UNIVERSITY OF CENTRAL LANCASHIRE

School of Physical Sciences and Computing

A study of the effect of Si:Al Ratio and ion-exchange on the ability of the zeolite ZSM-5 to adsorb common analgesics from waste water

A thesis submitted in partial fulfilment for the requirements for the degree of MSc (by Research) in Chemistry at the University of Central Lancashire

by

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August 2017

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Declaration

I confirm that this report is all my own work and that all references and quotations from both primary and secondary sources have been fully identified and properly acknowledged in footnotes and reference list.

Signed

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Date: 03/01/2017

Abstract

Due to the expansion of the pharmaceutical industry, the increase in demand and current inadequate removal methods, pharmaceutical waste has been increasing in concentration in environmental waters. It is unknown what the chronic effects this waste could have on humans and so more adequate removal methods are necessary. In this research project the zeolite ZSM-5's effectiveness at removing the analgesics paracetamol, aspirin and ibuprofen lysine from aqueous solution was investigated. ZSM-5's Si:Al ratio and charge balancing cation were also altered to ascertain the effects these attributes had on its ability to remove the analgesics from aqueous solution. Its ability to remove low concentrations of paracetamol from solution was also investigated. Ion exchange reactions were performed on commercial ZSM-5 ammonium with a Si:Al ratio of 30:1, this being the baseline zeolite for this research, changing the charge balancing cations to iron and sodium respectively. SEM-EDX spectroscopy was ran to ensure the ion exchanges had been successful. Then adsorption reactions using 0.005M paracetamol, 0.005M aspirin and 0.002M ibuprofen lysine were performed on commercial ZSM-5 ammonium with a 30:1 Si:Al ratio and one with a 200-400:1 Si:Al ratio as well as the iron ion exchanged ZSM-5 30:1 ratio and the sodium ion exchanged ZSM-5 30:1 ratio. Using HPLC and powder XRD analysis it was found that the optimum form of ZSM-5 for the adsorption of paracetamol and ibuprofen lysine was the commercial ZSM-5 ammonium with the 30:1 ratio, found to be due to its increased number of ammonium cations present relative to the other forms, and commercial ZSM-5 ammonium with a Si:Al ratio of 200-400:1 the optimum form for the adsorption of aspirin, found to be due to its hydrophobicity. At halved and quartered batch concentrations for paracetamol commercial ZSM-5 ammonium 30:1 was found to have a much lower ability to adsorb paracetamol, adsorbing only 3.62% at max at the halved concentration, relatively small when compared to its maximum of 64.39% at normal concentration.

Acknowledgements

I would like to thank Dr Jennifer Readman for allowing me to perform this research project and for her guidance and support throughout the year.

I would also like to thank the staff at UCLAN for their continued support, especially those in the analytical suite who helped me with and trained me in the use of the analytical equipment needed for my project.

Finally, I would like thank my friends and family who supported me throughout this research project and kept me on track.

Glossary

Si:Al	Silicon: Aluminium
ZSM-5	Zeolite Socony Mobil-5
SBU	Secondary building units
S4R	Single four ring
S6R	Single six ring
S8R	Single eight ring
D4R	Double four ring
D8R	Double eight ring
HSAB	Hard soft acid base
XRD	X-Ray diffraction
HPLC	High performance liquid chromatography
UV	Ultra violet
LC-MS	Liquid chromatography – Mass spectroscopy
LC-IR	Liquid chromatography – Infrared spectroscopy
LC-NMR	Liquid chromatography – Nuclear magnetic resonance
SEM	Scanning electron microscope
EDX	Energy dispersive X-Ray spectroscopy

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Introduction

1.1 – Zeolites and Zeotypes

1.1.1 – Background

Zeolites have been observed in nature since 1756, when the first one, stillbite, was discovered in Sweden by Baron Cronstedt.[1] The term 'molecular sieve', coined because of zeolite's ability to selectively take certain molecules into its porous structure whilst rejecting others based on their larger molecular dimensions[2], was first introduced in 1926 when the sorptive properties of chabazite were attributed to its small pores.[1] Through the early 1950s synthetic zeolites were first produced, these zeolites were given the prefix of 'Zeolite' to differentiate them from their natural counterparts. Examples from this time include zeolite A, zeolite X and zeolite Y. The first commercially available synthetic zeolite was made in 1953 by the Linde Corporation which was called Linde Type A zeolite or, more commonly, zeolite A.[1,2]

Zeolites are a class of microporous crystalline aluminosilicates which occur in nature and can be synthesised in the laboratory. Zeolites have the general formula of $M_{x/n}[(AlO_2)_x(SiO_2)y]$ $.mH_2O$, where n is the valency of the metal ion M which balances the negative charges in the aluminosilicate framework. These minerals have three dimensional structures which arise from a framework of $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ tetrahedra that are linked by all their four corners.[2] When these tetrahedra link they are governed by Lowenstein's rule. This rule states that the distribution of tetrahedra in a crystal is not entirely random in amorphous and crystalline aluminosilicates and that whenever two tetrahedra are linked by one oxygen bridge, the centre of only one of them can be occupied by aluminium while the other centre must be occupied by silicon. Also, whenever two aluminium ions are neighbours with the same oxygen anion, at least one of them must have a coordination number larger than four, either five or six, towards oxygen. These rules explain that there is a maximum substitution limit of 50% of the silicon in the framework.[3] The frameworks produced by these tetrahedra are generally open with channels and cavities, in which cation and water

molecules can reside. These cations have a high degree of mobility which give rise to easily achievable ion exchange and therefore zeolites are used industrially in ion exchange processes. The water molecules also have a large amount of freedom, being able to be easily lost and regained by the zeolite without any damage to the aluminosilicates framework.[2]

The word zeolite has its basis in Greek and means 'boiling stones'. This is due to the noticeable loss of water when zeolites are heated; this property visually illustrates how easily water is lost from the pores.[2] Materials that share the properties of zeolites, i.e. molecular sieving, easy loss and gain of water, and a similar structure to zeolites but that are non-aluminosilicates are known as zeotypes.

1.1.2 – Zeotypes

Zeotypes share all their major properties with zeolites and only differ in that they contain elements other than Si and Al in the tetrahedral framework sites and sometimes lack certain properties of zeolites.[4] The synthesis of these materials usually follows the logic of replacing one of the elements in a zeolite with another similar element to keep consistent properties. The most likely candidates for this replacement are elements in the same group as Al and Si on the periodic table such as Ga and Ge respectively, or that they share the same oxidation state as one of the two. However, the first commercially produced zeotype used neither of these elements.[4]

The first accepted zeotype was discovered in 1982, when Union Carbide research laboratories reported a family of framework structures based on $[AlO_4]^{5-}$ and $[PO_4]^{3-}$ known as aluminium phosphates.[4] This zeotype is more commonly known by the acronym $AlPO_4$. 24 compounds of this family have been described and all have the composition of $\chi RAl_2O_3 \cdot 1.0(\pm 0.2)P_2O_5 \cdot \gamma H_2O$ where R is the amine or quaternary ammonium species used as a component of the original gel synthesis[4] and the quantity of $(\chi + \gamma)$ represents the amount needed to fill the microporous void of the final framework[4]. The majority of these compounds are three-dimensional structures while some of them have P-O-H environments, some are dense phosphate phases and some have a layered structure, though this layered structure can sometimes have

different Al:P ratios.[3] 13 of these compounds are found to be three-dimensional while also being classified as molecular sieves. Unfortunately, these compounds lack ion exchange properties as the overall framework charge is neutral, due to an Al:P ratio of 1:1 and strict alternation of Al and P throughout the framework. Titanium silicates represent another possible zeotype and Titanium Silicate-1 (TS-1) was first successfully synthesised in 1983. They share similar sorptive properties to their corresponding zeolite, in the case of TS-1 this is ZSM-5 as they share the same MFI structure, though TS-1 seems to have a lower hydrophilic aspect than ZSM-5. They differ from zeolites in that they have an octahedral coordination in their Ti:S framework as opposed to a tetrahedral for zeolites.[5]

So, overall zeotypes differ from zeolites as they are not specifically aluminosilicates and they do not share all their properties.

1.1.3 – Structure

As previously mentioned, all zeolites are microporous aluminosilicates with a three-dimensional framework consisting of $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ tetrahedra. These tetrahedra are linked together by the vertices forming rings of varying size. Figure 1[6] shows a comparison of eight membered, ten membered and twelve membered rings. The formation of channels and cages has led to over 200 known zeolite framework types. The number of cations present is dependent on the ratio between the Al and Si in the framework. An increased number of Al^{3+} substituting into the framework over Si^{4+} leads to a residual negative charge on the oxygen framework. This negative charge leads to increase in cations to balance out the overall charge of the zeolite. The number and location of water molecules in the zeolite's framework depends on a few different factors. First the overall structure of the zeolite, the size, shape and number of channels present in the zeolite and secondly the number and type of cation located in the zeolitic framework. Zeolites that contain no aluminium and only silicon on the oxygen framework would be neutral charged and have no cations present. High silica zeolites have hydrophobic tendencies when compared to low silica zeolites that commonly have hydrophilic tendencies. [7]

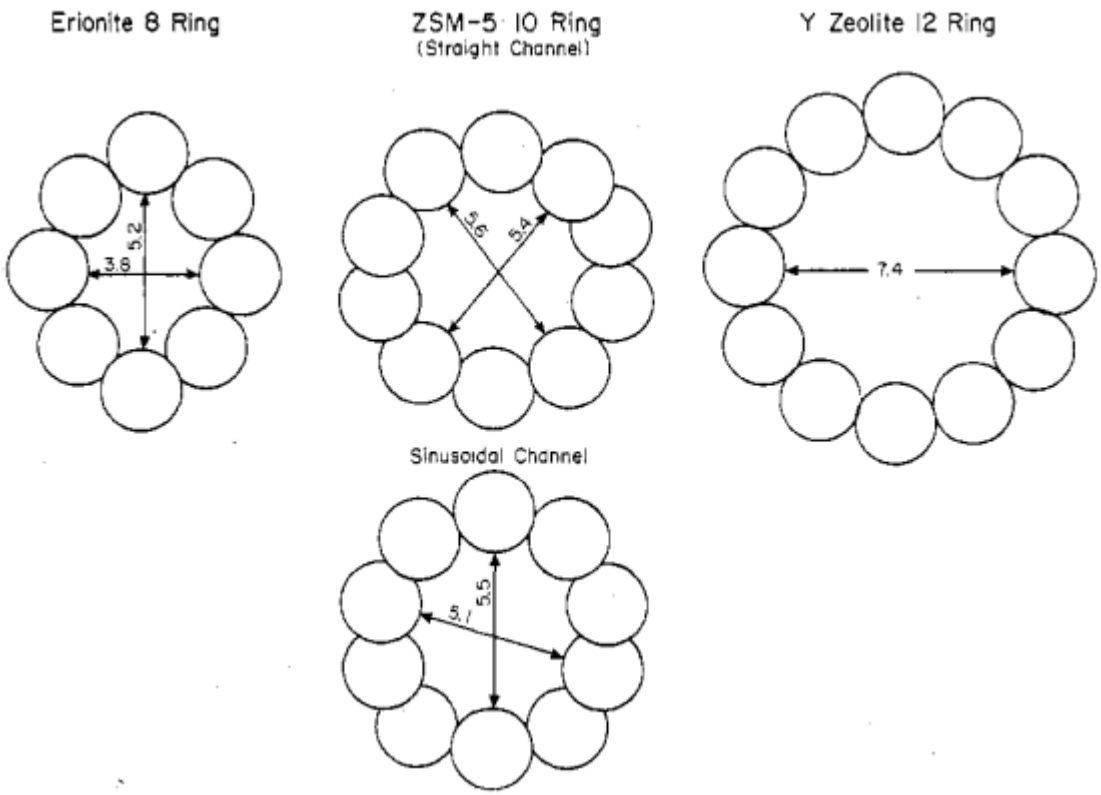


Figure 1. Comparison of the limiting ports of Erionite, ZSM-5 and Faujasite [6]

For the classification of zeolites, the usual process would be to relate them to the symmetry of their unit cells. This is troublesome however due their complex structure and so a simplified route has been found. The basis for this classification is the observation that zeolite structures often have very similar structural sub-units that repeat and lack the complexity of the repeating unit cells. These sub units are referred to as "secondary building units" (SBU)[4]. Using these SBUs a classification can be applied all of the known zeolite framework arrangements. There are eight SBUs total: single four ring (S4R), single six ring (S6R), single eight ring (S8R), double four ring (D4R), double eight ring (D8R), complex 4-1, complex 5-1 and complex 4-4-1. These are illustrated in the Figure 2 below.[7]

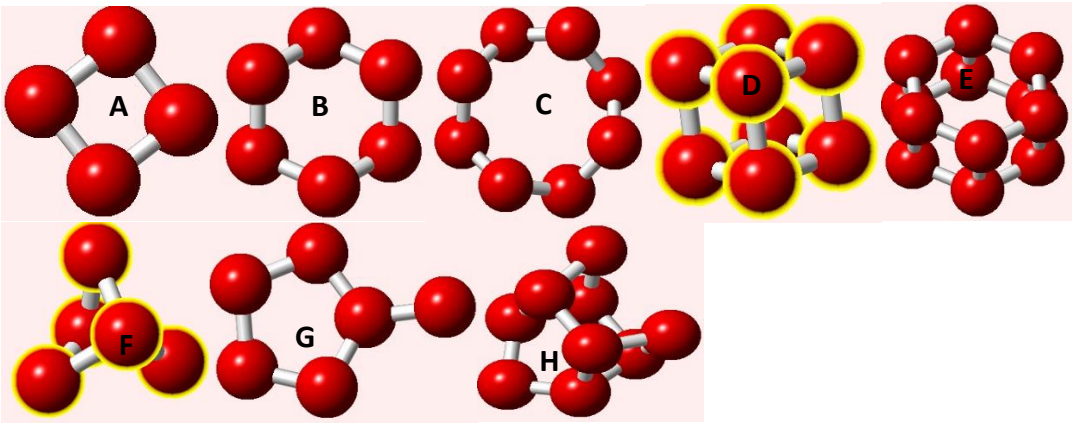


Figure 2: A) Single four ring SBU. B) Single six ring SBU. C) Single eight ring SBU. D) Double four ring SBU. E) Double eight ring SBU. F) Complex 4-1 SBU. G) Complex 5-1 SBU. H) Complex 4-4-1 SBU. [7]

The SBUs only represents the aluminosilicate skeleton, with the positions of Al, Si and O being relative to one another, and excludes the cations and water moieties with the pores and cavities within the zeolite framework. The sites for water and cations themselves are complex and specific to the zeolite and only fully defined for certain zeolites. [7]

1.1.4 – Uses

Due to the unique structure of zeolites they have four main uses: molecular sieve, drying agent, ion exchanger and heterogeneous catalyst.[8, 9, 10] Each of these will be described in turn.

Molecular Sieve

Zeolites themselves are not unique in their properties as molecular sieves, other compounds such as carbon and porous glass also have sieving properties but they are special in that they have highest flexibility of use for these kinds of materials. The structure of zeolites is responsible for their sieving properties as they possess a wide array of internal channels and cavities. The windows into the pore system are close in size to the dimensions of common organic and inorganic molecules and therefore

zeolites can separate mixtures of molecules, in either gas or liquid phase, as they allow molecules of certain sizes and dimensions to pass through. The size of the windows in the zeolite are dependent on the SBUs that make up the framework. The effective size of these windows is also affected by the nature and number of cations present in the pores and whether the zeolite is dehydrated. When water is removed from the zeolite the cations can move closer to the framework. This cation movement partially blocks access to the interstitial site via the window, reducing the effective pore size. The Si:Al ratio will also have an effect as that will limit the number of cations in the structure. The amount reduced is dependent on the size of the cation in the system, the larger the cation the more the effective pore size is reduced. This has been described as the sentinel effect.[7]

Drying Agent

The second use of zeolites are as drying agents in which they are used almost universally in laboratories around the world. Bottles of Molecular Sieve 3A, 4A and 5A[2] can be found in many laboratories and these contain beads made of zeolite A, the different notations referring to alternate names for different ion exchanged versions.[2,7] These beads are used as general purpose drying agents for purposes such as drying gas chromatography columns or drying an air-line for a vacuum. Dried, sealed cartridges of zeolites 3A, 4A and clinoptilolite are included in systems where water build up would cause malfunctions, these types of systems include vehicle braking and air conditioning systems and certain heavy duty transformers with hydrocarbon liquids stored inside of them. Another application where the use of zeolites is much preferred to the alternative is inside double glazed windows. The double-glazing units contain gases such as Ar, SF_6 and halocarbons in the cavity between the glass panes which improve heat and sound insulation. When molecular sieves other than zeolites are used they slowly absorb the gases over time and so reducing the windows life span. This is avoided if zeolites 3A and 4A are used as they do not absorb these gases. They also remove any residual vapour left behind by the sealant used to fix the panes together.[8]

Ion Exchangers

The third use, as ion exchangers, is based upon the property of zeolites which allows them to replace the cations held in their pores with cations present in solutions or melts. This property has been extensively researched and so modifications to zeolites through the changing of their cations have been performed. These modifications lead to changes in the catalytic or molecular sieving properties of the modified zeolite. Not all zeolites can perform simplistic ion exchange; zeolites that have a high density and low porosity, have limited and slow ion exchange properties. Unfortunately, despite the ease with zeolites can perform ion exchange their actual practical usefulness in this regard is very limited. One major limitation is their lack of compatibility with column use; synthetic zeolites usually crystallise with a particle size range of 0.1-1.0 μ. This size is too small for column use as it does not facilitate a reasonable liquid transport through a bed of particles. Synthetic zeolites are usually marketed as crystal compacts but they are not attrition resistant under liquid column use. Natural zeolites have a much higher compatibility with column use than their synthetic counterparts and clinoptilolite has been used in columns worldwide. Another problem with using zeolites as ion exchangers arises due to zeolites inherent instability in low pH conditions. Zeolites with an Si:Al ratio between 1 and 2 readily lose Al from their framework in acid environments and this leads to reduced capacity and eventually complete framework collapse. These properties mean that any use as an ion exchanger comes with the caveat that any reaction using zeolites must have very specific conditions.[9]

Zeolites have been used as ion exchangers in commercial laundry detergents as a replacement for polyphosphates. Polyphosphates were replaced because of their negative effect on the environment so less hazardous alternatives were investigated. Their use in detergents was to remove Ca^{2+} and Mg^{2+} ions from washing water to prevent them from co-precipitating with surfactant molecules. Zeolites were found to be a good alternative as they could effectively carry out the same function. Zeolite A and zeolite X in a mix were chosen as the best alternative. The sodium form of zeolite A was found to remove Ca^{2+} ions extremely well but was found to have much less

success when removing Mg^{2+} ions due to poor selectivity.[8] To make up for this the sodium form of zeolite X is used in conjunction with zeolite A as it removes the Mg^{2+} to a satisfactory amount. Zeolite P is sometimes used instead of zeolite A as it has a higher affinity for calcium ions than zeolite A but since there is less data on zeolite P's potential risks zeolite A is used more often.[10] Zeolites are also used in the nuclear industry to remove radioactive isotopes from radioactive waste water. Spent nuclear fuel rods are stored underwater in ponds[8] to allow thermal and radioactive cooling to take place before the elements are reprocessed. Unfortunately, this storage leads to a build of fission products, especially the radioactive isotopes of ^{137}Cs and $^{90}Sr/^{90}Y$, in the ponds. This pond water is a major source of medium level radioactive waste and so much be processed before it can be released into the environment. Zeolites such as clinoptilolite have been used to remove the harmful isotopes from these bodies of water. The Sellafield plant removes Cs and Sr isotopes from its liquid effluents via the use of clinoptilolite in the SIX GP process, greatly reducing the negative impact upon the environment once it is released into the Irish Sea.[9]

Catalysts

The last major use for zeolites, as heterogeneous catalysts, has been one of the major branches of research into these materials. Zeolites were first used as catalysts in 1959 when zeolite Y was used by Union Carbide as an isomerisation catalyst. The more important use however came in 1962 when zeolite X was first used as catalyst for cracking with zeolite Y now being used in fluid catalytic cracking. It was noted that small amounts of zeolites could be incorporated into the silica/alumina or silica/clay catalysts used at the time. This catalysis occurs via Brønsted acid sites produced by the aluminium sites in the zeolite's framework. The use of zeolites in petroleum cracking greatly increased their efficiency and has secured them a place as a catalyst in the petroleum industry. The savings produced from this improvement number in the billions of pounds per annum. These savings led to the huge amount of money invested into the research of zeolites.[11]

1.1.5 – ZSM-5

The zeolite ZSM-5 (Zeolite Socony Mobil-5) is a medium pore zeolite with channels defined by ten-membered rings which was patented by the Mobil Oil Company in 1975 and it has been widely used in the petroleum industry as a heterogeneous catalyst since. The chemical formula of ZSM-5 is $Na_nAl_nSi_{96-n}O_{192}$ where n is between zero and 27. It has a relatively low aluminium content and therefore has a low number of cations present in its pores making it less suited for ion exchange reactions when compared to other zeolites. Similarly, its use a drying agent will be low as well as it has low water content and its framework has hydrophobic properties as opposed to the highly hydrophilic properties of most other zeolites.[7]

Due to it having a medium pore size represented by a ten-membered ring, small being represented by an eight-membered ring and large being represented by a twelve-membered ring, ZSM-5 has distinct sorption and diffusion properties. ZSM-5 can be considered an end-member of the pentasil family and the structure is formed by the stacking of layers with the neighbouring layers being related via inversion. The structure contains two types of channels, straight and sinusoidal. The straight channel running parallel to [010] formed by ten membered rings with 5.4 X 5.6 Å free diameter and the sinusoidal channel runs parallel to the [100] direction having ten membered rings with 5.1 X 5.4 Å free diameter and this is known as the MFI topology. The sinusoidal channels, which have a near-circular cross-section, run in a zig-zag pattern between the straight channel pores, which have an elliptical shape. The pore size dictates how large of a molecule the zeolite can adsorb, for example adsorption of hydrocarbons by eight membered ring zeolites is limited to normal paraffin while the twelve membered ring zeolites can adsorb molecules as large as tributylamine, which is 9.1 Å. ZSM-5's ten membered ring and medium pore size means that it can adsorb as large as o- and m-xylene, 1,2,4-trimethylenzene and naphthalene all of which have minimum diameters of around 6.9Å, but these all adsorb slowly which would indicate some steric hindrance so these molecules would indicate the upper boundary. Hydrocarbons like pentamethylbenzene and 1,3,5-trimethylbenzenene, which have minimum diameters of around 7.8Å, do not adsorb at

all and are essentially excluded from the zeolite. ZSM-5's framework and structure is presented in figure 3 below. [7,12, 13]

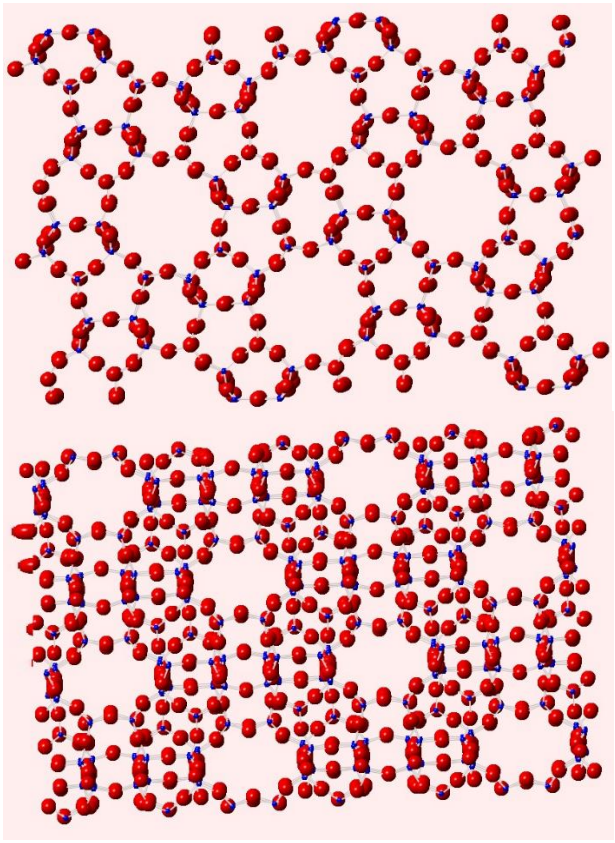


Figure 3. A) Structure of ZSM-5 with straight channel pores aligned and cations removed for simplicity. B) Structure of ZSM-5 with sinusoidal channel pores aligned and cations removed for simplicity.[13]

1.2 – Pharmaceuticals

1.2.1 – Levels of Detection

Over the last few decades the prevalence and production of pharmaceuticals in their many forms has increased dramatically due growing public demand. These chemicals have gone a long way to increase the quality of life and life expectancy of many. However, there has been a negative effect due to this, as the amount of waste from the production and use of these chemicals has increased and has accumulated in the environment.

Most of these pharmaceuticals and their metabolites are polar and so easily dissolve in water, this has led to them being found in concentrations of ng to pg/L in drinking water, ng to pg/L in ground water, µg to ng/L in surface water, mg to µg/L in wastewater and g to mg/L in domestic and non-domestic sources such as households, industries and healthcare establishments [14]. Relatively large amounts have been found in the effluent of waste water treatment plants indicating that they are not successfully removing all this pharmaceutical waste is not completely removed from our water supply. For example the average concentration of ibuprofen in the influent of investigated waste water treatment plants was found to be 14.6 µg/L and in the effluent it was reduced to 1.96 µg/L.[15] The average concentration of salicylic acid, a metabolite of aspirin, found in the influent of investigated waste water treatment plants was found to be 212 µg/L and in the effluent it was reduced to 2.50 µg/L.[15] Though these are large reductions the concentrations going into the water supply are still at the µg/L level and though these levels are way below what we expose ourselves to through the use of these pharmaceuticals very little is known about the long term effects of chronic low level exposure of this waste on humans.

More is known about the impact on aquatic life and bacterial resistances, as impaired reproductive and immune systems as well as structural and neurological damage in fish and amphibians has been linked to the increase of pharmaceutical waste along with increased antibiotic resistance in bacteria [16]. To prevent any more drastic effects in the long term effective and easily applicable water purification techniques need to be researched to ensure clean water and a healthy environment for the future. It is

especially important as the industries that are producing these chemicals and their use by the common public continue to increase.

1.2.2 – Environmental Concerns

With the advancement of the pharmaceutical industry as well as the increase in commercial availability of over the counter analgesics, the use of analgesics by the mass public has increased. This means that the amount of pharmaceutical waste released into the environment due to the production of these chemicals has increased and can be found at the highest concentrations in the effluents of sewage treatment plant. These pharmaceuticals are being detected in concentrations of µg/L such as ibuprofen being 1.96 µg/L. Analgesics and anti-inflammatory drugs waste have been found to have some of the highest influent concentrations, being over 292 µg/L, while hormones have the lowest at ng/L level.[15] Research comparing the influents and effluents of sewage treatment plants near the outflow of pharmaceutical factories has shown that the reduction of the pharmaceuticals found was a 100% reduction t the highest, varying from chemical to chemical but going as low as 0% uptake for some when using activated sludge processes.[2] Additionally most pharmaceuticals do not always break down completely in the body and so some of the drug and its metabolites are excreted, which in turn enter the water system through the sewage plant and other pathways illustrated in figure 4[17]. Due to their high use by the general public, pharmaceuticals such as analgesics are increasing being introduced into the environment in this manner[14].

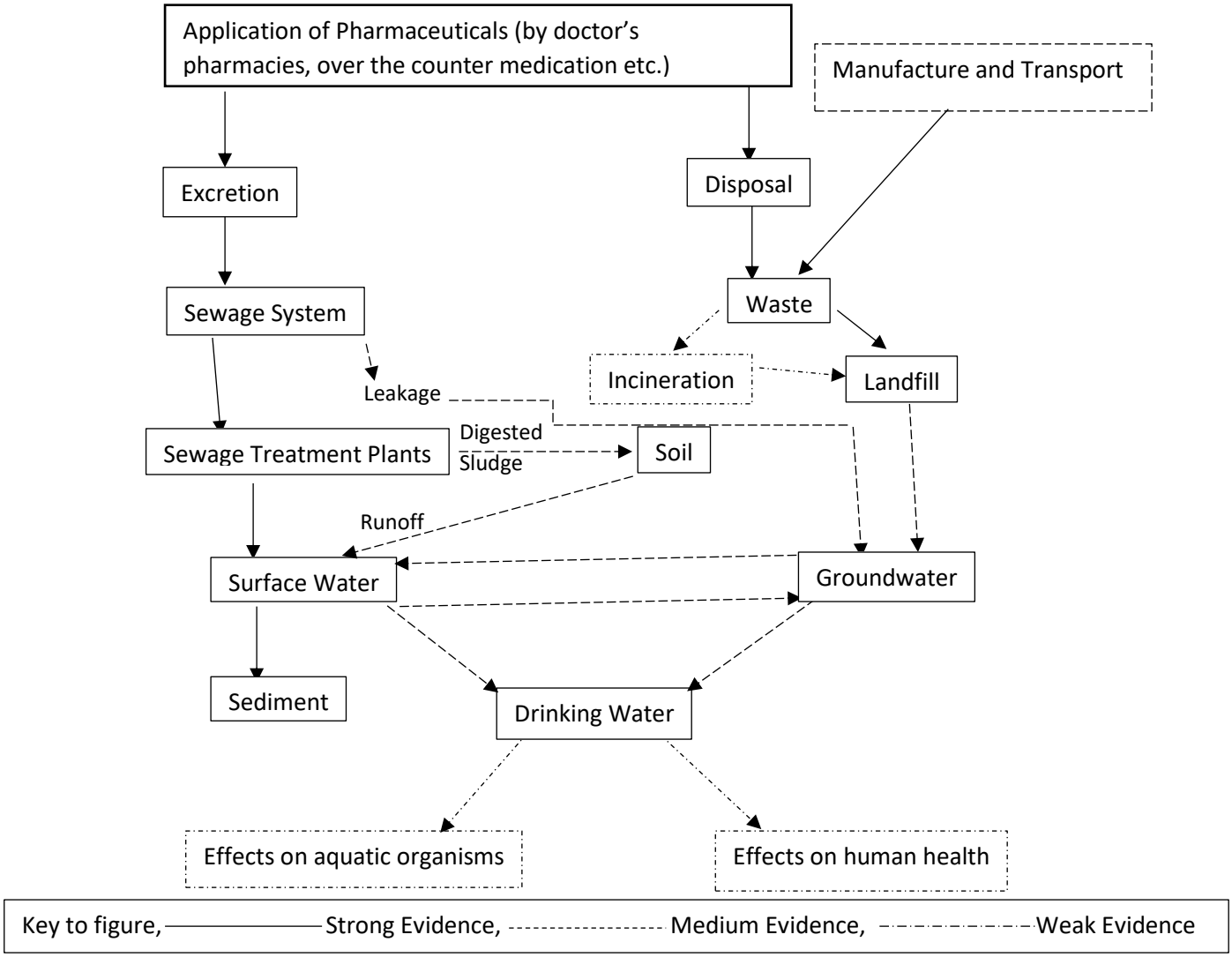


Figure 4. Possible pathways of pharmaceuticals into the environment.[17]

The effect on aquatic life has not been investigated thoroughly for all pharmaceuticals but the effects of oestrogen hormones on fish has been looked into. Work by Olsen *et al*[12] on the effects and incidence of oestrogenicity, found in the effluent of a Swedish sewage treatment plant, on juvenile rainbow trout were investigated. In the effluent of the sewage plant they found the synthetic oestrogen used in contraceptives 17α-ethinyloestradiol, the natural oestrogens oestrone and 17β-oestradiol and the weaker non-steroidal oestrogens 4-nonylphenol and bisphenol. All these oestrogens were found in ng/L levels but the amount of ethinyloestradiol found exceeded the levels shown to oestrogenic to fish by 45 times. [18]

When 17β-oestradiol is present in fish it acts as an inducer of vitellogenin, a complex precursor protein normally found in the blood of maturing female fish but very low in male or juvenile fish and is used in the production of yolk in all oviparous vertebrates. However, many other environmental oestrogens, which include alkyl-phenolic compounds, phyto-oestrogens, synthetic oestrogens and certain pesticides, have been found to also induce vitellogenin synthesis in male and female fish. Due to this the presence of vitellogenin in the blood of male or juvenile fish has become a biomarker for identifying oestrogenic contamination of an aquatic environment. The research was carried out by introducing juvenile rainbow trout downstream of the sewage treatment plants effluent and after two weeks samples of their bile and blood plasma were analysed using GC/MS for the bile and by ELISA and Western blotting for the blood plasma. All the oestrogens mentioned were found in the bile collected and large amounts of the vitellogenin was found in the blood plasma. This shows that a widely used synthetic oestrogen caused negative effects in the endocrine systems and hermaphroditic tendencies in fish exposed to sewage effluent water.[18] Considering that analgesics have the second highest incidence in sewage effluents[19] after hormones and that mostly their effects on the aquatic environment have not been thoroughly investigated, the introduction of a much more efficient removal system would be prudent and if successful this research could provide that.

1.2.3 – Current Filtering Techniques

As mentioned before[15] current techniques used for water purification do not completely remove pharmaceutical waste. Some of the most common removal techniques for organic compounds from wastewater are biological filters and activated sludge. Both techniques are similar in that they are both types of secondary wastewater treatment techniques that take place during secondary biological treatment and they both use two vessels, the first being a reactor containing large amounts of micro-organism populations. These micro-organisms oxidise the organic compounds so they are easier to remove, this is dependent on the biochemical oxygen demand and so oxygen is present in this reactor. The second vessel is a tank that removes the micro-organism from the effluent via sedimentation. The removal of organic micro-organism pollutants from during this process include the adsorption onto microbial

flocs and removed in waste sludge, through biological or chemical degradation or through transformation and volatilisation during aeration. These mechanisms are displayed on Figure 5[20] below but as shown in that diagram, some organic polar compounds are left unoxidised and are released into the next step of wastewater purification subsequently into the environment.[20]

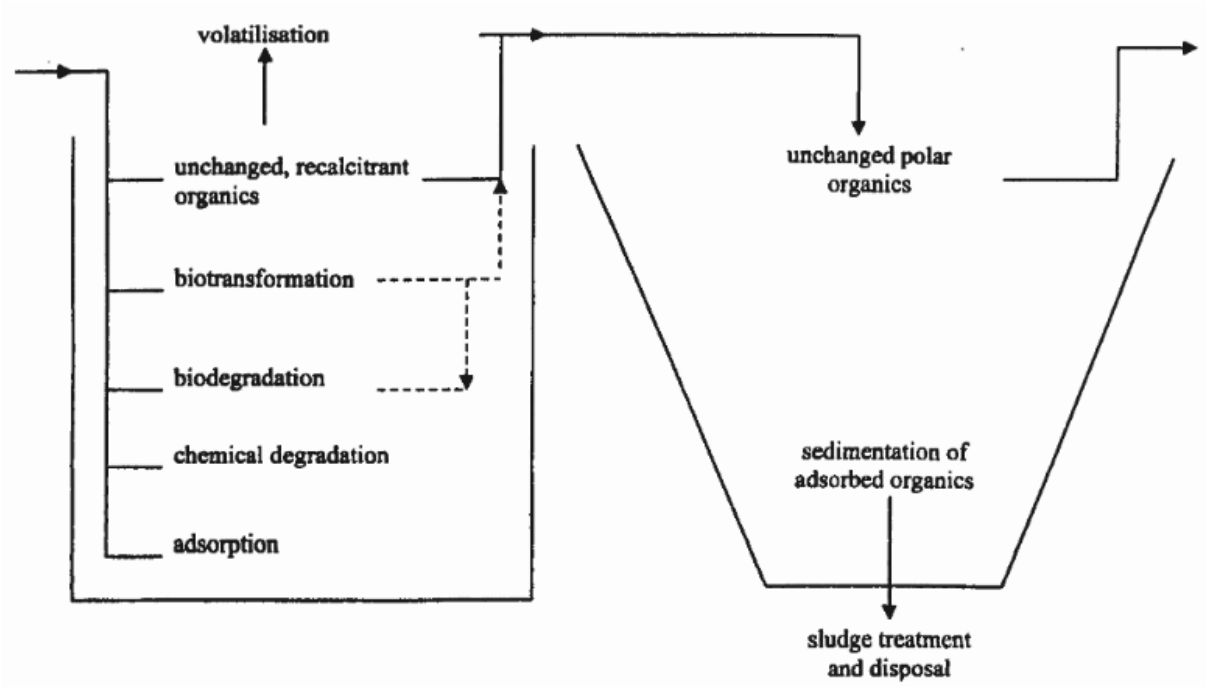


Figure 5. Removal mechanisms for organic micro-pollutants during secondary biological treatment.[20].

Most pharmaceuticals are polar molecules designed to dissolve in water and some are also designed to be resistant to biological degradation to improve therapeutic performance. Therefore, higher concentrations of these pharmaceuticals will be released into the environment because they are not fully removed by the wastewater purification techniques. However, treatment technologies based on advanced oxidation processes[21, 22, 23] or adsorption on to appropriate solid materials such as activated carbon cloth[24, 25] have been investigated and suggested as replacements or additions to the current system. Unfortunately, advanced oxidation processes are expensive and energy consuming, additionally total mineralisation of the pollutants cannot be reached. This can result in potentially dangerous products or by-products forming. Activated carbon cloth meanwhile has yet to demonstrate its ability to remove pharmaceutical waste. All this has led to an increased demand for adsorbent

materials that can achieve higher efficacy and better selectivity in the removal of pharmaceutical waste compounds in variable conditions.

1.3 – Zeolites and Pharmaceutical Waste

Previous research has proven that zeolites are useful when adsorbing organic compounds. Shu *et al*[17] investigated the use of zeolites in the adsorption of organic molecules form an aqueous solution. They used surfactant-modified pillared clays, silicalite and zeolite beta with high Si/Al ratios to remove phenol, chlorophenols and nitrophenol from an aqueous solution. They found that the surfactant-loaded pillared clays had a moderate capacity for the adsorption of the phenol and chlorophenols from an aqueous solution but were not seen to be a viable candidate as it had high adsorbance capacity for phenol, at low concentrations it fell lower than the silicalites. Also, it had the draw-back of discharging surfactant into the aqueous phase during the adsorption process. Hydrophobic silicalite, with a high Si/Al ratio, was found to have a high capacity for phenols and is efficient even at lower organic concentrations. Its capacity for phenols reaches a maximum value at a Si/Al ratio of 563 with further increases having no further effect on the adsorption capacity. Silicalites were found to be poor at adsorbing larger molecules as their internal pore structure limits access. Dealuminated zeolite beta with a Si/Al ratio of 170 however was found to be a good choice for an adsorbent for the larger phenols due to its larger pore size but was out performed by the silicalite on the smaller phenols, having only 60% the adsorption capacity, based on moles, of the silicalite for the smaller phenols. They also found that at higher Si/Al ratio that the adsorption capacity of both the silicates and zeolite beta were increased becoming comparable, but lower by a factor of two, to the capacities of organic resins XAD-2, XAD-4 and XAD-7 which were designed to adsorb organics from an aqueous solution. Overall this research shows that zeolites have been proven useful in the removal of small to large organic molecules from aqueous solution, thus adding credence to their use in this research.[17]

Khodaverdi at al[26] investigated the use of synthetic zeolites in adsorbing and then releasing anti-inflammatory drugs for use in modified-release drug delivery systems for the gastrointestinal tract. For a carrier to be ideal it must release the adsorbed drug into the intestine, which is the main area for absorption. They used zeolite X and Y as the carriers and sodium diclofenac and piroxicam as the drug molecules. They heated the zeolites for 48 hours to ensure the absence of water in the zeolites. Two methods

for loading the drugs onto the zeolites were used and analysed them using weight measurement, spectroscopy FTIR, thermogravimetry and scanning electron microscopy to confirm the drug loading into the zeolite. Simulated gastric fluid and simulated intestinal fluid were synthesised and used to determine how much of the drug the zeolites would desorb at the specific sites within the body. They found that the zeolites adsorbed over 90% of the drugs loaded onto them. The pure drugs without the zeolites were found to release around 90% of their concentration in the simulated gastric fluid within the first 15 minutes whereas the drugs adsorbed into the zeolites released a much smaller amount, around 10-20%, in the same time frame. However, they found that in the simulated intestinal fluid that the drug release from the zeolites was quite slow but a continuous process. They concluded that this was favourable as a drug delivery system as a large concentration of the drugs being released into the stomach caused irritation in the stomach lining, and that the overall performance for the release of diclofenac and piroxicam in the simulated gastric fluids and slow release in the simulated intestinal fluid was higher for zeolite Y compared to zeolite X. This research shows that synthetic zeolites can be used to adsorb anti-inflammatory drugs so theoretically so could ZSM-5.[26]

Research by Rakic *et al*[27] attempted to adsorb the following pharmaceuticals and pharmaceutical metabolites, salicylic acid, acetylsalicylic acid and atenolol from aqueous solutions onto clinoptilolite, which has been modified with sorbed metallic cations Cu(II), Zn(II), Ni(II) and Mn(II) as they will form stable complexes with N- and O-donor groups (following the Hard-Soft Acid-Base theory (HSAB theory)) that are present in the pharmaceuticals investigated. The HASB theory applies to Lewis acids and bases and explains the stability of compounds and the viability of reaction pathways. It assigns the terms hard or soft and acid or base to chemical species and if their ability to react together is shown in a like for like system. This means hard acids react well with hard bases and vice versa. This is important when designing reactions as it can help indicate what reactions will work well and can also help indicate the solubility of different compounds in water or mobile phases for analytical techniques such as high performance liquid chromatography. They also used the natural clays, kaolin and bentonite (pure or ion-exchanged by octadecyl dimethyl benzyl ammonium chloride), as adsorbents as well. All three of these are naturally occurring materials. The adsorption was observed at 30^{o}C (303.5K) by titration microcalorimetry which

was employed to obtain the heats evolved because of adsorption. These evolved heats were found to be directly linked to the strength of the interaction between the adsorbate and adsorbent and therefore the affinity of the pharmaceuticals used for the adsorbents were reflected by the evolved heats. They used volumetric experiments to indicate the adsorption capacities of the adsorbents used towards specific pharmaceuticals used. Their results showed that all the adsorbents investigated had affinities for the adsorption of the chosen pharmaceuticals with the maximal adsorption capacities within the range of 10^{-5}-10^{-6} mol/g. Their data also showed that the adsorption capacities of the adsorbents used could be tailored by applying modification procedures but that these procedures did not affect their structural characteristics. Overall they demonstrated that the removal of salicylic acid, acetylsalicylic acid and atenolol from aqueous solutions by aqueous phase adsorption was found to be highly dependent on the nature of the adsorbate. The presence of some organic functional groups appear to play an important part in the mechanism of adsorption of the specific adsorbate. Parameters such as hydrophobicity and the physical states of the adsorbate molecules in the aqueous solution are also important.[27] These results and their analysis show that the use of natural zeolites can be effective in the removal of salicylic acid, acetylsalicylic acid and atenolol from aqueous solution via adsorption and so the removal of the drugs investigated in this research from aqueous solution could be viable using ZSM-5.

Zeolites can be used to adsorb other groups of pharmaceutical apart from analgesics. Martucci *et al*[28] studied the sorption capacities of dilute solutions of drugs onto hydrophobic zeolites. They investigated the removal of the three drugs, erythromycin (an antibiotic), carbamazepine (an analgesic) and levofloxacin (an antibiotic) from a solution in water using the three synthetic zeolites Y, mordenite and ZSM-5. They added the zeolites to solutions of the pharmaceuticals in water and measured their concentration at different times to find out at what point an equilibrium is reached. They then determined the maximum adsorbance capacity of the zeolite by introducing a zeolite into a pharmaceutical aqueous solution until equilibrium is reached, they then separate the zeolite and solution and take the solution off the be tested using high pressure liquid chromatography/mass spectrometry. They then took the zeolite and introduced it to a fresh aqueous solution and the process repeated. Once the concentration of the solution ceased to change then maximum adsorbance had been

reached. Powder X-Ray diffraction patterns were collected and the presence of the drugs inside the zeolite pores was shown by variations in these unit cell parameters. Overall, it was shown that zeolite Y adsorbed high amounts of the three drugs tested compared to the other adsorbents. This data was then confirmed by thermogravimetric analysis. To test the ability of organophilic zeolites in removing drugs from wastewater they took samples of water from the outlet of a wastewater treatment plant located in Northern Italy and determined the adsorption of erythromycin, carbamazepine and levofloxacin onto zeolite Y. They found that the drugs were almost completely adsorbed by zeolite Y thus confirming its viability at removing pharmaceutical waste from wastewater.[28] This research shows that not only can zeolites be used to adsorb pharmaceuticals from wastewater, in this case antibiotics, but that synthetic zeolites can be used for this task. This means that though ZSM-5 was not useful in the adsorbance of the pharmaceuticals analysed in the paper it can be used to remove pharmaceuticals from water.

1.4 – Aim of Research

The aim of this research is to determine ZSM-5's viability in the removal of pharmaceutical waste from aqueous solution, specifically looking into the removal of the analgesics paracetamol, aspirin and ibuprofen lysine. Analgesics were chosen to be the focus of study because they were found in the effluent of investigated wastewater treatment plants in the second highest concentration second only to hormones, 20% for analgesics and 30% for hormones.[18] Ibuprofen lysine was chosen over ibuprofen as it was slightly more soluble in water and thus easier to analyse for the purposes of this research. A synthetic zeolite was chosen due to its ability to be mass-produced, any filtration system could have this easily applied to as its source is not necessarily finite, and research has been done into the use of naturally occurring zeolites and clays, like clinoptilolite and bentonite respectively, for the same purpose.[26] ZSM-5 was chosen out of the synthetic zeolites available due to a lack of research into its use in this manner, that other similar synthetic zeolites such as zeolite X and Y have had research into their use and adsorbents[27] and that its unique characteristics, like its intermediate pore sizes, might aid in its adsorption of the drug molecules of interest. Two Si:Al ratios were chosen for investigation because a change in this ratio can lead to changes in the sorptive characteristics of the ZSM-5, an increase leading to a lower number of charge balancing cations present and higher hydrophobic properties and vice versa. These changes could change the sorptive affinity of the drugs investigated for ZSM-5 and so should be explored. Similarly, a change in the charge balancing cation can change these affinities as well, therefore ion exchanged ZSM-5 shall be used. Iron is being used for one of the ion exchanges as it would imbue the ZSM-5 with ferro-magnetic properties allowing for easy removal from the water supply once adsorption of the drugs have taken place. The uptake levels of the drugs investigated shall be characterised by high performance liquid chromatography, powder X-ray diffraction and scanning electron microscope with energy dispersive X-ray spectroscopy.

2. Methodology

2.1 Experimental

The chemicals used in this research are the commercially available analgesics paracetamol[28], aspirin[29] and ibuprofen lysine[30] all purchased over the counter from the pharmacy Boots, commercially available zeolite ZSM-5 ammonium 30:1[7] and zeolite ZSM-5 ammonium 200-400:1[7] both purchased directly from the chemical supplier Alfa Aesar[31, 32], and iron chloride[33] and sodium chloride[34] both of which came from UCLan's laboratory stores. These chemicals were used for an adsorption experiment to determine the sorptive capacity of ZSM-5 with regards to the drugs used. First 0.005M, 0.005M and 0.002M aqueous solutions of paracetamol, aspirin and ibuprofen lysine respectively are prepared. These concentrations were chosen as mM is one order of magnitude higher than the highest concentration found in the effluent of wastewater treatment plants investigated by C. Miege *et al*[35], this increase would allow us to investigate whether ZSM-5 would be useful as a drug removal agent in the future if concentrations of these chemicals in the water system increase. 0.005M was found to be the highest concentration where all the solid dissolves in solution for paracetamol and aspirin, ibuprofen lysine being less polar than the other two analgesics used had its maximum concentration for full solid dissolution being found at 0.002M. 0.5g of ZSM-5 is then added to 250ml of the solution being analysed and the mixture stirred at room temperature for intervals between 2 and 48 hours at 400rpm. The solid is recovered using vacuum filtration and analysed using powder X-Ray Diffraction (XRD). The concentration of drug remaining in the filtrated solution is determined using High Performance Liquid Chromatography (HPLC). This basic template was used for all the experiments. To determine the effect that the charge balancing cations have on the adsorption reaction a form of ZSM-5 ammonium with an increased Si:Al ratio of 200-400:1 was used instead of the 30:1 form. Ion exchange experiments were also carried out on the 30:1 form of ZSM-5 prior to adsorption. The NH_4^+ containing ZSM-5 was exchanged with Fe(II) and Na. For the ion exchange 10g of the zeolite was stirred overnight in a 500ml 0.1M metal ion solution. The zeolite was then filtered, washed and the process repeated a further 3 times. Successful ion exchange was verified by SEM/EDX and XRD. Finally, the concentration of the paracetamol aqueous solution was reduced to verify if ZSM-5

could remove drug waste at lower concentrations effectively, these concentrations being 0.0025M and 0.00125M, half and a quarter of the original concentration used for the aqueous paracetamol solution.

2.2 Setup

The aqueous solutions of the analgesics were made in 1L batches from store bought packs of the drug being analysed. The concentration and mole equations were used to calculate the mass of the drug needed. Concentration was calculated using drug mass per tablet and not using total tablet mass. This is because the tablets themselves were not 100% pure as they have various other chemicals to help with their ingestion and stability, and so the percentage impurity (% impurity) was needed. To find this out this equation 1 was used.

$$\frac{Weight\ of\ Tablet\ as\ Advertised\ on\ the\ Packaging\ (g)}{Actual\ Weight\ of\ Tablet\ (g)} \times 100 = \%\ Impurity$$

Equation 1. Percentage impurity equation.

This equation is assuming that the weight on the packaging is referring to the weight of the drug in the tablet which seems likely as it does not correspond with the overall weight of the tablet. This % impurity is then used to work out the mass of tablet needed in equation 2.

$$Mass\ of\ Tablet\ Needed\ (g) = Mass\ (g) \times 1.\left(\frac{\%\ Impurity}{100}\right)$$

Equation 2. Mass of tablet needed equation.

This will give the concentrations needed.

2.3 High Performance Liquid Chromatography (HPLC)

High performance liquid chromatography (HPLC) is the analytical technique used to analyse the liquid filtrate from the ZSM-5 experiments. It was used ascertain the concentration of the drug remaining in the solution and therefore how much was adsorbed by the zeolite. For this a set of calibration concentrations needed to be made

to produce a calibration curve. The peaks produced by the HPLC are specific to the chemical producing them and the mobile phase used, i.e. the peak produced by paracetamol should always elute at the same time, if the mobile phase used is constant for all analyses'. The area of the peaks are proportional to their concentration so using set concentrations of the chemical being analysed a plot of their areas can be produced. A line of best fit is drawn and the equation for this line can be used to determine the concentrations of the drug peaks in the adsorption experiments. The calibration standards were produced using serial dilutions and these equations:

$$Concentration\ (M) = \frac{Moles\ (mol)}{Volume\ (L)}$$

$$Moles\ (mol) = \frac{Mass\ (g)}{Molar\ Mass\ (\frac{g}{mol})}$$

$$Concentration\ (M)_1 Volume\ (L)_1 = Concentration\ (M)_2 Volume\ (L)_2$$

A sample of the experiments solution is taken and injected into the HPLC and subsequently flows through the system shown in figure 6[36]. It passes through the column taking a certain amount of time to reach the detector, this time is referred to as the elution time. This elution time is dependent on two factors, the affinity of the chemical analysed for the mobile phase compared to the stationary phase and the chemical being analysed. If the sample has a higher affinity for the mobile phase than the stationary phase, then its elution time will be less. The opposite is also true, a higher affinity for the stationary phase leads to a longer elution time. The chemical being analysed will have a set range for elution times based upon the mobile and stationary phases used. This allows for the identity of chemicals to be found if used with other techniques as multiple chemicals have overlapping elution time ranges.

The detector used in the HPLC can change what chemicals can be identified as there is no perfect universal detector yet available. There are four main types detector that differ by taking advantage of different physical or chemical attributes of the analyte or the mobile phase. The first and closest to a universal detector are bulk property detectors, these measure properties that are common to all analytes by measuring differences in the mobile phase with and without the sample, and the refractive index

detector is one of the most common bulk property detectors. Because bulk property detectors react to all analytes more emphasis is placed on the selectivity of the chromatographic column used, though overall this type of detector is limited in its sensitivity due to its bulk identification technique being the equivalent of determining the weight of a person by weighing their car before and after they get in to it.[37]

The second type of detector is the analyte specific property detector; these respond to unique characteristics of certain analytes. The most commonly used of this type is the Ultra Violet (UV) detector which responds to analytes that absorb UV light at particular wavelengths. Though usually specific to analytes with chromophores the range of detection for UV detectors can be increased by using low wavelengths, <210nm, as almost all organic compounds absorb UV radiation at this wavelength. Other types of analyte specific detector include fluorescence, conductivity and electrochemical detectors.[37]

Mobile phase modification detectors are the third type and these change the mobile phase post-column to produce a change in the properties of the analyte such as creating particles suspended in a gas phase. Detectors that fit into this category include evaporative light scattering and corona discharge detectors.[37]

The final type of detectors use hyphenated techniques; this refers to the use of independent analytical technologies alongside a HPLC system. These include mass spectrometry (LC-MS), which is the most common, infrared spectrometry (LC-IR) and nuclear magnetic resonance (LC-NMR).[37]

Once identified its concentration can be established though the use of previously mentioned calibration curves. These properties are why HPLC has been chosen for this analysis.

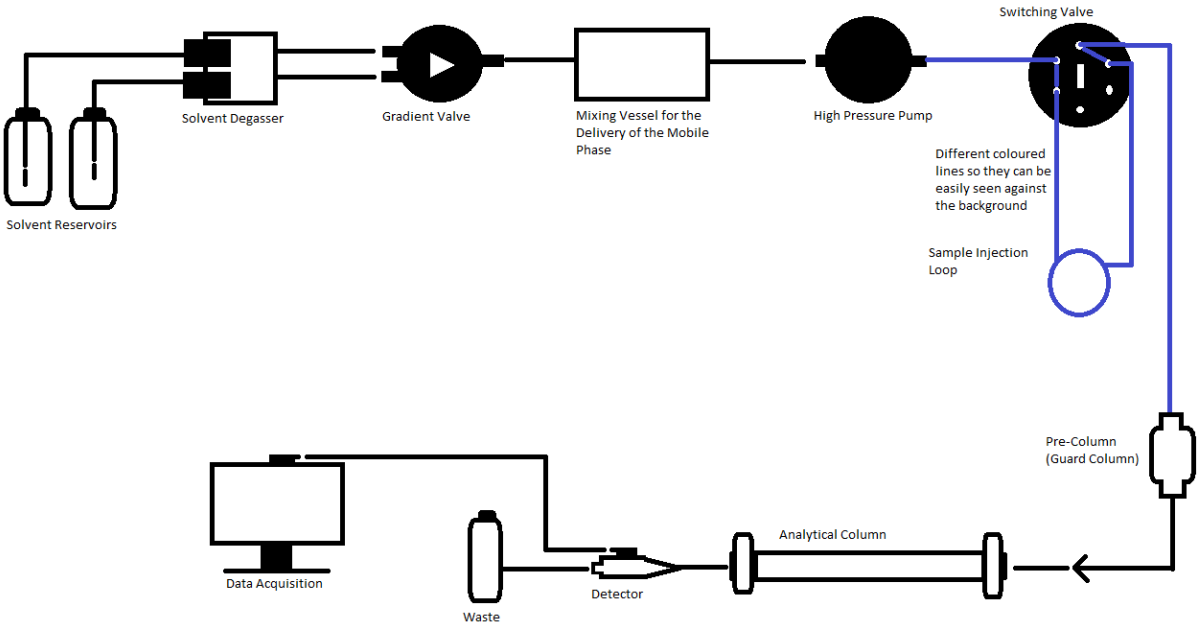


Figure 6. Diagram of HPLC machine.[36]

The HPLC used in this work was a Perkin Elmer LC 90 BIO. The Supercosil™ LC-18 HPLC column with C18 as the matrix active group and a UV detector was used. To analyse the three drugs being looked into two different mobile phases and wavelengths were required. For the analysis of paracetamol and aspirin the wavelength of the machine was set to 254nm and the mobile phase consisted of methanol: water: acetic acid with the ratios of 40: 60: 1.6. For ibuprofen lysine, however the wavelength was set to 220nm and the mobile phase consisted of water: acetonitrile: phosphoric acid with the ratios of 45: 55: 0.045.

2.4 Powder X-Ray Diffraction (XRD)

Powder X-Ray Diffraction (XRD) produces patterns based upon the crystal structure of the compound and gives us information on the composition and structure of the compound analysed, i.e. the unit cell, its thermal parameters, its particle size and the location and nature of its atoms. Any changes in the XRD pattern can be related to a change in the structure or in the shape and contents of the unit cell.

Crystalline substances act like three-dimensional diffraction gratings towards X-ray wavelengths that are similar to the spacing of planes in crystal lattices XRD is based upon the constructive interference of monochromatic waves by a crystalline sample.

The X-rays are generated in a cathode ray tube and then, based on the diffractometer, sometimes filtered to produce monochromatic radiation, collimated to concentrate and then directed towards the sample. The interaction of the incident rays with the sample produces constructive interference and a diffracted ray when the conditions satisfy Bragg's law.

$$n\lambda = 2d\sin\theta$$

Equation 3. Bragg's Law[38]

Equation 3[38] is Bragg's Law, where n is the order of reflection and an integer, λ is the wavelength of the incident X-rays, d is the interplanar spacing of the crystal and θ is the angle of incidence. This law is shown in figure 7[38] and it relates the wavelength of the electromagnetic radiation to the diffraction angle and the lattice spacing in crystalline samples. The diffracted X-rays are detected, processed and counted by the detector. By scanning the sample through a range of angles of incidence all the possible directions of the lattice can be attained due to the random orientation of the powdered material. The d-spacing of the crystal system can be calculated by using the d-spacing equation, though the crystal geometry must be known beforehand as the equation differs dependent on them. For example, equation 4 is the d-spacing equation for cubic crystal systems.

$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2}$$

Equation 4. d-spacing equation for cubic crystal system.[39]

In equation 4 h, k and l represent the miller indices, d represents the d-spacing and a represents the lattice parameters, there is only one as for cubic they are all equal. ZSM-5 is not a cubic crystal system and so this equation does not apply to it. ZSM-5's crystal system is orthorhombic and equation 5 is the d-spacing equation for orthorhombic, with h, k and l representing the miller indices, d representing the d-spacing and a, b and c representing the lattice parameters.

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

Equation 5. d-spacing equation for orthorhombic crystal system.[39]

The intensity of the peaks in the diffraction patterns can be calculated using equation 6 where I_{hkl} is the intensity, K is a proportionality constant, $(Lp)_{hkl}$ is the Lorentz-Polarisation factor, which contains two parts, the Lorentz factor and the polarisation factor, j_{hkl} is the multiplicity of the {hkl} planes, W_{hkl} is the Debye temperature correction factor, A_{hkl} is the absorption factor and F_{hkl} is the structure factor.

$$I_{hkl} = K(Lp)_{hkl} j_{hkl} F_{hkl}^2 e^{-2w} . A_{hkl}$$

Equation 6. Intensity equation for a diffracted X-ray peak[40]

The Lorentz factor is a function of θ and is dependent on the geometry of the experiment and the polarisation factor is used to correct for the unpolarised nature of the X-rays produced by the X-ray tube. These X-rays are at their most intense when either parallel or antiparallel to the incident beam and at their weakest when perpendicular. The correction done by these factors is in the form of $\frac{1}{2}(1 + cos^2 2\theta)$. The multiplicity term, j_{hkl}, takes into account the amount of equivalent reflections that can give rise to a single powder line, for example the (122), (212) and (221) reflections for a cubic material will all have the same d-spacing and so make a single line. The absorption factor is related to the geometry of the experiment and the Debye temperature corrects for the thermal motion of the atoms in the crystal, as when they vibrate the intensity is reduced. The structure factor of a particular lattice plane is shown in equation 7[40], where f_i, the atomic scattering factor, is the sum of the scattering from each electron and therefore is dependent on the atomic number.

$$F_{hkl} = \sum_{\substack{all \\ lattice \\ points}} \sum_{n=1}^{n=N} f_i [\cos 2\pi (hx_i + ky_i + lz_i) + i \sin 2\pi (hx_i + ky_i + lz_i)]$$

Equation 7. Structure factor equation[40]

The powder XRD data were collected on a Bruker D2 phaser using $CuK_{\alpha 1 \alpha 2}$ radiation (λ = 1.5418Å average) operating in θ-θ geometry and equipped with a LynxEye PSD detector. The scan range was 5-80°2θ with a scan time of 20 minutes. Pawley fits were performed on the data using the programs TOPAS and Jedit, Pawley fits themselves being a process in which observed peaks in a powder pattern are fitted

without a structural model but with 2-theta values that are constrained by the size and symmetry of the unit cell and can be used to give an indication of the best fit possible from a structural refinement.

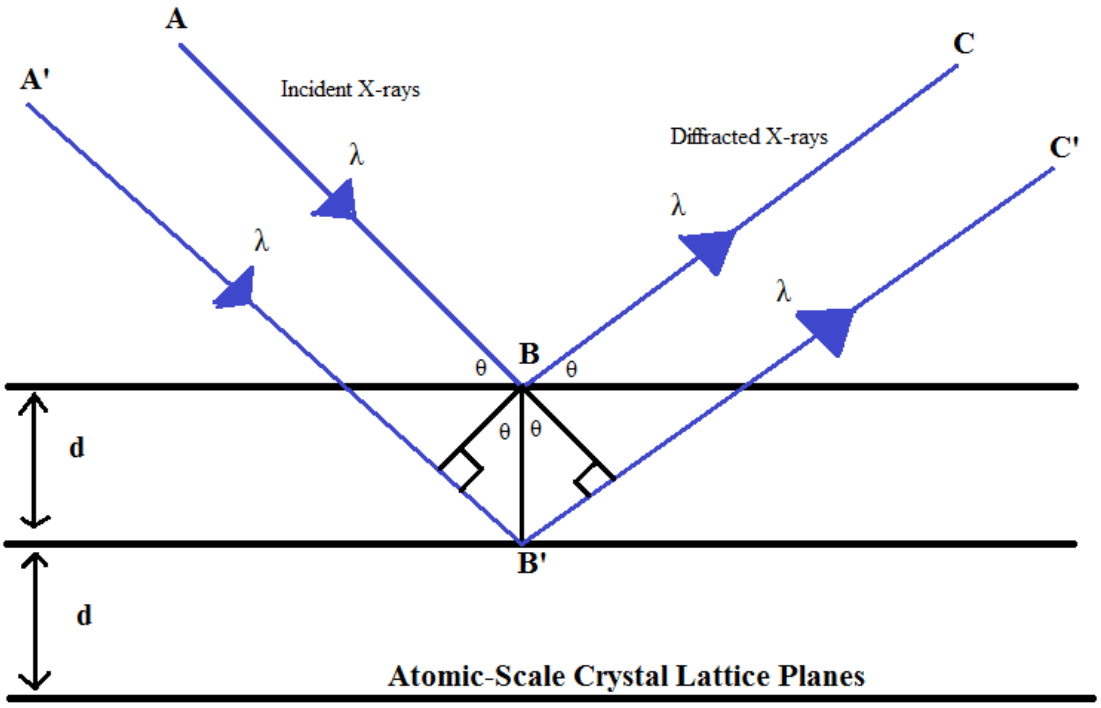


Figure 7. Bragg's Law reflection. The diffracted X-rays exhibit constructive interference when the distance between paths ABC and A''C' differs by an integer number of wavelengths (λ).[38]

If the relative intensities of the peaks change then this indicates a change in the chemical contents of the unit cell. If this change was shown in a ZSM-5 XRD pattern after being introduced to the aqueous drug solutions it would indicate that something has been taken up into the zeolite, and when taken in context, that the drug had been adsorbed. If for example the peaks were to shift to the left or right this would indicate a change in the unit cell, either compressing or expanding it. If the peaks shift to the right, towards the higher 2-theta values, then the unit cell would be compressed whereas if the peaks shifted towards the left, towards the lower 2-theta values, then the unit cell would be stretched though this can be somewhat dependent on the cell symmetry. This effect is illustrated by equation 3, Bragg's Law, the 2-theta value being inversely proportional to the d-spacing. Due to ZSM-5 and zeolites in general

having a rather high level of flexibility when it comes to their unit cells this could be caused by the adsorption of the drug in the solution. This technique shall be used alongside HPLC analysis to confirm that the drug being analysed has been taken up into the ZSM-5 and not lost in some other fashion. An example of a XRD pattern is shown in figure 8, this pattern being from pure ZSM-5 ammonium 30:1.

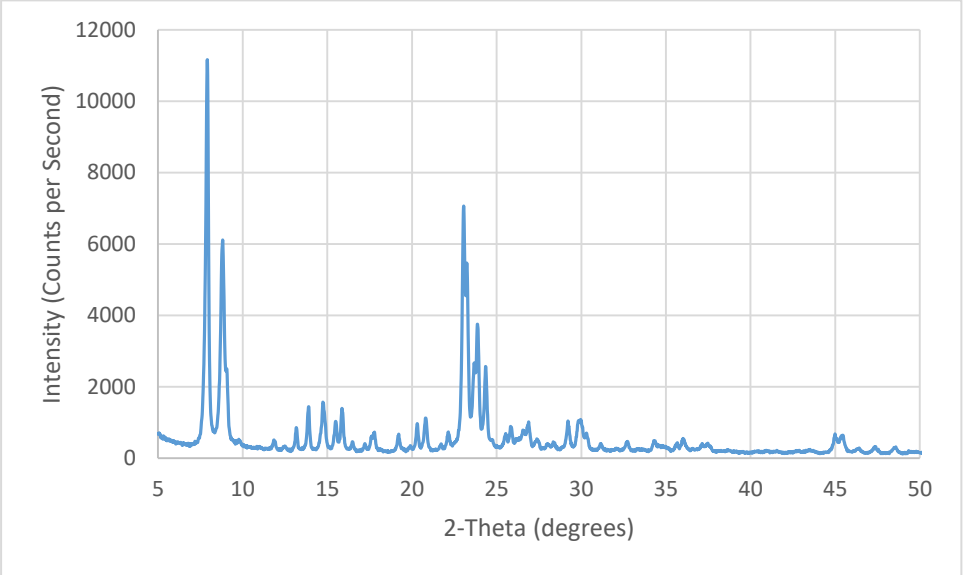


Figure 8. The powder XRD pattern for ZSM-5 ammonium 30:1.

2.5 Scanning Electron Microscope with Energy Dispersive X-Ray Spectroscopy (SEM EDX)

Scanning Electron Microscopes (SEM) allows for the production of high resolution images of the surface of materials with resolution better than 1 nanometre. An electron beam is scanned across a sample's surface and when the electrons strike the sample a variety of signals are generated. The interpretation of these signals is how the images produced by an SEM are formed. The three signals most important in an SEM and the ones that provide the most information are the secondary electrons, backscattered electrons and secondary X-rays. Secondary electrons are emitted from the surface of the atoms occupying the top surface of the sample and produce a readily interpretable image of the surface, the contrast of which is determined by the samples morphology. A high-resolution image can be obtained because of the small diameter of the primary electron beam. The backscattered electrons are the primary beam electrons that are 'reflected' by the atoms in the solid. The contrast in the

image produced is determined by the atomic number of the elements in the sample. Therefore, the image will show the distribution of different chemical phases in the sample, but because these electrons are emitted from a depth in the sample the resolution of the image produced is not as good as the one from the secondary electrons.

Interaction of the primary electron beam with atoms in the sample causes shell transitions which result in the emission of an X-ray. This emitted X-ray has an energy that is characteristic of the element that produced it or the parent element. Detection and measurement of these X-rays and their energy allows for elemental analysis; this is known as Energy Dispersive X-ray Spectroscopy (EDX). It is this aspect of SEM EDX that is useful for this research as it is needed to confirm whether the ion exchanges performed in the experiments are successful as it will allow us to gauge the elemental changes to the ZSM-5 used.

The SEM EDX used for the analysis in this work was a FEI Quanta 200 SEM EDAX. The accelerating voltage of the system was 20kV, a spot size of 6 was used for the EDX analysis as well as having the sample set at a 10mm working distance inside the SEM. Samples were sputter coated with gold before putting them into the SEM to make them more conducting.

3. Results and Discussion – Adsorptions Using Commercial ZSM-5 Ammonium 30:1

3.1 Introduction

The data presented in this chapter has been taken from the adsorptions of paracetamol, aspirin and ibuprofen lysine by the commercial ZSM-5 30:1 used in these experiments. The later chapter will go into the data from the adsorptions where certain properties of ZSM-5 have been changed such as the Si:Al ratio being changed, the charge balancing cation being changed through ion exchange and conditions like reduced concentration of the drug in the solution. The ZSM-5 used for the experiments in this chapter has a Si:Al ratio of 30:1 and its charge balancing cation is ammonium.

3.2 – Paracetamol

A HPLC calibration curve for aqueous paracetamol was produced for the concentrations 0.001M – 0.01M, increasing in 0.001M increments. Table 1 shows the results for this curve. The peak area was plotted against the concentration and a line of best fit was applied and the first five data points were used for the line equation as they produced a straight line with an intercept through zero. This graph is shown in figure 9.

Table 1. Paracetamol HPLC calibration curve.

Paracetamol Standards Concentration (M)	Peak Area (mVmin)	Retention Time (mins)	Height (mV)
0.005	517.1415	2.979	2272.58
0.004	463.3413	2.978	2141.348
0.003	355.0007	2.975	1746.598
0.002	248.4916	2.973	1229.889
0.001	132.6921	2.969	636.163

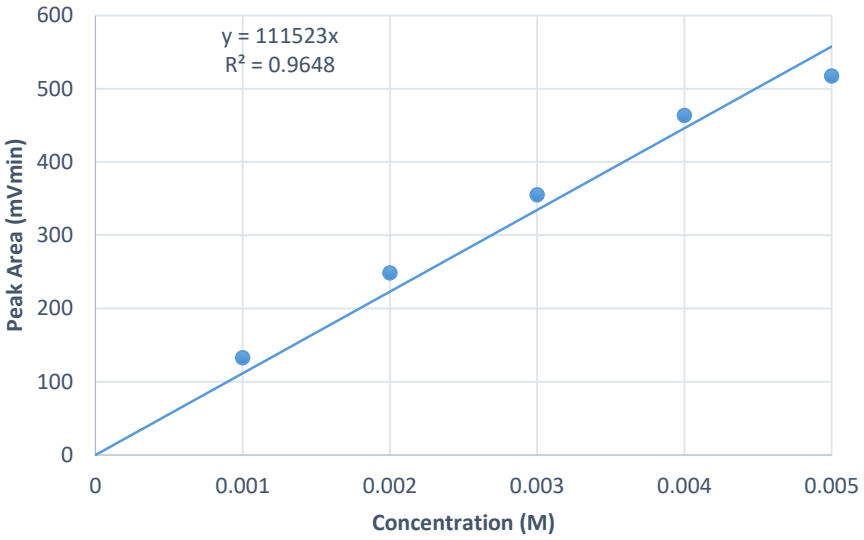


Figure 9. Paracetamol HPLC calibration curve with the equation of the line included.

This calibration curve's equation was used to calculate the concentration of the paracetamol left in the solution after the adsorptions. This calibration curve was used for all paracetamol adsorptions presented in this work. Table 2 shows the HPLC data produced by the adsorption reactions between 2 and 48 hours. Included are the concentration of the drug left in solution, the concentration of the drug that was adsorbed and the percentage of the overall concentration that was adsorbed. A plot showing concentration adsorbed by the zeolite against contact time is presented in figure 10.

Table 2. HPLC results for the paracetamol adsorptions by ZSM-5 ammonium 30:1.

Paracetamol Concentration Left in Solution (M)	Peak Area (mVmin)	Contact Time (Hours)	Retention Time (mins)	Height (mV)	Concentration Adsorbed by the Zeolite (M)	% Concentration Adsorbed
0.00219	244.2899	2	1.765	1892.936	0.00281	56.1902
0.00228	254.2914	4	1.779	2057.026	0.00272	54.3966
0.00230	256.1782	6	1.775	2022.073	0.00270	54.0582
0.00178	198.5878	8	3.513	1133.016	0.00322	64.3862
0.00414	461.4787	10	3.690	2175.915	0.00086	17.2406
0.00221	246.1849	24	1.779	1927.387	0.00279	55.8504
0.00224	249.8804	48	1.776	1940.49	0.00276	55.1876

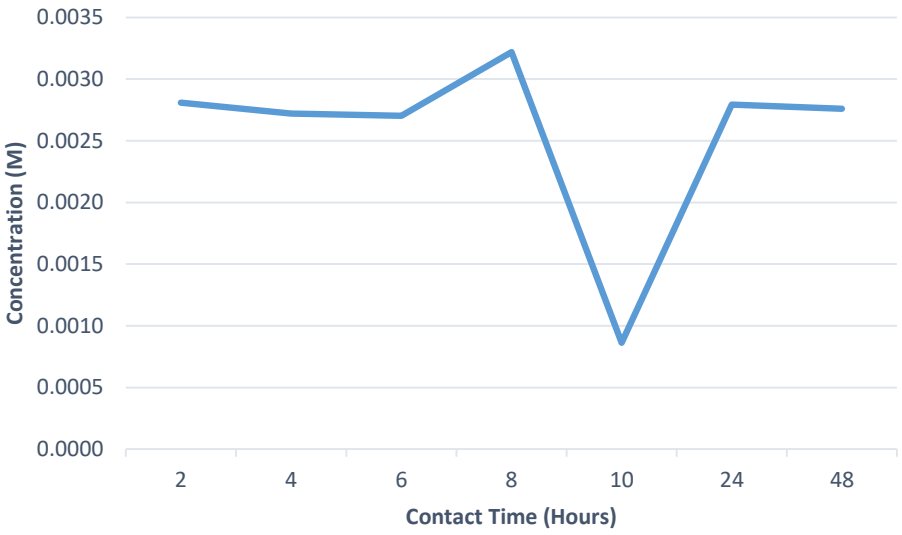
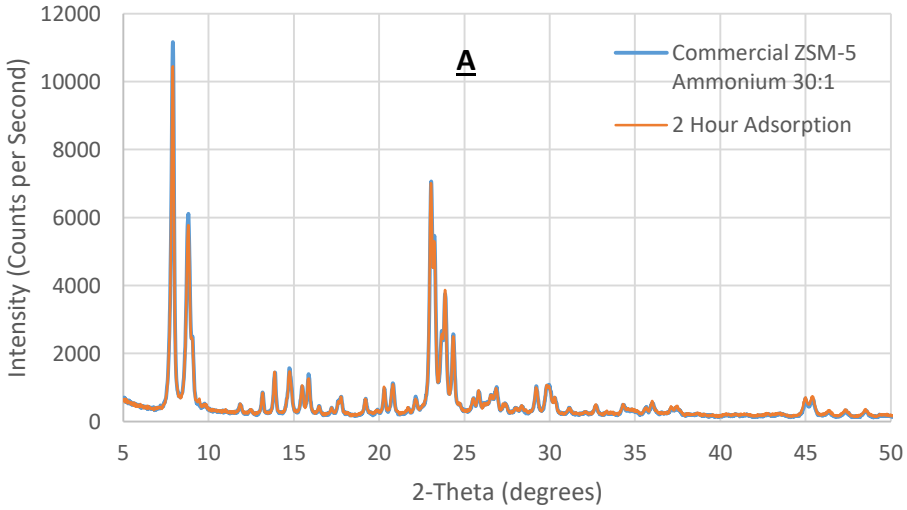


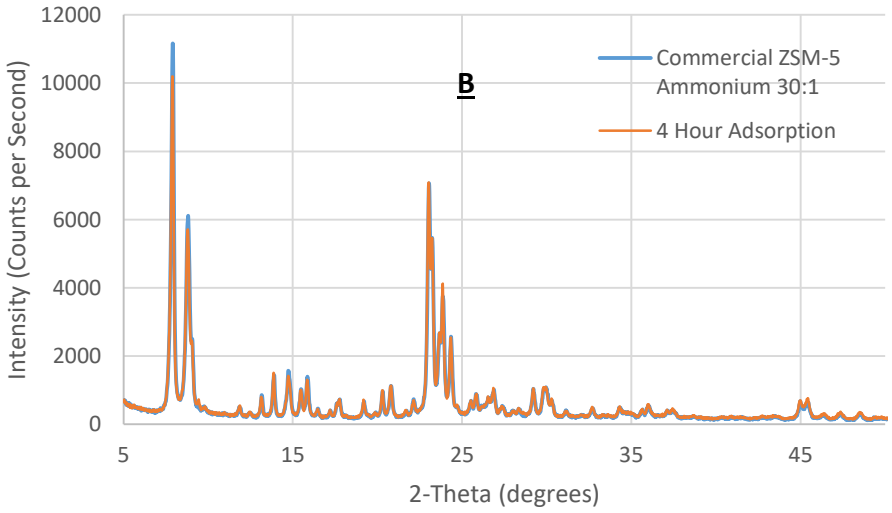
Figure 10. Graph depicting concentration of paracetamol adsorbed by ZSM-5 ammonium 30:1 against contact time.

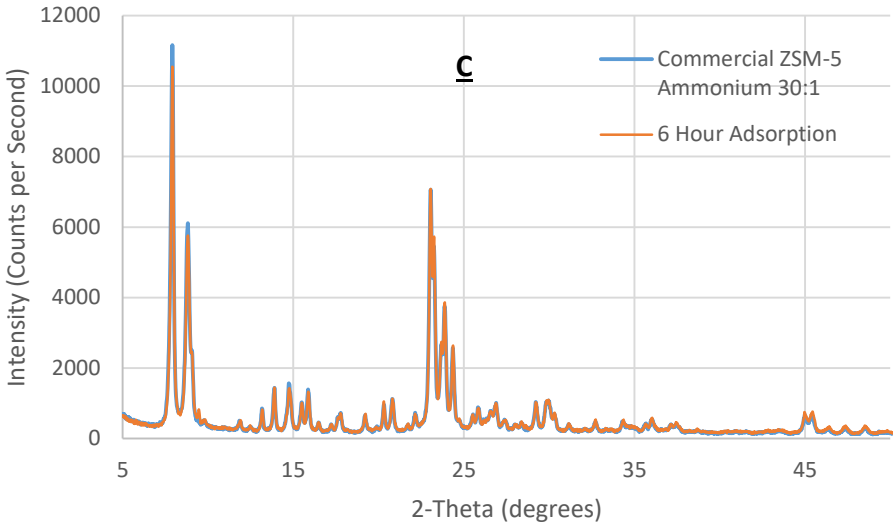
As the data shows it seems that the optimum contact time for the maximum adsorption is eight hours, with an adsorption of 0.0032M equating to 64.39% of the initial concentration being adsorbed. This then drops drastically between eight and ten hours, adsorbing only 0.0009M or 17.24% of the overall concentration at this contact time. The retention times for the eight and ten hour adsorptions differ from the retention times for the rest of the adsorptions as these were completely redone to verify the validity of their concentrations and were ran in a separate batch of mobile phase, this different batch is the reason for their differing retention times. The data was kept because the concentrations being found were congruent with the previously found concentration for these adsorptions. After this the adsorption increases to 0.0028M or 55.19% adsorbed for 24 and 48 hours. It seems that this is the equilibrium concentration adsorbed as two to six hours have similar adsorptions, ranging from 54-56% adsorbed. Further research is required to find out the exact point at which is starts to desorb the paracetamol between eight and ten hours because 8 hours is not necessarily the point at which the concentration adsorbed starts to drop but as it stands with a contact time of eight hours ZSM-5 ammonium 30:1 seems to be suitable for removing paracetamol from an aqueous solution. To confirm that the paracetamol has been adsorbed into the pores of ZSM-5 and not absorbed on to the surface of the particles powder XRD was performed on the filtered solid after adsorption had occurred. As a basis, the commercial ZSM-5 ammonium 30:1 XRD

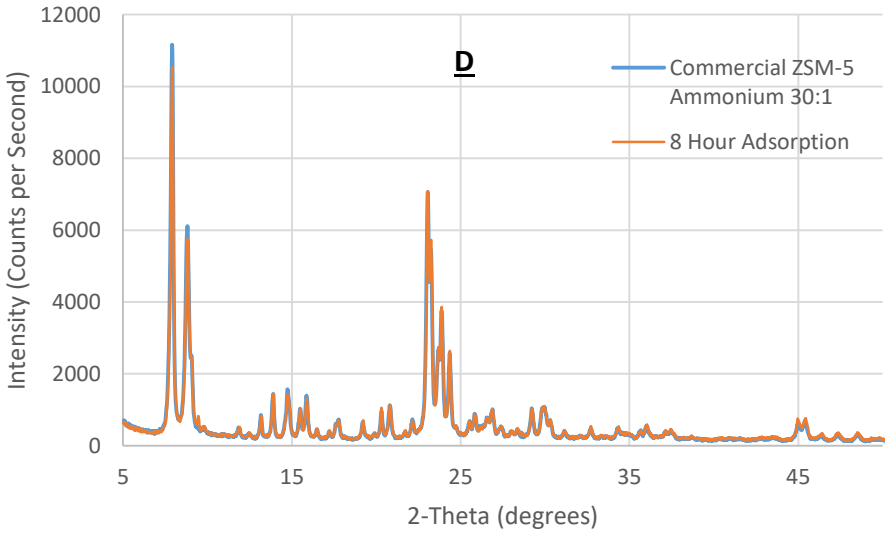
pattern is included in figure 8 and shall have the adsorption patterns overlaid onto it in any further XRD patterns in this chapter.

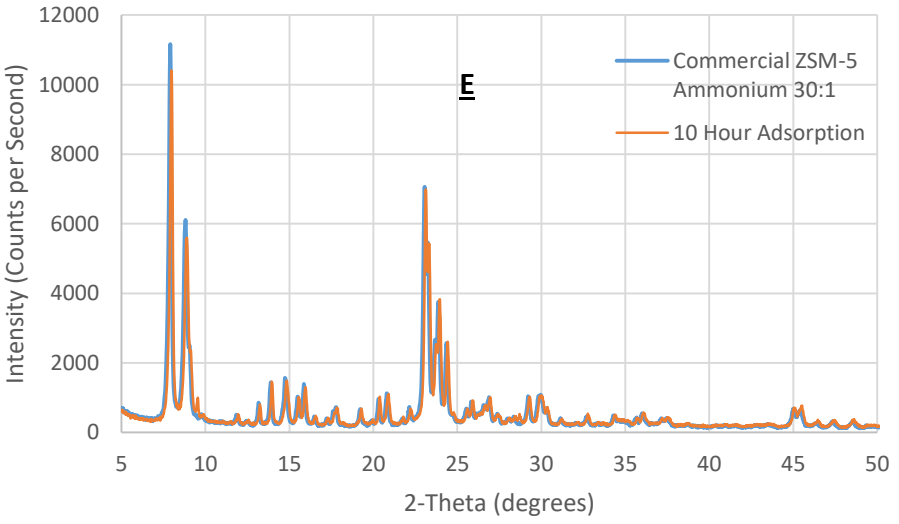
The diffraction patterns for the post adsorption ZSM-5 is shown in figure 11 with the post adsorption pattern overlaid onto the pre-adsorption pattern.






C
Commercial ZSM-5 Ammonium 30:1
6 Hour Adsorption
Intensity (Counts per Second)
2-Theta (degrees)
12000
10000
8000
6000
4000
2000
0
5
15
25
35
45


D
Commercial ZSM-5 Ammonium 30:1
8 Hour Adsorption
Intensity (Counts per Second)
2-Theta (degrees)
12000
10000
8000
6000
4000
2000
0
5
15
25
35
45


E
Commercial ZSM-5 Ammonium 30:1
10 Hour Adsorption
Intensity (Counts per Second)
2-Theta (degrees)
12000
10000
8000
6000
4000
2000
0
5
10
15
20
25
30
35
40
45
50

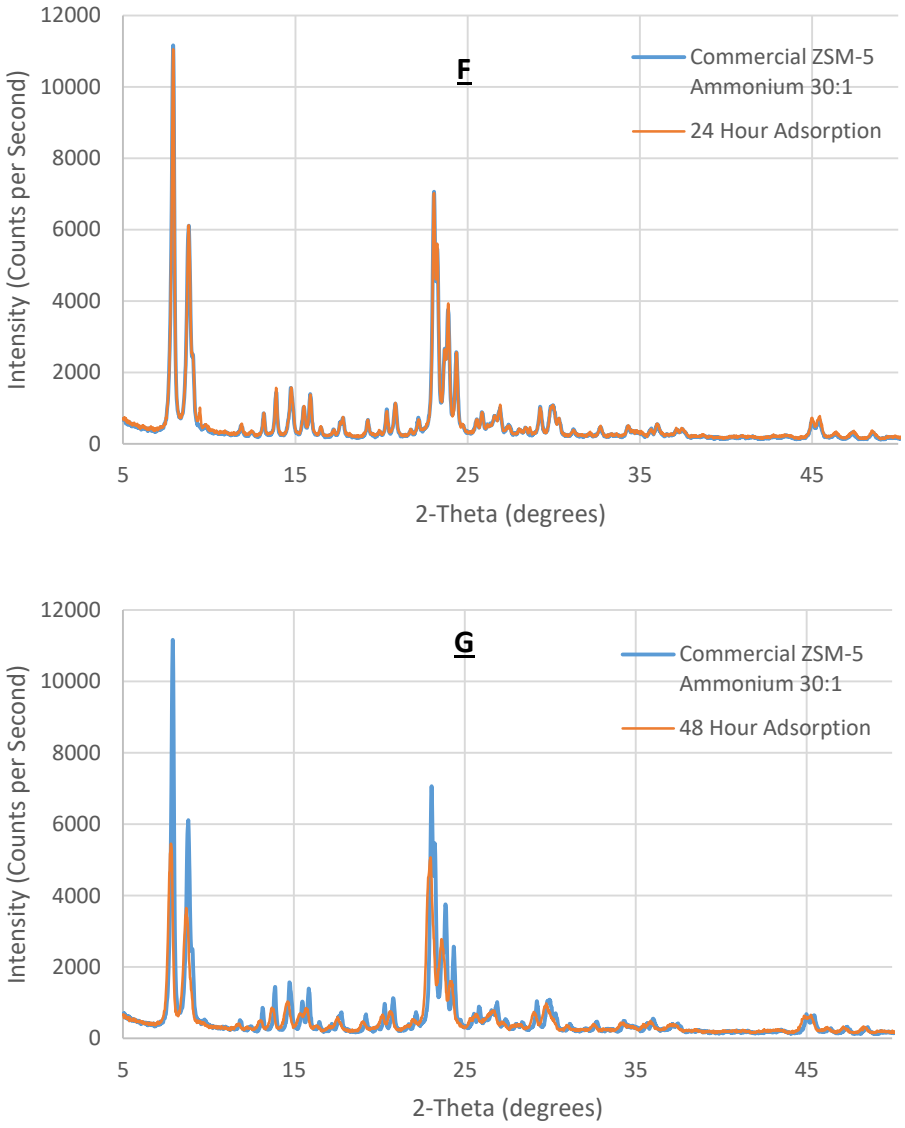


Figure 11. A) Commercial ZSM-5 Ammonium 30:1 + ZSM-5 30:1 post 2-hour paracetamol adsorption. B) Commercial ZSM-5 Ammonium 30:1 + ZSM-5 30:1 post 4-hour paracetamol adsorption. C) Commercial ZSM-5 Ammonium 30:1 + ZSM-5 30:1 post 6-hour paracetamol adsorption. D) Commercial ZSM-5 Ammonium 30:1 + ZSM-5 30:1 post 8-hour paracetamol adsorption. E) Commercial ZSM-5 Ammonium 30:1 + ZSM-5 30:1 post 10-hour paracetamol adsorption. F) Commercial ZSM-5 Ammonium 30:1 + ZSM-5 30:1 post 24-hour paracetamol adsorption. G) Commercial ZSM-5 Ammonium 30:1 + ZSM-5 30:1 post 48-hour paracetamol adsorption.

All seven XRD patterns show some difference when compared to the original, commercial ZSM-5. All the patterns have some form of reduction in relative peak intensity in multiple peaks within the range of 5^{o}-23^{o} 2-theta. The biggest difference is seen in the first two peaks at 7.91^{o} 2-theta and 8.82^{o} 2-theta, with the commercial

ZSM-5 having peak intensities of 11162 counts per second and 6111 counts per second respectively. Post adsorption these peaks were reduced to between 9242-11052 counts per second and 5030-6121 counts per second with the lowest peaks being produced by the 8-hour adsorption and highest being produced by the 24-hour adsorption. This change in relative peak intensity indicates that the contents of the unit cell have changed in some way which would indicate that the adsorption of the paracetamol has been successful. Another indicator is that the post adsorption patterns are shifted to the right a small amount, most notable on the 8 hour and 10 hour adsorptions. The 8-hour adsorption shifts to the right by 0.0606^{o} 2-theta and the 10-hour adsorption by 0.0808^{o} 2-theta. This shift towards a higher 2-theta value indicates a contraction of the zeolite unit cell is occurring. The zeolite framework has a high degree of flexibility and this peak position shift is a further indication that a species has been adsorbed into the pores of the zeolite, in this case paracetamol, though the relatively low shift indicates that this change is negligible. I have not included the 48-hour adsorption XRD pattern into my discussion as I believe this to be an outlier result due to its inconsistent data with respect to the rest of the paracetamol XRD and HPLC results, going from the trend set by the other data it should have a similar XRD pattern to the 2, 4, 6 or 24 hour adsorptions.

The HPLC and XRD data indicate that the paracetamol has been adsorbed by the commercial ZSM-5 30:1 and successfully removed from the solution. The data from the XRD patterns were used to determine the cell parameters to see how the cell structure changed to accommodate the adsorbed paracetamol. The unit cell parameters for commercial ZSM-5 30:1 pre-and post paracetamol adsorption were determined using Topas and J-edit and shown in table 3. A Pawley fit was done using a Chebyshev function background and Pseudo-Voight peak shape function, the zero background and unit cell parameters (*a*, *b*, *c*) were refined to determine errors. The Pawley fit of the commercial ZSM-5 30:1 pre-adsorption is shown in figure 12, as is shown the cif file used[13] is a good fit.

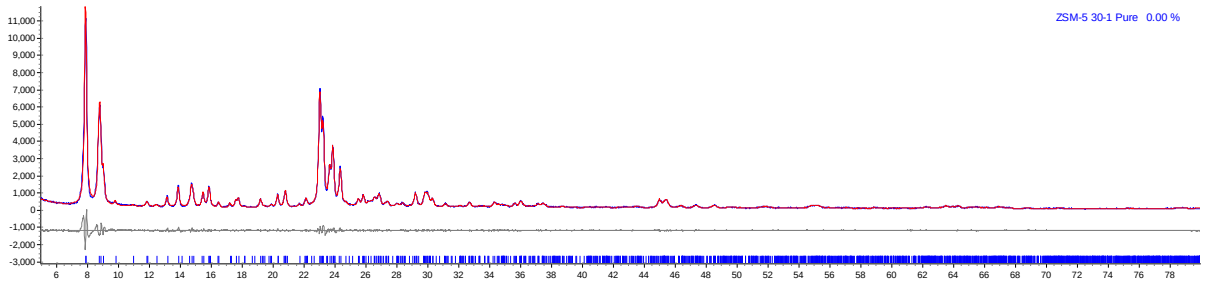


Figure 12. Commercial ZSM-5 30:1 Ammonium Pawley fit against its XRD data.

Table 3. Lattice parameters of commercial ZSM-5 30:1 pre-and post paracetamol adsorption with errors included in brackets.

Contact Time with Paracetamol Solution (Hours)	**RWP**	***a*** **(Å)**	***b*** **(Å)**	***c*** **(Å)**
0	7.466	20.11848(3)	19.92388(2)	13.41704(2)
2	7.369	20.12475(3)	19.93059(2)	13.42273(2)
4	7.479	20.12271(3)	19.92646(2)	13.42233(2)
6	7.378	20.12378(3)	19.92806(2)	13.42322(2)
8	7.059	20.12952(3)	19.92966(2)	13.42709(2)
10	8.192	20.11720(4)	19.92717(3)	13.41934(3)
24	7.963	20.11900(4)	19.92830(3)	13.42093(3)
48	7.672	20.18986(9)	19.91643(9)	13.45545(5)

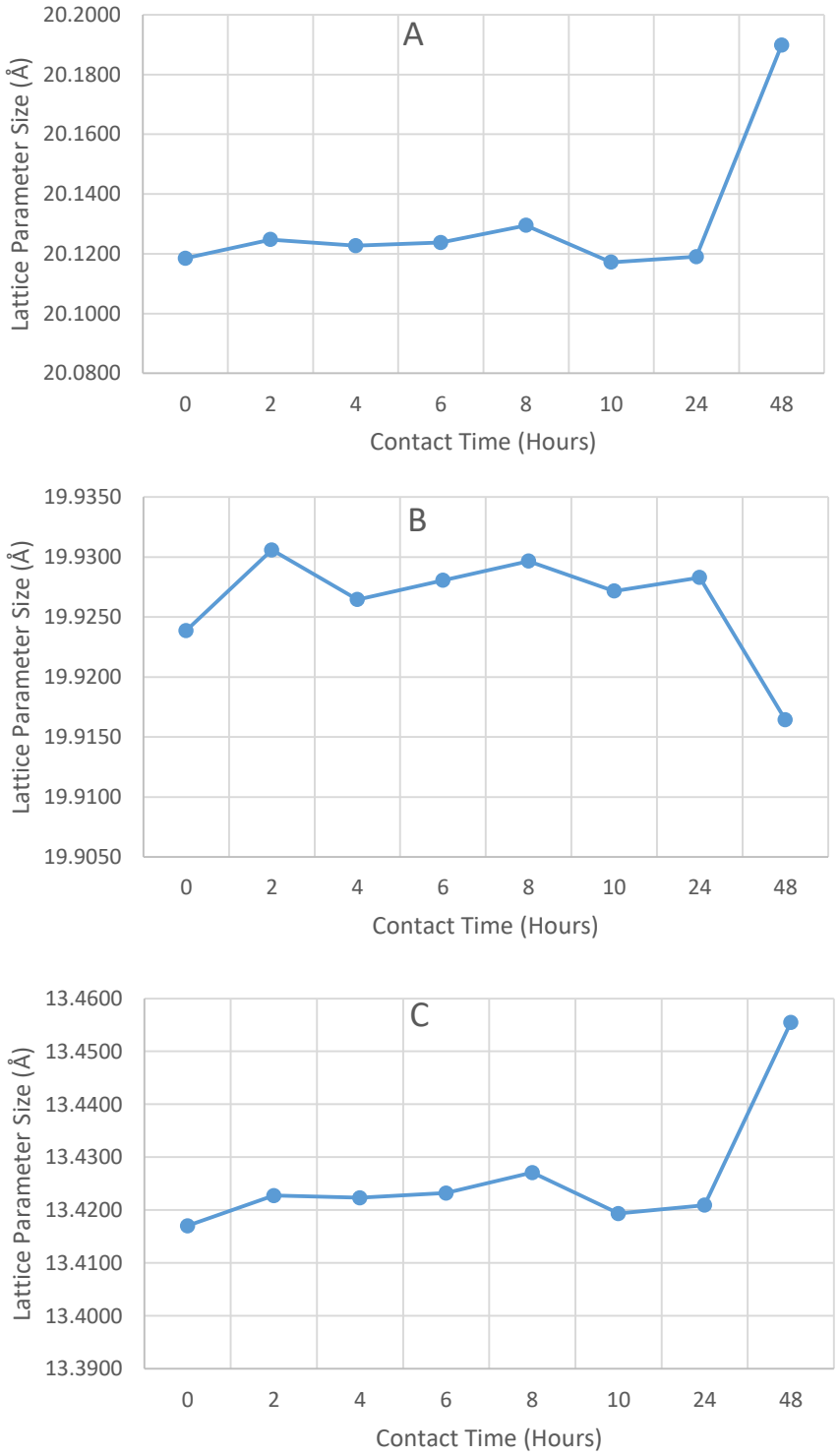


Figure 13. A) Change in lattice parameter *a* against ZSM-5 30:1 contact time with paracetamol. B) Change in lattice parameter *b* against ZSM-5 30:1 contact time with paracetamol. C) Change in lattice parameter *c* against ZSM-5 30:1 contact time with paracetamol.

Figure 13 shows the change in the lattice parameters of ZSM-5 pre-and post paracetamol adsorption and shows all three lattice parameter size changes are related to each other. All three have very similar relative size changes with the only major differences being that parameter *b* has a larger increase in size at 2 hours when compared to parameters *a* and *c*, and that it has a reduction in size for its 48-hour adsorption whereas parameters *a* and *c* increase in size at this contact time. Though as before the results for the 48-hour adsorption is not being considered with regards to the rest of the discussion as it seems to be an outlier with false XRD data. Taking that out then the lattice parameter size changes in relation to the amount of paracetamol adsorbed by ZSM-5. The concentration adsorbed of paracetamol plateaued from 2 to 6 hours and then increased to its most adsorbed at 8 hours, similarly the lattice parameters *a* and *c* size increased from zero contact hours to 2 hours and then plateaued until 6 hours before increasing in size to its largest size at 8 hours, showing an increase of 0.055% for parameter *a* and a 0.075% increase for parameter *c*, which correlates to 64.39% of the paracetamol being adsorbed by ZSM-5. Parameter *b* starts with an increase in size from zero contact hours to 2 seemingly much larger than that of parameter *a* and *c*, increasing by 0.034%, but is in fact similar to the increase for parameter *a* which is an increase of 0.031%. Parameter *c* has the highest initial increase of 0.042%. After 2 hours parameter *b* increases in size steadily up to 8 hours where it has an increase in size of 0.029% from the norm. All three parameters size the drops at 10 hours before increasing in size at 24 hours. Paracetamol is 7.8Å X 4.2Å [41] in size, considering the pore sizes of ZSM-5 are 5.4 X 5.6Å and 5.1 X 5.5Å it would be logical to conclude that some pore expansion would be required for paracetamol to be adsorbed and with the upper limit for molecule adsorption size for ZM-5 being 9.1Å[6] it is completely possible for paracetamol to be adsorbed.

These changes in size corresponding with the changes in the concentration of paracetamol adsorbed indicate that these changes are due to the unit cell expanding to accommodate the paracetamol being adsorbed into the pores of ZSM-5, which confirms that the paracetamol is being adsorbed by the ZSM-5.

3.3 – Ibuprofen Lysine

Ibuprofen lysine was used instead of ibuprofen as it is more polar and more soluble in water making it more suitable for the adsorption experiments. A HPLC calibration curve for aqueous ibuprofen lysine was produced for the concentrations 0.001M – 0.01M, increasing in 0.001M increments. Table 4 shows the results for this curve. The peak area was plotted against the concentration and a line of best fit was applied an intercept through zero. This graph is shown in figure 14.

Table 4. Ibuprofen lysine HPLC calibration curve.

Ibuprofen Lysine Standards Concentrations (M)	Peak Area (mVmin)	Retention Time (mins)	Height (mV)
0.01	760.5942	8.795	1837.132
0.009	707.4346	8.801	1748.334
0.008	644.6036	8.800	1636.957
0.007	562.1113	8.807	1463.294
0.006	493.8933	8.807	1314.598
0.005	415.9444	8.802	1121.824
0.004	329.1105	8.808	889.091
0.003	252.4453	8.816	691.038
0.002	170.936	8.817	472.958
0.001	82.3878	8.825	228.722

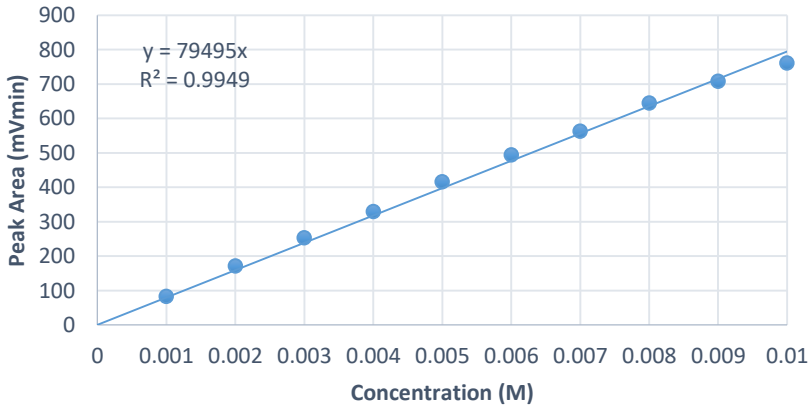


Figure 14. Ibuprofen lysine HPLC calibration curve graph.

This calibration curve's equation was used to calculate the concentration of the ibuprofen lysine left in the solution after the adsorptions. This calibration curve has been used for all ibuprofen lysine adsorptions presented in this work. Table 5 shows

the HPLC data produced by the adsorption reactions. Included are the concentration of the drug left in solution, the concentration of the drug that was adsorbed and the percentage of the overall concentration that was adsorbed. The data is plotted in figure 15.

Table 5. HPLC results for the ibuprofen lysine adsorptions by ZSM-5 ammonium 30:1

Ibuprofen Lysine Samples Concentration Left in Solution (M)	Peak Area (mVmin)	Contact Time (Hours)	Retention Time (mins)	Height (mV)	Concentration Adsorbed by the Zeolite (M)	% Concentration Adsorbed
0.00086	68.6539	2	8.377	259.063	0.00114	56.8187
0.00197	156.9875	4	8.390	809.574	0.00003	1.2595
0.00225	179.2554	6	8.386	919.555	0.00000*	0.0000
0.00156	124.3634	8	8.392	641.871	0.00044	21.7791
0.00211	167.4259	10	9.108	407.518	0.00000*	0.0000
0.00163	129.6220	24	8.388	668.371	0.00037	18.4716
0.00223	177.2387	48	8.389	912.151	0.00000*	0.0000

*These values have been normalised to zero as HPLC data came out with a negative concentration

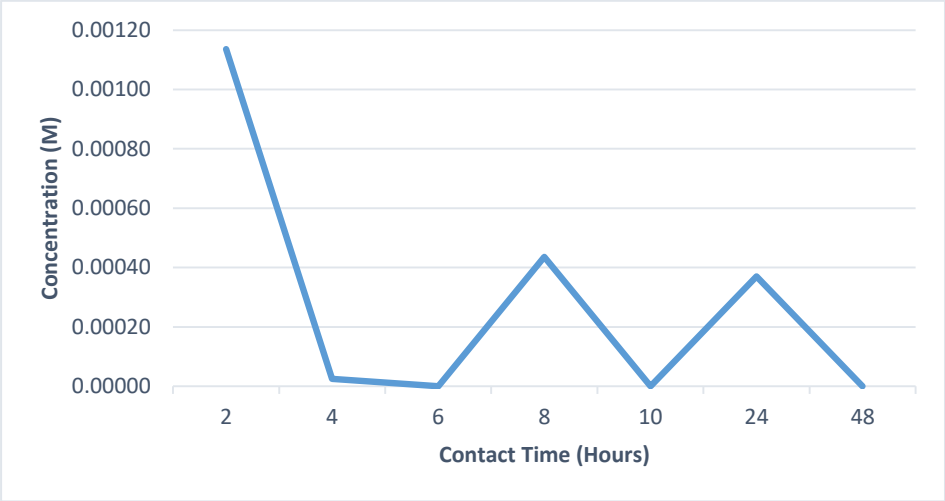
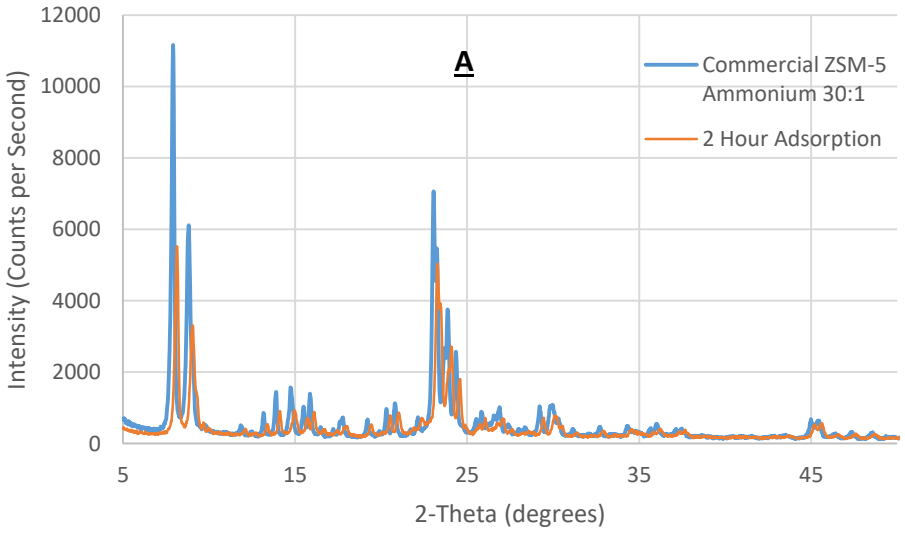


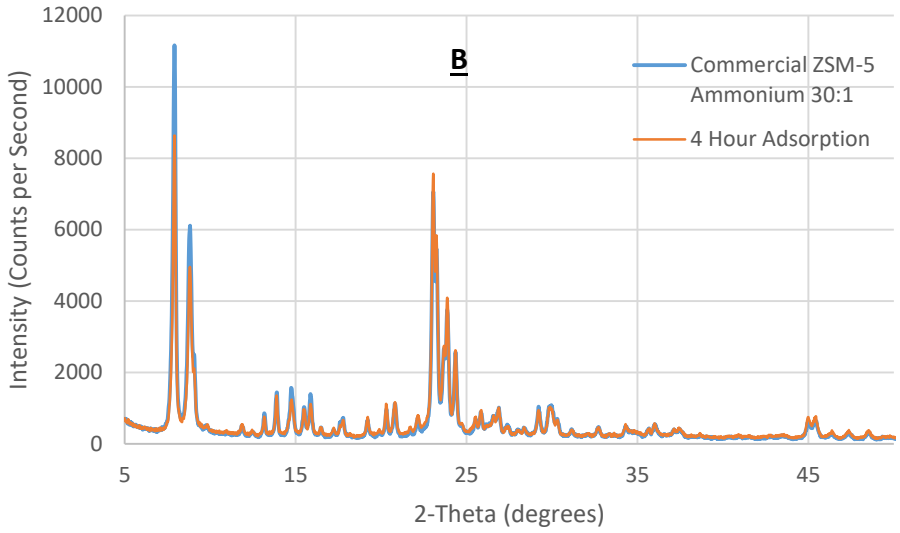
Figure 15. Graph depicting the concentration of ibuprofen lysine adsorbed by ZSM-5 ammonium 30:1 against contact time.

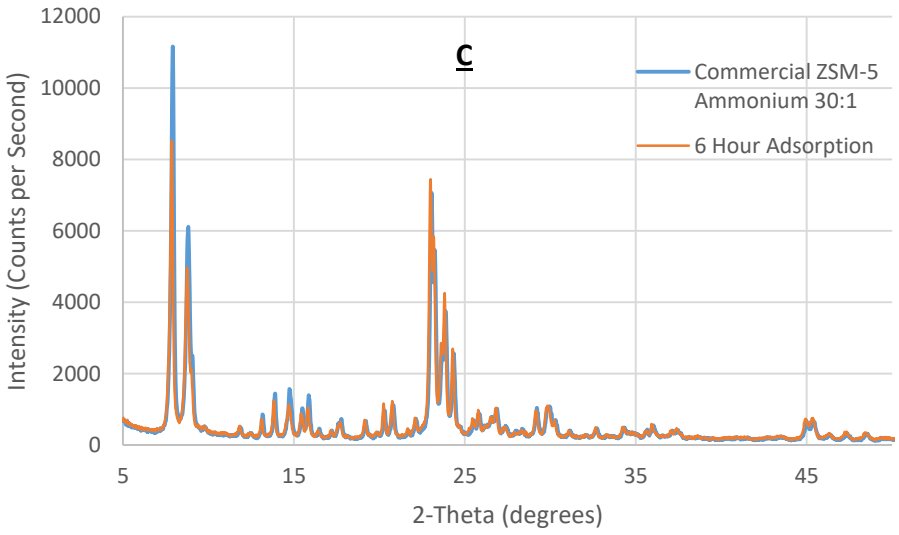
This data indicates that the optimum time for adsorption is two hours and after that the concentration adsorbed drops, going from 56.82% down to at most 21.78% and at least no adsorption occurring at all. The HPLC data indicated that the data points with stars next to them had a negative concentration being adsorbed, as for this to be

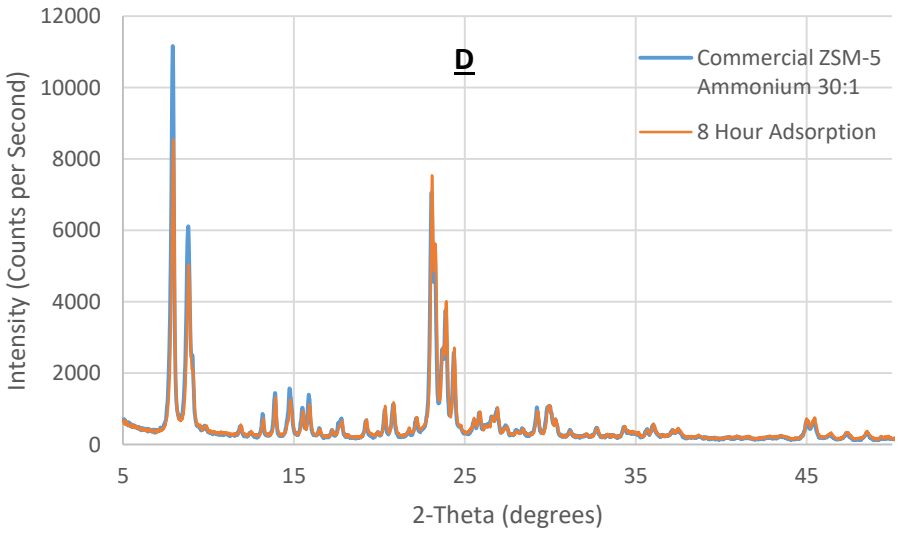
true ibuprofen lysine would have to increase in concentration in the solution spontaneously. Due to its low concentration and the low relative solubility of ibuprofen lysine in general the HPLC machine may have picked up a higher result than possible, if only slightly, causing negative results to appear. These adsorptions were repeated to check validity and consistent results were produced. For the purposes of this research any negative concentration results have been changed to indicate that no ibuprofen lysine was adsorbed, though some may have been the amount is negligible, and these results will be clearly marked on any tables presented in this work. The incongruous retention time of the 10 hour adsorption is due to this adsorption being ran in a different batch of mobile phase to the rest of the adsorptions and was repeated to confirm its validity.

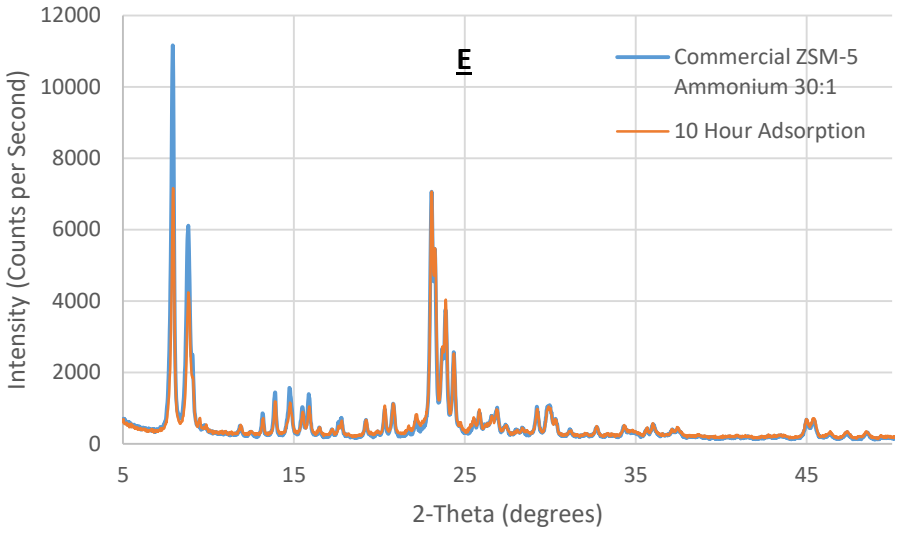
To ascertain that ibuprofen lysine had been adsorbed into the pores of the zeolite and not the surface of the particles XRD was carried out and the data analysed using Pawley fits. The post adsorption XRD patterns overlaid onto the commercial ZSM-5 30:1 XRD pattern, shown in figure 8, are plotted in figure 16 below.

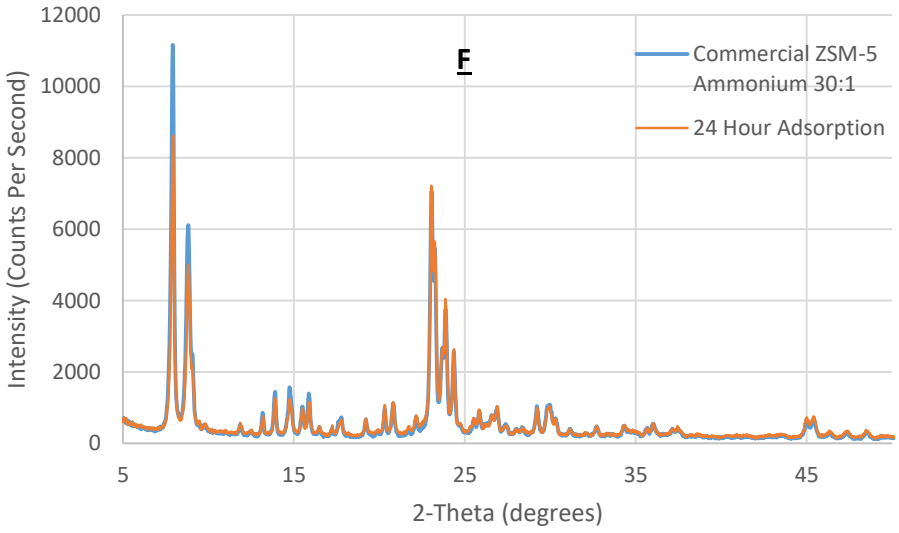



B
Commercial ZSM-5 Ammonium 30:1
4 Hour Adsorption
Intensity (Counts per Second)
2-Theta (degrees)
12000
10000
8000
6000
4000
2000
0
5
15
25
35
45


C
Commercial ZSM-5 Ammonium 30:1
6 Hour Adsorption
Intensity (Counts per Second)
2-Theta (degrees)
12000
10000
8000
6000
4000
2000
0
5
15
25
35
45


D
Commercial ZSM-5 Ammonium 30:1
8 Hour Adsorption
Intensity (Counts per Second)
2-Theta (degrees)
12000
10000
8000
6000
4000
2000
0
5
15
25
35
45


E
Commercial ZSM-5 Ammonium 30:1
10 Hour Adsorption
Intensity (Counts per Second)
2-Theta (degrees)
12000
10000
8000
6000
4000
2000
0
5
15
25
35
45


F
Commercial ZSM-5 Ammonium 30:1
24 Hour Adsorption
Intensity (Counts Per Second)
2-Theta (degrees)
12000
10000
8000
6000
4000
2000
0
5
15
25
35
45

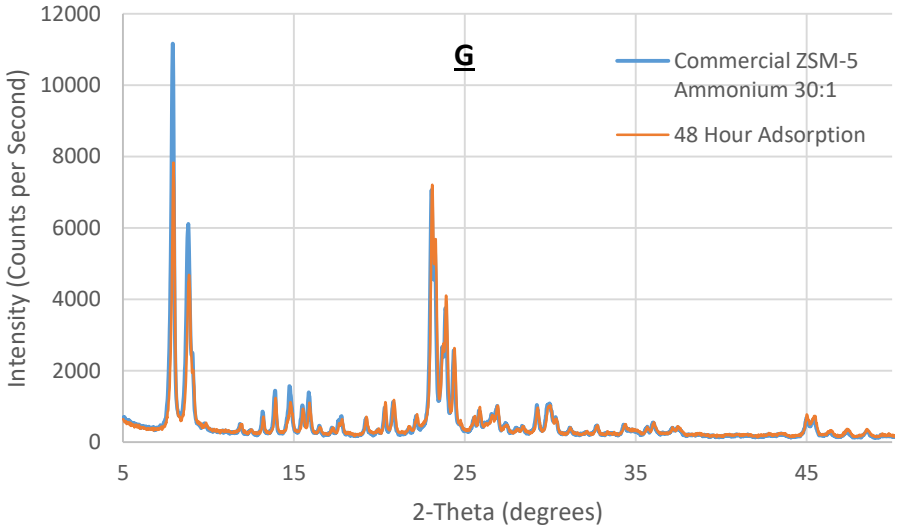

G
Commercial ZSM-5 Ammonium 30:1
48 Hour Adsorption
Intensity (Counts per Second)
2-Theta (degrees)
12000
10000
8000
6000
4000
2000
0
5
15
25
35
45

Figure 16. A) Commercial ZSM-5 Ammonium 30:1 + ZSM-5 30:1 post 2-hour ibuprofen lysine adsorption. B) Commercial ZSM-5 Ammonium 30:1 + ZSM-5 30:1 post 4-hour ibuprofen lysine adsorption. C) Commercial ZSM-5 Ammonium 30:1 + ZSM-5 30:1 post 6-hour ibuprofen lysine adsorption. D) Commercial ZSM-5 Ammonium 30:1 + ZSM-5 30:1 post 8-hour ibuprofen lysine adsorption. F) Commercial ZSM-5 Ammonium 30:1 + ZSM-5 30:1 post 24-hour ibuprofen lysine adsorption. G) Commercial ZSM-5 Ammonium 30:1 + ZSM-5 30:1 post 48-hour ibuprofen lysine adsorption.

All seven XRD patterns show some difference when compared to the original, commercial ZSM-5. All the patterns have some form of reduction in relative peak intensity in multiple peaks within the range of 5^{o}-23^{o} 2-theta and a large overall reduction in relative intensity with the 2-hour adsorption. The biggest difference is seen in the first two peaks at 7.91^{o} 2-theta and 8.82^{o} 2-theta, with the commercial ZSM-5 having peak intensities of 11162 counts per second and 6111 counts per second respectively. Post adsorption these peaks were reduced to 5393 counts per second and 3309 counts per second respectively for the 2-hour adsorption and between 7162-8636 counts per second and 4244-5042 counts per second for the rest of the adsorptions with the lowest peaks being produced by the 10-hour adsorption and highest being produced by the 4-hour adsorption for the 7.91^{o} 2-theta peak and the 8-hour adsorption for the 8.82^{o} 2-theta peak. Further noticeable changes in relative intensity are shown in the 2-hour adsorption, a reduction from 1555 counts per second on the 14.75^{o} 2-theta peak to 932 counts per second, from 7062 counts per second on the 23.05^{o} 2-theta peak to 5034 counts per second and from 3753 counts per second on the 23.86^{o} 2-theta peak to 2715 counts per second. These changes in relative peak intensity indicate that the contents of the unit cell have changed in some way which would indicate that the adsorption of the ibuprofen has been successful. Another indicator is that the post adsorption patterns are shifted a small amount, most notable on the 2-hour adsorption, shifting to the right, and the 6-hour adsorption shifting to the left. The 2-hour adsorption shifts to the right by 0.2423^{o} 2-theta and the 6-hour adsorption shifting to the left by 0.0808^{o} 2-theta. This shift towards a higher 2-theta value indicates a contraction of the zeolite unit cell is occurring. The zeolite framework has a high degree of flexibility and this peak position shift is a further indication that a species has been adsorbed into the pores of the zeolite, in this case ibuprofen, though the relatively low level of shift occurring indicates that this

change is negligible. The biggest change seems to be occurring within the 2-hour adsorption pattern, which lines up with the HPLC results as the 2-hour adsorption has the highest amount of concentration adsorbed.

The data from the XRD patterns were used to determine the cell parameters to see how the cell structure changed to accommodate the adsorbed ibuprofen lysine. The unit cell parameters for commercial ZSM-5 30:1 pre-and post ibuprofen adsorption were determined using Topas and J-edit and presented in table 6. A Pawley fit was done using a Chebyshev function background and Pseudo-Voight peak shape function, the zero background and unit cell parameters (*a*, *b*, *c*) were refined to determine errors.

Table 6. Lattice parameters of commercial ZSM-5 30:1 pre-and post ibuprofen lysine adsorption with errors included in brackets.

Contact Time with Ibuprofen Lysine Solution (Hours)	**RWP**	***a*** **(Å)**	***b*** **(Å)**	***c*** **(Å)**
0	7.466	20.11848(3)	19.92388(2)	13.41704(2)
2	7.634	20.20457(5)	19.94301(3)	13.43105(3)
4	6.799	20.12280(3)	19.93512(2)	13.42727(2)
6	7.170	20.12198(4)	19.93152(2)	13.42720(2)
8	7.195	20.11385(4)	19.92755(2)	13.42167(2)
10	7.047	20.14066(4)	19.94453(2)	13.43933(2)
24	6.847	20.12434(4)	19.93571(2)	13.42845(2)
48	6.855	20.12592(4)	19.93224(2)	13.42836(2)

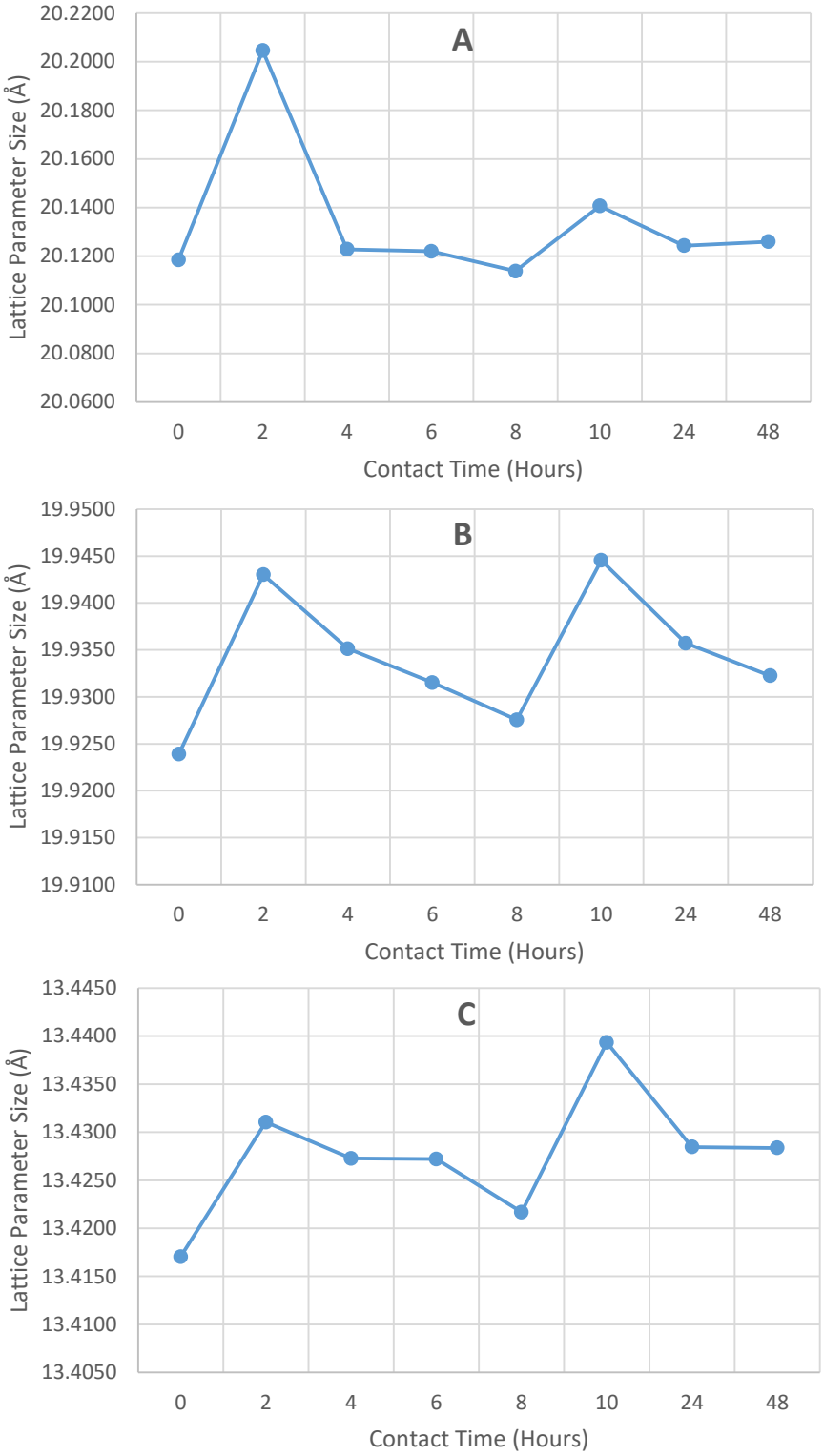


Figure 17. A) Change in lattice parameter *a* against ZSM-5 30:1 contact time with ibuprofen lysine. B) Change in lattice parameter *b* against ZSM-5 30:1 contact time with ibuprofen lysine. C) Change in lattice parameter *c* against ZSM-5 30:1 contact time with ibuprofen lysine.

Figure 17 shows the change in the lattice parameters of ZSM-5 pre-and post ibuprofen lysine adsorption and shows all three lattice parameter size changes are related to each other in some capacity. All three increase from 0-2 hours a large amount, 0.43% for parameter *a* and 0.10% for parameters *b* and *c*. Then all three reduce in overall size between 2-8 hours, -0.45% for parameter *a*, -0.08% for parameter *b* and -0.07% for parameter *c*. This coincides with the HPLC results as 56.82% of the concentration was adsorbed from the solution at 2 hours and this was reduced to 0% at 6 hours and 21.78% at 8 hours. All three then increase in size from 8-10 hour and then reduce in size again from 10-48 hours, except for parameter *a* having a slight increase from 24-48 hours. Having an increase in size from 8-10 seems to indicate that the desorption of ibuprofen lysine caused the lattice parameters to increase in size, this is inconsistent with the rest of the data which shows a relative reduction in size at 6 hours and 48 hours when the concentration adsorbed is also 0. Taking out 10 hours there is a correlation with the HPLC results that a higher percentage of concentration leads to a larger size for all 3 lattice parameters. Ibuprofen lysine is 8.9Å X 3.8Å[42] in size, the pore sizes of ZSM-5 are 5.4 X 5.6Å and 5.1 X 5.5Å so it would be logical to conclude that some pore expansion would occur to allow for ibuprofen lysine to be adsorbed and with the upper limit for molecule adsorption size for ZM-5 being 9.1Å[6] it is completely possible for ibuprofen to be adsorbed, conversely though it may be this large size that is inhibiting its adsorption into ZSM-5. Due to this commercial ZSM-5 ammonium 30:1 has been found to not be a viable compound for the removal of ibuprofen lysine from aqueous solution.

3.4 – Aspirin

The aspirin solution post adsorption produced HPLC result with two peaks instead of one. This indicated that the aspirin degraded into at least two products. For this some experimentation was required and it was found out that the first peak corresponded with pure acetylsalicylic acid (i.e. aspirin) and salicylic acid. This means that sometime while it was in its aqueous form it partially broke down into salicylic acid and acetic acid. The mechanism for the degradation of aspirin in aqueous solution is shown in figure 18[43]. For the HPLC calibration curves for aspirin two were made up, one from pure acetylsalicylic acid and one from pure salicylic acid. These are

represented in table 7 and figure 19 for acetylsalicylic acid and table 8 and figure 20 for salicylic acid. The line equation from figure 19 being used to determine the concentration of the first HPLC peak, the line equation from figure 20 being used for the concentration of the second HPLC peak.

$$Aspirin + Water \rightarrow Salicylic\ Acid + Acetic\ Acid$$

$$C_9H_8O_4 + H_2O \rightarrow C_7H_6O_3 + C_2H_4O_2$$

Figure 18. Aspirin degradation mechanism.[43]

Table 7. Acetylsalicylic acid HPLC calibration curve.

Acetyl Salicylic Acid Standards Concentration (M)	Peak Area (mVmin)	Retention Time (min)	Height (mV)
0.001	9.9330	6.749	35.479
0.002	19.8956	6.740	70.903
0.003	29.4265	6.714	104.295
0.004	39.1061	6.724	137.71
0.005	49.0458	6.713	171.942
0.006	59.0977	6.713	206.907
0.007	69.3670	6.711	242.319
0.008	77.6219	6.705	269.304
0.009	88.4570	7.420	279.23
0.01	97.5896	7.349	307.972

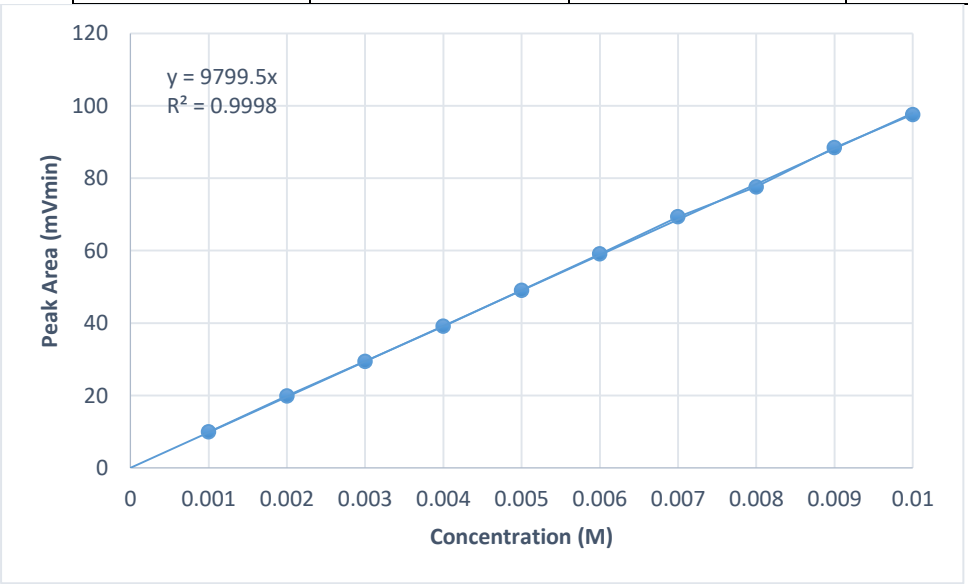


Figure 19. Acetylsalicylic acid HPLC calibration curve graph.

Table 8. Salicylic acid HPLC calibration curve.

Salicylic Acid Standards Concentration (M)	Peak Area (mVmin)	Retention Time (mins)	Height (mV)
0.01	86.1949	10.046	223.323
0.009	73.9693	10.065	201.481
0.008	74.8316	10.063	189.282
0.007	68.1971	10.060	166.64
0.006	53.7704	10.092	140.216
0.005	45.6968	10.097	118.49
0.004	40.0593	10.125	98.005
0.003	29.806	10.169	73.802
0.002	20.1126	10.212	49.353
0.001	9.7841	10.287	24.224

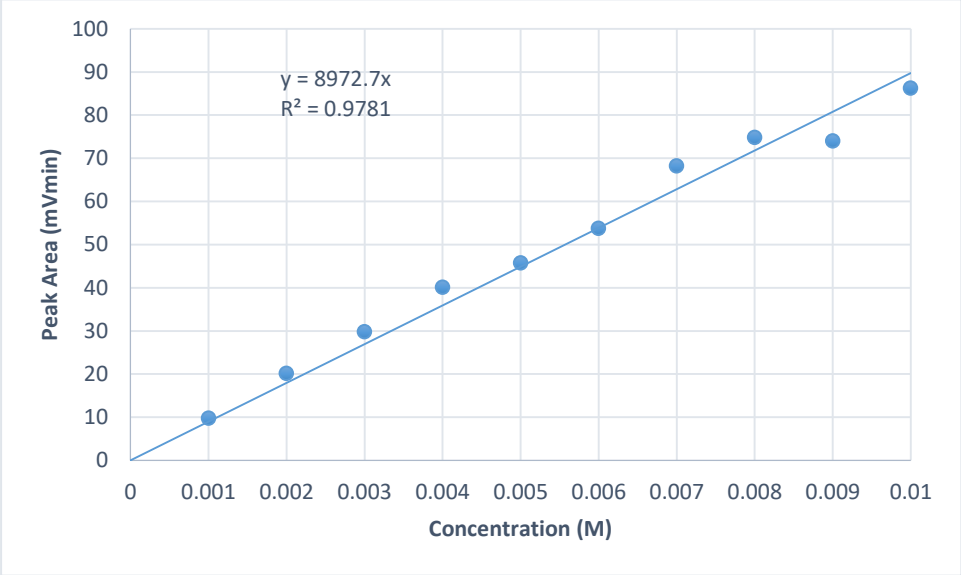


Figure 20. Salicylic acid HPLC calibration curve graph.

Using the line equations, the concentrations of the peaks were calculated separately and then added together to produce the overall concentration left in the aqueous solution and from there the concentration adsorbed by ZSM-5. The results from the first HPLC peak are depicted in table 9 and table 10 for the second peak. The combined concentration results as well as the concentration adsorbed and percentage adsorbed by ZSM-5 are shown in table 11. A graph with combined concentration adsorbed against contact time is shown in figure 21.

Table 9. Aspirin peak 1 HPLC results

Aspirin Tablet Samples Peak 1 Concentration Left in Solution (M)	Peak Area (mVmin)	Contact Time (Hours)	Retention Time (min)	Height (mV)
0.0020	19.3766	2	8.037	97.393
0.0019	19.0242	4	8.004	95.762
0.0021	20.6857	6	8.130	102.869
0.0002	2.0689	8	7.040	11.487
0.0012	12.0469	10	4.248	68.765
0.0014	13.7907	24	8.065	66.972
0.0013	12.6718	48	8.011	64.19

Table 10. Aspirin peak 2 HPLC results.

Aspirin Tablet Samples Peak 2 Concentration Left in Solution (M)	Peak Area (mVmin)	Contact Time (Hours)	Retention Time (mins)	Height (mV)
0.0013	11.9075	2	11.806	42.234
0.0013	11.9620	4	11.766	42.202
0.0009	8.0997	6	11.935	28.913
0.0027	24.5764	8	10.635	94.237
0.0010	8.8900	10	7.058	31.836
0.0011	9.8382	24	11.898	33.926
0.0020	17.9634	48	11.77	62.784

Table 11. Aspirin combined concentrations HPLC results.

Aspirin Tablet Samples Combined Concentrations Left in Solution (M)	Contact Time	Concentration Adsorbed by the Zeolite	% Concentration Adsorbed
0.0033	2	0.0017	33.9123
0.0033	4	0.0017	34.5100
0.0030	6	0.0020	39.7280
0.0030	8	0.0020	40.9972
0.0022	10	0.0028	55.5976
0.0025	24	0.0025	49.9251
0.0033	48	0.0017	34.0977

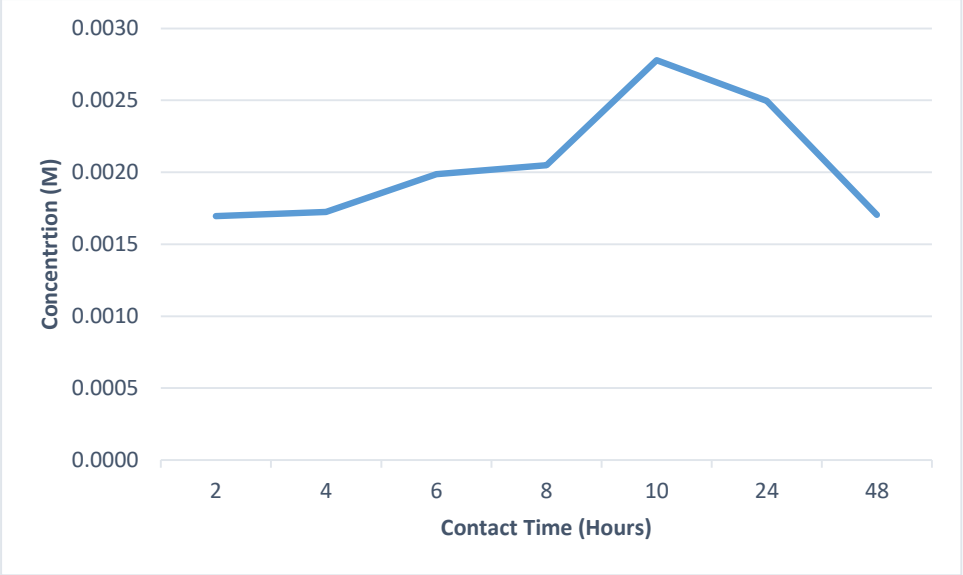
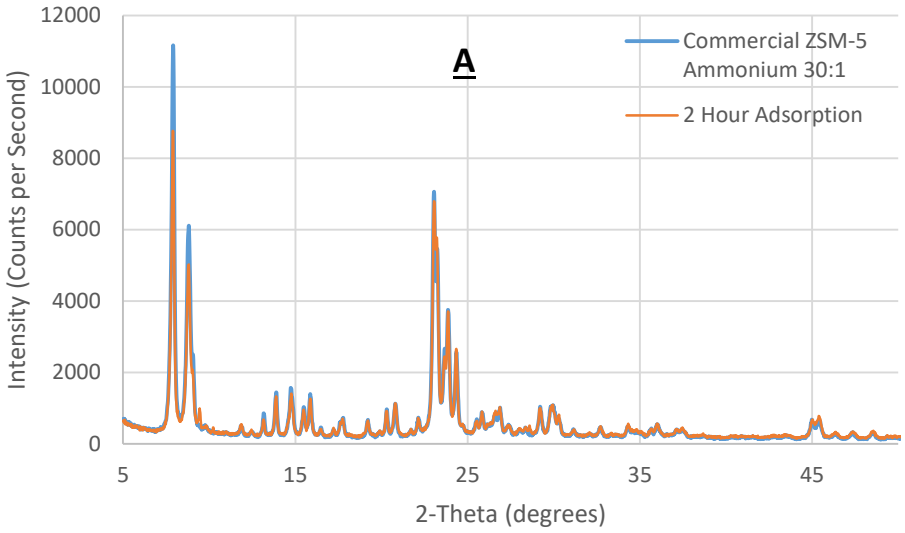


Figure 21. Graph of aspirin combined concentration adsorbed against contact time.

The HPLC results indicate that the optimum adsorption time is 10 hours with the maximum adsorption being 55.60% of the concentration in the solution, the retention time for both peaks vary greatly from the rest of the adsorptions as its HPLC analysis was ran at a different time using a different batch of mobile phase which caused this anomaly, the time between the peaks is consistent though and so the data was kept. Overall the adsorption seems to plateau at around 34% with it rising and falling as it approaches and passes the optimum adsorption time of 10 hours. Though this is lower overall than the adsorption of paracetamol it does indicate that ZSM-5 ammonium 30:1 is an adequate choice for the removal of aspirin from aqueous solution.

Again, to determine of the molecules had been adsorbed in to the pores powder XRD was carried out and the data obtained shown in figure 22.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2 Hour Adsorption
Intensity (Counts per Second)
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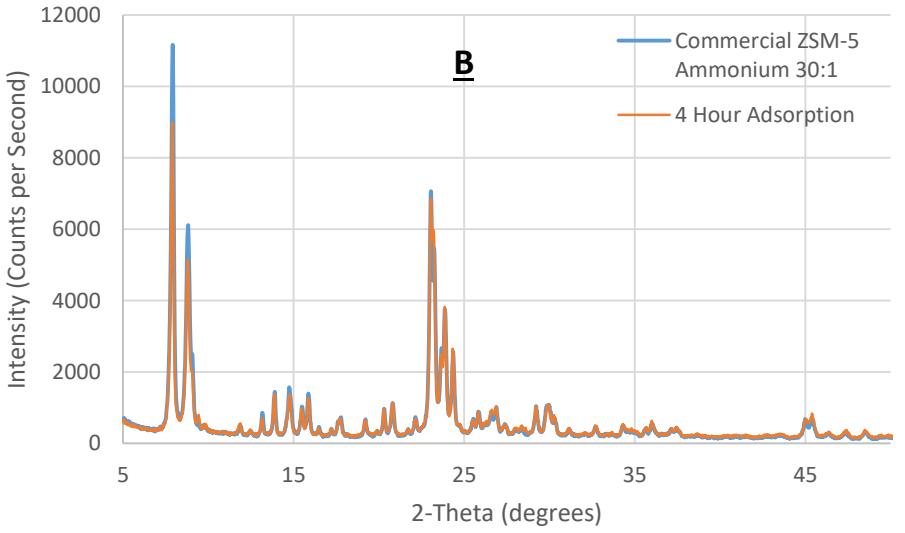
10000
8000
6000
4000
2000
0
5
15
25
35
45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Commercial ZSM-5 Ammonium 30:1
4 Hour Adsorption
Intensity (Counts per Second)
2-Theta (degrees)
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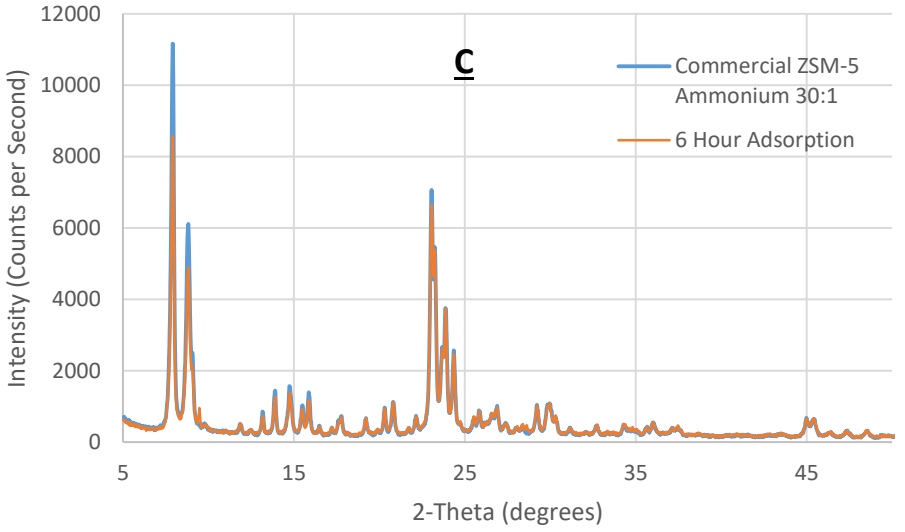
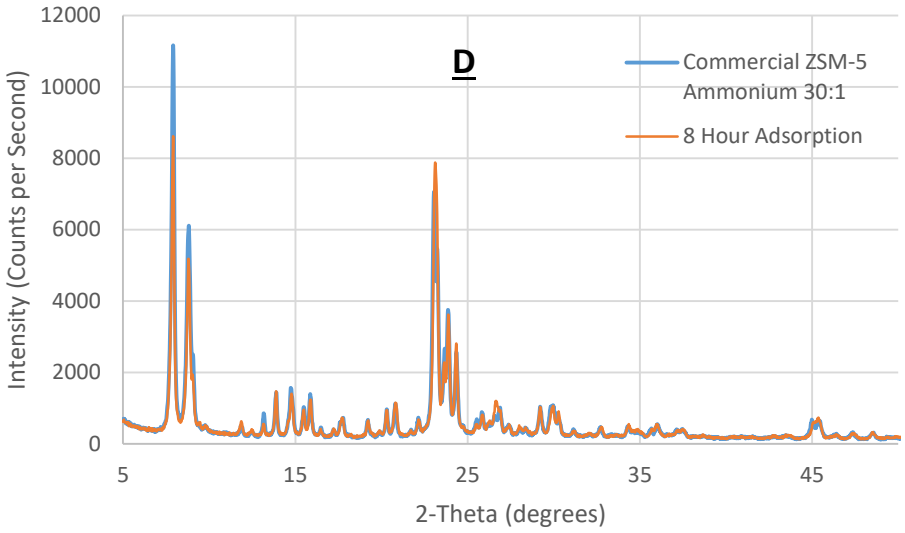
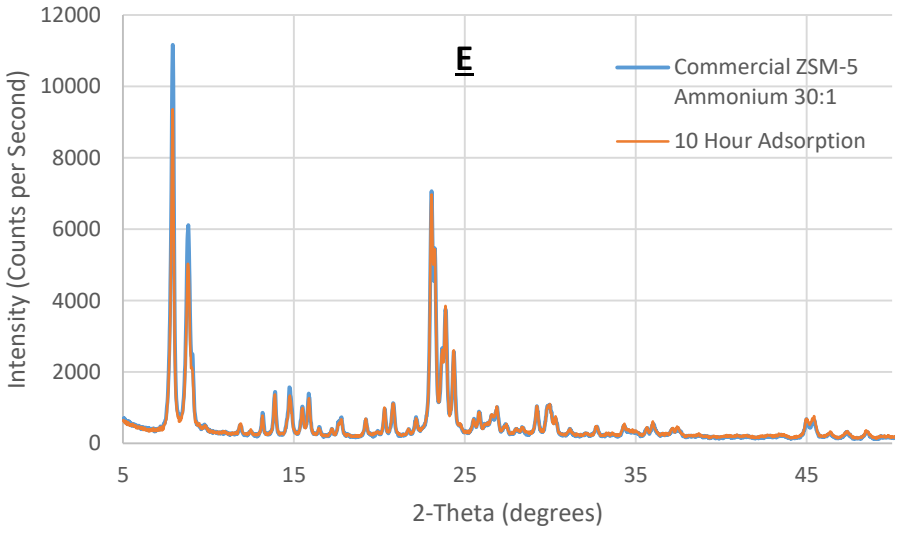
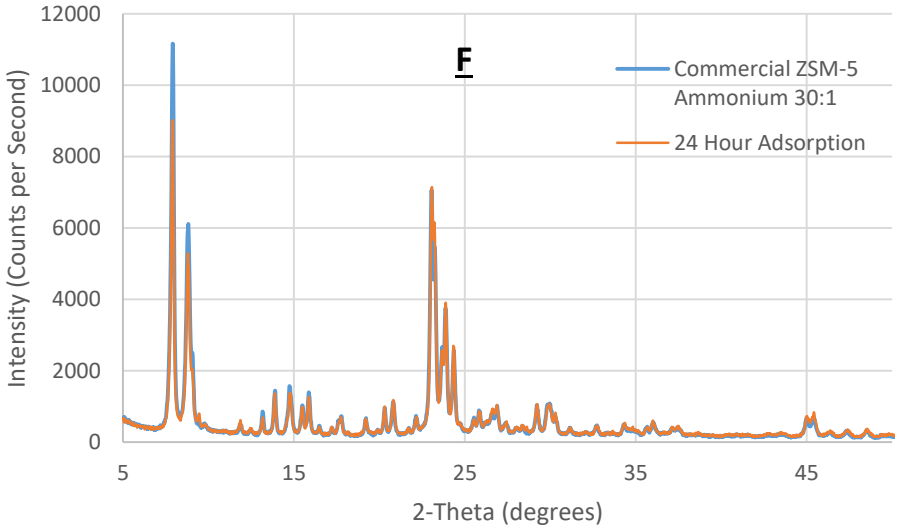
10000
8000
6000
4000
2000
0
5
15
25
35
45


C
Commercial ZSM-5 Ammonium 30:1
6 Hour Adsorption
Intensity (Counts per Second)
2-Theta (degrees)
12000
10000
8000
6000
4000
2000
0
5
15
25
35
45


D
Commercial ZSM-5 Ammonium 30:1
8 Hour Adsorption
Intensity (Counts per Second)
2-Theta (degrees)
12000
10000
8000
6000
4000
2000
0
5
15
25
35
45


E
Commercial ZSM-5 Ammonium 30:1
10 Hour Adsorption
Intensity (Counts per Second)
2-Theta (degrees)
12000
10000
8000
6000
4000
2000
0
5
15
25
35
45


F
Commercial ZSM-5 Ammonium 30:1
24 Hour Adsorption
Intensity (Counts per Second)
2-Theta (degrees)
12000
10000
8000
6000
4000
2000
0
5
15
25
35
45

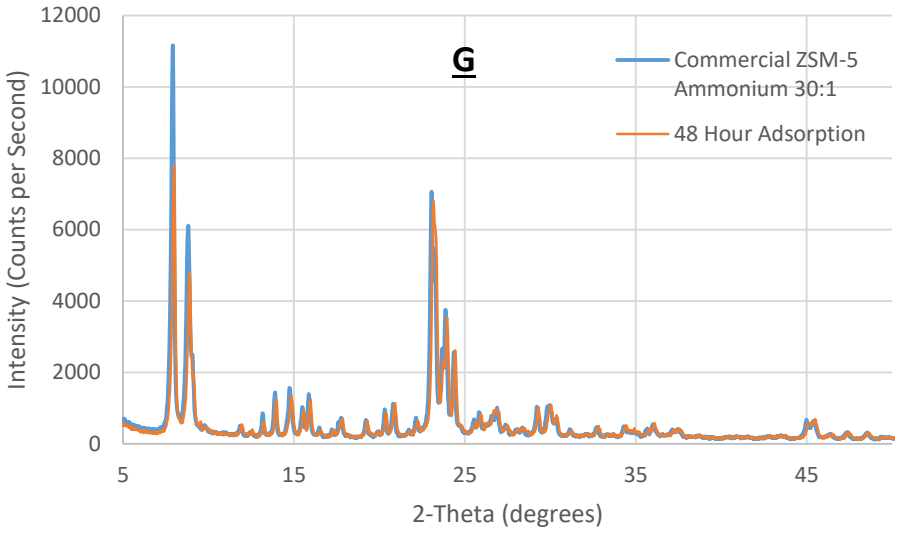


Figure 22. A) Commercial ZSM-5 Ammonium 30:1 + ZSM-5 30:1 post 2-hour aspirin adsorption. B) Commercial ZSM-5 Ammonium 30:1 + ZSM-5 30:1 post 4-hour aspirin adsorption. C) Commercial ZSM-5 Ammonium 30:1 + ZSM-5 30:1 post 6-hour aspirin adsorption. D) Commercial ZSM-5 Ammonium 30:1 + ZSM-5 30:1 post 8-hour aspirin adsorption. E) Commercial ZSM-5 Ammonium 30:1 + ZSM-5 30:1 post 10-hour aspirin adsorption. F) Commercial ZSM-5 Ammonium 30:1 + ZSM-5 30:1 post 24-hour aspirin adsorption. G) Commercial ZSM-5 Ammonium 30:1 + ZSM-5 30:1 post 48-hour aspirin adsorption.

All seven patterns show differences between the original and the post adsorption pattern. This is most prominently shown in a reduction in the relative peak intensity in the first two major peaks at 7.91^{o} 2-theta and 8.82^{o} 2-theta, with the commercial ZSM-5 having peak intensities of 11162 counts per second and 6111 counts per second respectively. Post adsorption these peaks were reduced to 7795-9359 counts per second, with 48 hours accounting for the lower value and 10 hours for the higher value, and 4795-5283 counts per second, with 48 hours accounting for the lower value and 24 hours the higher value, respectively. The 48-hour adsorption is the only one with a significant shift, as it shifts towards the right by 0.0808 2-theta. This presence of a change in the relative peak intensity indicates that the contents of the unit cell have been altered and the partial shifting to the right indicates a contraction in the zeolite's unit cell thus indicating that the aspirin has not been successfully adsorbed into the ZSM-5, though the relatively low level of shift occurring indicates that this change is negligible.

The data from the XRD patterns were used to determine the cell parameters to see how the cell structure changed to accommodate the adsorbed aspirin. A Pawley fit was done using a Chebyshev function background and Pseudo-Voight peak shape function, the zero background and unit cell parameters (*a*, *b*, *c*) were refined to determine errors.

Table 12. Lattice parameters of commercial ZSM-5 30:1 pre-and post aspirin adsorption with errors included in brackets.

Contact Time with Aspirin Solution (Hours)	**RWP**	***a*** **(Å)**	***b*** **(Å)**	***c*** **(Å)**
0	7.466	20.11848(3)	19.92388(2)	13.41704(2)
2	9.063	20.11648(4)	19.93417(3)	13.42123(3)
4	7.417	20.10842(4)	19.93362(3)	13.42091(3)
6	7.931	20.11721(7)	19.93039(5)	13.41920(5)
8	7.22	20.08936(4)	19.94652(3)	13.41488(2)
10	6.976	20.11527(3)	19.93053(2)	13.42048(2)
24	6.974	20.10132(6)	19.93409(5)	13.41659(4)
48	7.616	20.10199(4)	19.92641(3)	13.41310(3)

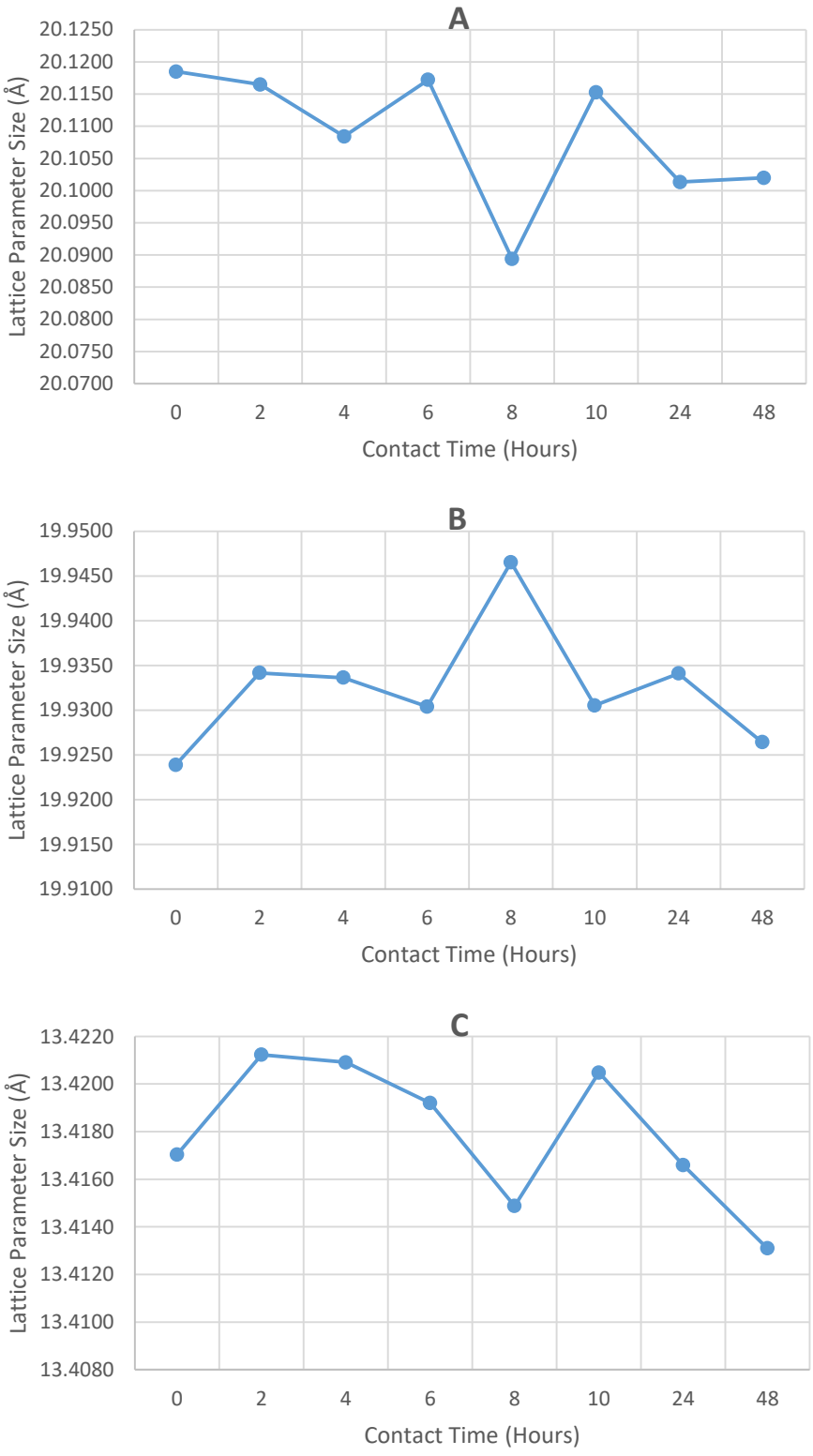


Figure 23. A) Change in lattice parameter *a* against ZSM-5 30:1 contact time with aspirin. B) Change in lattice parameter *b* against ZSM-5 30:1 contact time with aspirin. C) Change in lattice parameter *c* against ZSM-5 30:1 contact time with aspirin.

Figure 23 shows the change in the lattice parameters of ZSM-5 pre and post aspirin adsorption and shows all three follow similar trends in relative size changes, parameter *b* and *c* having similar size changes from 0-6 hours, a and c both having a large reduction in size at 8 hours, a size change of -0.14% for parameter *a* and -0.03% for parameter *c*, and then increase again at 10 hours, a size change of 0.13% for parameter *a* and 0.04% for parameter *c*, while parameter *b* the inverse happens for these contact times, increasing by 0.17% from 6-8 hours and reducing by 0.08% from 8-10 hours, parameter *a* and *c* having a similar drop from 10-24 hours while parameter *b* increases in size, parameter *a* and *c* reducing by 0.07% and 0.03% respectively and parameter *b* increasing by 0.02%, and then a final reduction in size for parameters *b* and *c* from 24-48 hours, a reduction of 0.04% and 0.03% respectively, while parameter *a* increases in size during that time by 0.003%. These changes in lattice parameter size indicate that an increase in concentration of aspirin adsorbed by the zeolite leads to an increase in size of parameter *a* and *c* and reduction in size for parameter *c* as shown at 10 hours when the maximum concentration was adsorbed, 55.60%. This would seem to indicate that these two lattice parameters are expanding in size to accommodate the aspirin. Considering aspirin has a size of 7.1Å X 4.9Å[44] it could easily fit into the 5.4 X 5.6Å and 5.1 X 5.5Å sized pores of ZSM-5 as their upper limit for adsorption is larger than aspirin, being 9.1Å[6], so it would be logical to conclude that some pore expansion would occur to allow for the aspirin to be adsorbed. The data indicates that ZSM-5 did remove aspirin from the solution and would be a viable option for its removal from water systems.

4. Results and Discussion – Adsorptions Using Commercial ZSM-5 Ammonium 200-400:1

4.1 – Introduction

The data presented in this chapter has been taken from the adsorptions of paracetamol, aspirin and ibuprofen lysine by the commercial ZSM-5 200-400:1 used in these experiments. The Si:Al ratio has been increased to ascertain the effect the ammonium cation has on the adsorption rates of the drugs investigated as this increase will reduce the number of cations present. The ZSM-5 used for the experiments in this chapter has a Si:Al ratio of 200-400:1 and its charge balancing cation is ammonium.

4.2 – Paracetamol

The previous paracetamol HPLC calibration curve's equation was used to calculate the concentration of the paracetamol left in the solution after the adsorptions. Table 13 shows the HPLC data produced by the adsorption reactions between 2 and 48 hours. Included are the concentration of the drug left in solution, the concentration of the drug that was adsorbed and the percentage of the overall concentration that was adsorbed. A plot showing concentration adsorbed by the zeolite against contact time is presented in figure 24.

Table 13. HPLC results for the paracetamol adsorptions by commercial ZSM-5 ammonium 200-400:1.

Paracetamol Concentration Left in Solution (M)	Peak Area (mVmin)	Contact Time (Hours)	Retention Time (mins)	Height (mV)	Concentration Adsorbed by the Zeolite (M)	% Concentration Adsorbed
0.00402	447.7846	2	3.553	2191.053	0.00098	19.6965
0.00379	422.8537	4	3.532	2195.389	0.00121	24.1674
0.00360	401.6719	6	3.531	2276.892	0.00140	27.9661
0.00361	402.3755	8	3.534	2270.588	0.00139	27.8399
0.00376	419.5940	10	3.520	2252.319	0.00124	24.7520
0.00386	430.8252	24	3.324	2288.548	0.00114	22.7379
0.00368	409.9684	48	3.388	2321.145	0.00132	26.4782

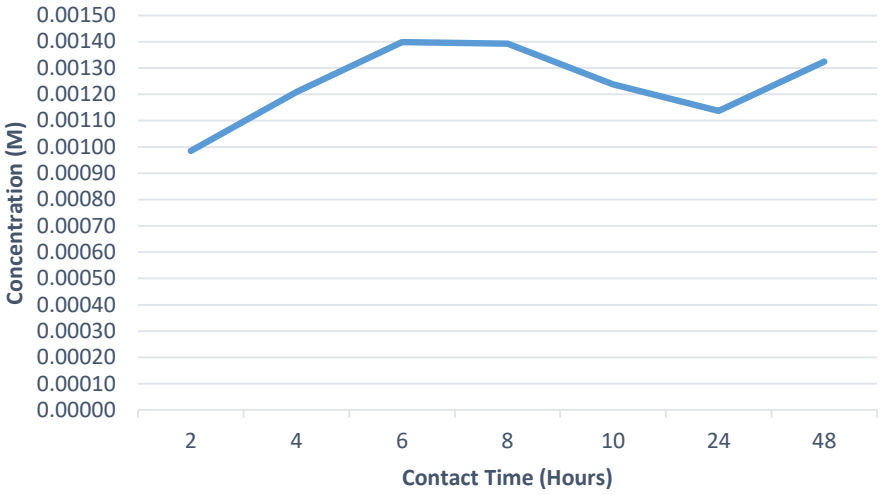


Figure 24. Graph depicting concentration of paracetamol adsorbed by commercial ZSM-5 ammonium 200-400:1 against contact time.

The concentration adsorbed stays fairly constant throughout as the percentage adsorbed only had a range of 19.70-27.97% with the contact time of 2 hours accounting for the lowest concentration adsorbed of 0.00098M and the highest occurring during the 6-hour adsorption of 0.0014M. From 2-6 hours, a steady increase in concentration adsorbed is observed followed by a 0.13% concentration adsorbed decrease from 6-8 hours before a drop of 5.1% from 8-24 hours. Between 24-48 hours the concentration adsorbed increased by 3.7%, to 26.48%, this indicates that the equilibrium of concentration adsorbed is within the range of 22-28%. This overall decrease in the concentration adsorbed by ZSM-5 indicates that fewer ammonium cations present lowers the affinity of paracetamol for ZSM-5.

To confirm that the paracetamol has been adsorbed into the pores of ZSM-5 and not absorbed on to the surface of the particles powder XRD was performed on the filtered solid after adsorption had occurred. As a basis, the commercial ZSM-5 ammonium 200-400:1 XRD pattern is included in figure 25 and shall have the adsorption patterns overlaid onto it in any further XRD patterns in this chapter.

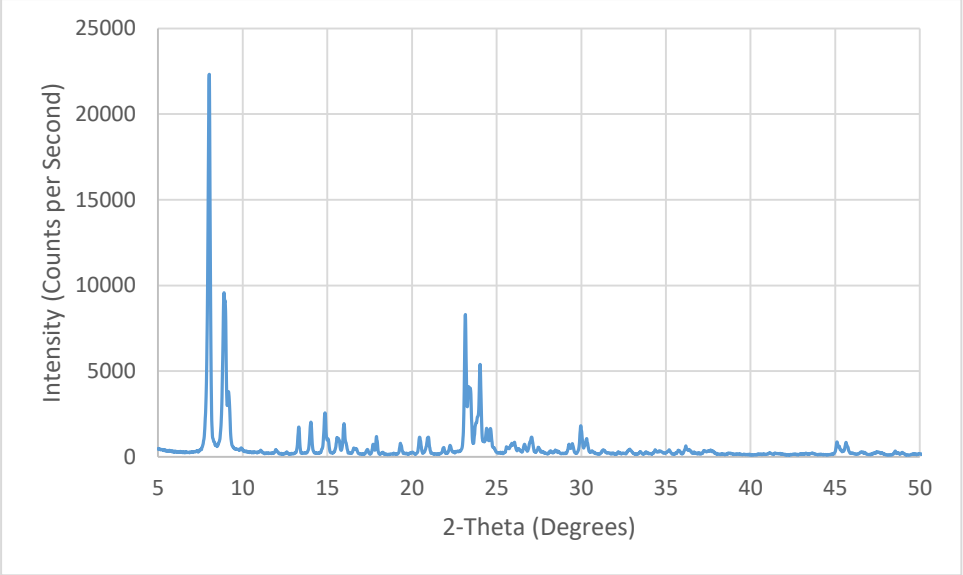
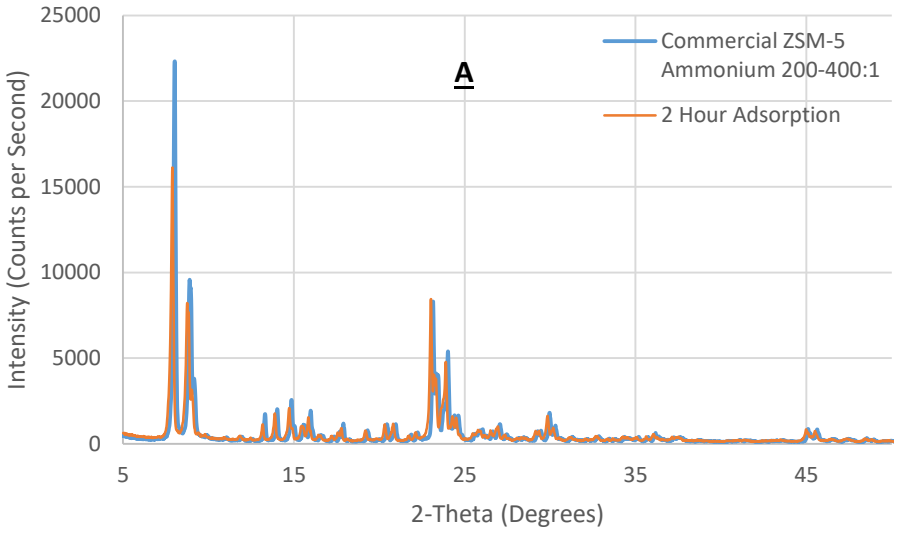


Figure 25. Commercial ZSM-5 ammonium 200-400:1 XRD pattern.

The diffraction patterns for the post adsorption ZSM-5 is shown in figure 26 with the post adsorption pattern overlaid onto the pre-adsorption pattern.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2 Hour Adsorption
Intensity (Counts per Second)
2-Theta (Degrees)
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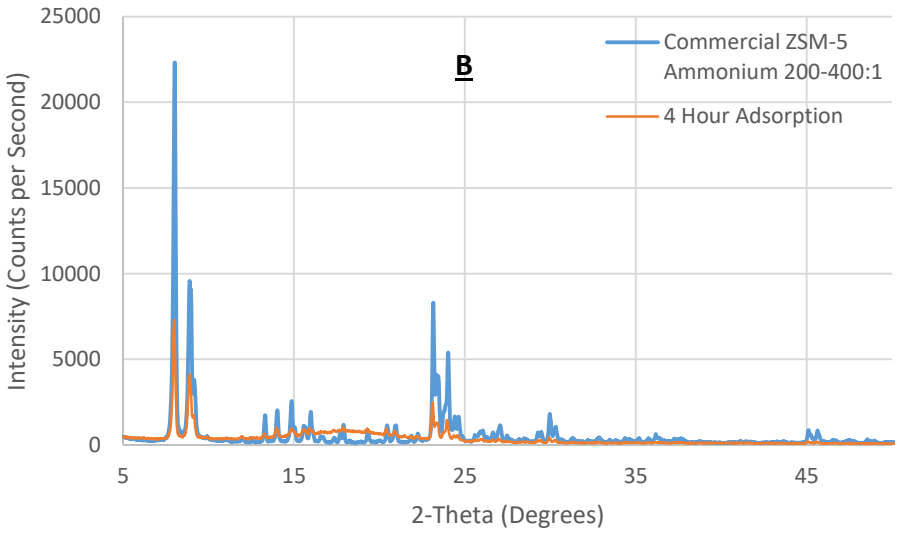
20000
15000
10000
5000
0
5
15
25
35
45


B
Commercial ZSM-5 Ammonium 200-400:1
4 Hour Adsorption
Intensity (Counts per Second)
2-Theta (Degrees)
25000
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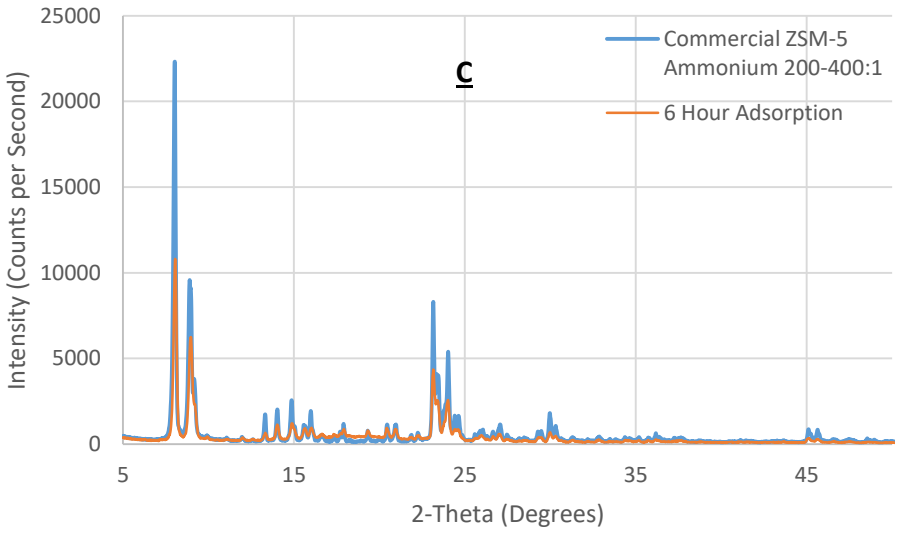
15000
10000
5000
0
5
15
25
35
45


C
Commercial ZSM-5 Ammonium 200-400:1
6 Hour Adsorption
Intensity (Counts per Second)
2-Theta (Degrees)
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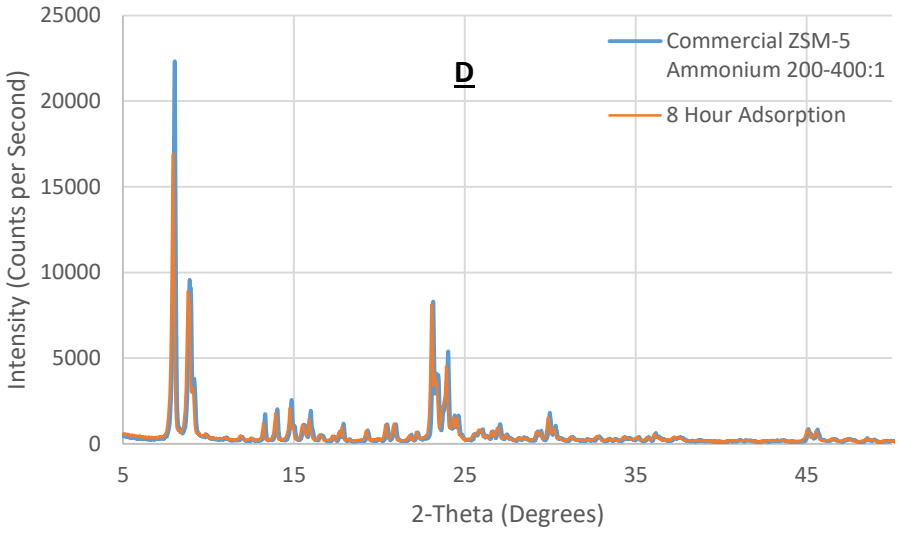
10000
5000
0
5
15
25
35
45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8 Hour Adsorption
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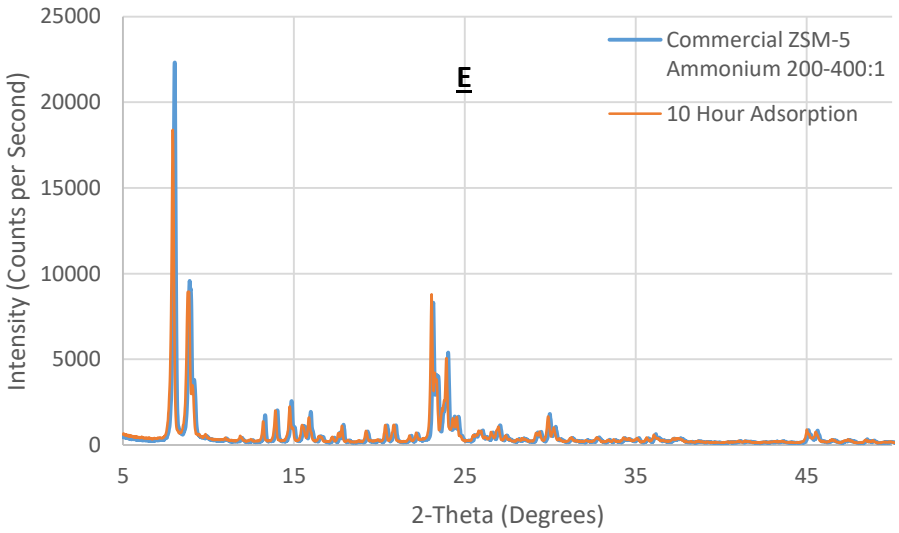
25
35
45
2-Theta (Degrees)


E
Commercial ZSM-5 Ammonium 200-400:1
10 Hour Adsorption
Intensity (Counts per Second)
25000
20000
15000
10000
5000
0
5
15
25
35
45
2-Theta (Degrees)

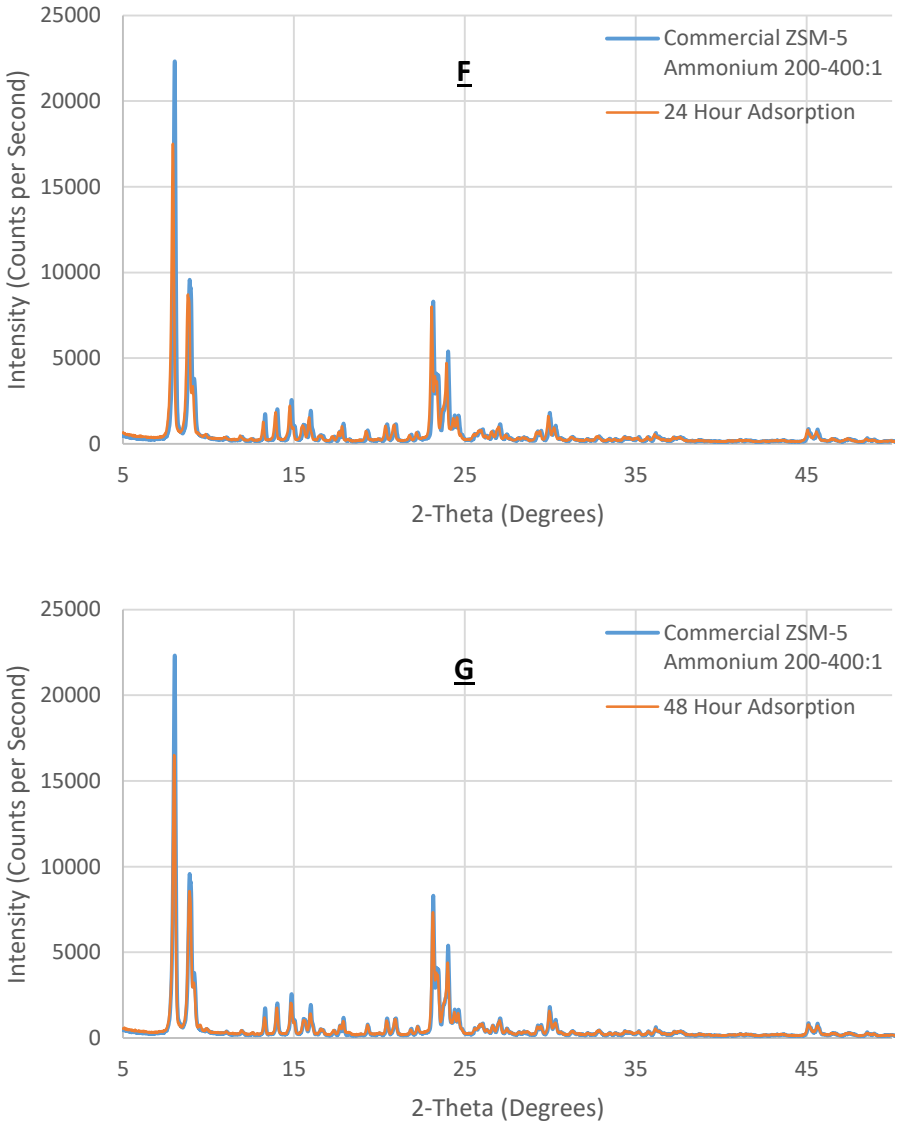


Figure 26. A) Commercial ZSM-5 Ammonium 200-400:1 + ZSM-5 200-400:1 post 2-hour paracetamol adsorption. B) Commercial ZSM-5 Ammonium 200-400:1 + ZSM-5 200-400:1 post 4-hour paracetamol adsorption. C) Commercial ZSM-5 Ammonium 200-400:1 + ZSM-5 200-400:1 post 6-hour paracetamol adsorption. D) Commercial ZSM-5 Ammonium 200-400:1 + ZSM-5 200-400:1 post 8-hour paracetamol adsorption. E) Commercial ZSM-5 Ammonium 200-400:1 + ZSM-5 200-400:1 post 10-hour paracetamol adsorption. F) Commercial ZSM-5 Ammonium 200-400:1 + ZSM-5 200-400:1 post 24-hour paracetamol adsorption. G) Commercial ZSM-5 Ammonium 200-400:1 + ZSM-5 200-400:1 post 48-hour paracetamol adsorption.

All seven XRD patterns show some difference when compared to the original, commercial ZSM-5. All the patterns have some form of reduction in relative peak intensity in multiple peaks within the range of 5^{o}-23^{o} 2-theta. The biggest difference is seen in the first two peaks at 8.03^{o} 2-theta and 8.90^{o} 2-theta, with the commercial

ZSM-5 pre-adsorption having peak intensities of 22321 counts per second and 9576 counts per second respectively. Post adsorption these peaks were reduced to between 10809-18329 counts per second and 6240-8945 counts per second with the lowest peaks being produced by the 6-hour adsorption and highest being produced by the 10-hour adsorption. For the 6-hour adsorption there was also a notable reduction in relative peak intensity at the four peaks at 13.32^{o}, 14.03^{o}, 14.85^{o} and 15.99^{o} 2-theta, with the commercial ZSM-5 pre-adsorption having peak intensities of 1737, 2026, 2558 and 1937 counts per second respectively. Post adsorption these peaks were reduced to 659, 1137, 1211 and 955 counts per second respectively. This change in relative peak intensity indicates that the contents of the unit cell have changed in some way which would indicate that the adsorption of the paracetamol has been successful. Another indicator is that the post adsorption pattern for 10 hours has been shifted to the left by 0.1212^{o} 2-theta. This shift towards a lower 2-theta value indicates an expansion of the zeolite unit cell is occurring. The zeolite framework has a high degree of flexibility and this peak position shift is a further indication that a species has been adsorbed into the pores of the zeolite, in this case paracetamol, though the relatively low level of shift occurring indicates that this change is negligible. I have not included the 4-hour adsorption XRD pattern into my discussion as I believe this to be an outlier result due to its inconsistent data with respect to the rest of the paracetamol XRD and HPLC results, going from the trend set by the other data it should have a similar XRD pattern to the 2 and 24 hour adsorptions. The loss of definite peaks within the range 16^{o}-23^{o} 2-theta indicates a loss of crystallinity in the zeolite but there doesn't seem to be any other indication that this should be occurring.

The HPLC and XRD data indicate that the paracetamol has been adsorbed by the commercial ZSM-5 200-400:1 and successfully removed from the solution. The data from the XRD patterns were used to determine the cell parameters to see how the cell structure changed to accommodate the adsorbed paracetamol. The unit cell parameters for commercial ZSM-5 200-400:1 pre-and post paracetamol adsorption were determined using Topas and J-edit and shown in table 14. A Pawley fit was done using a Chebyshev function background and Pseudo-Voight peak shape function, the zero background and unit cell parameters (*a*, *b*, *c*) were refined to determine errors.

Table 14. Lattice parameters of commercial ZSM-5 200-400:1 pre-and post paracetamol adsorption with errors included in brackets.

Contact Time with Paracetamol Solution (Hours)	**RWP**	***a*** **(Å)**	***b*** **(Å)**	***c*** **(Å)**
0	14.083	20.11858(3)	19.87802(2)	13.38665(2)
2	12.142	20.10968(6)	19.87911(5)	13.38614(5)
4	10.364	20.12285(5)	19.89023(5)	13.41291(5)
6	11.918	20.15622(4)	19.90739(3)	13.41809(4)
8	10.93	20.12050(4)	19.89147(4)	13.39455(3)
10	11.903	20.11053(4)	19.87947(3)	13.38668(3)
24	11.263	20.10687(4)	19.87512(4)	13.38366(3)
48	10.665	20.11650(4)	19.88051(4)	13.38748(3)

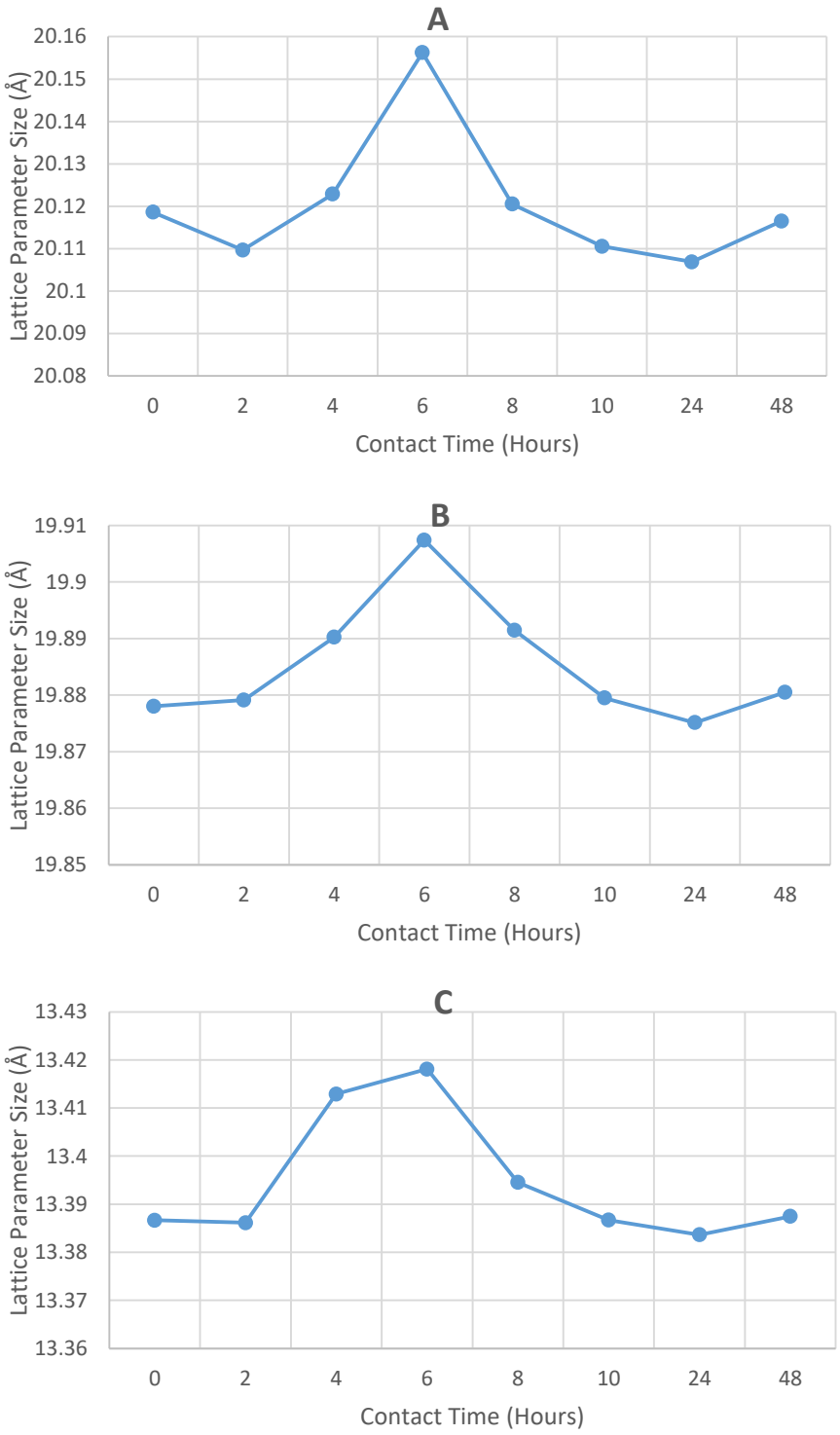


Figure 27. A) Change in lattice parameter *a* against ZSM-5 200-400:1 contact time with paracetamol. B) Change in lattice parameter *b* against ZSM-5 200-400:1 contact time with paracetamol. C) Change in lattice parameter *c* against ZSM-5 200-400:1 contact time with paracetamol.

Figure 27 shows the change in the lattice parameters of ZSM-5 pre-and post paracetamol adsorption and shows all three lattice parameter size changes follow the same pattern. All three increase from 0-6 hours where their size peaks, they then reduce in size between 6-24 hours before increasing in size gain from 24-48 hours. Their graphs are visually similar because of this with the main exception being parameter *c* having a larger relative increase in size from 2-4 hours due to a higher 4-hour value, though as before the results for the 4-hour adsorption are not being considered with regards to the rest of the discussion as it seems to be an outlier with false XRD data. Taking that out then the lattice parameter sizes change in relation to the amount of paracetamol adsorbed by ZSM-5. The concentration adsorbed of paracetamol increased from 2-6 hours, peaking at 6 hours, and then decreasing from 6-24 hours before increasing again from 24-48 hours, mirroring the lattice parameter sizes. Between 2-6 hours there is an increase in concentration adsorbed of 8.27% followed by a reduction of 5.23% concentration adsorbed between 6-24 hours and an increase of 3.74% concentration adsorbed between 24-48 hours. Similarly between 2-6 hours there are increase in size of lattice parameters *a*, *b* and *c* of 0.23%, 0.14% and 0.24% respectively, between 6-24 hours there is a reduction in size of lattice parameters *a*, *b* and *c* of 0.24%, 0.16% and 0.26% respectively, and between 24-48 hours there is an increase in size of 0.05% for parameter *a*, 0.03% for parameters *b* and *c*. Paracetamol is 7.8Å X 4.2Å [41] in size, considering the pore sizes of ZSM-5 are 5.4 X 5.6Å and 5.1 X 5.5Å it would be logical to conclude that some pore expansion would be required for paracetamol to be adsorbed and with the upper limit for molecule adsorption size for ZMS-5 being 9.1Å[6] it is completely possible for paracetamol to be adsorbed.

These changes in size corresponding with the changes in the concentration of paracetamol adsorbed indicate that these changes are due to the unit cell expanding to accommodate the paracetamol being adsorbed into the pores of ZSM-5 200-400:1, which confirms that the paracetamol is being adsorbed by the ZSM-5 200-400:1. However considering its overall amount of concentration removed from solution is reduced by over half of the ZSM-5 30:1 equivalent we would consider commercial ZSM-5 ammonium 200-400:1 appropriate for the removal of paracetamol from aqueous solution but to not use it if commercial ZSM-5 ammonium 30:1 is available. This would indicate that the lowered number of ammonium cations in the zeolite led

to the lowered affinity of paracetamol for ZSM-5 though it could also be due to the higher hydrophobicity of the ZSM-5 due to the increased Si:Al ratio. A change in charge balancing cation could help indicate which is more probable.

4.3 – Ibuprofen Lysine

The previous ibuprofen lysine HPLC calibration curve's equation was used to calculate the concentration of the ibuprofen lysine left in the solution after the adsorptions. Table 15 shows the HPLC data produced by the adsorption reactions between 2 and 48 hours. Included are the concentration of the drug left in solution, the concentration of the drug that was adsorbed and the percentage of the overall concentration that was adsorbed. A plot showing concentration adsorbed by the zeolite against contact time is presented in figure 28.

Table 15. HPLC results for the paracetamol adsorptions by commercial ZSM-5 ammonium 200-400:1.

Ibuprofen Lysine Concentration Left in Solution (M)	**Peak Area (mVmin)**	**Contact Time (Hours)**	**Retention Time (mins)**	**Height (mV)**	**Concentration Adsorbed by the Zeolite (M)**	**% Concentration Adsorbed**
0.00210	167.0034	2	12.812	355.352	0.000*	0.0000
0.00214	170.0308	4	10.996	312.878	0.000*	0.0000
0.00205	162.6876	6	10.973	308.117	0.000*	0.0000
0.00204	162.3697	8	11.058	310.110	0.000*	0.0000
0.00204	162.3697	10	8.709	313.649	0.000*	0.0000
0.00211	167.7182	24	13.023	297.059	0.000*	0.0000
0.00213	169.4421	48	11.000	317.040	0.000*	0.0000

*These values have been normalised to zero as HPLC data came out with a negative concentration

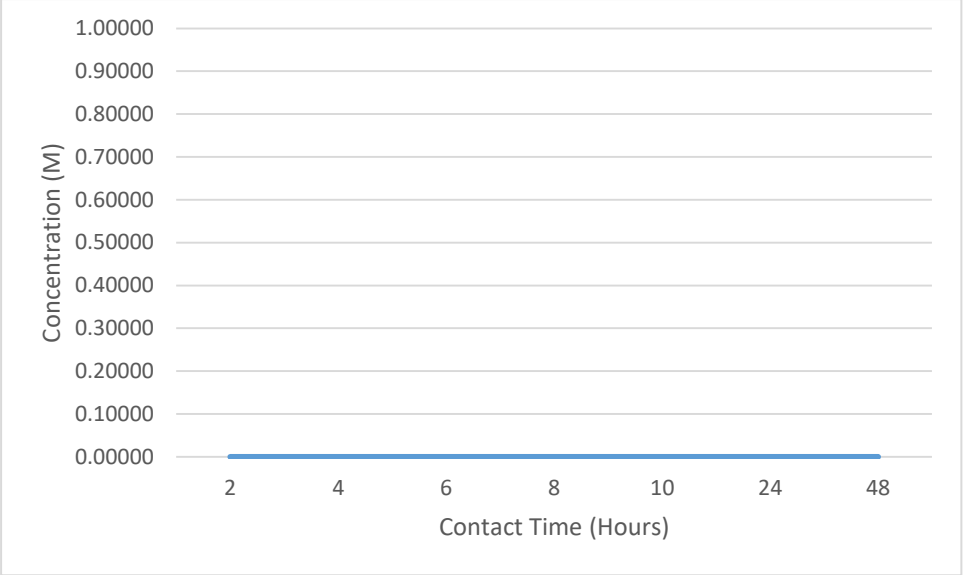
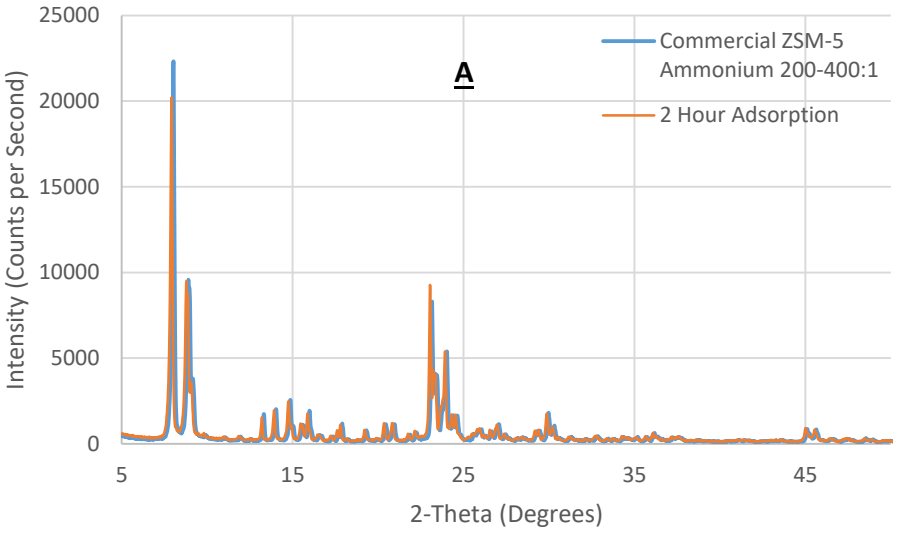
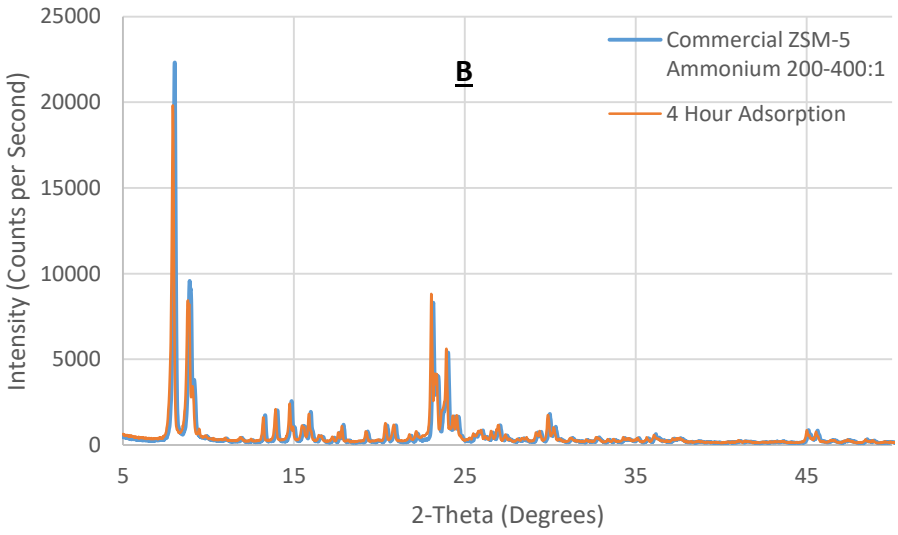


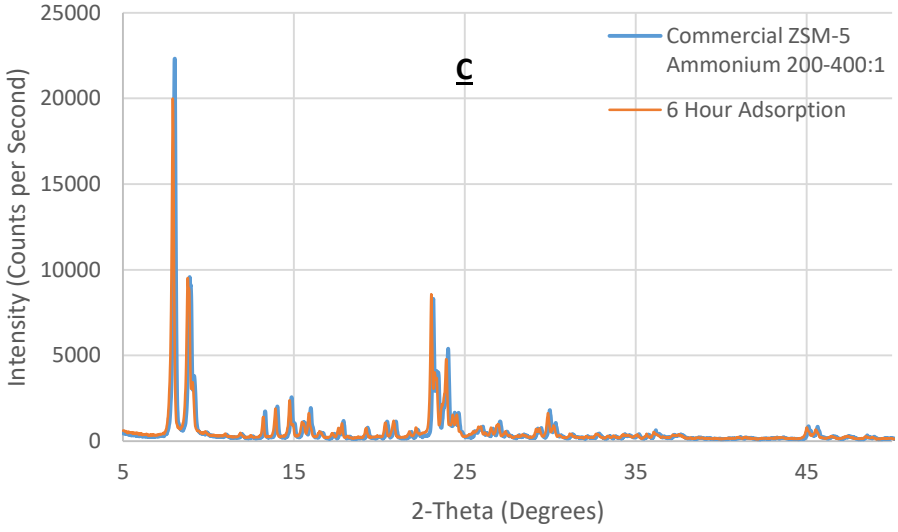
Figure 28. Graph depicting concentration of ibuprofen lysine adsorbed by ZSM-5 ammonium 200-400:1 against contact time.

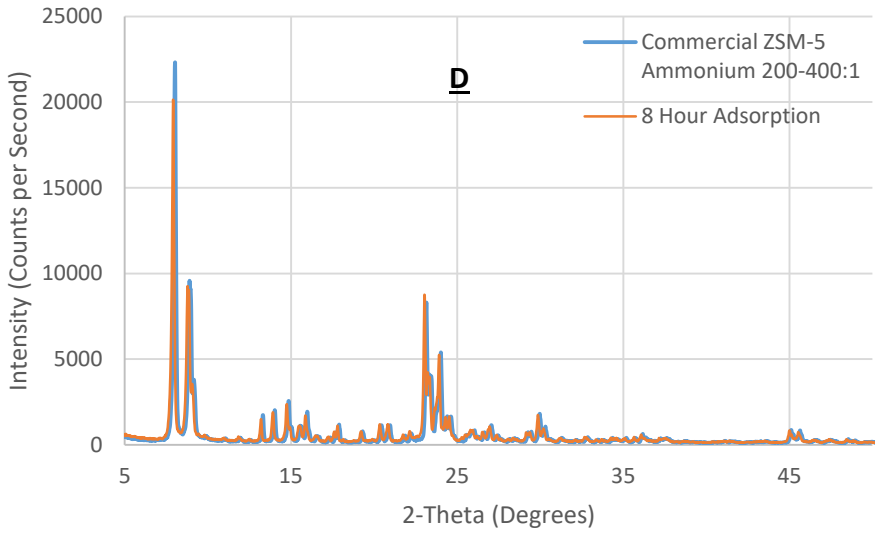
Due to its low concentration and the low relative solubility of ibuprofen lysine in general the HPLC machine may have picked up a higher result than possible, if only slightly, causing negative results to appear. These adsorptions were repeated to check validity and consistent results were produced. For the purposes of this research any negative concentration results have been changed to indicate that no ibuprofen lysine was adsorbed, though some may have been the amount is negligible. Since all the results presented produced higher results than possible they were all normalised to zero. This indicates that the increase in the Si:Al ratio, and therefore the decrease in the amount of ammonium ions present, decreases the affinity of ibuprofen lysine towards ZSM-5 considerably. The incongruous retention time of the 10 hour adsorption is due to this adsorption being ran in a different batch of mobile phase to the rest of the adsorptions and was repeated to confirm its validity.

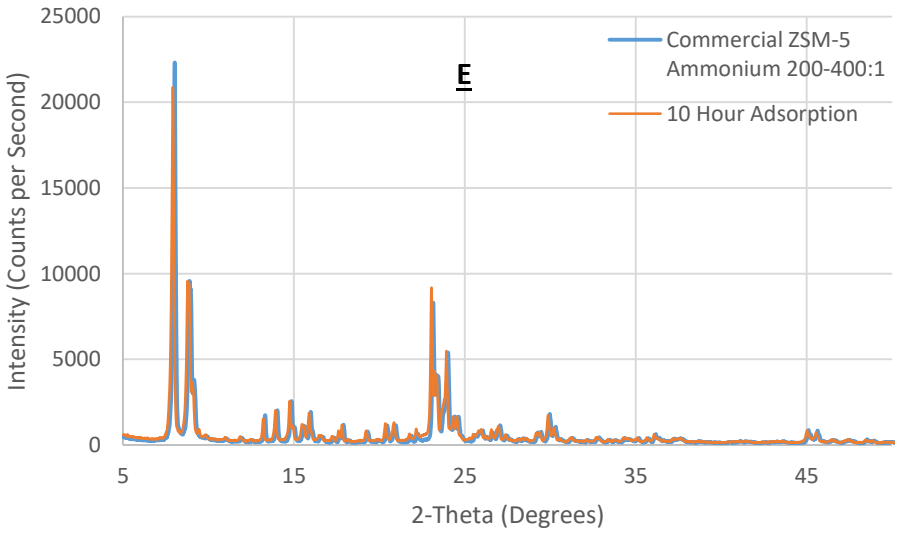
To ascertain that ibuprofen lysine had been adsorbed into the pores of the zeolite and not the surface of the particles XRD was carried out and the data analysed using Pawley fits. The post adsorption XRD patterns overlaid onto the commercial ZSM-5 200-400:1 XRD pattern, shown in figure 25, are plotted in figure 29 below.

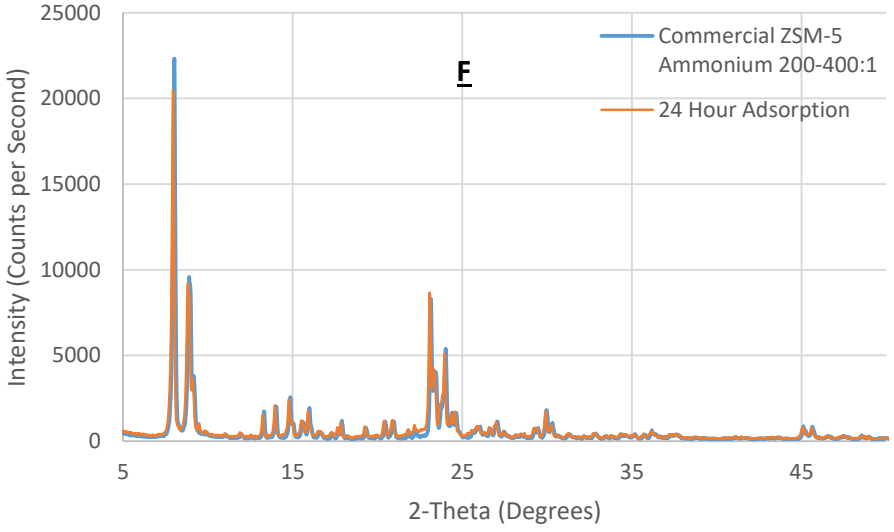

A
Commercial ZSM-5 Ammonium 200-400:1
2 Hour Adsorption
Intensity (Counts per Second)
2-Theta (Degrees)
25000
20000
15000
10000
5000
0
5
15
25
35
45


B
Commercial ZSM-5 Ammonium 200-400:1
4 Hour Adsorption
Intensity (Counts per Second)
2-Theta (Degrees)
25000
20000
15000
10000
5000
0
5
15
25
35
45


C
Commercial ZSM-5 Ammonium 200-400:1
6 Hour Adsorption
Intensity (Counts per Second)
2-Theta (Degrees)
25000
20000
15000
10000
5000
0
5
15
25
35
45


D
Commercial ZSM-5 Ammonium 200-400:1
8 Hour Adsorption
Intensity (Counts per Second)
2-Theta (Degrees)
25000
20000
15000
10000
5000
0
5
15
25
35
45


E
Commercial ZSM-5 Ammonium 200-400:1
10 Hour Adsorption
Intensity (Counts per Second)
2-Theta (Degrees)
25000
20000
15000
10000
5000
0
5
15
25
35
45


F
Commercial ZSM-5 Ammonium 200-400:1
24 Hour Adsorption
Intensity (Counts per Second)
2-Theta (Degrees)
25000
20000
15000
10000
5000
0
5
15
25
35
45

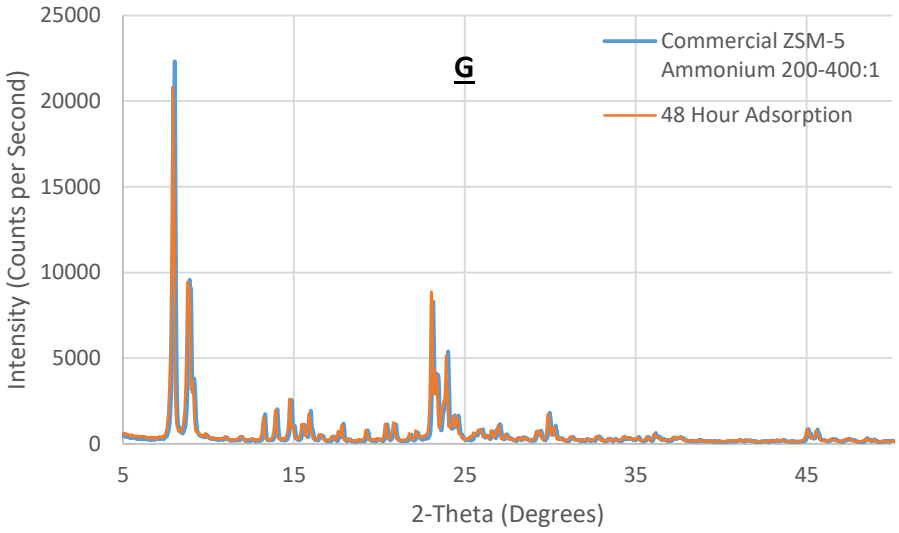


Figure 29. A) Commercial ZSM-5 Ammonium 200-400:1 + ZSM-5 200-400:1 post 2-hour ibuprofen lysine adsorption. B) Commercial ZSM-5 Ammonium 200-400:1 + ZSM-5 200-400:1 post 4-hour ibuprofen lysine adsorption. C) Commercial ZSM-5 Ammonium 200-400:1 + ZSM-5 200-400:1 post 6-hour ibuprofen lysine adsorption. D) Commercial ZSM-5 Ammonium 200-400:1 + ZSM-5 200-400:1 post 8-hour ibuprofen lysine adsorption. E) Commercial ZSM-5 Ammonium 200-400:1 + ZSM-5 200-400:1 post 10-hour ibuprofen lysine adsorption. F) Commercial ZSM-5 Ammonium 200-400:1 + ZSM-5 200-400:1 post 24-hour ibuprofen lysine adsorption. G) Commercial ZSM-5 Ammonium 200-400:1 + ZSM-5 200-400:1 post 48-hour ibuprofen lysine adsorption.

All seven XRD patterns show some slight difference when compared to the original, commercial ZSM-5. All the patterns have some form of reduction in relative peak intensity in multiple peaks within the range of 5^{o}-23^{o} 2-theta. The biggest difference is seen in the first two peaks at 8.03^{o} 2-theta and 8.90^{o} 2-theta, with the commercial ZSM-5 pre-adsorption having peak intensities of 22321 counts per second and 9576 counts per second respectively. Post adsorption these peaks were reduced to between 19814-20874 counts per second and 9579-8438 counts per second with the lowest peaks being produced by the 4-hour adsorption and highest being produced by the 10-hour adsorption. This change in relative peak intensity indicates that the contents of the unit cell have changed in some way which would indicate that the adsorption of the ibuprofen lysine has been successful, but considering the HPLC results these changes are most likely due to the negligible concentration of ibuprofen lysine adsorbed which would explain the relatively small reduction in relative peak intensity. All seven of the XRD patterns show some shifting towards the left, a shift of 0.0606-0.1212 2-theta with the smallest shift being produced by the 24-hour

adsorption and the largest shift being produced by the 2, 6, 8, 10 and 48-hour adsorption. This shift towards a lower 2-theta value indicates an expansion of the zeolite unit cell is occurring. The zeolite framework has a high degree of flexibility and this peak position shift is a further indication that a species has been adsorbed into the pores of the zeolite, in this case ibuprofen lysine, though the relatively low level of shift occurring indicates that this change is negligible.

The HPLC and XRD data indicate that the ibuprofen lysine has not been adsorbed by the commercial ZSM-5 200-400:1 and unsuccessfully removed from the solution. The data from the XRD patterns were used to determine the cell parameters to see how the cell structure changed to accommodate the adsorbed ibuprofen lysine. The unit cell parameters for commercial ZSM-5 200-400:1 pre-and post ibuprofen lysine adsorption were determined using Topas and J-edit and shown in table 16. A Pawley fit was done using a Chebyshev function background and Pseudo-Voight peak shape function, the zero background and unit cell parameters (*a*, *b*, *c*) were refined to determine errors.

Table 16. Lattice parameters of commercial ZSM-5 200-400:1 pre-and post ibuprofen lysine adsorption with errors included in brackets.

Contact Time with Ibuprofen Lysine Solution (Hours)	**RWP**	***a*** **(Å)**	***b*** **(Å)**	***c*** **(Å)**
0	14.083	20.11858(3)	19.87802(2)	13.38665(2)
2	12.741	20.11985(3)	19.88012(3)	13.38896(3)
4	13.965	20.12178(4)	19.87836(3)	13.38860(3)
6	11.918	20.13450(4)	19.89147(3)	13.39826(3)
8	12.164	20.12244(4)	19.88052(3)	13.39051(3)
10	12.601	20.12215(4)	19.88367(3)	13.38941(3)
24	12.117	20.12277(4)	19.88158(4)	13.38950(3)
48	12.255	20.12666(4)	19.89167(3)	13.39527(3)

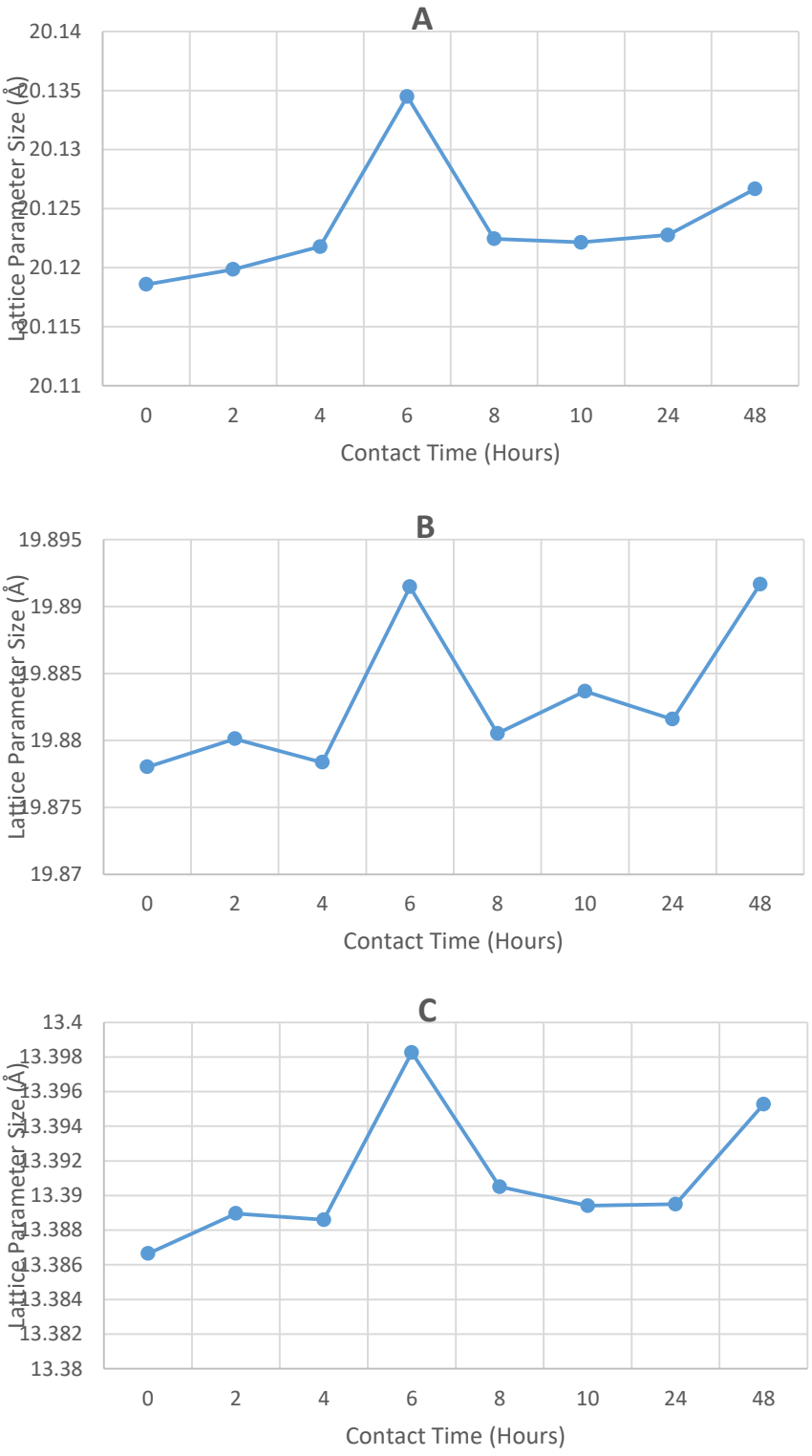


Figure 30. A) Change in lattice parameter *a* against ZSM-5 200-400:1 contact time with ibuprofen lysine. B) Change in lattice parameter *b* against ZSM-5 200-400:1 contact time with ibuprofen lysine. C) Change in lattice parameter *c* against ZSM-5 200-400:1 contact time with ibuprofen lysine.

Figure 30 shows the change in the lattice parameters of ZSM-5 pre-and post ibuprofen lysine adsorption and shows all three lattice parameter size changes follow the same pattern. All three plateau from 0-4 hours then increase in size between 4-6 hours before decreasing in size from 6-8 hours, they then plateau from 8-24 hours before a final increase from 24-48 hours. Their graphs are visually similar because of this with the main exception being parameter *b* and *c* having an increase between 0-2 hours and parameter *b* having an increase between 8-10 hours before reducing back down to a similar relative size as the other two parameters. The largest increase, from 4-6 hours, accounts for an increase of 0.06% for parameter *a*, 0.07% for parameter *b* and *c*. This change in size would indicate that some ibuprofen lysine was adsorbed into the zeolite, but coupled with the HPLC, XRD and low increase in overall size it would be safe to assume that the amount adsorbed was so small as to be negligible. Ibuprofen lysine is 8.9Å X 3.8Å[42] in size, considering the pore sizes of ZSM-5 are 5.4 X 5.6Å and 5.1 X 5.5Å it would be logical to conclude that some pore expansion would be required for ibuprofen lysine to be adsorbed and with the upper limit for molecule adsorption size for ZMS-5 being 9.1Å[6] it is completely possible for ibuprofen lysine to be adsorbed but considering that the previous ibuprofen lysine adsorption had produced a maximum lattice parameter increase of 0.43% the 0.07% maximum from this adsorption would indicate that not enough expansion has occurred for adsorption to occur. This lines up with the HPLC data showing that no adsorption did occur.

This data indicates that ZSM-5 200-400:1 ammonium is not an appropriate compound for the removal of ibuprofen lysine from aqueous solution. This may be due to the lower number of ammonium cations present due to the higher Si:Al ratio or could be due to the increased hydrophobicity a higher Si:Al ratio produces. A change in the charge balancing cation could help determine which is more probable.

4.4 – Aspirin

The previous aspirin HPLC calibration curve's equations for aspirin peak 1 and 2 was used to calculate the concentration of the aspirin left in the solution after the

adsorptions by combining the concentrations. Table 17 shows the HPLC data produced by the adsorption reactions between 2 and 48 hours for peak 1, table 18 shows peak 2 and table 19 are the two sets of concentrations combined. Included are the concentration of the drug left in solution, the concentration of the drug that was adsorbed and the percentage of the overall concentration that was adsorbed. A plot showing the aspirin combined concentration adsorbed by the zeolite against contact time is presented in figure 31.

Table 17. Aspirin peak 1 HPLC results

Aspirin Tablet Samples Peak 1 Concentration Left in Solution (M)	**Peak Area (mVmin)**	**Contact Time (Hours)**	**Retention Time (min)**	**Height (mV)**
0.00138	13.5547	2	7.203	49.615
0.00145	14.2320	4	7.235	50.566
0.00200	19.5517	6	7.235	68.437
0.00196	19.1874	8	7.185	66.860
0.00160	15.6785	10	7.200	55.619
0.00156	15.3361	24	7.141	54.115
0.00077	7.5558	48	7.253	27.495

.

Table 18. Aspirin peak 2 HPLC results.

Aspirin Tablet Samples Peak 2 Concentration Left in Solution (M)	**Peak Area (mVmin)**	**Contact Time (Hours)**	**Retention Time (mins)**	**Height (mV)**
0.00069	6.1941	2	10.841	14.979
0.00074	6.6261	4	10.922	16.209
0.00063	5.6723	6	10.906	13.671
0.00060	5.4208	8	10.826	12.894
0.00060	5.4059	10	10.828	13.434
0.00050	4.4691	24	10.732	11.234
0.00115	10.3435	48	10.987	24.786

Table 19. Aspirin combined concentrations HPLC results.

Aspirin Tablet Samples Combined Concentrations Left in Solution (M)	Contact Time	Concentration Adsorbed by the Zeolite	% Concentration Adsorbed
0.00207	2	0.00293	58.5294
0.00219	4	0.00281	56.1842
0.00263	6	0.00237	47.4531
0.00256	8	0.00244	48.7572
0.00220	10	0.00280	55.9518
0.00206	24	0.00294	58.7387
0.00192	48	0.00308	61.5237

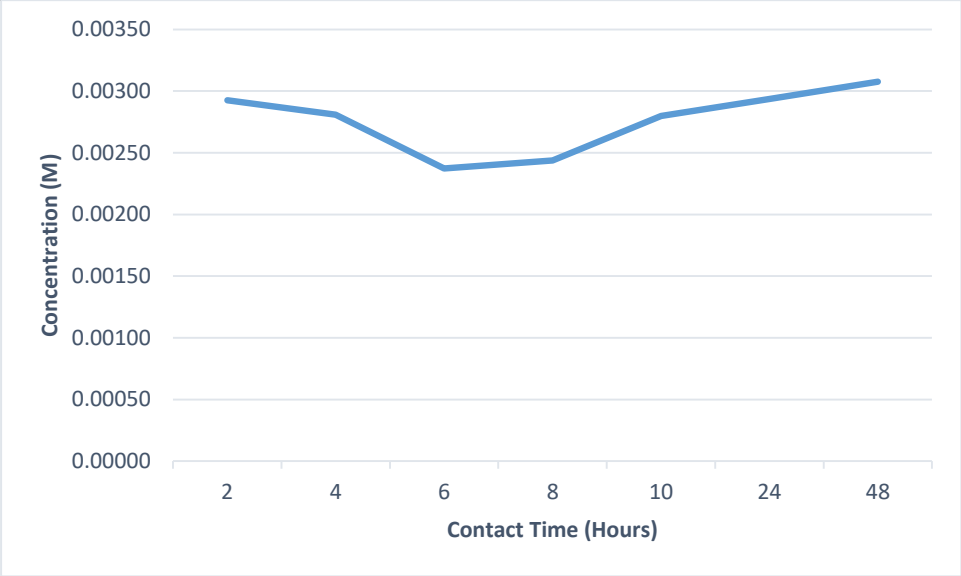
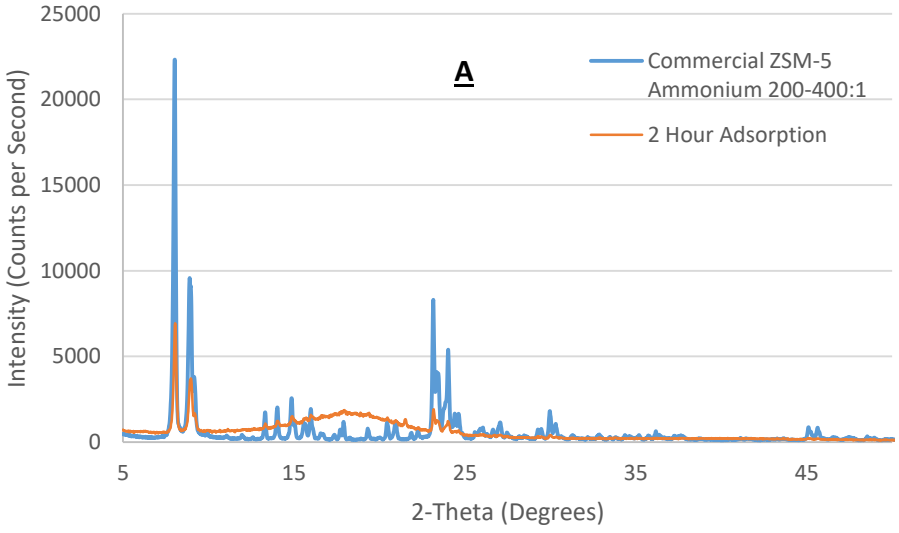


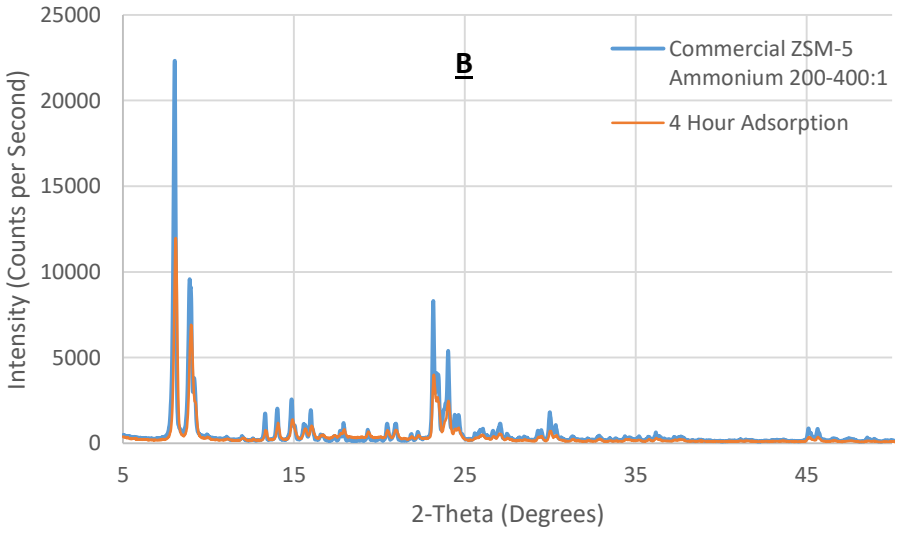
Figure 31. Graph depicting concentration of aspirin adsorbed by ZSM-5 ammonium 200-400:1 against contact time.

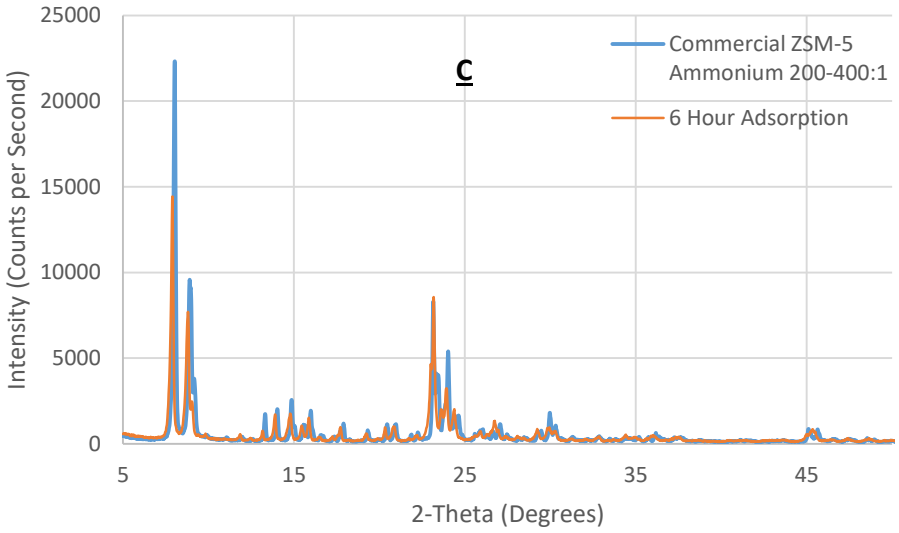
The concentration adsorbed stays fairly constant throughout as the percentage adsorbed only had a range of 47.45-61.52% with the contact time of 6 hours accounting for the lowest concentration adsorbed of 0.0024M and the highest occurring during the 48-hour adsorption of 0.0031M. An equilibrium seems to have been found at around 56-61%, 2 and 4 hours being within this range before dropping down to 47.45% at 6 hours. From 6-8 hours, there is a slight increase in percentage adsorbed, from 47.45% to 48.76%, before increasing again between 8-48 hours quite

steadily, going from 48.76% to the maximum of 61.52% and seemingly the equilibrium point. This overall relative increase in the concentration adsorbed by ZSM-5 indicates that fewer ammonium cations present increases the affinity of aspirin for ZSM-5.

To confirm that the aspirin has been adsorbed into the pores of ZSM-5 and not absorbed on to the surface of the particles powder XRD was performed on the filtered solid after adsorption had occurred. As a basis, the commercial ZSM-5 ammonium 200-400:1 XRD pattern is included in figure 25 and the diffraction patterns for the post adsorption ZSM-5 is shown in figure 32 with the post adsorption pattern overlaid onto the pre-adsorption pattern.



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6 Hour Adsorption
Intensity (Counts per Second)
2-Theta (Degrees)
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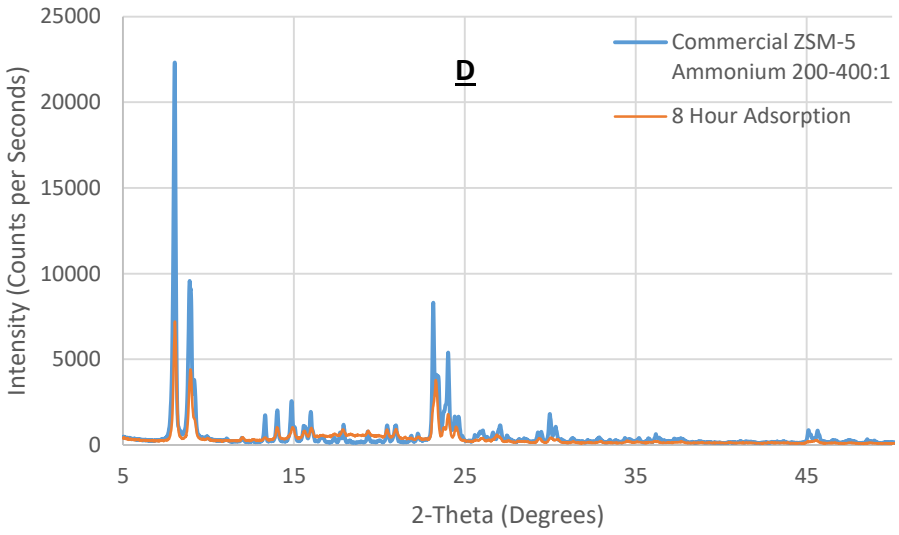
20000
15000
10000
5000
0
5
15
25
35
45


D
Commercial ZSM-5 Ammonium 200-400:1
8 Hour Adsorption
Intensity (Counts per Seconds)
2-Theta (Degrees)
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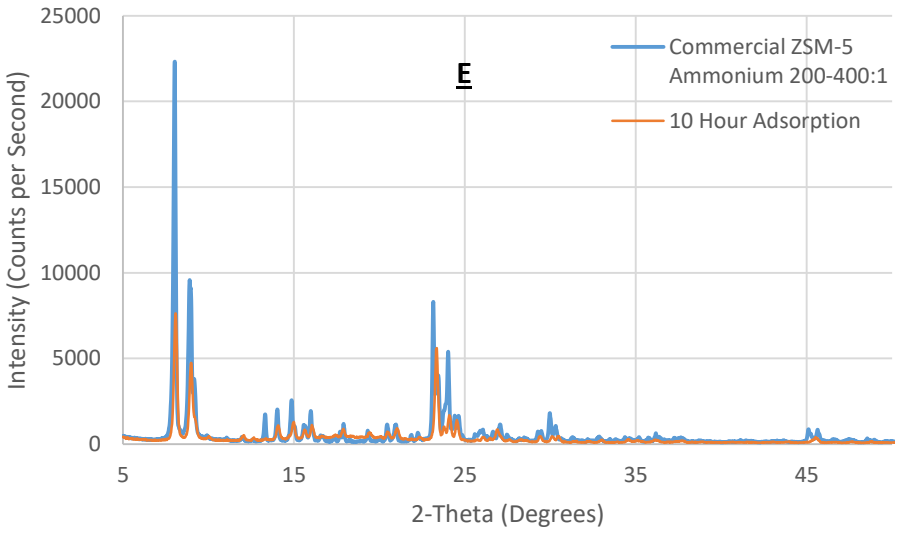
20000
15000
10000
5000
0
5
15
25
35
45


E
Commercial ZSM-5 Ammonium 200-400:1
10 Hour Adsorption
Intensity (Counts per Second)
2-Theta (Degrees)
25000
20000
15000
10000
5000
0
5
15
25
35
45

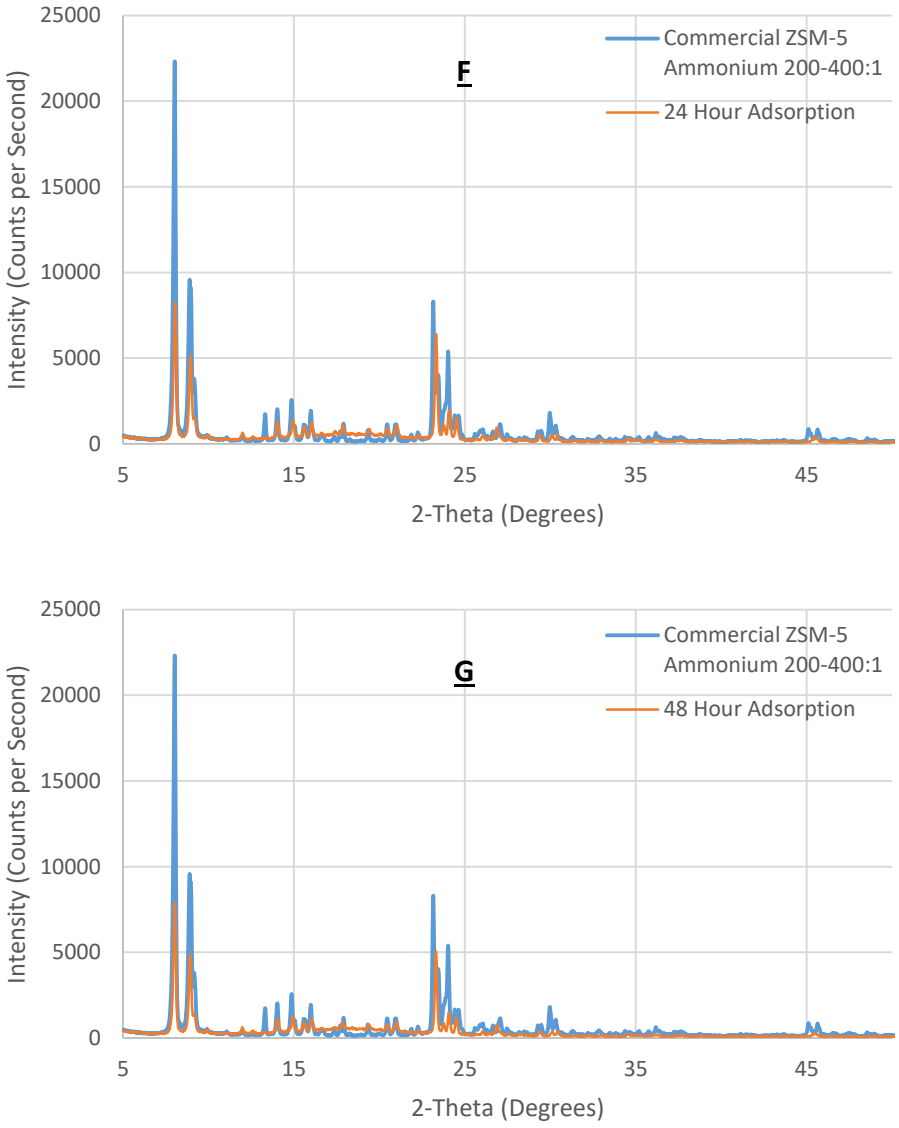


Figure 32. A) Commercial ZSM-5 Ammonium 200-400:1 + ZSM-5 200-400:1 post 2-hour aspirin adsorption. B) Commercial ZSM-5 Ammonium 200-400:1 + ZSM-5 200-400:1 post 4-hour aspirin adsorption. C) Commercial ZSM-5 Ammonium 200-400:1 + ZSM-5 200-400:1 post 6-hour aspirin adsorption. D) Commercial ZSM-5 Ammonium 200-400:1 + ZSM-5 200-400:1 post 8-hour aspirin adsorption. E) Commercial ZSM-5 Ammonium 200-400:1 + ZSM-5 200-400:1 post 10-hour aspirin adsorption. F) Commercial ZSM-5 Ammonium 200-400:1 + ZSM-5 200-400:1 post 24-hour aspirin adsorption. G) Commercial ZSM-5 Ammonium 200-400:1 + ZSM-5 200-400:1 post 48-hour aspirin adsorption.

All seven XRD patterns show noticeable difference when compared to the original, commercial ZSM-5 200-400:1. All the patterns have some form of reduction in relative peak intensity in multiple peaks within the range of 5^{o}-25^{o} 2-theta. The first two peaks at 8.03^{o} 2-theta and 8.90^{o} 2-theta show consistently large changes in

relative peak intensity, with the commercial ZSM-5 pre-adsorption having peak intensities of 22321 counts per second and 9576 counts per second respectively. Post adsorption these peaks were reduced to between 7205-14430 counts per second and 4415-7702 counts per second with the lowest peaks being produced by the 8-hour adsorption and highest being produced by the 6-hour adsorption. There was also notable reduction in relative peak intensity at the four peaks at 13.32^{o}, 14.03^{o}, 14.85^{o} and 15.99^{o} 2-theta, with the commercial ZSM-5 pre-adsorption having peak intensities of 1737, 2026, 2558 and 1937 counts per second respectively. Post adsorption these peaks were reduced to ranges of 330-762 counts per second for 13.32^{o}, the largest being produced by the 6-hour adsorption and lowest the 10-hour adsorption, 1042-1714 counts per second for 14.03^{o}, 1036-1759 counts per second for 14.85^{o} and 994-1521 counts per second for 15.99^{o}, these last three points having their largest peak intensity produced by the 6-hour adsorption and their lowest by the 8-hour adsorption. The last two notable changes occur at the peaks at 23.15^{o} and 24.02^{o} 2-theta, with the commercial ZSM-5's pre-adsorption peak intensities being 8304 and 5395 counts per second respectively. These became 3790-8565 counts per second for 23.15^{o}, with the largest peak intensity produced by the 6-hour adsorption and the lowest by the 8-hour adsorption, and 1504-3225 counts per second for 24.02^{o}, the largest peak intensity being produced by the 6-hour adsorption and the lowest the 48-hour adsorption. This change in relative peak intensity indicates that the contents of the unit cell have changed in some way which would indicate that the adsorption of the aspirin has been successful. Another indicator is that the all the patterns show some shift either towards the left or right to a greater or lesser degree. The largest of these shifts occurs in the 6-hour adsorption as it is shifted to the left by 0.1414^{o} 2-theta. This shift towards a lower 2-theta value indicates an expansion of the zeolite unit cell is occurring. The rest of the patterns show a shift towards the higher 2-theta values which indicates a contraction of the zeolite unit cell is occurring. The zeolite framework has a high degree of flexibility and this peak position shift is a further indication that a species has been adsorbed into the pores of the zeolite, in this case aspirin, though the relatively low level of shift occurring indicates that this change is negligible. I have not included the 2-hour adsorption XRD pattern into my discussion as I believe this to be an outlier result due to its inconsistent data with respect to the rest of the aspirin XRD and HPLC results, going from the trend set by the other data it should have a similar XRD pattern to the 4 and 24 hour adsorptions but its relative

peak intensities are much lower than these two. The loss of definite peaks within the range 16^{o}-23^{o} 2-theta indicates a loss of crystallinity in the zeolite but there doesn't seem to be any other indication that this should be occurring.

The HPLC and XRD data indicate that the aspirin has been adsorbed by the commercial ZSM-5 200-400:1 and successfully removed from the solution. The data from the XRD patterns were used to determine the cell parameters to see how the cell structure changed to accommodate the adsorbed aspirin. The unit cell parameters for commercial ZSM-5 200-400:1 pre-and post aspirin adsorption were determined using Topas and J-edit and shown in table 20. A Pawley fit was done using a Chebyshev function background and Pseudo-Voight peak shape function, the zero background and unit cell parameters (*a*, *b*, *c*) were refined to determine errors.

Table 20. Lattice parameters of commercial ZSM-5 200-400:1 pre-and post aspirin adsorption with errors included in brackets.

Contact Time with Paracetamol Solution (Hours)	**RWP**	***a*** **(Å)**	***b*** **(Å)**	***c*** **(Å)**
0	14.083	20.11858(3)	19.87802(2)	13.38665(2)
2	8.422	20.09008(19)	19.85840(17)	13.39895(14)
4	12.619	20.15887(5)	19.90917(4)	13.40750(3)
6	11.089	20.12000(6)	19.94505(3)	13.37450(3)
8	9.749	20.13646(5)	19.94842(4)	13.42013(4)
10	10.557	20.12037(7)	19.95905(4)	13.40383(4)
24	10.585	20.07175(6)	19.95104(4)	13.39697(3)
48	11.859	20.10364(7)	19.96116(4)	13.38733(4)

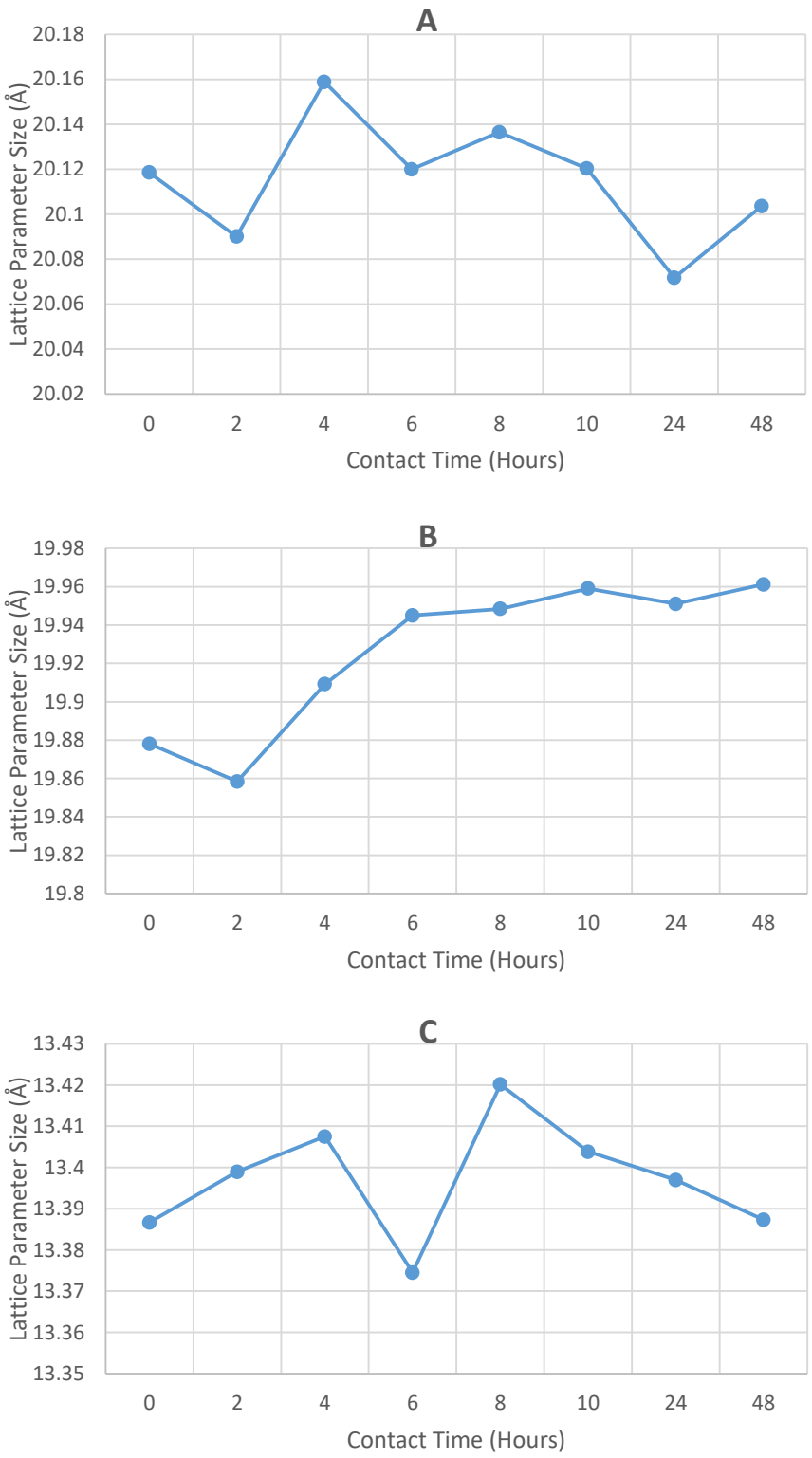


Figure 33. A) Change in lattice parameter *a* against ZSM-5 200-400:1 contact time with aspirin. B) Change in lattice parameter *b* against ZSM-5 200-400:1 contact time with aspirin. C) Change in lattice parameter *c* against ZSM-5 200-400:1 contact time with aspirin.

Figure 33 shows the change in the lattice parameters of ZSM-5 pre-and post aspirin adsorption and all three lattice parameters do not follow a similar path to one another. Lattice parameter *a* and *b* both decrease in size from 0-2 hours but lattice parameter *a* then peaks at 4 hours while *b* steadily increases until 6 hours where it then plateaus till its peak at 48 hours. Between 0 hours to its peak at 48 there is an increase of 0.42%. Lattice parameter *a* decreases from its peak at 4 hours to 6 hours before rising slightly at 8 hours. It then drops from 8-24 hours before a slight increase at 48 hours. Overall there is shown to be a 0.07% reduction in lattice parameter *a*'s size from 0-48 hours. Lattice parameter *c* shows a steady increase in size from 0-4 hours before a large drop at 6 hours. It then jumps back up at 8 hours before steady decline in size between 8-48 hours. Overall there was a 0.01% increase in lattice parameter *c*'s size from 0-48 hours. Considering aspirin has a size of 7.1Å X 4.9Å[44] it could easily fit into the 5.4 X 5.6Å and 5.1 X 5.5Å sized pores of ZSM-5 as their upper limit for adsorption is larger than aspirin, being 9.1Å[6], so it would be logical to conclude that some pore expansion would occur to allow for the aspirin to be adsorbed. At the maximum concentration adsorbed, the 48-hour adsorption, lattice parameter *b* and *c* show an increase in size whereas *a* shows a decrease in size. This trend is shown throughout the data as the amount adsorbed is relatively stable and high.

These changes in size corresponding with the changes in the concentration of aspirin adsorbed indicate that these changes are due to the unit cell expanding and contracting to accommodate the aspirin being adsorbed into the pores of ZSM-5 200-400:1, which confirms that the aspirin is being adsorbed by the ZSM-5 200-400:1. ZSM-5 200-400:1 shows a higher concentration adsorbed than ZSM-5 30:1, an increase of 5.9% adsorbed at maximum. From this the conclusion that ZSM-5 200-400:1 ammonium would be an appropriate compound for the removal of aspirin from aqueous solution, more so than ZSM-5 30:1. This increase in affinity after an increase in the Si:Al ratio indicates that the charge balancing cation had a large effect on aspirin's affinity for ZSM-5 as a reduction in this cation increased it. A change in the charge balancing cation may produce similar results and shall be explored later in this research. It could also be due to the increase hydrophobic tendencies of ZSM-5 with an increase amount of silicon, the change in the charge balancing cation will indicate whether this is probable or not.

5. Results and Discussion – Adsorptions Using Fe Ion Exchanged ZSM-5 30:1

5.1 – Introduction

The data presented in this chapter has been taken from the adsorptions of paracetamol, aspirin and ibuprofen lysine by the commercial ZSM-5 30:1 after it had undergone an ion exchange reaction using $Fe(II)Cl_2$. The charge balancing cation has been changed to see if this would change the investigated drug's affinity for ZSM-5 and whether this change in cation will have a positive effect on their adsorption. The ZSM-5 used for the experiments in this chapter has a Si:Al ratio of 30:1 and its charge balancing cation is Fe^{3+}. To confirm that a successful ion exchange had occurred SEM EDX spectroscopy was ran before and after the reaction. The results of this are presented in table 21 below, five sets of EDX were run on different areas of the zeolite and an average was found. These results show that successful ion exchange has occurred and this allowed me to carry on with my adsorption reactions.

Table 21. ZSM-5 30:1 EDX Wt% data before and after Fe ion exchange reaction.

Sample Analysed	Silicon Wt% (%)	Aluminium Wt% (%)	Oxygen Wt% (%)	Nitrogen Wt% (%)	Iron Wt% (%)
ZSM-5 30:1 NH4 #1	47.62	3.30	46.79	2.30	0.00
ZSM-5 30:1 NH4 #2	34.61	2.75	52.84	9.80	0.00
ZSM-5 30:1 NH4 #3	46.89	3.42	44.06	5.63	0.00
ZSM-5 30:1 NH4 #4	49.10	3.74	43.28	3.87	0.00
ZSM-5 30:1 NH4 #5	54.25	4.08	38.55	3.12	0.00
Average	46.49	3.46	45.10	4.94	0.00
ZSM-5 30:1 FeCl2 Ion Exchange #1	35.83	3.26	47.49	0.00	13.42
ZSM-5 30:1 FeCl2 Ion Exchange #2	47.50	3.93	47.13	0.00	1.45
ZSM-5 30:1 FeCl2 Ion Exchange #3	42.89	3.20	51.95	0.00	1.95
ZSM-5 30:1 FeCl2 Ion Exchange #4	45.97	3.52	48.29	0.00	2.22
ZSM-5 30:1 FeCl2 Ion Exchange #5	42.96	3.40	52.48	0.00	1.16
Average	43.03	3.46	49.47	0.00	4.04

5.2 – Paracetamol

The previous paracetamol HPLC calibration curve's equation was used to calculate the concentration of the paracetamol left in the solution after the adsorptions. Table 22 shows the HPLC data produced by the adsorption reactions between 2 and 48 hours. Included are the concentration of the drug left in solution, the concentration of the drug that was adsorbed and the percentage of the overall concentration that was adsorbed. A plot showing concentration adsorbed by the zeolite against contact time is presented in figure 34.

Table 22. HPLC results for the paracetamol adsorptions by Fe ion exchanged ZSM-5 30:1.

Paracetamol Concentration Left in Solution (M)	Peak Area (mVmin)	Contact Time (Hours)	Retention Time (mins)	Height (mV)	Concentration Adsorbed by the Zeolite (M)	% Concentration Adsorbed
0.00393	438.8005	2	3.512	2312.091	0.00107	21.3076
0.00392	436.9443	4	3.496	2302.634	0.00108	21.6405
0.00386	430.0410	6	3.484	2285.780	0.00114	22.8785
0.00383	427.3773	8	3.482	2275.059	0.00117	23.3562
0.00372	414.7077	10	3.493	2237.827	0.00128	25.6283
0.00391	436.0245	24	3.490	2285.189	0.00109	21.8055
0.00390	435.0501	48	3.483	2280.047	0.00110	21.9802

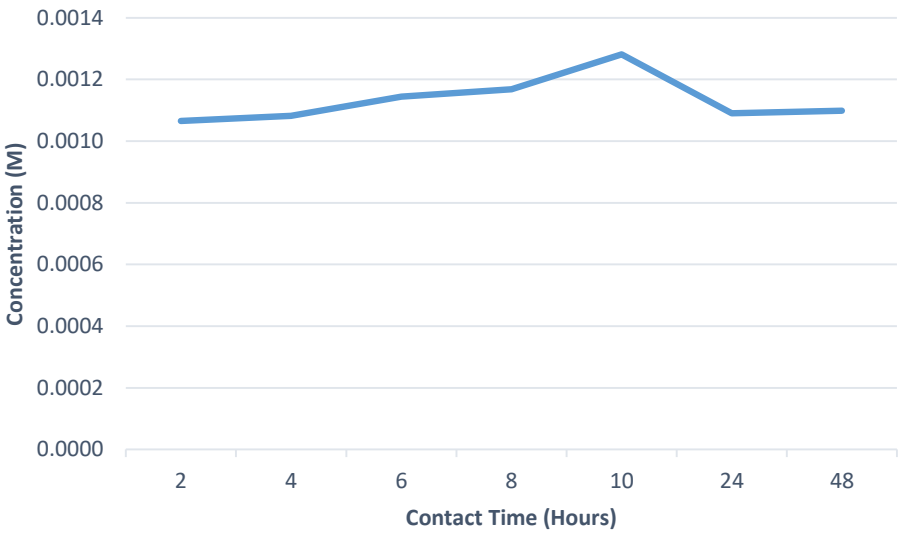


Figure 34. Graph depicting concentration of paracetamol adsorbed by Fe ion exchanged ZSM-5 30:1 against contact time.

The concentration adsorbed stays fairly constant throughout as the percentage adsorbed only had a range of 21.31-25.63% with the contact time of 2 hours

accounting for the lowest concentration adsorbed of 0.00107M and the highest occurring during the 10-hour adsorption of 0.00128M, indicating that 10 hours is the optimum contact time. The equilibrium seems to be between 21-22% as the 2, 4, 6, 24 and 48 hour adsorptions all fall within this range. Overall this shows a decrease in the concentration adsorbed by ZSM-5 when compared to the ZSM-5 with ammonium as the charge balancing cation. This indicates that replacing the ammonium cations with iron cations lowers the affinity of paracetamol for ZSM-5.

To confirm that the paracetamol has been adsorbed into the pores of ZSM-5 and not absorbed on to the surface of the particles powder XRD was performed on the filtered solid after adsorption had occurred. As a basis, the Fe ion exchanged ZSM-5 30:1 pre-adsorption XRD pattern is included in figure 35 and shall have the adsorption patterns overlaid onto it in any further XRD patterns in this chapter.

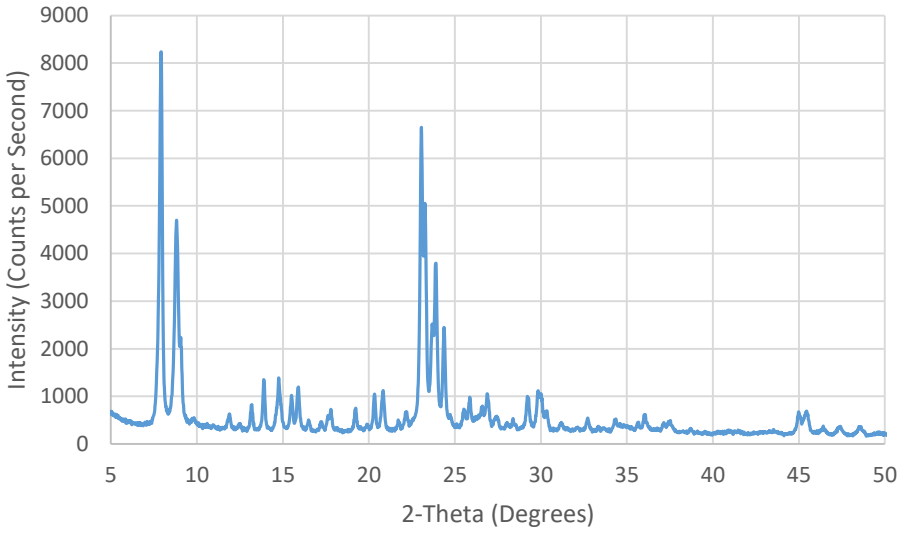
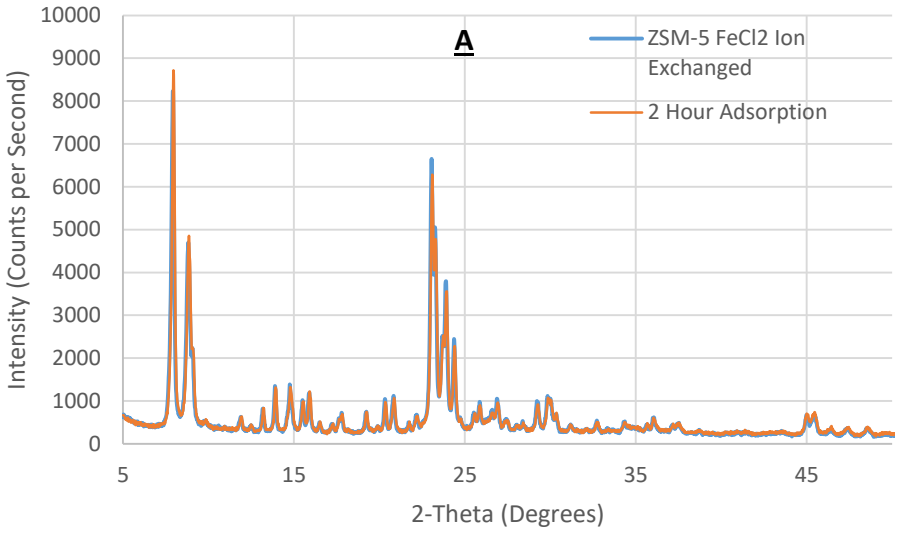


Figure 35. Fe ion exchanged ZSM-5 30:1 pre-adsorption XRD pattern.

The diffraction patterns for the post adsorption ZSM-5 is shown in figure 36 with the post adsorption pattern overlaid onto the pre-adsorption pattern.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2 Hour Adsorption
Intensity (Counts per Second)
2-Theta (Degrees)
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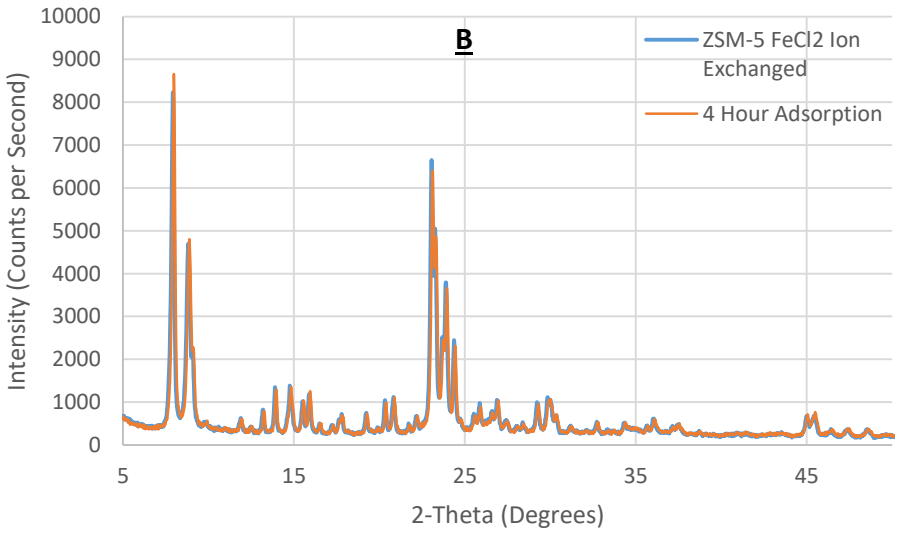
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
5
15
25
35
45


B
ZSM-5 FeCl2 Ion Exchanged
4 Hour Adsorption
Intensity (Counts per Second)
2-Theta (Degrees)
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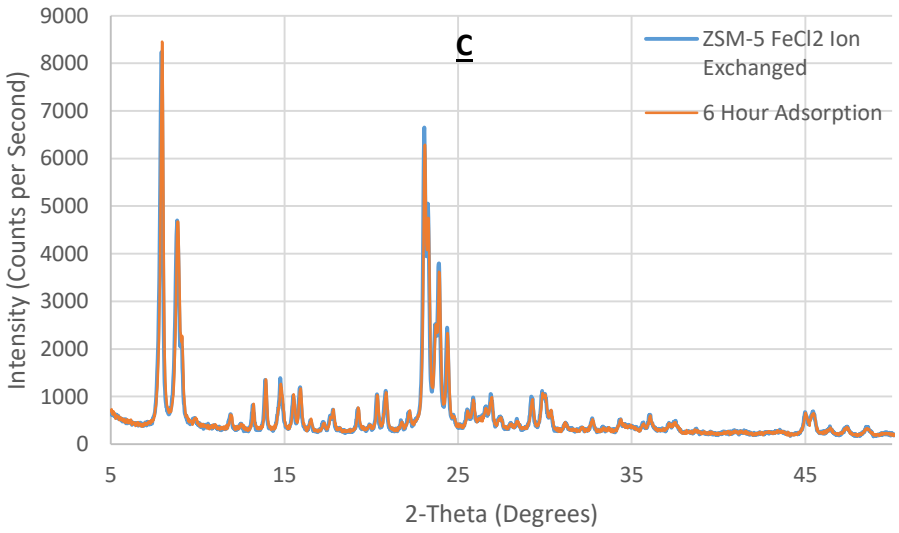
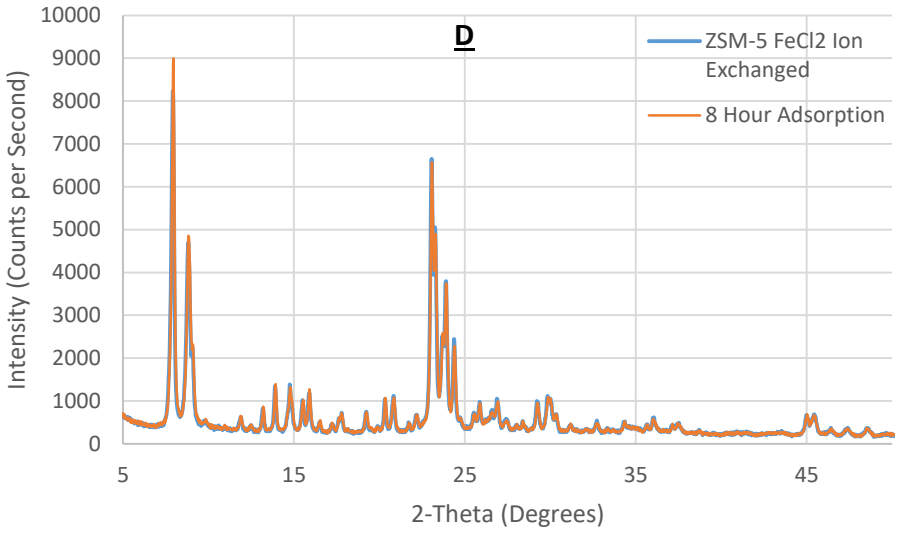
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
5
15
25
35
45


C
ZSM-5 FeCl2 Ion Exchanged
6 Hour Adsorption
Intensity (Counts per Second)
2-Theta (Degrees)
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
5
15
25
35
45


D
ZSM-5 FeCl2 Ion Exchanged
8 Hour Adsorption
Intensity (Counts per Second)
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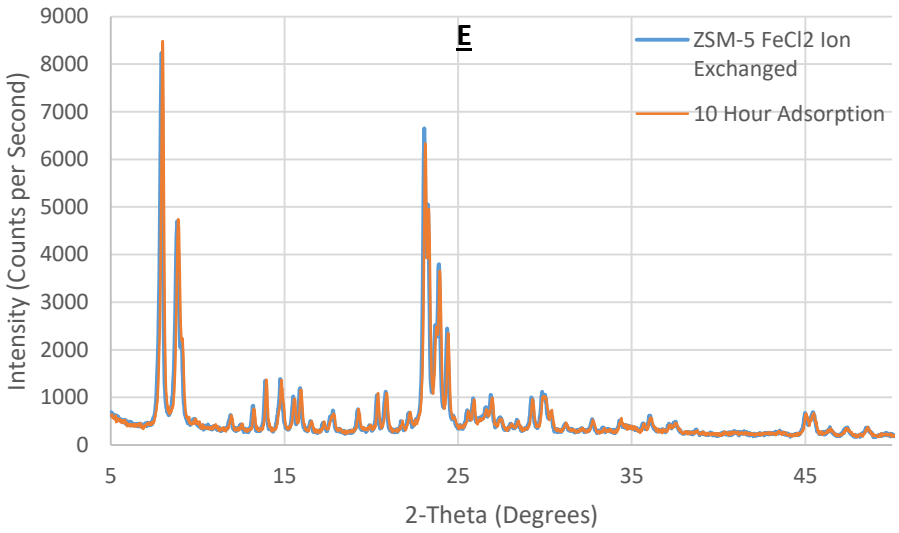
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
5
15
25
35
45
2-Theta (Degrees)


E
ZSM-5 FeCl2 Ion Exchanged
10 Hour Adsorption
Intensity (Counts per Second)
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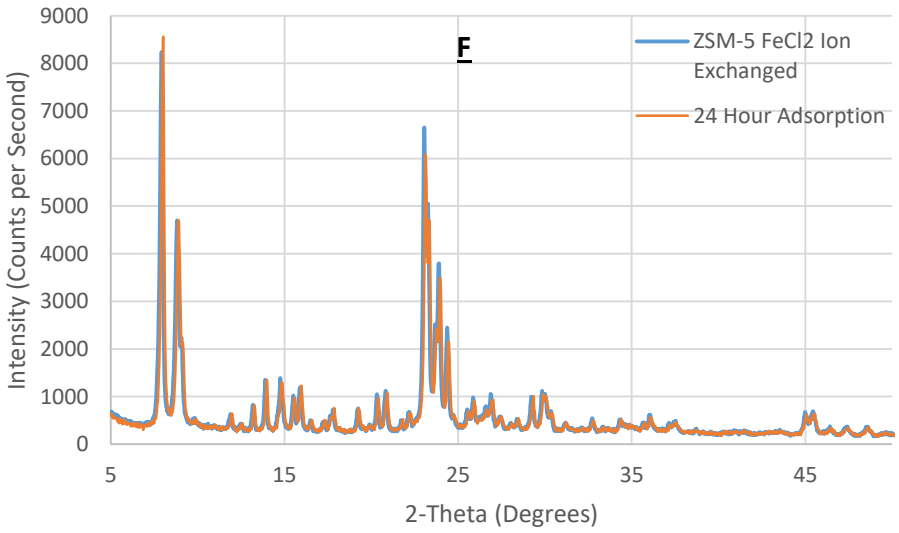
8000
7000
6000
5000
4000
3000
2000
1000
0
5
15
25
35
45
2-Theta (Degrees)


F
ZSM-5 FeCl2 Ion Exchanged
24 Hour Adsorption
Intensity (Counts per Second)
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7000
6000
5000
4000
3000
2000
1000
0
5
15
25
35
45
2-Theta (Degrees)

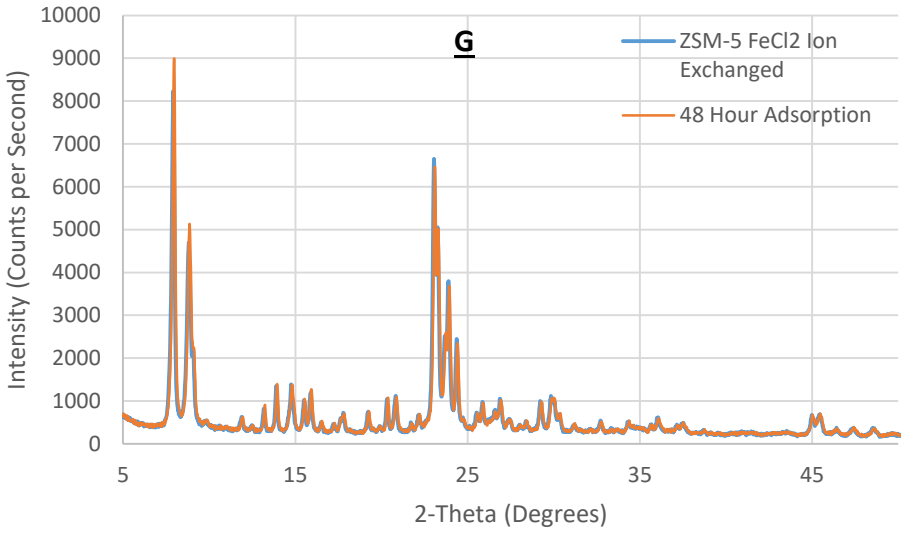


Figure 36. A) Fe ion exchanged ZSM-5 30:1 pre-adsorption + Fe ion exchanged ZSM-5 30:1 post 2-hour paracetamol adsorption. B) Fe ion exchanged ZSM-5 30:1 pre-adsorption + Fe ion exchanged ZSM-5 30:1 post 4-hour paracetamol adsorption. C) Fe ion exchanged ZSM-5 30:1 pre-adsorption + Fe ion exchanged ZSM-5 30:1 post 6-hour paracetamol adsorption. D) Fe ion exchanged ZSM-5 30:1 pre-adsorption + Fe ion exchanged ZSM-5 30:1 post 8-hour paracetamol adsorption. E) Fe ion exchanged ZSM-5 30:1 pre-adsorption + Fe ion exchanged ZSM-5 30:1 post 10-hour paracetamol adsorption. F) Fe ion exchanged ZSM-5 30:1 pre-adsorption + Fe ion exchanged ZSM-5 30:1 post 24-hour paracetamol adsorption. G) Fe ion exchanged ZSM-5 30:1 pre-adsorption + Fe ion exchanged ZSM-5 30:1 post 48-hour paracetamol adsorption.

All seven XRD patterns show some difference when compared to the pre-adsorption ZSM-5. All the patterns have some form of change in relative peak intensity in multiple peaks within the range of 5^{o}-23^{o} 2-theta. The most consistent difference is seen in the first two peaks at 7.93^{o} 2-theta and 8.82^{o} 2-theta, with the Fe ion exchanged ZSM-5 pre-adsorption having peak intensities of 8236 counts per second and 4700 counts per second respectively. Post adsorption these peaks were changed to between 8456-8999counts per second and 4675-5135 counts per second with the lowest peaks being produced by the 6-hour adsorption and highest being produced by the 48-hour adsorption. This change in relative peak intensity indicates that the contents of the unit cell have changed in some way which would indicate that the adsorption of the paracetamol has been successful. Another indicator is that all the post adsorption patterns have been shifted to the right by 0.0202^{o}-0.0808^{o} 2-theta with the 10-hour adsorption being shifted the most and the 8-hour adsorption the least. This shift towards a higher 2-theta value indicates a contraction of the zeolite

unit cell is occurring. The zeolite framework has a high degree of flexibility and this peak position shift is a further indication that a species has been adsorbed into the pores of the zeolite, in this case paracetamol, though the relatively low level of shift occurring indicates that this change is negligible.

The HPLC and XRD data indicate that the paracetamol has been adsorbed by the Fe ion exchanged ZSM-5 30:1 and successfully removed from the solution. The data from the XRD patterns were used to determine the cell parameters to see how the cell structure changed to accommodate the adsorbed paracetamol. The unit cell parameters for Fe ion exchanged ZSM-5 30:1 pre-and post paracetamol adsorption were determined using Topas and J-edit and shown in table 23. A Pawley fit was done using a Chebyshev function background and Pseudo-Voight peak shape function, the zero background and unit cell parameters (*a*, *b*, *c*) were refined to determine errors.

Table 23. Lattice parameters of Fe ion exchanged ZSM-5 30:1 pre-and post paracetamol adsorption with errors included in brackets.

Contact Time with Paracetamol Solution (Hours)	**RWP**	***a*** **(Å)**	***b*** **(Å)**	***c*** **(Å)**
0	6.791	20.11923(4)	19.92074(2)	13.41776(2)
2	6.294	20.12903(4)	19.92670(2)	13.41817(2)
4	6.225	20.12127(3)	19.92243(2)	13.41232(2)
6	6.156	20.13228(3)	19.92865(2)	13.42065(2)
8	6.305	20.12280(6)	19.92317(2)	13.41237(2)
10	6.221	20.13241(3)	19.93416(2)	13.42308(2)
24	6.379	20.12665(3)	19.92374(2)	13.41350(2)
48	6.457	20.11770(3)	19.91986(2)	13.41179(2)

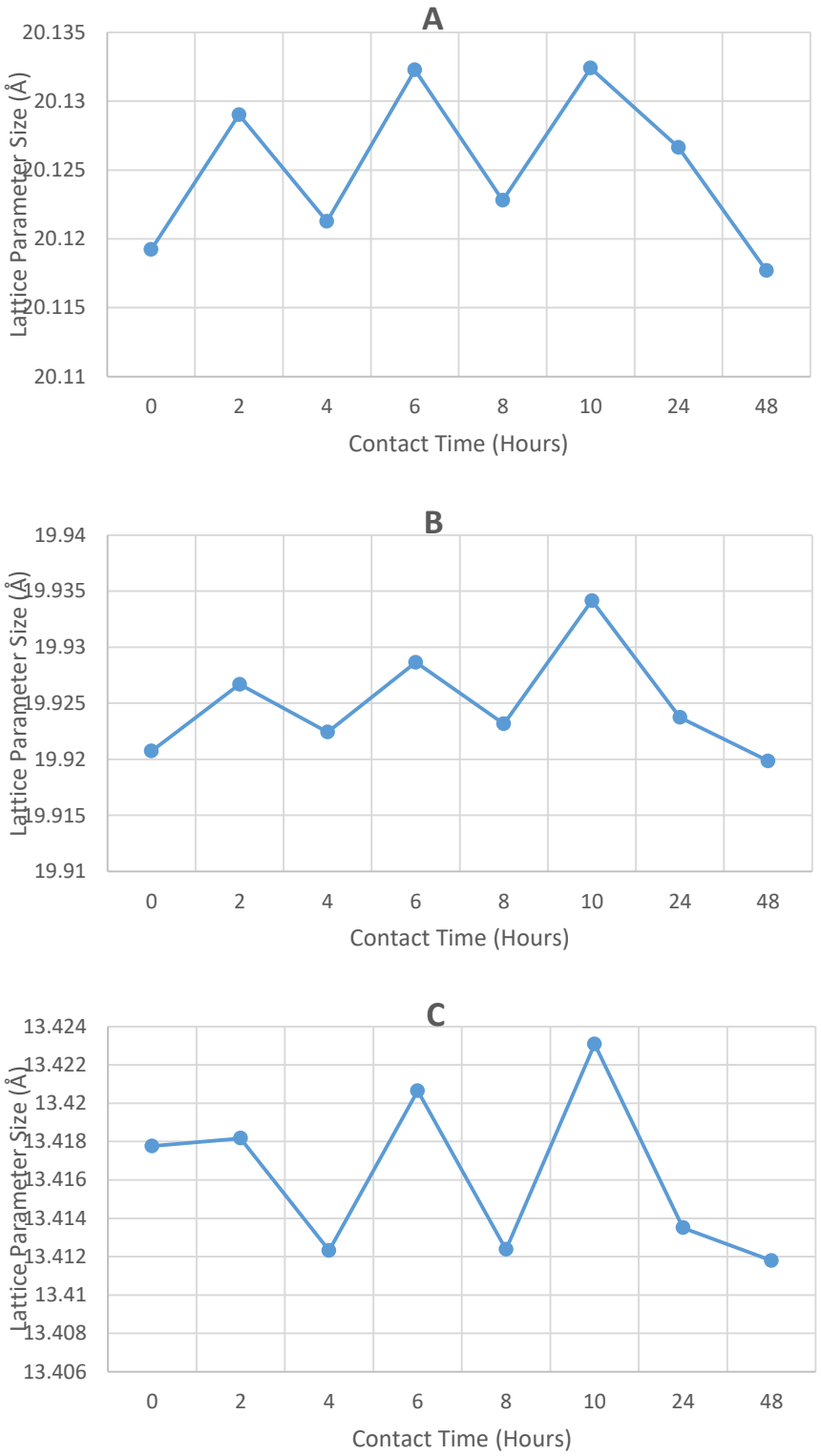


Figure 37. A) Change in lattice parameter *a* against Fe ion exchanged ZSM-5 30:1 contact time with paracetamol. B) Change in lattice parameter *b* against Fe ion exchanged ZSM-5 30:1 contact time with paracetamol. C) Change in lattice parameter *c* against Fe ion exchanged ZSM-5 30:1 contact time with paracetamol.

Figure 37 shows the change in the lattice parameters of ZSM-5 pre-and post paracetamol adsorption and shows all three lattice parameter size changes follow the same pattern. All three increase from 0-2 hours, they then reduce in size between 2-4 hours, followed by another increase in size from 4-6 hours, they reduce in size from 6-8 hours then increase in size from 8-10 hours and then a final reduction in size from 10-48 hours. Their graphs are visually similar because of this with only the relative size changes varying. These peaks and valleys do not seem to correlate with the steady yet small increase in concentration adsorbed shown in the HPLC data but there are some definite similarities. The concentration adsorbed of paracetamol increased steadily from 2-10 hours, peaking at 10 hours, and then decreasing from 10-48 hours. Between 2-10 hours there is an increase in concentration adsorbed of 4.32% followed by a reduction of 3.65% concentration adsorbed between 10-48 hours. Similarly, between 0-10 hours there is an increase in size of lattice parameters *a*, *b* and *c* of 0.07%, 0.07% and 0.04% respectively, between 10-48 hours there is a reduction in size of lattice parameters *a*, *b* and *c* of 0.07%, 0.07% and 0.08% respectively. Paracetamol is 7.8Å X 4.2Å [41] in size, considering the pore sizes of ZSM-5 are 5.4 X 5.6Å and 5.1 X 5.5Å it would be logical to conclude that some pore expansion would be required for paracetamol to be adsorbed and with the upper limit for molecule adsorption size for ZMS-5 being 9.1Å[6] it is completely possible for paracetamol to be adsorbed.

These changes in size corresponding with the changes in the concentration of paracetamol adsorbed indicate that these changes are due to the unit cell expanding to accommodate the paracetamol being adsorbed into the pores of the Fe ion exchanged ZSM-5 30:1, which confirms that the paracetamol is being adsorbed by the Fe ion exchanged ZSM-5 30:1. However considering its overall amount of concentration removed from solution is reduced by over half of the commercial ZSM-5 30:1 equivalent we would consider the Fe ion exchanged ZSM-5 30:1 appropriate for the removal of paracetamol from aqueous solution but to not use it if commercial ZSM-5 ammonium 30:1 is available. This would indicate that the presence of iron cations instead of ammonium reduced paracetamol's affinity for ZSM-5. From this we can infer that it is more likely that the reduction in adsorption of paracetamol by the commercial ZSM-5 ammonium 200-400:1 was due to the reduction of ammonium cations present rather than its increased hydrophobicity.

5.3 – Ibuprofen Lysine

The previous ibuprofen lysine HPLC calibration curve's equation was used to calculate the concentration of the ibuprofen lysine left in the solution after the adsorptions. Table 24 shows the HPLC data produced by the adsorption reactions between 2 and 48 hours. Included are the concentration of the drug left in solution, the concentration of the drug that was adsorbed and the percentage of the overall concentration that was adsorbed. A plot showing concentration adsorbed by the zeolite against contact time is presented in figure 38.

Table 24. HPLC results for the ibuprofen lysine adsorptions by Fe ion exchanged ZSM-5 30:1.

Ibuprofen Lysine Concentration Left in Solution (M)	Peak Area (mVmin)	Contact Time (Hours)	Retention Time (mins)	Height (mV)	Concentration Adsorbed by the Zeolite (M)	% Concentration Adsorbed
0.00205	162.9501	2	8.258	450.885	0.00000*	0.0000
0.00214	170.3202	4	8.203	395.462	0.00000*	0.0000
0.00151	120.1861	6	8.079	345.410	0.00049	24.4065
0.00145	115.5099	8	8.070	331.811	0.00055	27.3477
0.00147	117.2509	10	8.068	336.472	0.00053	26.2527
0.00206	163.6923	24	8.234	457.206	0.00000*	0.0000
0.00205	162.8823	48	8.243	451.870	0.00000*	0.0000

*These values have been normalised to zero as HPLC data came out with a negative concentration

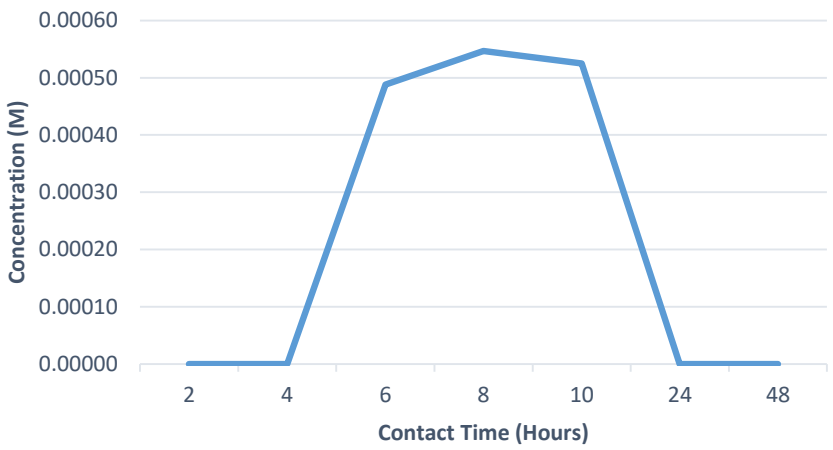
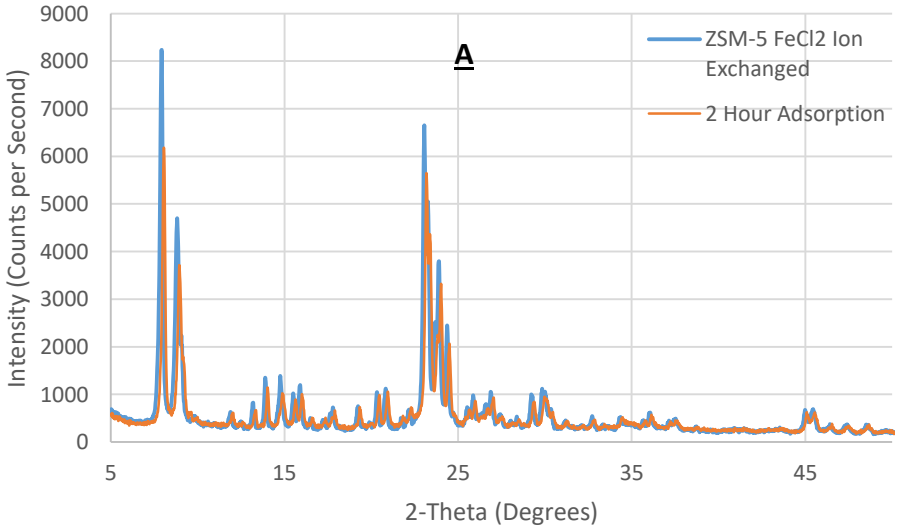
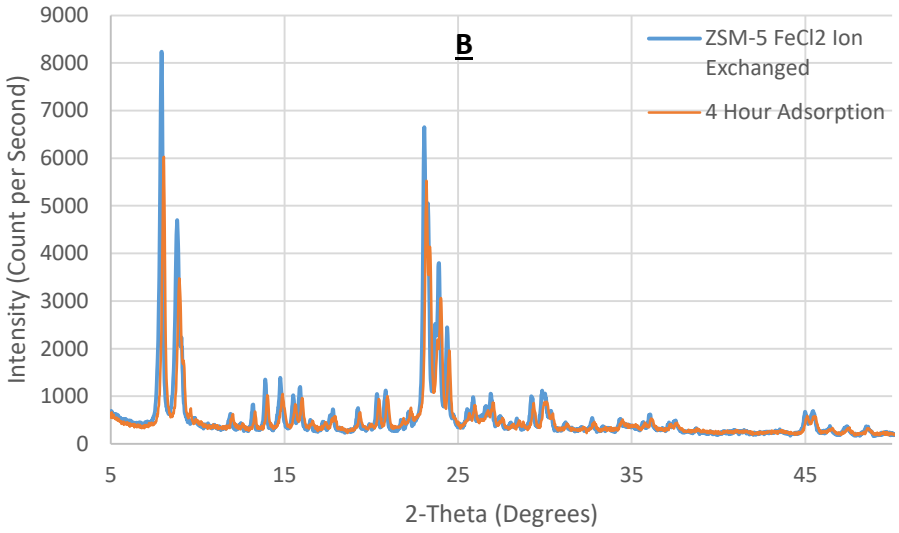


Figure 38. Graph depicting concentration of ibuprofen lysine adsorbed by Fe ion exchanged ZSM-5 30:1 against contact time.

Due to its low concentration and the low relative solubility of ibuprofen lysine in general the HPLC machine may have picked up a higher result than possible, if only slightly, causing negative results to appear. These adsorptions were repeated to check validity and consistent results were produced. For the purposes of this research any negative concentration results have been changed to indicate that no ibuprofen lysine was adsorbed, though some may have been the amount is negligible. The amount adsorbed seems to be rather stable when it is adsorbed, being within the range of 24.4-27.35%. This data would indicate that the optimum adsorption time is 8 hours as after this the concentration adsorbed starts to drop. This would indicate that while better than commercial ZSM-5 200-400:1, Fe ion exchanged ZSM-5 30:1 is not appropriate for the removal of ibuprofen lysine from aqueous solution if commercial ZSM-5 30:1 is available.

To ascertain that ibuprofen lysine had been adsorbed into the pores of the zeolite and not the surface of the particles XRD was carried out and the data analysed using Pawley fits. The post adsorption XRD patterns overlaid onto the Fe ion exchanged ZSM-5 30:1 XRD pattern, shown in figure 35, are plotted in figure 39 below.

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ZSM-5 FeCl2 Ion Exchanged
4 Hour Adsorption
Intensity (Count per Second)
2-Theta (Degrees)
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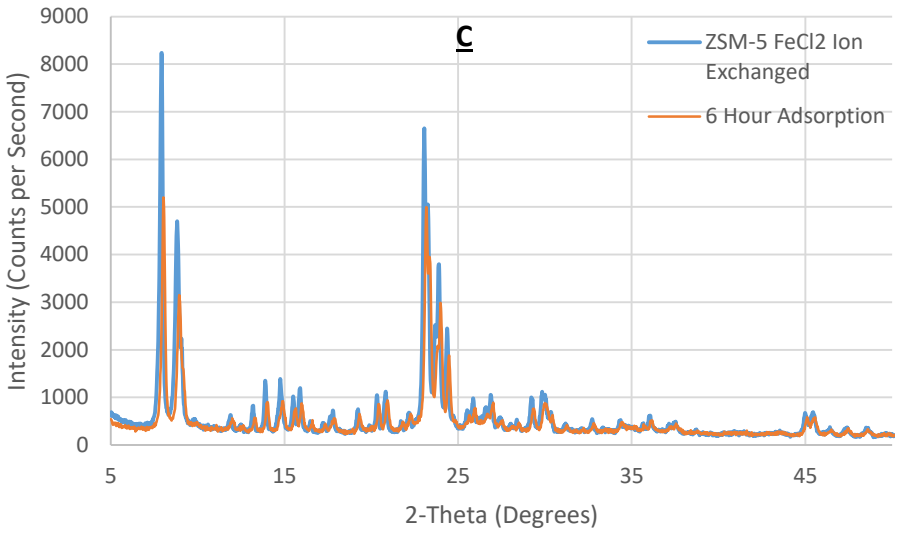
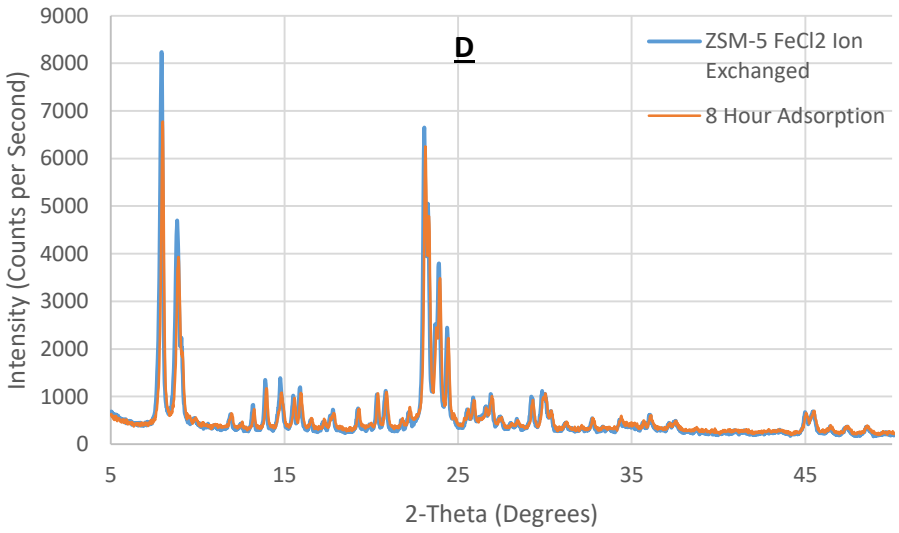
8000
7000
6000
5000
4000
3000
2000
1000
0
5
15
25
35
45


C
ZSM-5 FeCl2 Ion Exchanged
6 Hour Adsorption
Intensity (Counts per Second)
2-Theta (Degrees)
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
5
15
25
35
45


D
ZSM-5 FeCl2 Ion Exchanged
8 Hour Adsorption
Intensity (Counts per Second)
2-Theta (Degrees)
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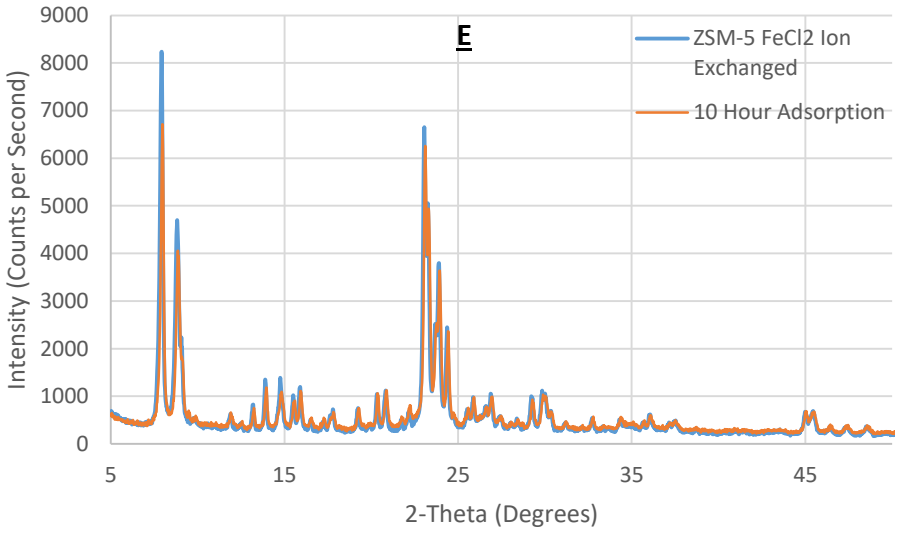
8000
7000
6000
5000
4000
3000
2000
1000
0
5
15
25
35
45


E
ZSM-5 FeCl2 Ion Exchanged
10 Hour Adsorption
Intensity (Counts per Second)
2-Theta (Degrees)
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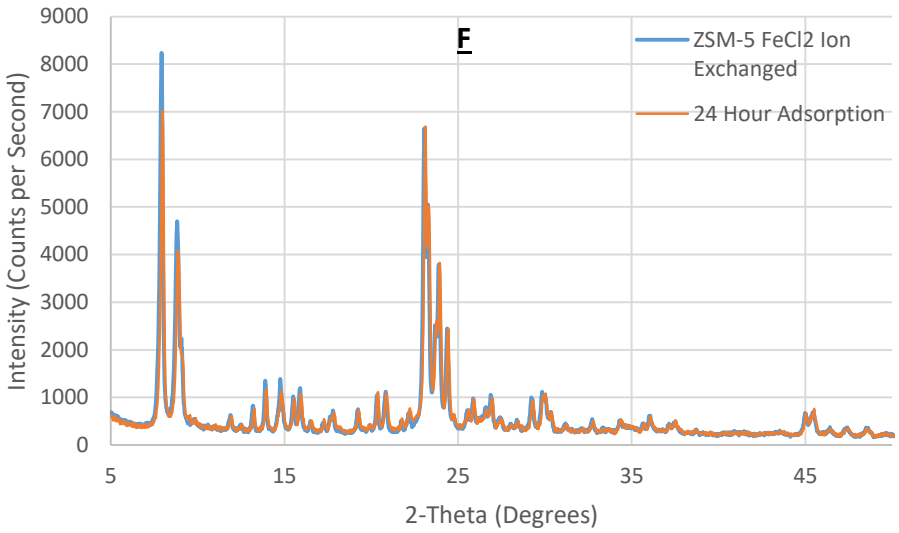
8000
7000
6000
5000
4000
3000
2000
1000
0
5
15
25
35
45


F
ZSM-5 FeCl2 Ion Exchanged
24 Hour Adsorption
Intensity (Counts per Second)
2-Theta (Degrees)
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8000
7000
6000
5000
4000
3000
2000
1000
0
5
15
25
35
45

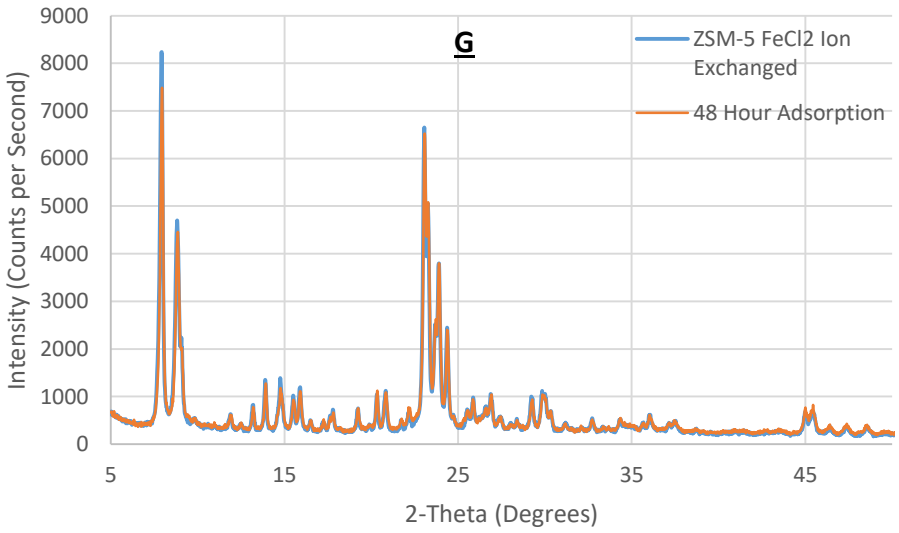
G
ZSM-5 FeCl2 Ion Exchanged
48 Hour Adsorption
Intensity (Counts per Second)
2-Theta (Degrees)
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
5
15
25
35
45

Figure 39. A) Fe Ion Exchanged ZSM-5 30:1 pre-adsorption + Fe Ion Exchanged ZSM-5 30:1 post 2-hour ibuprofen lysine adsorption. B) Fe Ion Exchanged ZSM-5 30:1 pre-adsorption + Fe Ion Exchanged ZSM-5 30:1 post 4-hour ibuprofen lysine adsorption. C) Fe Ion Exchanged ZSM-5 30:1 pre-adsorption + Fe Ion Exchanged ZSM-5 30:1 post 6-hour ibuprofen lysine adsorption. D) Fe Ion Exchanged ZSM-5 30:1 pre-adsorption + Fe Ion Exchanged ZSM-5 30:1 post 8-hour ibuprofen lysine adsorption. E) Fe Ion Exchanged ZSM-5 30:1 pre-adsorption + Fe Ion Exchanged ZSM-5 30:1 post 10-hour ibuprofen lysine adsorption. F) Fe Ion Exchanged ZSM-5 30:1 pre-adsorption + Fe Ion Exchanged ZSM-5 30:1 post 24-hour ibuprofen lysine adsorption. G) Fe Ion Exchanged ZSM-5 30:1 pre-adsorption + Fe Ion Exchanged ZSM-5 30:1 post 48-hour ibuprofen lysine adsorption.

All seven XRD patterns show some slight difference when compared to the pre-adsorption ZSM-5. All the patterns have some form of reduction in relative peak intensity in multiple peaks within the range of 5^{o}-23^{o} 2-theta. The biggest difference is seen in the first two peaks at 7.93^{o} 2-theta and 8.82^{o} 2-theta, with the commercial ZSM-5 pre-adsorption having peak intensities of 8236 counts per second and 4700 counts per second respectively. Post adsorption these peaks were reduced to between 5201-6777 counts per second and 3150-4058 counts per second with the lowest peaks being produced by the 6-hour adsorption and highest being produced by the 8 and 10 hour adsorptions respectively. The 6-hour adsorption also has noticeable reductions in the peaks at 13.89^{o} 2-theta, 14.75^{o} 2-theta, 15.50^{o} 2-theta, 15.90^{o} 2-theta, 23.05^{o} 2-theta and 23.90^{o} 2-theta. These initially had peak intensities of 1351, 1388, 1021, 1196, 6652 and 3797 counts per second respectively. These were reduced to 902, 917, 769, 836, 4998 and 2986 counts per second respectively. This change in relative peak intensity indicates that the contents of the unit cell have changed in some way which would indicate that the adsorption of the ibuprofen lysine has been successful. The 6-hour adsorption's XRD pattern show some shifting towards the right, a shift of 0.1212^{o} 2-theta. This shift towards a higher 2-theta value indicates a contraction of the zeolite unit cell is occurring. The zeolite framework has a high degree of flexibility and this peak position shift is a further indication that a species has been adsorbed into the pores of the zeolite, in this case ibuprofen lysine, though the relatively low level of shift occurring indicates that this change is negligible. I have not included the 2, 4, 24 and 48-hour adsorption's XRD patterns in my conclusions as the peaks they display are inconsistent with what would be expected and each other, 2 and 4 hours being similar to each other and 24 and 48 hours being similar but both sets being dissimilar to each other. This could be due to small amount of

ibuprofen lysine being adsorbed and the HPLC not picking it up properly but since 2 and 4 hours have a similar pattern to the 6-hour adsorption and 24 and 48 hours have a similar pattern to the 10-hour adsorption it is still inconsistent. Any further analysis shall exclude these data points also.

The HPLC and XRD data indicate that the ibuprofen lysine has been adsorbed at certain times by the Fe ion exchanged ZSM-5 30:1 and successfully removed from the solution. The data from the XRD patterns were used to determine the cell parameters to see how the cell structure changed to accommodate the adsorbed ibuprofen lysine. The unit cell parameters for Fe ion exchanged ZSM-5 30:1 pre-and post ibuprofen lysine adsorption were determined using Topas and J-edit and shown in table 25. A Pawley fit was done using a Chebyshev function background and Pseudo-Voight peak shape function, the zero background and unit cell parameters (*a*, *b*, *c*) were refined to determine errors.

Table 25. Lattice parameters of Fe ion exchanged ZSM-5 30:1 pre-and post ibuprofen lysine adsorption with errors included in brackets.

Contact Time with Ibuprofen Lysine Solution (Hours)	**RWP**	***a*** **(Å)**	***b*** **(Å)**	***c*** **(Å)**
0	6.791	20.11923(4)	19.92074(2)	13.41776(2)
2	6.270	20.13753(4)	19.93231(2)	13.42492(3)
4	6.170	20.12901(5)	19.92952(3)	13.42435(3)
6	6.031	20.13959(4)	19.93073(3)	13.42675(3)
8	5.939	20.13039(4)	19.93160(2)	13.42568(2)
10	6.086	20.12244(4)	19.92341(2)	13.42254(2)
24	6.565	20.12246(4)	19.92455(2)	13.42109(2)
48	6.253	20.12771(4)	19.93093(2)	13.42469(2)

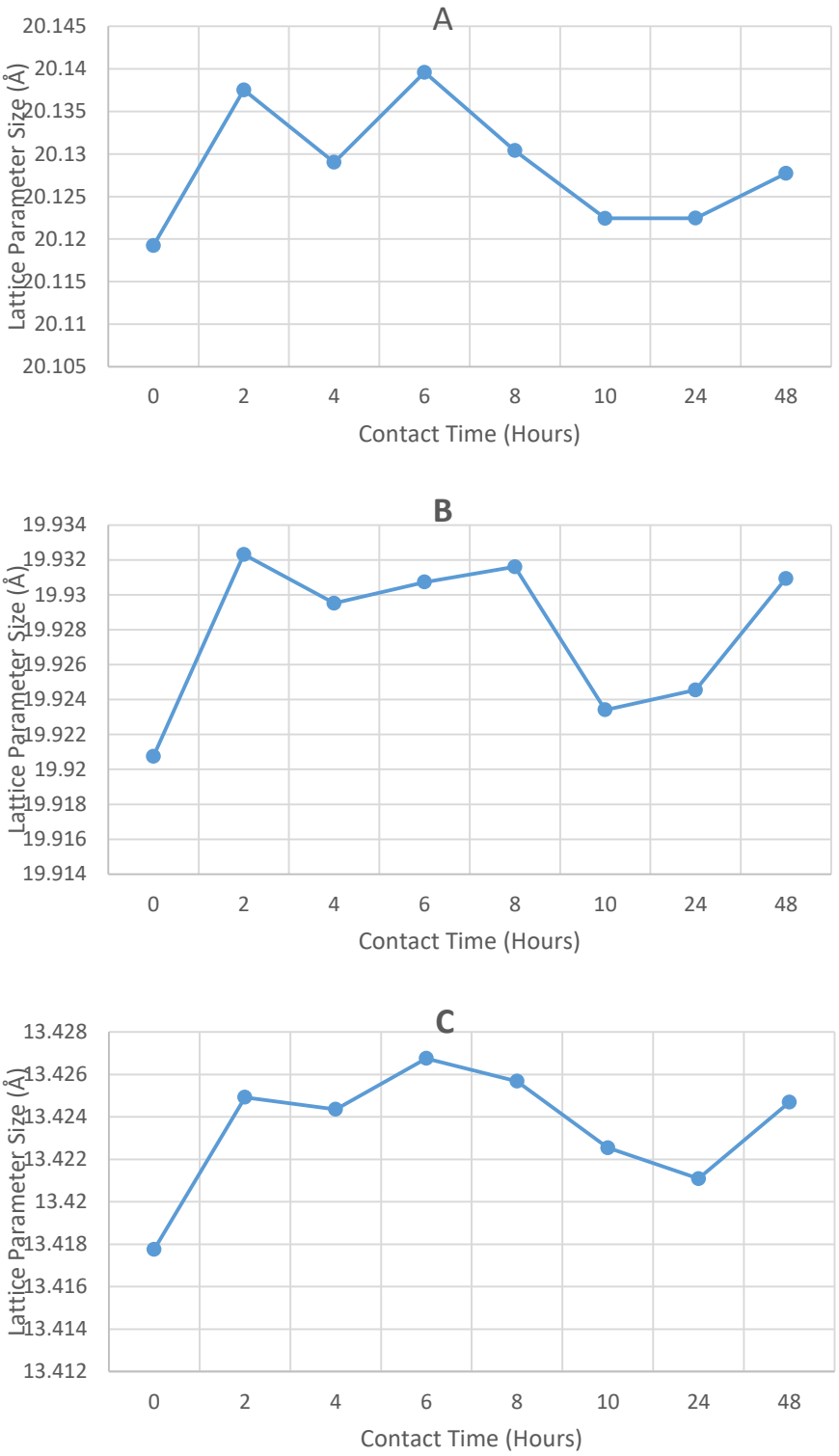

Figure 40. A) Change in lattice parameter *a* against Fe ion exchanged ZSM-5 30:1 contact time with ibuprofen lysine. B) Change in lattice parameter *b* against Fe ion exchanged ZSM-5 30:1 contact time with ibuprofen lysine. C) Change in lattice parameter *c* against Fe ion exchanged ZSM-5 30:1 contact time with ibuprofen lysine.

Figure 40 shows the change in the lattice parameters of ZSM-5 pre-and post ibuprofen lysine adsorption and shows all three lattice parameter size changes follow a similar pattern. All three increase in size from 0-2 hours then reduce in size between 2-4 hours before increasing in size again from 4-6 hours. Then parameters *a* and *c* decrease in size from 6-10 hours, with parameter *c* further decreasing in size from 10-24 hours and parameter *a* plateauing at this point. Parameter *b* increases in size between 4-6 hours before dropping down from 8-10 hours followed by a slight increase in size from 10-24 hours. All three parameters then increase in size from 24-48 hours. Disregarding the XRD data from 2, 4, 24 and 48 hours, as done previously, then it seems that all the parameters increase in size when ibuprofen lysine is adsorbed but that parameter *b* increases in size the higher the concentration is adsorbed while parameters *a* and *c* decrease in size. From 6-8 hours, there is an increase in adsorption by 2.94%, this produced an increase in size for parameter *b* of 0.004% and reductions in size of parameters *a* and *c* by 0.046% and 0.008% respectively. All three behave inconsistently with this though at 10 hours, as there is a reduction in concentration so parameter *b* should reduce in size, as it does, but its reduction seems too large for the reduction in concentration that is occurring. Similarly, at 10 hours there should be an increase in size of parameters *a* and *c* as there is a reduction in concentration adsorbed but both are shown to decrease in size alongside parameter *b*. The concentration adsorbed is reduced by 1.10% and this leads to a reduction in size for parameters *a*, *b* and *c* of 0.039%, 0.041% and 0.023% respectively. These inconsistencies indicate that the lattice parameters were changing independently of the amount of ibuprofen lysine adsorbed and that they do not change to accommodate the ibuprofen lysine. Ibuprofen lysine is 8.9Å X 3.8Å[42] in size, considering the pore sizes of ZSM-5 are 5.4 X 5.6Å and 5.1 X 5.5Å it would be logical to conclude that some pore expansion would be required for ibuprofen lysine to be adsorbed and with the upper limit for molecule adsorption size for ZMS-5 being 9.1Å[6] it is completely possible for ibuprofen lysine to be adsorbed, but due to the inconsistencies presented in the lattice parameters sizes it does not seem likely that the expansions occurring are purely due to the adsorption of ibuprofen lysine.

This data indicates that Fe ion exchanged ZSM-5 30:1 is not an appropriate compound for the removal of ibuprofen lysine from aqueous solution. The presence of a lower amount of adsorption than that of commercial ZSM-5 ammonium 30:1

would indicate that the change to the iron charge balancing cation decreased the affinity of ibuprofen lysine for ZSM-5 and it is more likely that the reduction in the number of charge balancing cations and not the hydrophobicity of the commercial ZSM-5 200-400:1 that caused the reduction in ibuprofen lysine's affinity for it.

5.4 – Aspirin

The previous aspirin HPLC calibration curve's equations for aspirin peak 1 and 2 was used to calculate the concentration of the aspirin left in the solution after the adsorptions by combining the concentrations. Table 26 shows the HPLC data produced by the adsorption reactions between 2 and 48 hours for peak 1, table 27 shows peak 2 and table 28 are the two sets of concentrations combined. Included are the concentration of the drug left in solution, the concentration of the drug that was adsorbed and the percentage of the overall concentration that was adsorbed. A plot showing the aspirin combined concentration adsorbed by the zeolite against contact time is presented in figure 41.

Table 26. Aspirin peak 1 HPLC results

Aspirin Tablet Samples Peak 1 Concentration Left in Solution (M)	**Peak Area (mVmin)**	**Contact Time (Hours)**	**Retention Time (min)**	**Height (mV)**
0.0014	13.7629	2	7.291	46.359
0.0014	13.8948	4	7.212	46.576
0.0019	18.6756	6	6.987	65.442
0.0019	18.1783	8	6.872	62.975
0.0008	7.8051	10	6.835	27.295
0.0018	17.4385	24	6.802	60.180
0.0010	9.4389	48	6.793	32.345

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Table 27. Aspirin peak 2 HPLC results.

Aspirin Tablet Samples Peak 2 Concentration Left in Solution (M)	Peak Area (mVmin)	Contact Time (Hours)	Retention Time (mins)	Height (mV)
0.0014	12.8839	2	11.044	30.142
0.0015	13.3165	4	10.927	30.141
0.0013	11.9726	6	10.448	39.060
0.0013	11.4244	8	10.304	38.590
0.0017	15.1906	10	10.221	35.969
0.0013	11.2748	24	10.148	28.011
0.0019	17.2676	48	10.425	40.242

Table 28. Aspirin combined concentrations HPLC results.

Aspirin Tablet Samples Combined Concentrations Left in Solution (M)	Contact Time	Concentration Adsorbed by the Zeolite	% Concentration Adsorbed
0.0028	2	0.0022	43.1930
0.0029	4	0.0021	41.9596
0.0032	6	0.0018	35.1979
0.0031	8	0.0019	37.4347
0.0025	10	0.0025	50.2108
0.0030	24	0.0020	39.2781
0.0029	48	0.0021	42.2468

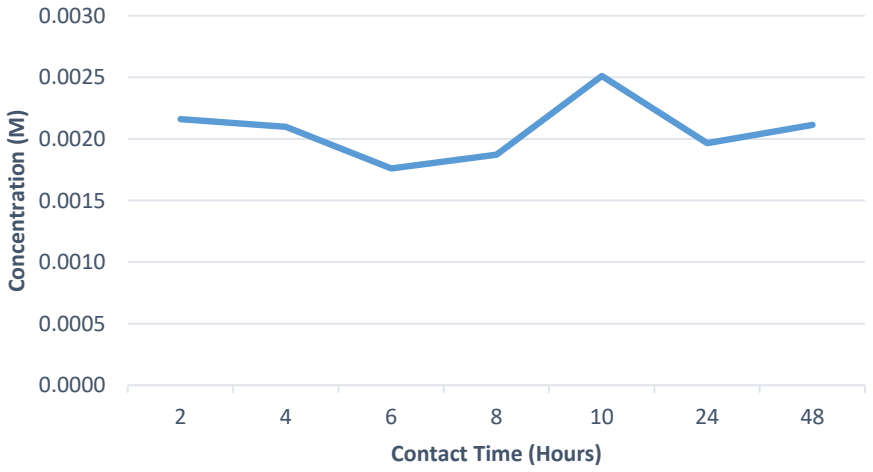
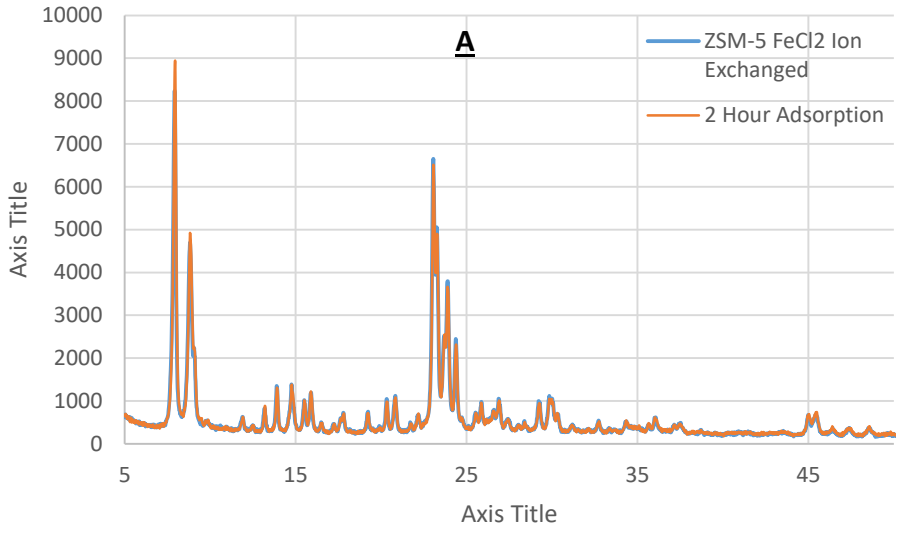


Figure 41. Graph depicting concentration of aspirin adsorbed by Fe ion exchanged ZSM-5 30:1 against contact time.

The concentration adsorbed stays fairly constant throughout as the percentage adsorbed only had a range of 35.20-50.21% with the contact time of 6 hours accounting for the lowest concentration adsorbed of 0.0018M and the highest occurring during the 10-hour adsorption of 0.0025M, indicating that this is the optimum adsorbance time. An equilibrium seems to have been found at around 41-43%, 2 and 4 hours being within this range before dropping down to 35.20% at 6 hours. From 6-8 hours, there is a slight increase in percentage adsorbed, from 35.20% to 37.43%, before increasing again between 8-10 hours, going from 37.43% to the maximum of 50.21% before dropping down to 39.28% at 24 hours. It then increases again to 42.25% at 48 hours, seemingly approaching the equilibrium once again. This overall relative decrease in the concentration adsorbed by ZSM-5 when compared the commercial ZSM-5 ammonium 30:1 indicates that changing the charge balancing cation to iron reduced aspirin's affinity for ZSM-5. It also shows a relative decrease in the concentration adsorbed when compared to the commercial ZSM-5 ammonium 200-400:1, this would indicate that aspirin's increased affinity for ZSM-5 200-400:1 was more likely due to its increased hydrophobicity than its reduced amount of ammonium cations.

To confirm that the aspirin has been adsorbed into the pores of ZSM-5 and not absorbed on to the surface of the particles powder XRD was performed on the filtered solid after adsorption had occurred. As a basis, the Fe ion exchanged ZSM-5 30:1 XRD pattern is included in figure 35 and the diffraction patterns for the post adsorption ZSM-5 is shown in figure 42 with the post adsorption pattern overlaid onto the pre-adsorption pattern.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ZSM-5 FeCl2 Ion Exchanged
2 Hour Adsorption
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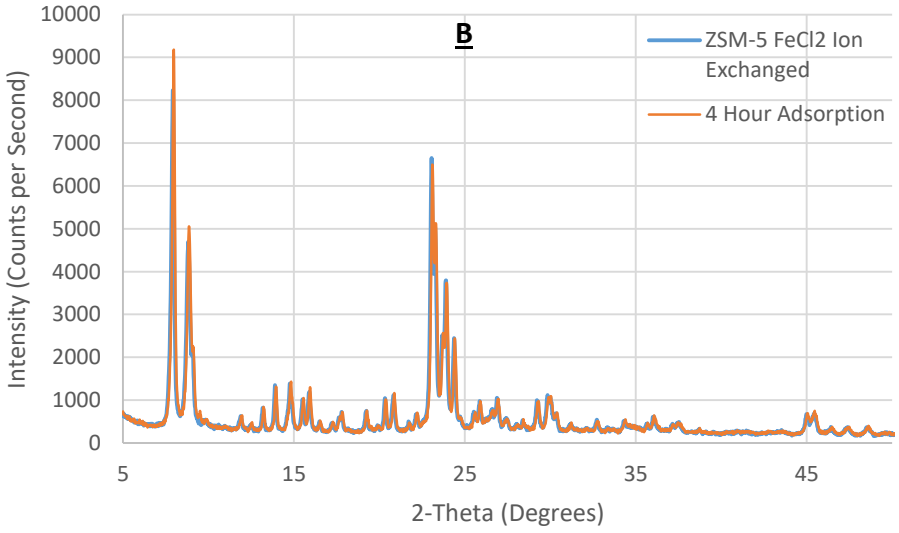
B
ZSM-5 FeCl2 Ion Exchanged
4 Hour Adsorption
Intensity (Counts per Second)
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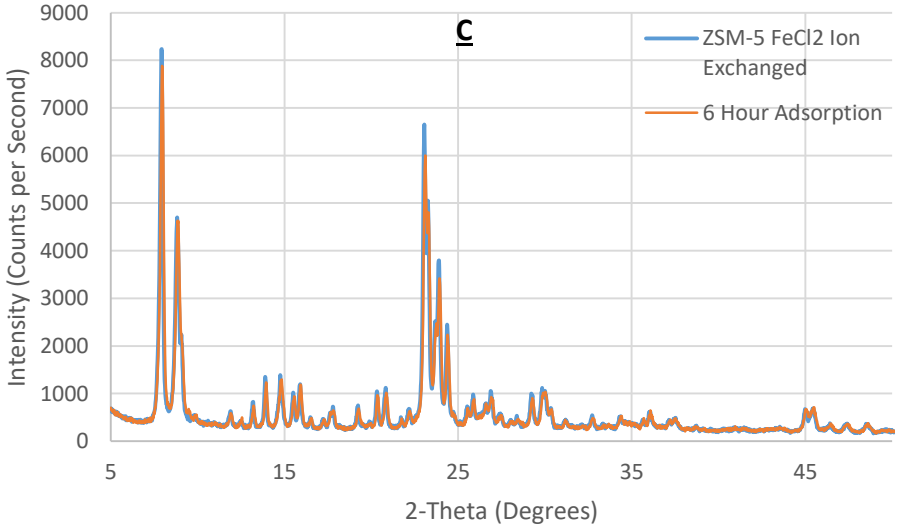
C
ZSM-5 FeCl2 Ion Exchanged
6 Hour Adsorption
Intensity (Counts per Second)
2-Theta (Degrees)
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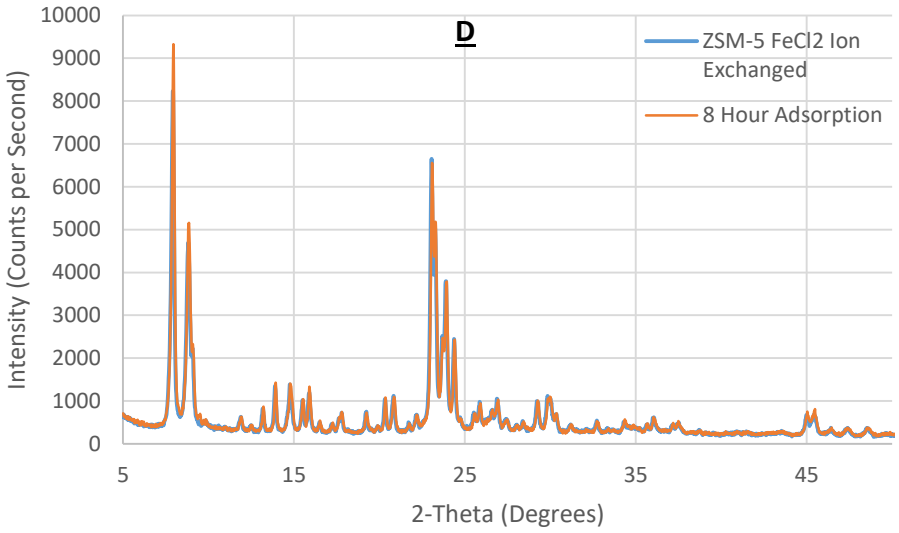
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ZSM-5 FeCl2 Ion Exchanged
8 Hour Adsorption
Intensity (Counts per Second)
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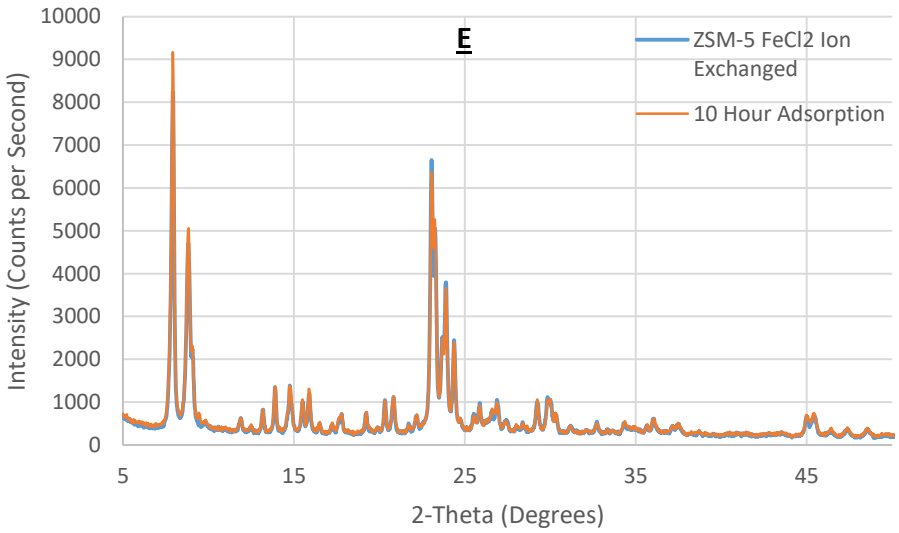
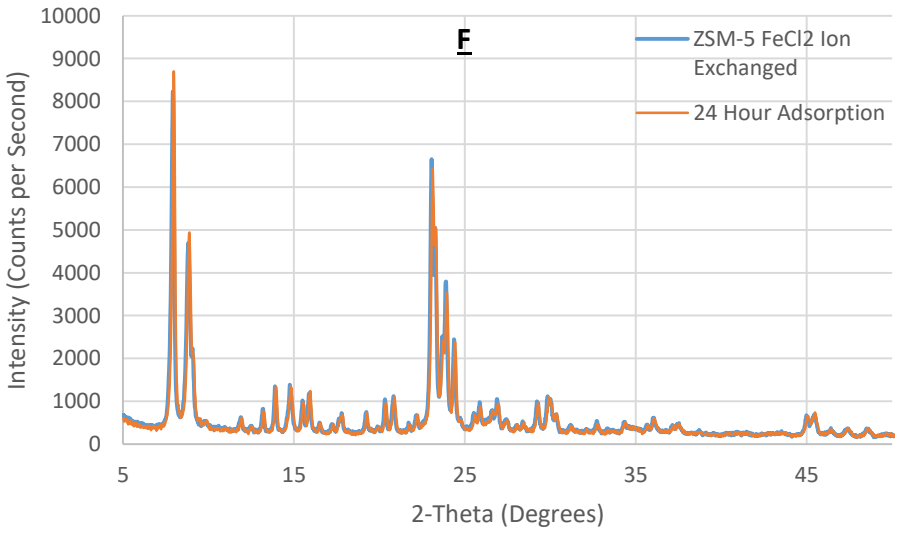
2-Theta (Degrees)


E
ZSM-5 FeCl2 Ion Exchanged
10 Hour Adsorption
Intensity (Counts per Second)
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
5
15
25
35
45
2-Theta (Degrees)


F
ZSM-5 FeCl2 Ion Exchanged
24 Hour Adsorption
Intensity (Counts per Second)
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
5
15
25
35
45
2-Theta (Degrees)

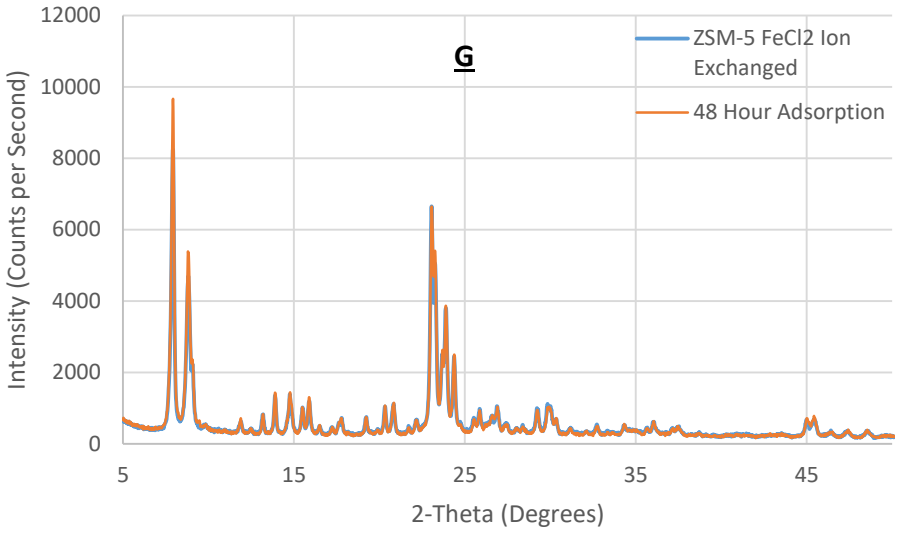


Figure 42. A) Fe ion exchanged ZSM-5 30:1 pre-adsorption + Fe ion exchanged ZSM-5 30:1 post 2-hour aspirin adsorption. B) Fe ion exchanged ZSM-5 30:1 pre-adsorption + Fe ion exchanged ZSM-5 30:1 post 4-hour aspirin adsorption. C) Fe ion exchanged ZSM-5 30:1 pre-adsorption + Fe ion exchanged ZSM-5 30:1 post 6-hour aspirin adsorption. D) Fe ion exchanged ZSM-5 30:1 pre-adsorption + Fe ion exchanged ZSM-5 30:1 post 8-hour aspirin adsorption. E) Fe ion exchanged ZSM-5 30:1 pre-adsorption + Fe ion exchanged ZSM-5 30:1 post 10-hour aspirin adsorption. F) Fe ion exchanged ZSM-5 30:1 pre-adsorption + Fe ion exchanged ZSM-5 30:1 post 24-hour aspirin adsorption. G) Fe ion exchanged ZSM-5 30:1 pre-adsorption + Fe ion exchanged ZSM-5 30:1 post 48-hour aspirin adsorption.

All seven XRD patterns show noticeable difference when compared to pre-adsorption ZSM-5. All the patterns have some form of change in relative peak intensity in the first two peaks at 7.93^{o} 2-theta and 8.82^{o} 2-theta. These show a consistent increase in relative peak intensity, except for 6 hours which shows a reduction of relative peak intensity, with the commercial ZSM-5 pre-adsorption having peak intensities of 8236 counts per second and 4700 counts per second respectively. Post adsorption these peaks were changed to between 7883-9663 counts per second and 4415-7702 counts per second with the lowest peaks being produced by the 6-hour adsorption and highest being produced by the 48-hour adsorption. This change in relative peak intensity indicates that the contents of the unit cell have changed in some way which would indicate that the adsorption of the aspirin has been successful. Another indicator is that the 24-hour adsorption pattern has been shifted to the right by a noticeable amount, being shifted by 0.0606^{o} 2-theta. This shift towards a higher 2-theta value indicates a contraction of the zeolite unit cell is occurring. The rest of the

patterns also show a shift towards the higher 2-theta values which indicating that a contraction of the zeolite unit cell is occurring there as well. The zeolite framework has a high degree of flexibility and this peak position shift is a further indication that a species has been adsorbed into the pores of the zeolite, in this case aspirin, though the relatively low level of shift occurring indicates that this change is negligible.

The HPLC and XRD data indicate that the aspirin has been adsorbed by the Fe ion exchanged ZSM-5 30:1 and successfully removed from the solution. The data from the XRD patterns were used to determine the cell parameters to see how the cell structure changed to accommodate the adsorbed aspirin. The unit cell parameters for Fe ion exchanged ZSM-5 30:1 pre-and post aspirin adsorption were determined using Topas and J-edit and shown in table 29. A Pawley fit was done using a Chebyshev function background and Pseudo-Voight peak shape function, the zero background and unit cell parameters (*a*, *b*, *c*) were refined to determine errors.

Table 29. Lattice parameters of Fe ion exchanged ZSM-5 30:1 pre-and post aspirin adsorption with errors included in brackets.

Contact Time with Paracetamol Solution (Hours)	**RWP**	***a*** **(Å)**	***b*** **(Å)**	***c*** **(Å)**
0	6.791	20.11923(4)	19.92074(2)	13.41776(2)
2	6.489	20.12965(3)	19.92964(2)	13.41955(2)
4	6.418	20.11964(4)	19.92586(3)	13.41366(3)
6	6.747	20.12342(4)	19.92081(3)	13.41465(3)
8	6.809	20.11310(4)	19.92608(2)	13.41296(2)
10	6.694	20.10625(4)	19.92351(2)	13.41111(2)
24	6.444	20.11578(4)	19.92679(2)	13.41478(2)
48	7.04	20.10644(4)	19.92032(2)	13.40841(3)

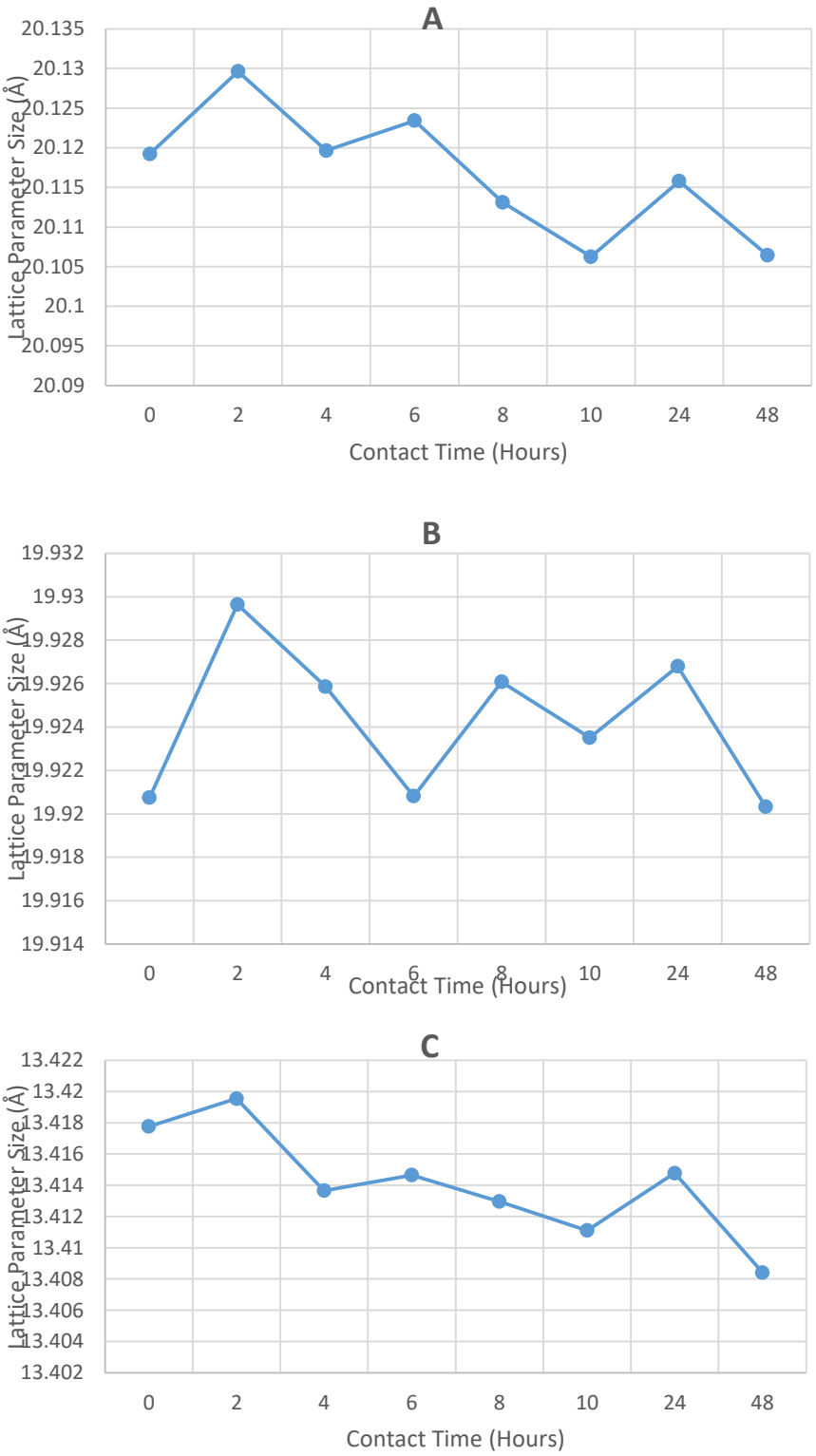


Figure 43. A) Change in lattice parameter *a* against Fe ion exchanged ZSM-5 30:1 contact time with aspirin. B) Change in lattice parameter *b* against Fe ion exchanged ZSM-5 30:1 contact time with aspirin. C) Change in lattice parameter *c* against Fe ion exchanged ZSM-5 30:1 contact time with aspirin.

Figure 43 shows the change in the lattice parameters of ZSM-5 pre-and post aspirin adsorption and all three lattice parameters do follow a similar path to one another. All three increase from 0-2 hours, lattice parameter *a* increasing by 0.05%, parameter *b* by 0.04% and parameter *c* by 0.1%. They then slowly decrease in size between 2-48 hours with lattice parameter *a* reducing by 0.12%, lattice parameter *b* reducing by 0.05% and lattice parameter *c* by 0.08%. These changes in size do not correlate to the change in concentration adsorbed by the zeolite, this indicates that the changes in lattice parameter's sizes are independent and therefore they are not changing to accommodate adsorbing the aspirin.

From this we conclude that Fe ion exchanged ZSM-5 30:1 would be an appropriate compound for the removal of aspirin from aqueous solution, though slightly less useful than commercial ZSM-5 30:1 ammonium and commercial ZSM-5 200-400:1 ammonium. This reduction in affinity after changing the charge balancing cation to iron indicates that the charge balancing cation influences aspirin's affinity for ZSM-5, though this effect may be quite small as it isn't that large a reduction in relative concentration adsorbed. Taken in conjunction with the increase in affinity for ZSM-5 200-400:1 seems to indicate that it was more likely that the increase in aspirin's affinity for ZSM-5 200-400:1 was due to the increase in its hydrophobicity rather than the reduction of the number of charge balancing cations present. Overall using Fe ion exchanged ZSM-5 30:1 to remove aspirin from aqueous solution is viable though unadvised if commercial ZSM-5 30:1 ammonium or commercial ZSM-5 200-400:1 ammonium is available as these are preferable.

6. Results and Discussion – Adsorptions Using Na Ion Exchanged ZSM-5 30:1

6.1 – Introduction

The data presented in this chapter has been taken from the adsorptions of paracetamol, aspirin and ibuprofen lysine by the commercial ZSM-5 30:1 after it had undergone an ion exchange reaction using NaCl. The charge balancing cation has been changed to see if this would change the investigated drug's affinity for ZSM-5. The ZSM-5 used for the experiments in this chapter has a Si:Al ratio of 30:1 and its charge balancing cation is Na^+. To confirm that a successful ion exchange had occurred SEM EDX spectroscopy was ran before and after the reaction. The results of this are presented in table 30 below, five sets of EDX were run on different areas of the zeolite and an average was found. These results show that successful ion exchange has occurred and this allowed me to carry on with my adsorption reactions.

Table 30. ZSM-5 30:1 EDX Wt% data before and after Na ion exchange reaction.

Sample Analysed	Silicon Wt% (%)	Aluminium Wt% (%)	Oxygen Wt% (%)	Nitrogen Wt% (%)	Sodium Wt% (%)
ZSM-5 30:1 NH4 #1	47.62	3.30	46.79	2.30	0.00
ZSM-5 30:1 NH4 #2	34.61	2.75	52.84	9.80	0.00
ZSM-5 30:1 NH4 #3	46.89	3.42	44.06	5.63	0.00
ZSM-5 30:1 NH4 #4	49.10	3.74	43.28	3.87	0.00
ZSM-5 30:1 NH4 #5	54.25	4.08	38.55	3.12	0.00
Average	46.49	3.46	45.10	4.94	0.00
ZSM-5 30:1 NaCl Ion Exchange #1	43.19	3.54	51.03	0.00	2.24
ZSM-5 30:1 NaCl Ion Exchange #2	46.21	3.45	48.55	0.00	1.79
ZSM-5 30:1 NaCl Ion Exchange #3	47.74	3.36	47.22	0.00	1.68
ZSM-5 30:1 NaCl Ion Exchange #4	44.89	3.53	49.49	0.00	2.08
ZSM-5 30:1 NaCl Ion Exchange #5	46.35	3.60	48.38	0.00	1.66
Average	45.68	3.50	48.93	0.00	1.89

6.2 – Paracetamol

The previous paracetamol HPLC calibration curve's equation was used to calculate the concentration of the paracetamol left in the solution after the adsorptions. Table 31 shows the HPLC data produced by the adsorption reactions between 2 and 48 hours. Included are the concentration of the drug left in solution, the concentration of the drug that was adsorbed and the percentage of the overall concentration that was adsorbed. A plot showing concentration adsorbed by the zeolite against contact time is presented in figure 44.

Table 31. HPLC results for the paracetamol adsorptions by Na ion exchanged ZSM-5 30:1.

Paracetamol Concentration Left in Solution (M)	Peak Area (mVmin)	Contact Time (Hours)	Retention Time (mins)	Height (mV)	Concentration Adsorbed by the Zeolite (M)	% Concentration Adsorbed
0.004007	446.8445	2	3.471	2307.533	0.000993	19.8651
0.003971	442.8634	4	3.435	2270.959	0.001029	20.5790
0.004127	460.2138	6	3.470	2325.131	0.000873	17.4675
0.003935	438.8704	8	3.436	2274.801	0.001065	21.2951
0.003943	439.7617	10	3.438	2271.731	0.001057	21.1352
0.004022	448.5706	24	3.469	2303.159	0.000978	19.5555
0.004111	458.5221	48	3.451	2311.202	0.000889	17.7708

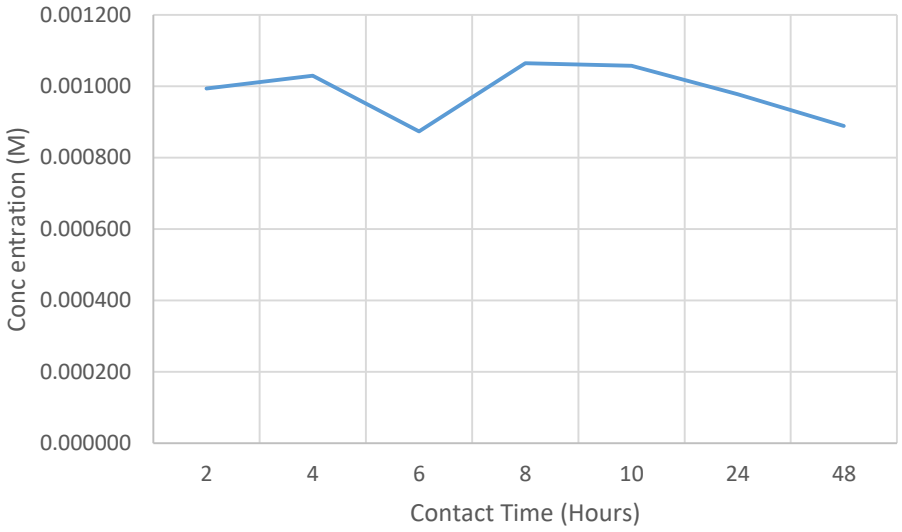


Figure 44. Graph depicting concentration of paracetamol adsorbed by Na ion exchanged ZSM-5 30:1 against contact time.

The concentration adsorbed stays fairly constant throughout as the percentage adsorbed only had a range of 17.47-21.30% with the contact time of 6 hours

accounting for the lowest concentration adsorbed of 0.000873M and the highest occurring during the 8-hour adsorption of 0.001065M, indicating that 8 hours is the optimum contact time. The equilibrium seems to be between 19-21% as the 2, 4, 8, 10 and 24 hour adsorptions all fall within this range. There is a drop at 6 hours, with a concentration adsorbed of 17.47%, and at 48 hours with a concentration at 17.77%. Overall this shows a decrease in the concentration adsorbed by ZSM-5 when compared to the ZSM-5 with ammonium as the charge balancing cation. This indicates that replacing the ammonium cations with sodium cations lowers the affinity of paracetamol for ZSM-5.

To confirm that the paracetamol has been adsorbed into the pores of ZSM-5 and not absorbed on to the surface of the particles powder XRD was performed on the filtered solid after adsorption had occurred. As a basis, the Fe ion exchanged ZSM-5 30:1 pre-adsorption XRD pattern is included in figure 45 and shall have the adsorption patterns overlaid onto it in any further XRD patterns in this chapter.

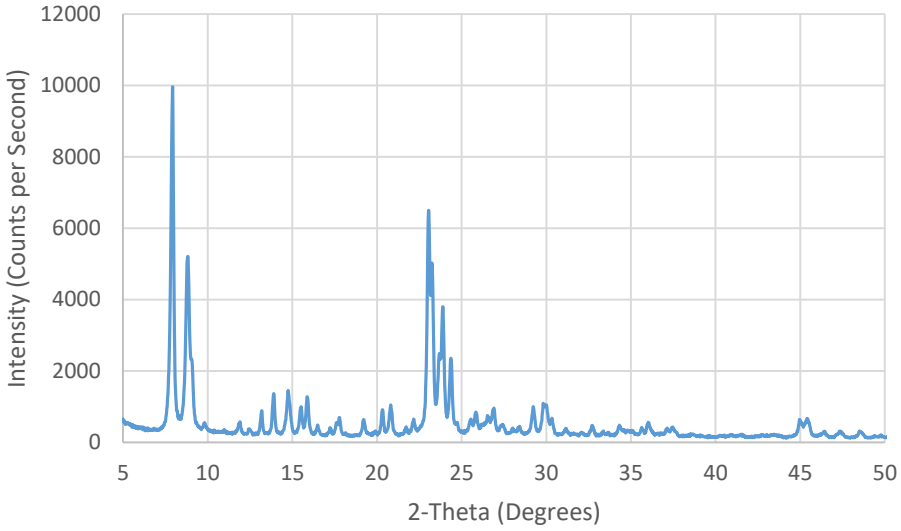
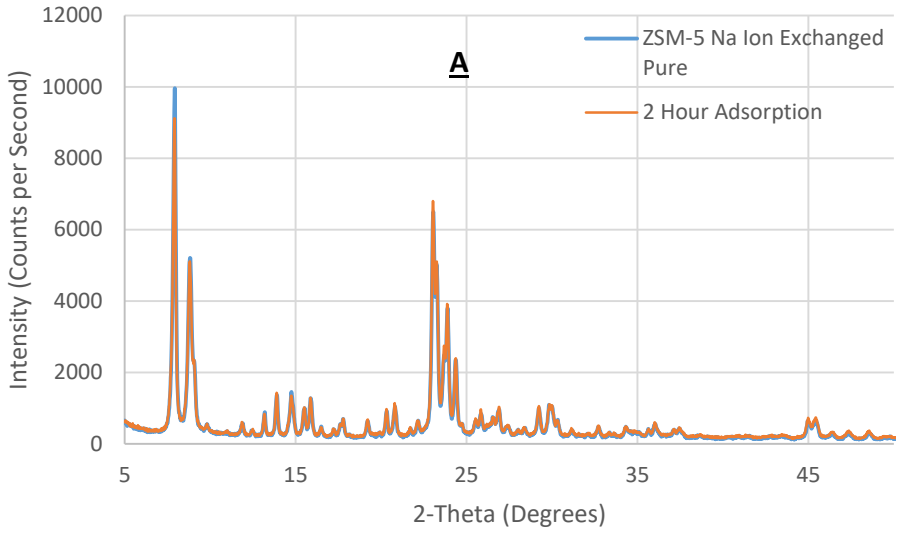
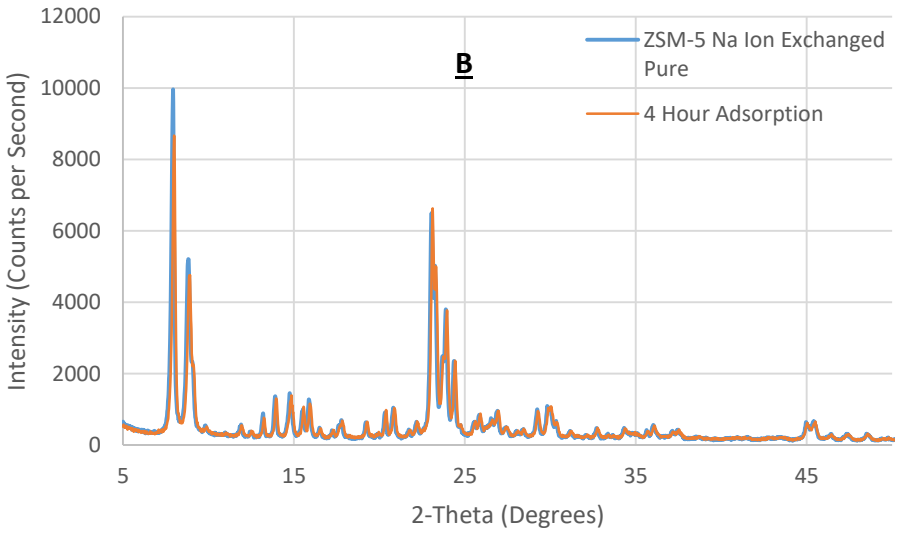
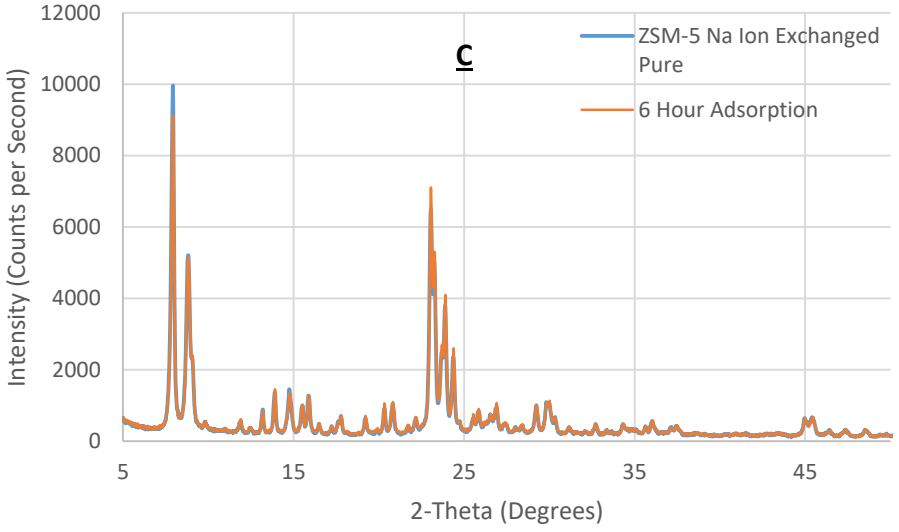


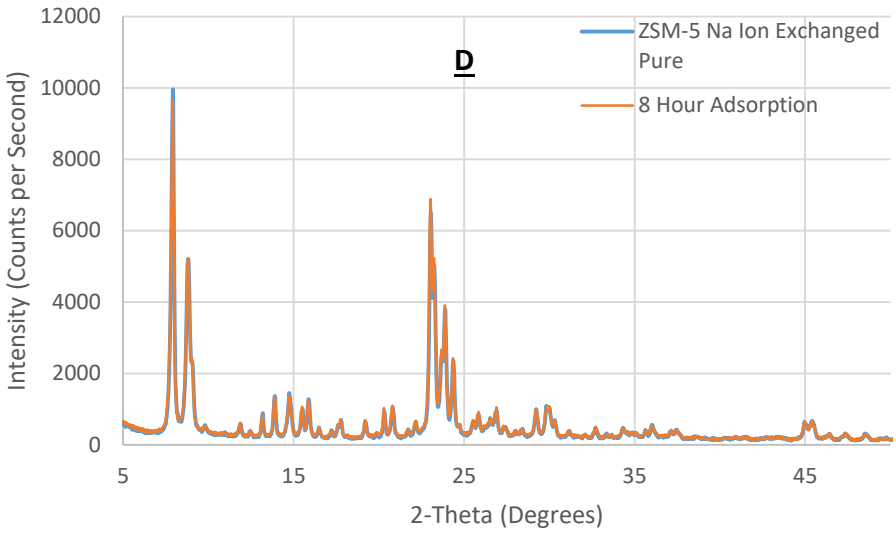
Figure 45. Na ion exchanged ZSM-5 30:1 pre-adsorption XRD pattern.

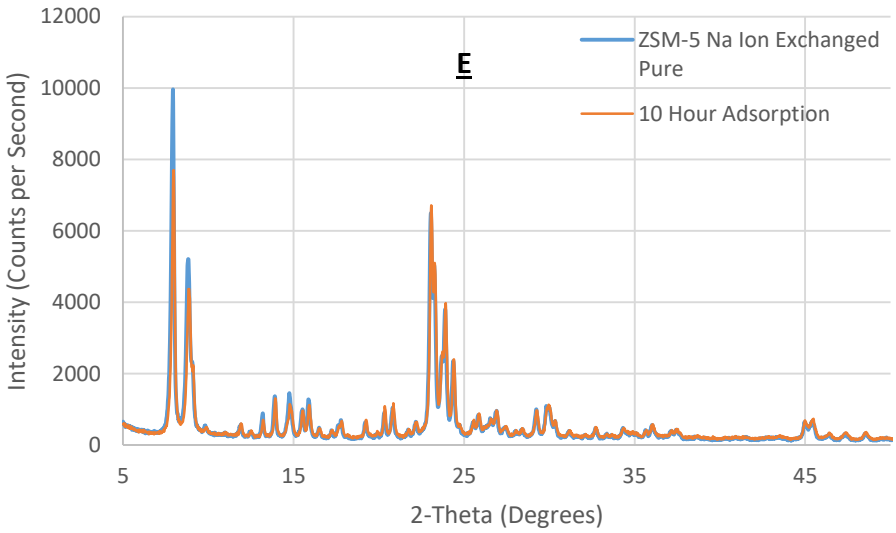
The diffraction patterns for the post adsorption ZSM-5 is shown in figure 46 with the post adsorption pattern overlaid onto the pre-adsorption pattern.

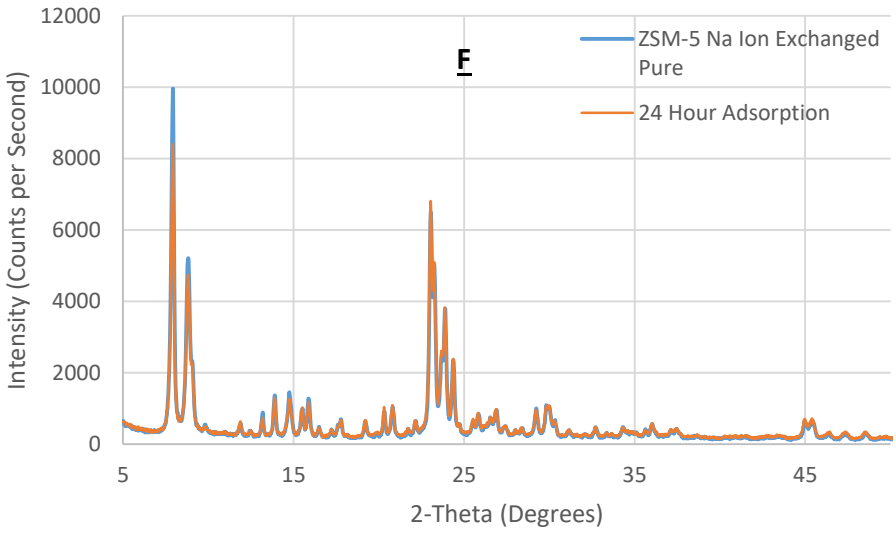

A
ZSM-5 Na Ion Exchanged Pure
2 Hour Adsorption
Intensity (Counts per Second)
2-Theta (Degrees)
12000
10000
8000
6000
4000
2000
0
5
15
25
35
45


B
ZSM-5 Na Ion Exchanged Pure
4 Hour Adsorption
Intensity (Counts per Second)
2-Theta (Degrees)
12000
10000
8000
6000
4000
2000
0
5
15
25
35
45


C
ZSM-5 Na Ion Exchanged Pure
6 Hour Adsorption
Intensity (Counts per Second)
2-Theta (Degrees)
12000
10000
8000
6000
4000
2000
0
5
15
25
35
45


D
ZSM-5 Na Ion Exchanged Pure
8 Hour Adsorption
Intensity (Counts per Second)
2-Theta (Degrees)
12000
10000
8000
6000
4000
2000
0
5
15
25
35
45


E
ZSM-5 Na Ion Exchanged Pure
10 Hour Adsorption
Intensity (Counts per Second)
2-Theta (Degrees)
12000
10000
8000
6000
4000
2000
0
5
15
25
35
45


F
ZSM-5 Na Ion Exchanged Pure
24 Hour Adsorption
Intensity (Counts per Second)
2-Theta (Degrees)
12000
10000
8000
6000
4000
2000
0
5
15
25
35
45

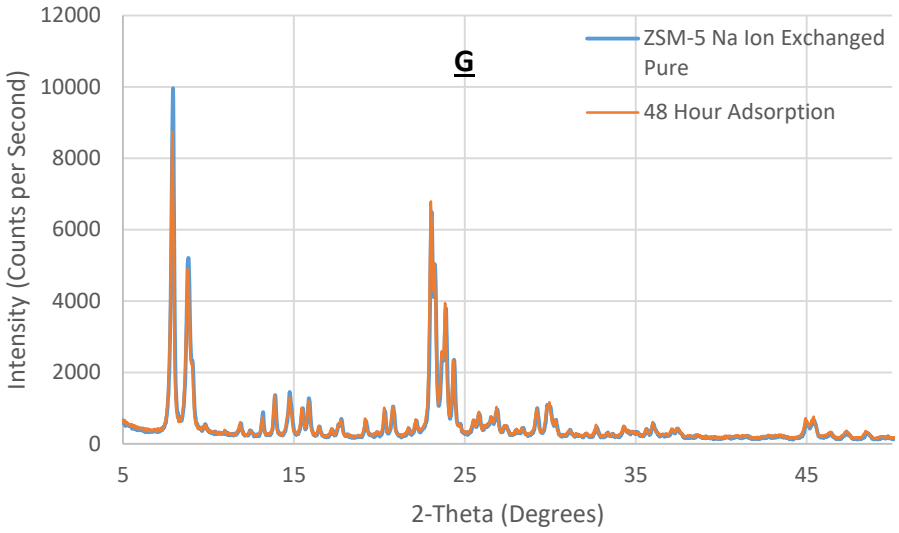


Figure 46. A) Na ion exchanged ZSM-5 30:1 pre-adsorption + Na ion exchanged ZSM-5 30:1 post 2-hour paracetamol adsorption. B) Na ion exchanged ZSM-5 30:1 pre-adsorption + Na ion exchanged ZSM-5 30:1 post 4-hour paracetamol adsorption. C) Na ion exchanged ZSM-5 30:1 pre-adsorption + Na ion exchanged ZSM-5 30:1 post 6-hour paracetamol adsorption. D) Na ion exchanged ZSM-5 30:1 pre-adsorption + Na ion exchanged ZSM-5 30:1 post 8-hour paracetamol adsorption. E) Na ion exchanged ZSM-5 30:1 pre-adsorption + Na ion exchanged ZSM-5 30:1 post 10-hour paracetamol adsorption. F) Na ion exchanged ZSM-5 30:1 pre-adsorption + Na ion exchanged ZSM-5 30:1 post 24-hour paracetamol adsorption. G) Na ion exchanged ZSM-5 30:1 pre-adsorption + Na ion exchanged ZSM-5 30:1 post 48-hour paracetamol adsorption.

All seven XRD patterns show some difference when compared to the pre-adsorption ZSM-5. All the patterns have some form of change in relative peak intensity in multiple peaks within the range of 5^{o}-23^{o} 2-theta. The most consistent differences are seen in the first two peaks at 7.93^{o} 2-theta and 8.82^{o} 2-theta, with the Na ion exchanged ZSM-5 pre-adsorption having peak intensities of 9961 counts per second and 5208 counts per second respectively, and the peaks at 23.05^{o} 2-theta and 23.88^{o} 2-theta, with the Na ion exchanged ZSM-5 pre-adsorption having peak intensities of 6498 counts per second and 3800 counts per second respectively. Post adsorption these peaks were changed to between 7699-9119 counts per second and 4369-5199 counts per second for 7.93^{o} 2-theta and 8.82^{o} 2-theta respectively, with the lowest peaks being produced by the 10-hour adsorption and highest being produced by the 2 and 8 hour adsorptions respectively. For the peaks at 23.05^{o} 2-theta and 23.88^{o} 2-theta the post-adsorption peaks were changed to between 6627-7105 counts per second and 3770-4096 counts per second respectively with the lowest peaks being

produced by the 4-hour adsorption and the highest being produced by the 6-hour adsorption. This change in relative peak intensity indicates that the contents of the unit cell have changed in some way which would indicate that the adsorption of the paracetamol has been successful. Another indicator is that 4-hour adsorption pattern has been shifted to the right by 0.0808^{o} 2-theta. This shift towards a higher 2-theta value indicates a contraction of the zeolite unit cell is occurring. The zeolite framework has a high degree of flexibility and this peak position shift is a further indication that a species has been adsorbed into the pores of the zeolite, in this case paracetamol, though this could be seen to be negligible due to the low levels.

The HPLC and XRD data indicate that the paracetamol has been adsorbed by the Fe ion exchanged ZSM-5 30:1 and successfully removed from the solution. The data from the XRD patterns were used to determine the cell parameters to see how the cell structure changed to accommodate the adsorbed paracetamol. The unit cell parameters for Na ion exchanged ZSM-5 30:1 pre-and post paracetamol adsorption were determined using Topas and J-edit and shown in table 32. A Pawley fit was done using a Chebyshev function background and Pseudo-Voight peak shape function, the zero background and unit cell parameters (*a*, *b*, *c*) were refined to determine errors.

Table 32. Lattice parameters of Na ion exchanged ZSM-5 30:1 pre-and post paracetamol adsorption with errors included in brackets.

Contact Time with Paracetamol Solution (Hours)	**RWP**	***a*** **(Å)**	***b*** **(Å)**	***c*** **(Å)**
0	7.228	20.13230(3)	19.92958(2)	13.42249(2)
2	6.892	20.12666(3)	19.92248(2)	13.41696(2)
4	6.949	20.13635(3)	19.93184(2)	13.41977(2)
6	6.999	20.12648(3)	19.92326(2)	13.41727(2)
8	7.109	20.12705(4)	19.92628(2)	13.41622(2)
10	6.499	20.13911(3)	19.93545(2)	13.42536(2)
24	6.786	20.13384(3)	19.93107(2)	13.42559(2)
48	6.824	20.13339(4)	19.93369(2)	13.42343(2)

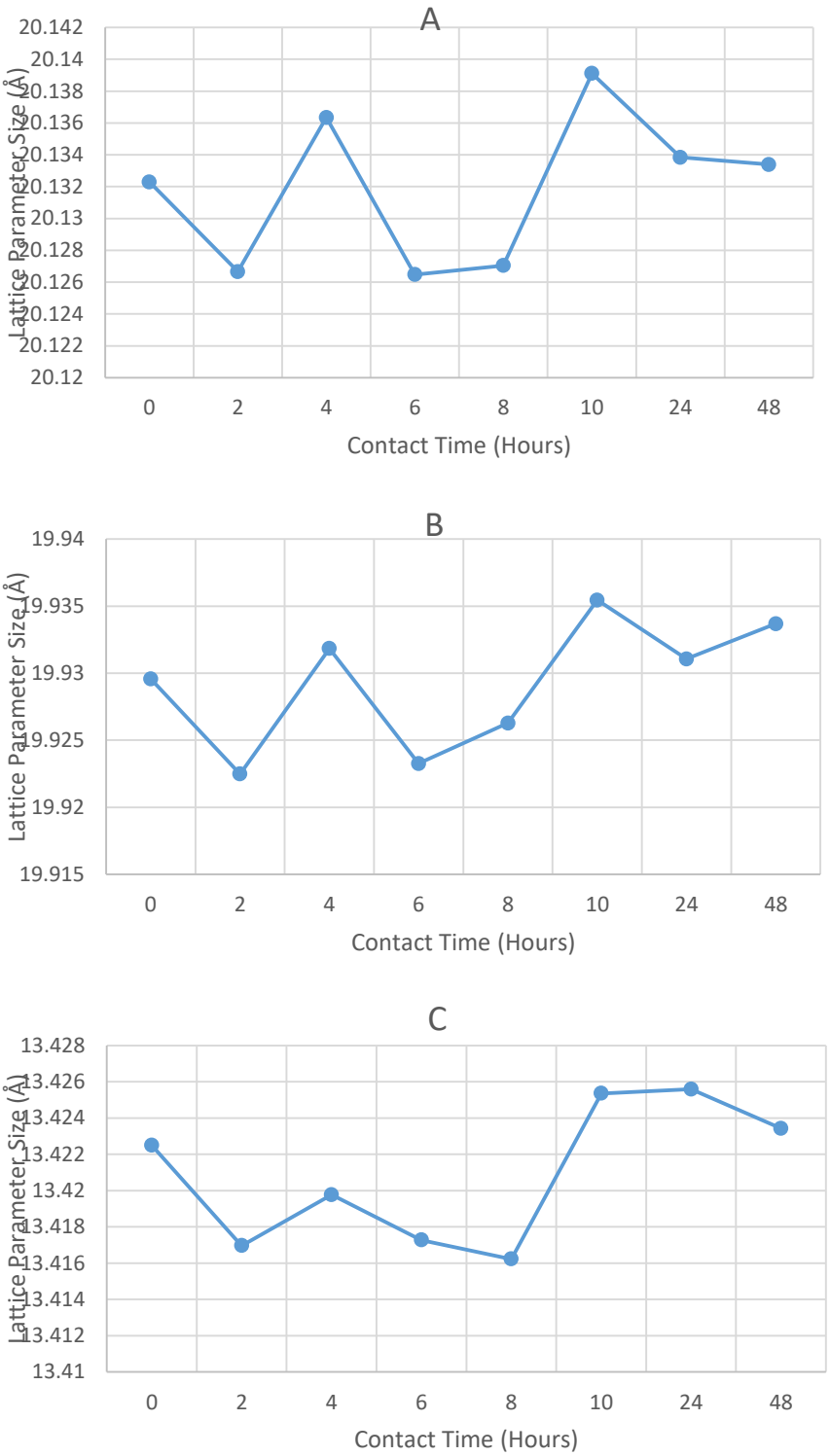


Figure 47. A) Change in lattice parameter *a* against Na ion exchanged ZSM-5 30:1 contact time with paracetamol. B) Change in lattice parameter *b* against Na ion exchanged ZSM-5 30:1 contact time with paracetamol. C) Change in lattice parameter *c* against Na ion exchanged ZSM-5 30:1 contact time with paracetamol.

Figure 47 shows the change in the lattice parameters of ZSM-5 pre-and post paracetamol adsorption and shows all three lattice parameter size changes follow a similar pattern. All three decrease in size from 0-2 hours, then increase in size between 2-4 hours, followed by another decrease in size from 4-6 hours, then an increase in size from 6-10 hours before a final decrease in size from 10-48 hours overall. Parameter *c* differs from this pattern in two ways, first having a decrease in size from 6-8 hours before the increase at 10 hours and second a small increase between 10-24 hours before the final decrease at 48 hours and parameter *b* increases in size between 24 and 48 hours instead of decreasing. From 2-48 hours, there is an overall increase of 0.03% for parameter *a*, a 0.06% increase for parameter *b* and a 0.05% increase for parameter *c*. The data points seem to fit with the HPLC data, increasing from 2-4 hours and then decreasing from 4-6 hours in conjunction with the HPLC data. They differ however in that if they are directly proportional to one another then the peak point for size in all three parameters should be 8 hours but as shown it is 10 hours, and the increase from 8-10 hours is too large in comparison. From this we can conclude that overall the changes in the lattice parameters' size are independent to the changes in concentration adsorbed and therefore do not change to accommodate the paracetamol adsorbed.

The overall amount of concentration removed from solution is reduced by over half of the commercial ZSM-5 30:1 equivalent we would consider the Na ion exchanged ZSM-5 30:1 appropriate for the removal of paracetamol from aqueous solution but to not use it if commercial ZSM-5 ammonium 30:1 is available. This would indicate that the presence of sodium cations instead of ammonium reduced paracetamol's affinity for ZSM-5. From this we can infer that it is more likely that the reduction in adsorption of paracetamol by the commercial ZSM-5 ammonium 200-400:1 was due to the reduction of ammonium cations present rather than its increased hydrophobicity.

6.3 – Ibuprofen Lysine

The previous ibuprofen lysine HPLC calibration curve's equation was used to calculate the concentration of the ibuprofen lysine left in the solution after the adsorptions. Table 33 shows the HPLC data produced by the adsorption reactions between 2 and 48 hours. Included are the concentration of the drug left in solution, the concentration of the drug that was adsorbed and the percentage of the overall concentration that was adsorbed. A plot showing concentration adsorbed by the zeolite against contact time is presented in figure 48.

Table 33. HPLC results for the ibuprofen lysine adsorptions by Na ion exchanged ZSM-5 30:1.

Ibuprofen Lysine Concentration Left in Solution (M)	**Peak Area (mVmin)**	**Contact Time (Hours)**	**Retention Time (mins)**	**Height (mV)**	**Concentration Adsorbed by the Zeolite (M)**	**% Concentration Adsorbed**
0.00206	163.3818	2	8.415	345.897	0.00000*	0.0000
0.00199	158.2332	4	8.399	334.504	0.00001	0.4760
0.00216	171.6196	6	8.315	346.323	0.00000*	0.0000
0.00210	167.3168	8	8.304	336.573	0.00000*	0.0000
0.00208	165.6775	10	8.283	333.887	0.00000*	0.0000
0.00211	167.4967	24	8.377	352.131	0.00000*	0.0000
0.00212	168.1853	48	8.287	337.790	0.00000*	0.0000

*These values have been normalised to zero as HPLC data came out with a negative concentration

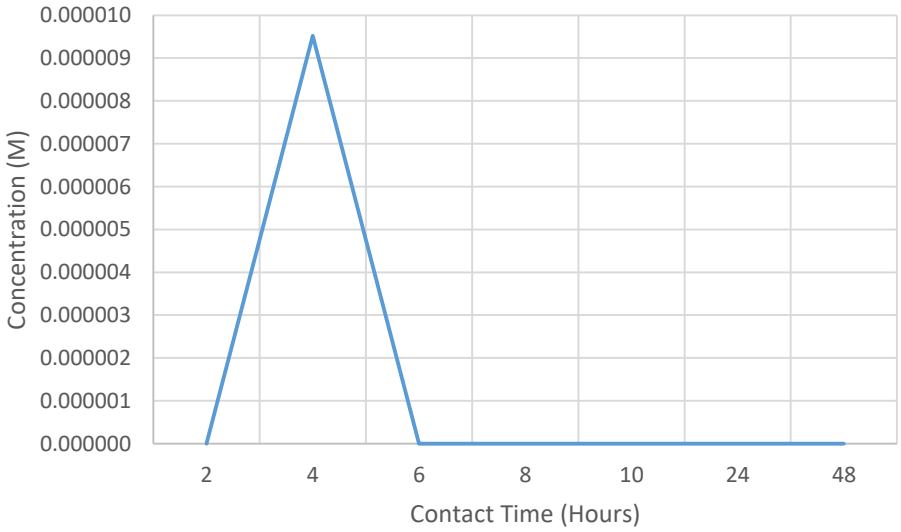
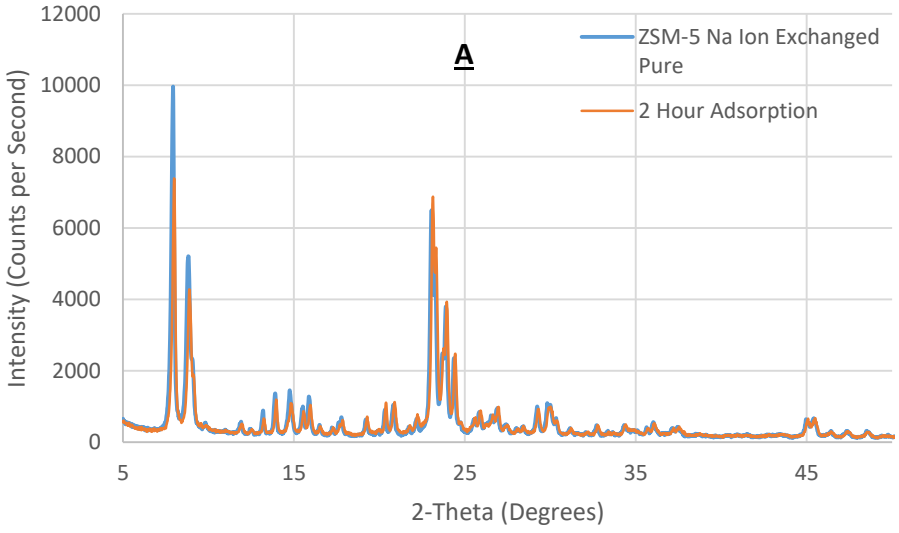
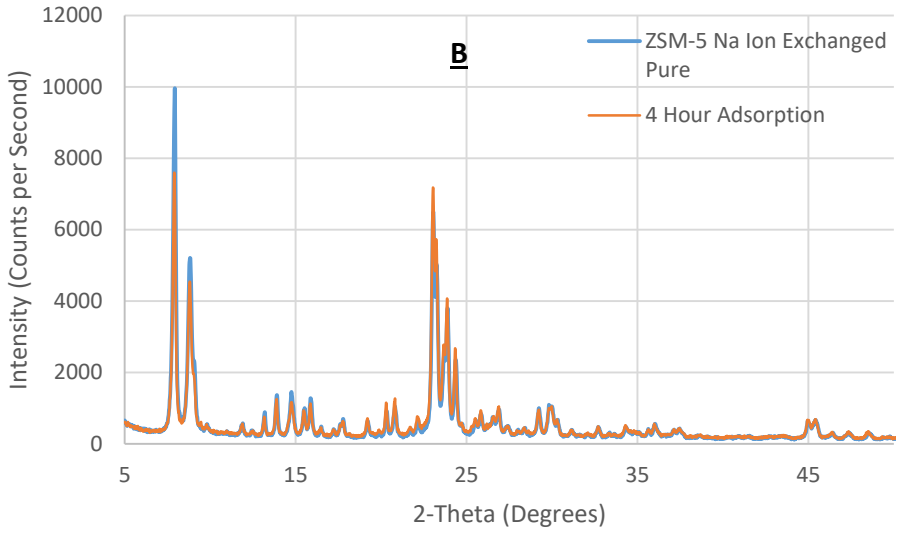


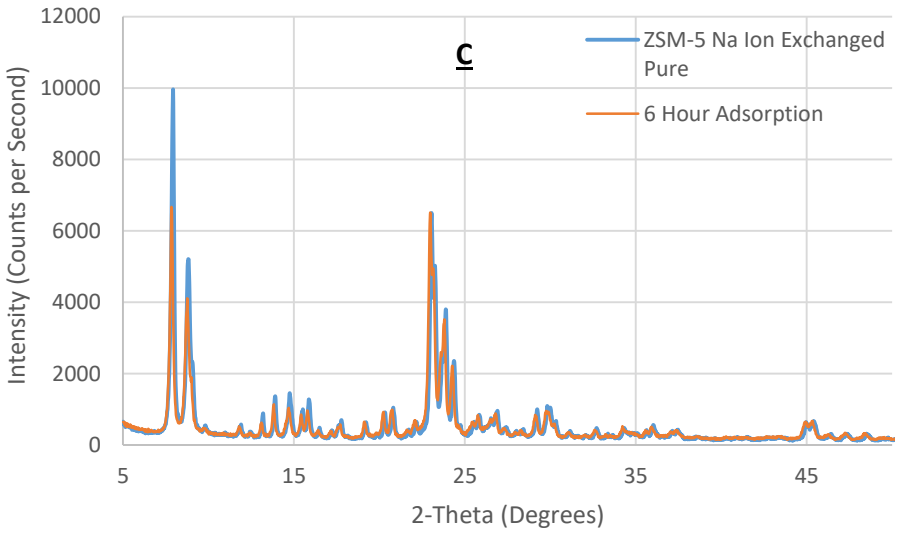
Figure 48. Graph depicting concentration of ibuprofen lysine adsorbed by Na ion exchanged ZSM-5 30:1 against contact time.

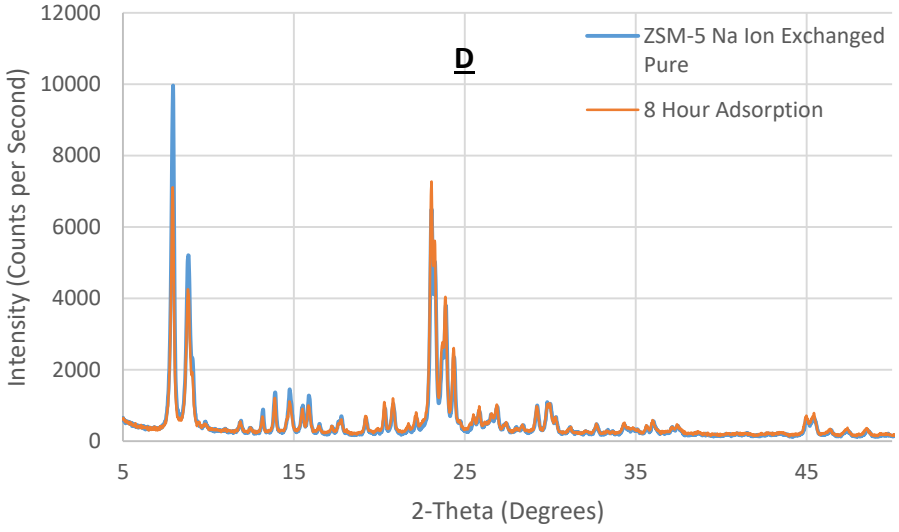
Due to its low concentration and the low relative solubility of ibuprofen lysine in general the HPLC machine may have picked up a higher result than possible, if only slightly, causing negative results to appear. These adsorptions were repeated to check validity and consistent results were produced. For the purposes of this research any negative concentration results have been changed to indicate that no ibuprofen lysine was adsorbed, though some may have been the amount is negligible. The only contact time where any ibuprofen lysine was adsorbed was 4 hours, adsorbing 0.48% of the overall amount in solution. This would indicate that while marginally better than commercial ZSM-5 200-400:1, Na ion exchanged ZSM-5 30:1 is not appropriate for the removal of ibuprofen lysine from aqueous solution as the positive amount removed could itself be easily negligible.

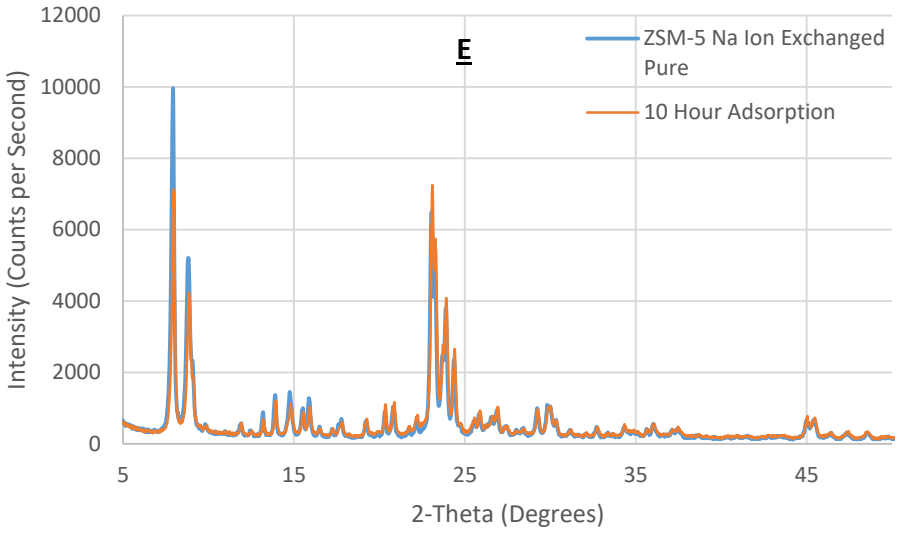
To ascertain that ibuprofen lysine had been adsorbed into the pores of the zeolite and not the surface of the particles XRD was carried out and the data analysed using Pawley fits. The post adsorption XRD patterns overlaid onto the Na ion exchanged ZSM-5 30:1 XRD pattern, shown in figure 45, are plotted in figure 49 below.




B
ZSM-5 Na Ion Exchanged Pure
4 Hour Adsorption
Intensity (Counts per Second)
2-Theta (Degrees)
12000
10000
8000
6000
4000
2000
0
5
15
25
35
45


C
ZSM-5 Na Ion Exchanged Pure
6 Hour Adsorption
Intensity (Counts per Second)
2-Theta (Degrees)
12000
10000
8000
6000
4000
2000
0
5
15
25
35
45


D
ZSM-5 Na Ion Exchanged Pure
8 Hour Adsorption
Intensity (Counts per Second)
2-Theta (Degrees)
12000
10000
8000
6000
4000
2000
0
5
15
25
35
45


E
ZSM-5 Na Ion Exchanged Pure
10 Hour Adsorption
Intensity (Counts per Second)
2-Theta (Degrees)
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10000
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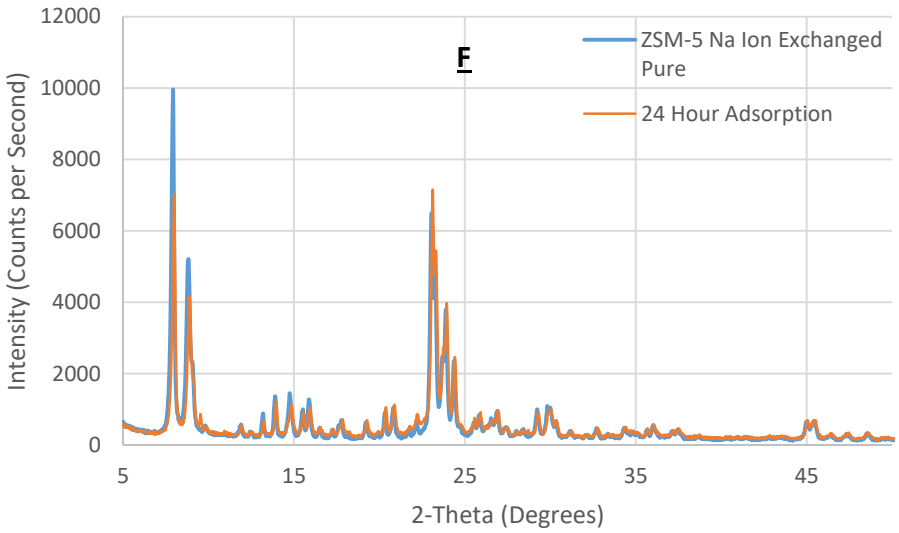
6000
4000
2000
0
5
15
25
35
45


F
ZSM-5 Na Ion Exchanged Pure
24 Hour Adsorption
Intensity (Counts per Second)
2-Theta (Degrees)
12000
10000
8000
6000
4000
2000
0
5
15
25
35
45

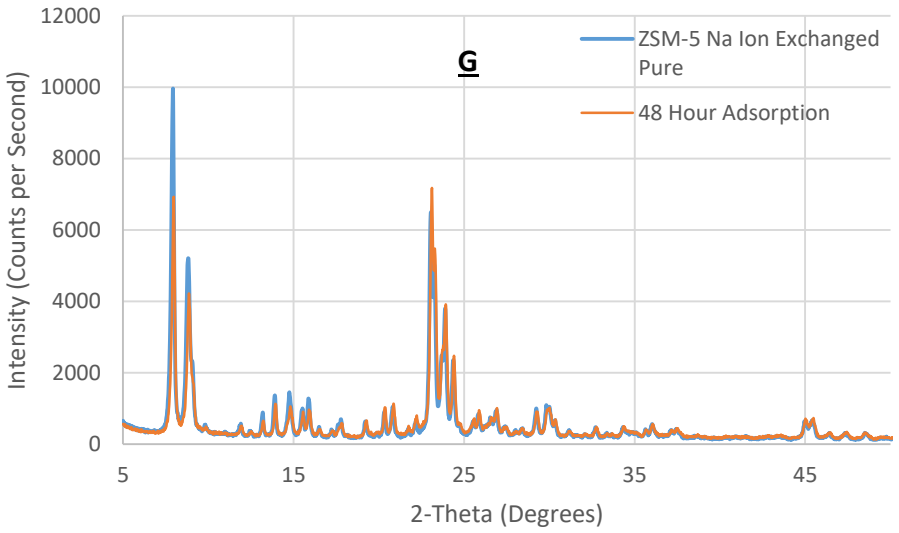

G
ZSM-5 Na Ion Exchanged Pure
48 Hour Adsorption
Intensity (Counts per Second)
2-Theta (Degrees)
12000
10000
8000
6000
4000
2000
0
5
15
25
35
45

Figure 49. A) Na Ion Exchanged ZSM-5 30:1 pre-adsorption + Na Ion Exchanged ZSM-5 30:1 post 2-hour ibuprofen lysine adsorption. B) Na Ion Exchanged ZSM-5 30:1 pre-adsorption + Na Ion Exchanged ZSM-5 30:1 post 4-hour ibuprofen lysine adsorption. C) Na Ion Exchanged ZSM-5 30:1 pre-adsorption + Na Ion Exchanged ZSM-5 30:1 post 6-hour ibuprofen lysine adsorption. D) Na Ion Exchanged ZSM-5 30:1 pre-adsorption + Na Ion Exchanged ZSM-5 30:1 post 8-hour ibuprofen lysine adsorption. E) Na Ion Exchanged ZSM-5 30:1 pre-adsorption + Na Ion Exchanged ZSM-5 30:1 post 10-hour ibuprofen lysine adsorption. F) Na Ion Exchanged ZSM-5 30:1 pre-adsorption + Na Ion Exchanged ZSM-5 30:1 post 24-hour ibuprofen lysine adsorption. G) Na Ion Exchanged ZSM-5 30:1 pre-adsorption + Na Ion Exchanged ZSM-5 30:1 post 48-hour ibuprofen lysine adsorption.

All seven XRD patterns show some differences when compared to the pre-adsorption ZSM-5. All the patterns have similar forms of change in relative peak intensity in multiple peaks within the range of 5^{o}-23^{o} 2-theta. The biggest differences are seen in the first two peaks at 7.93^{o} 2-theta and 8.82^{o} 2-theta, with the Na ion exchanged ZSM-5 pre-adsorption having peak intensities of 9961 counts per second and 5208 counts per second respectively, and the peaks at 23.05^{o} 2-theta and 23.88^{o} 2-theta, with the Na ion exchanged ZSM-5 pre-adsorption having peak intensities of 6498 counts per second and 3800 counts per second respectively. Post adsorption these peaks were reduced to between 6668-7593 counts per second and 4108-4542 counts per second, with the lowest peaks being produced by the 6-hour adsorption and highest being produced by the 4-hour adsorption. For the peaks at 23.05^{o} 2-theta and 23.88^{o} 2-theta the post-adsorption peaks were changed to between 6511-7272 counts per second and 3519-4080 counts per second respectively with the lowest peaks being produced by the 6-hour adsorption and the highest being produced by the 8 and 10 hour adsorptions respectively. This change in relative peak intensity indicates that the contents of the unit cell have changed in some way which would indicate that the adsorption of the ibuprofen lysine has been successful. The 6-hour adsorption's XRD pattern show some shifting towards the right, a shift of 0.1212^{o} 2-theta. This shift towards a higher 2-theta value indicates a contraction of the zeolite unit cell is occurring. The zeolite framework has a high degree of flexibility and this peak position shift is a further indication that a species has been adsorbed into the pores of the zeolite, in this case ibuprofen lysine, though considering the HPLC results it would indicate that the amounts adsorbed are negligible.

The HPLC and XRD data indicate that the ibuprofen lysine has not been adsorbed by the Na ion exchanged ZSM-5 30:1 and has not been successfully removed from the solution. The data from the XRD patterns were used to determine the cell parameters to see how the cell structure changed to accommodate the adsorbed ibuprofen lysine. The unit cell parameters for Na ion exchanged ZSM-5 30:1 pre-and post ibuprofen lysine adsorption were determined using Topas and J-edit and shown in table 34. A Pawley fit was done using a Chebyshev function background and Pseudo-Voight peak shape function, the zero background and unit cell parameters (*a*, *b*, *c*) were refined to determine errors.

Table 34. Lattice parameters of Na ion exchanged ZSM-5 30:1 pre-and post ibuprofen lysine adsorption with errors included in brackets.

Contact Time with Ibuprofen Lysine Solution (Hours)	**RWP**	***a*** **(Å)**	***b*** **(Å)**	***c*** **(Å)**
0	7.228	20.13230(3)	19.92958(2)	13.42249(2)
2	6.854	20.12407(3)	19.93208(2)	13.42822(2)
4	6.98	20.12411(4)	19.93551(2)	13.42837(2)
6	6.048	20.14328(4)	19.94898(3)	13.44385(3)
8	6.751	20.12614(3)	19.93327(2)	13.43024(2)
10	6.75	20.12972(4)	19.93658(2)	13.43051(2)
24	7.115	20.13689(4)	19.93856(2)	13.43180(3)
48	6.45	20.12734(3)	19.93482(2)	13.43062(2)

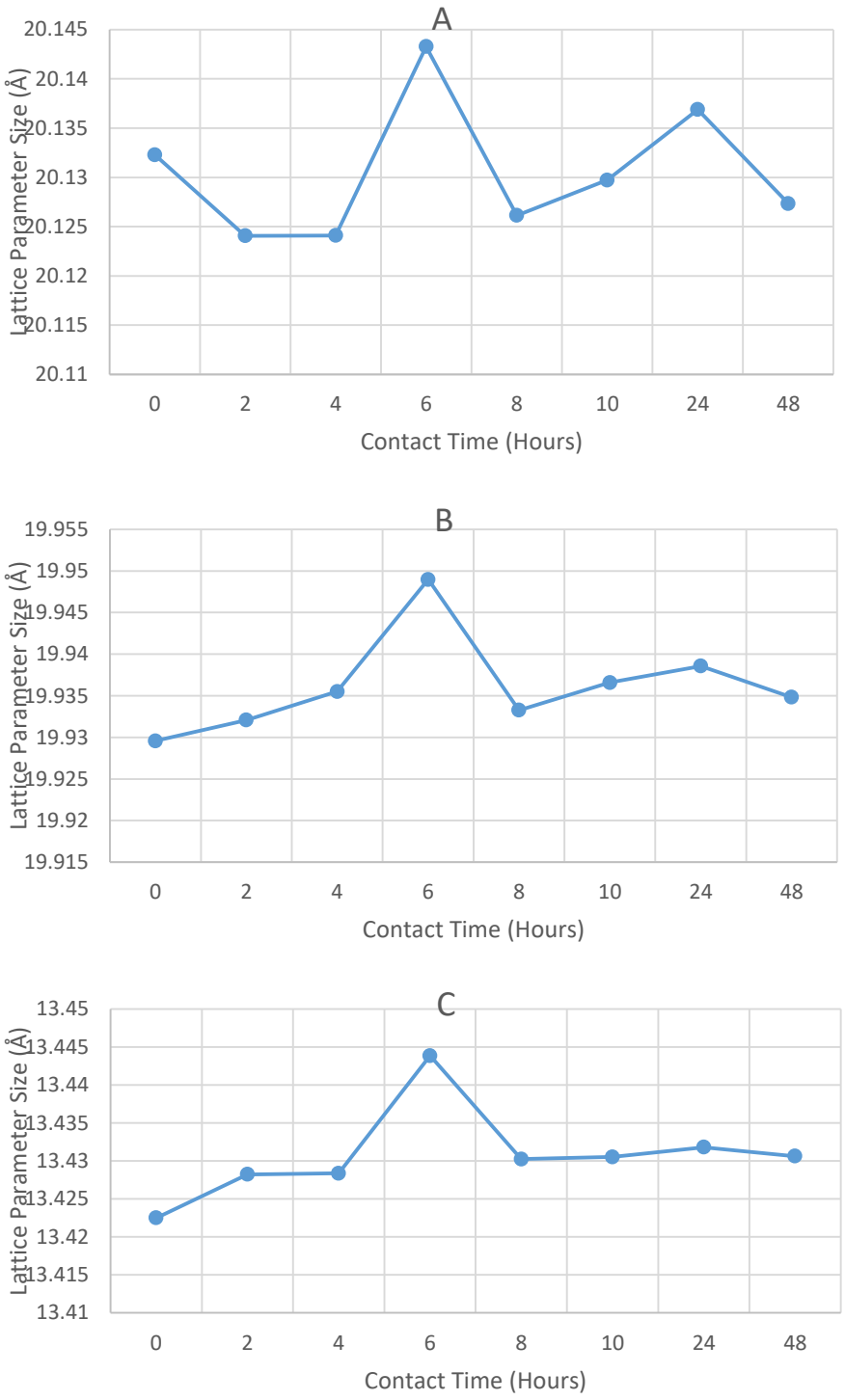


Figure 50. A) Change in lattice parameter *a* against Na ion exchanged ZSM-5 30:1 contact time with ibuprofen lysine. B) Change in lattice parameter *b* against Na ion exchanged ZSM-5 30:1 contact time with ibuprofen lysine. C) Change in lattice parameter *c* against Na ion exchanged ZSM-5 30:1 contact time with ibuprofen lysine.

Figure 50 shows the change in the lattice parameters of ZSM-5 pre-and post paracetamol adsorption and shows all three lattice parameter size changes follow a

mostly similar pattern. Parameter *a* decreases in size from 0-2 hours while parameters *b* and *c* increase during this time. All three then plateau between 2-4 hours and then increasing to their peak sizes at 6 hours before decreasing in size from 6-8 hours. All three then increase in size from 8-24 hours with parameter *a* showing the largest increase in this range, then there is a final reduction in size from 24-48 hours. The largest change in size is produced by the 6-hour adsorption accounting for an increase in size for lattice parameter *a* of 0.05%, for parameter *b* of 0.10% and parameter *c* of 0.16% and these would indicate that it is expanding to accommodate ibuprofen lysine adsorption, but taking the HPLC data into account this is inconsistent and therefore the lattice parameters are independent and not altered by the adsorption of ibuprofen lysine.

This data indicates that Na ion exchanged ZSM-5 30:1 is not an appropriate compound for the removal of ibuprofen lysine from aqueous solution as it is unsuccessful in doing so. The lack of any viable adsorption when compare with that of commercial ZSM-5 ammonium 30:1 would indicate that the change to the sodium charge balancing cation decreased the affinity of ibuprofen lysine for ZSM-5 and therefore it is more likely that the reduction in the number of charge balancing cations and not the hydrophobicity of the commercial ZSM-5 200-400:1 that caused the reduction in ibuprofen lysine's affinity for it.

6.4 – Aspirin

The previous aspirin HPLC calibration curve's equations for aspirin peak 1 and 2 was used to calculate the concentration of the aspirin left in the solution after the adsorptions by combining the concentrations. Table 35 shows the HPLC data produced by the adsorption reactions between 2 and 48 hours for peak 1, table 36 shows peak 2 and table 37 are the two sets of concentrations combined. Included are the concentration of the drug left in solution, the concentration of the drug that was adsorbed and the percentage of the overall concentration that was adsorbed. A plot showing the aspirin combined concentration adsorbed by the zeolite against contact time is presented in figure 51.

Table 35. Aspirin peak 1 HPLC results

Aspirin Tablet Samples Peak 1 Concentration Left in Solution (M)	Peak Area (mVmin)	Contact Time (Hours)	Retention Time (min)	Height (mV)
0.0040	38.8928	2	6.868	132.108
0.0040	38.7591	4	6.789	128.004
0.0039	37.9694	6	6.827	126.190
0.0032	31.0207	8	6.892	98.752
0.0031	30.0074	10	6.036	99.405
0.0040	39.5102	24	6.761	130.499
0.0031	30.8190	48	6.820	100.380

Table 36. Aspirin peak 2 HPLC results.

Aspirin Tablet Samples Peak 2 Concentration Left in Solution (M)	Peak Area (mVmin)	Contact Time (Hours)	Retention Time (mins)	Height (mV)
0.0007	5.9046	2	10.311	13.979
0.0006	5.8091	4	10.200	13.266
0.0008	6.9036	6	10.284	15.396
0.0017	15.5030	8	10.402	34.673
0.0016	14.2309	10	9.283	33.657
0.0005	4.6416	24	10.140	10.580
0.0018	16.1409	48	10.275	35.314

Table 37. Aspirin combined concentrations HPLC results.

Aspirin Tablet Samples Combined Concentrations Left in Solution (M)	Contact Time	Concentration Adsorbed by the Zeolite	% Concentration Adsorbed
0.00463	2	0.00037	7.4616
0.00460	4	0.00040	7.9474
0.00464	6	0.00036	7.1195
0.00489	8	0.00011	2.1333
0.00465	10	0.00035	7.0368
0.00455	24	0.00045	9.0168
0.00494	48	0.00006	1.1231

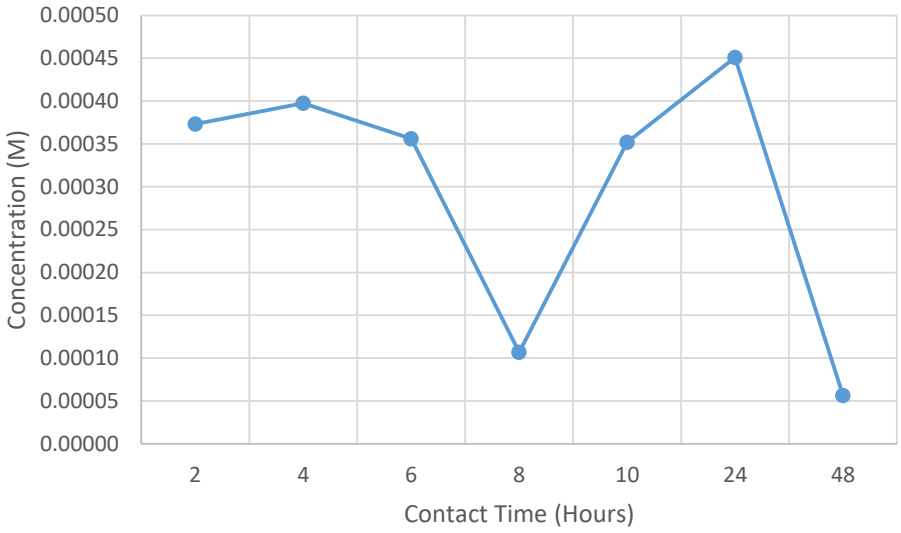
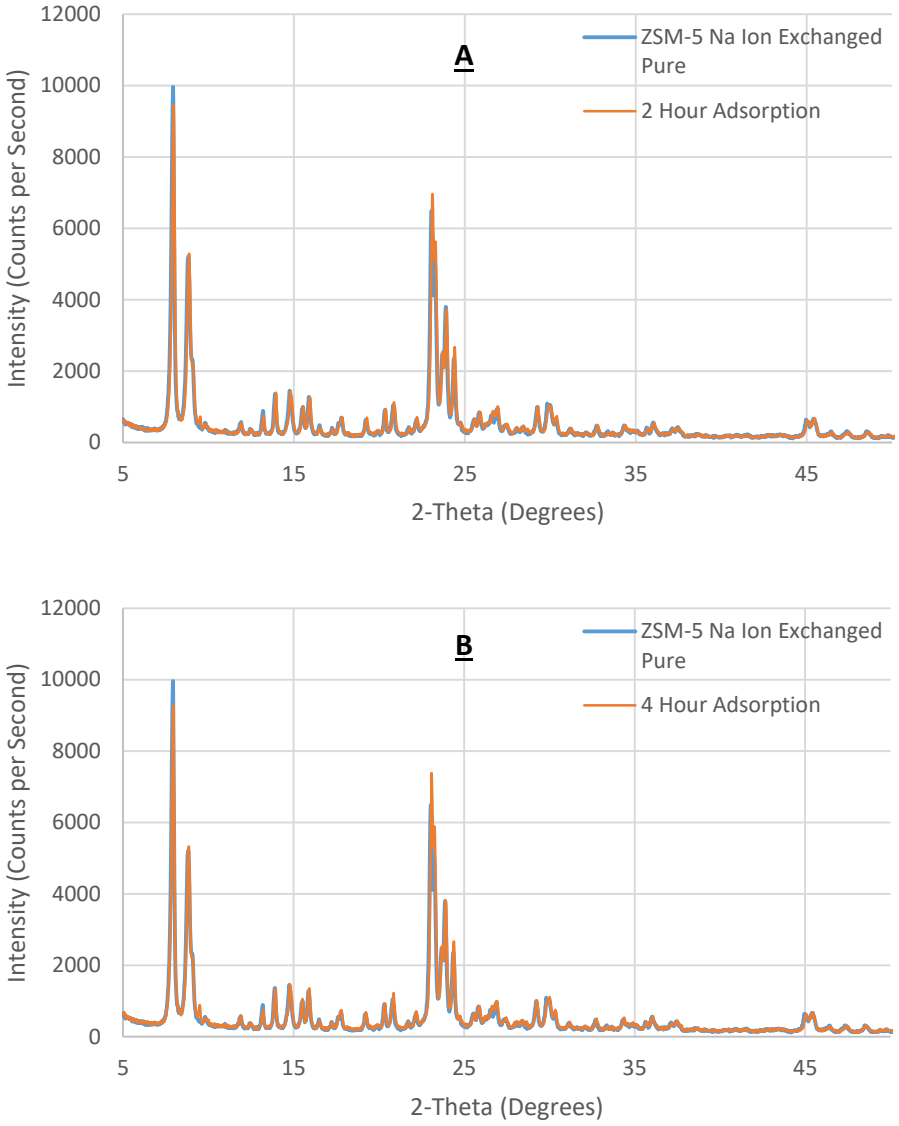


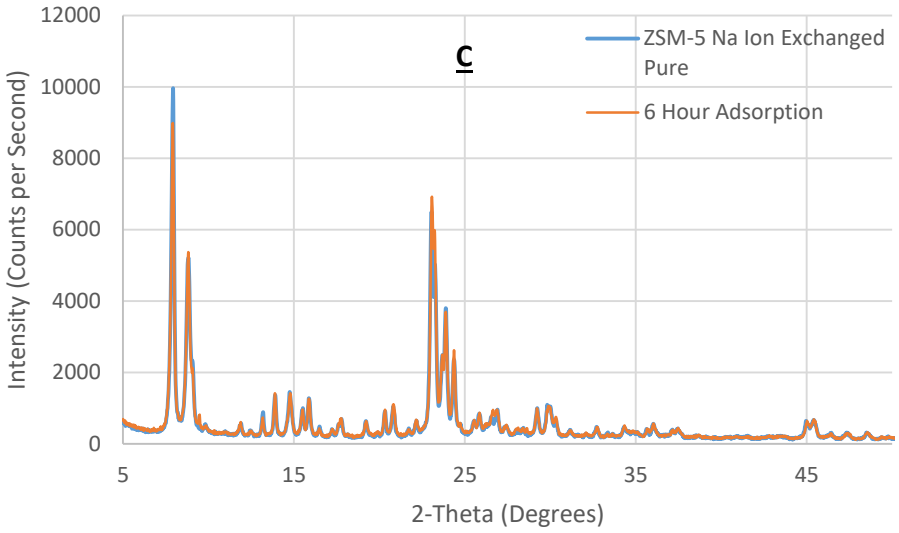
Figure 51. Graph depicting concentration of aspirin adsorbed by Na ion exchanged ZSM-5 30:1 against contact time.

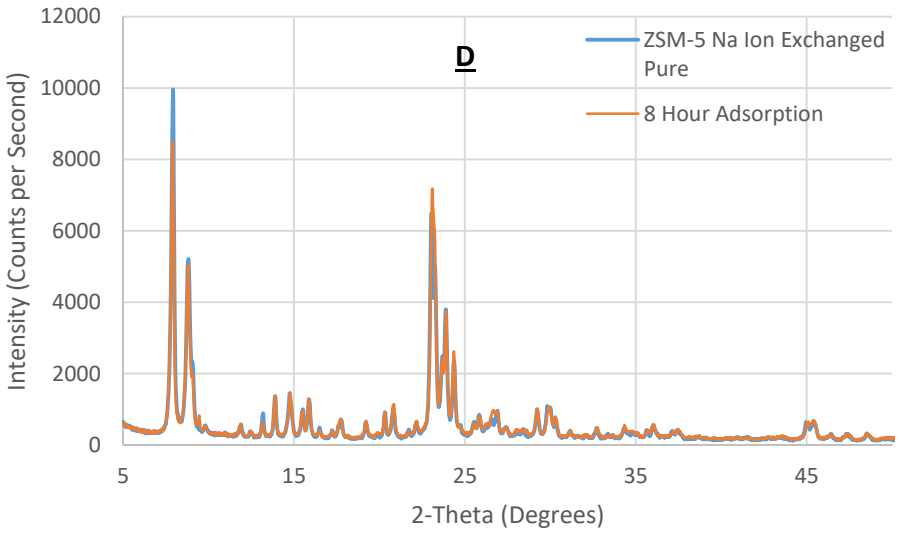
The concentration adsorbed stays fairly constant throughout, with the exception for 8 and 48 hours, as the percentage adsorbed has a range of 1.12-9.02% with the contact time of 48 hours accounting for the lowest concentration adsorbed of 0.00006M and the highest occurring during the 24-hour adsorption of 0.00045M, indicating that this is the optimum adsorbance time. 2-6 hours plateau, from 7.46% to 7.12%, before dropping down to 2.1% at 8 hours. From 8-24 hours, there is an increase of 6.9% up to the peak of 9.02% before the final reduction at 48 hours, reducing in concentration adsorbed by 7.9% to 1.1% adsorbed. The equilibrium is shown to be between 7.0-7.9% as the 2, 4, 6 and 10 hour adsorptions fall into this range. This overall relative decrease in the concentration adsorbed by ZSM-5 when compared the commercial ZSM-5 ammonium 30:1 indicates that changing the charge balancing cation to sodium reduced aspirin's affinity for ZSM-5. It also shows a relative decrease in the concentration adsorbed when compared to the commercial ZSM-5 ammonium 200-400:1, this would indicate that aspirin's increased affinity for ZSM-5 200-400:1 was more likely due to its increased hydrophobicity than its reduced amount of ammonium cations. Overall it has the lowest concentration adsorbed out of all the aspirin adsorptions ran.

To confirm that the aspirin has been adsorbed into the pores of ZSM-5 and not absorbed on to the surface of the particles powder XRD was performed on the

filtered solid after adsorption had occurred. As a basis, the Na ion exchanged ZSM-5 30:1 XRD pattern is included in figure 45 and the diffraction patterns for the post adsorption ZSM-5 is shown in figure 52 with the post adsorption pattern overlaid onto the pre-adsorption pattern.




C
ZSM-5 Na Ion Exchanged Pure
6 Hour Adsorption
Intensity (Counts per Second)
2-Theta (Degrees)
12000
10000
8000
6000
4000
2000
0
5
15
25
35
45


D
ZSM-5 Na Ion Exchanged Pure
8 Hour Adsorption
Intensity (Counts per Second)
2-Theta (Degrees)
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10000
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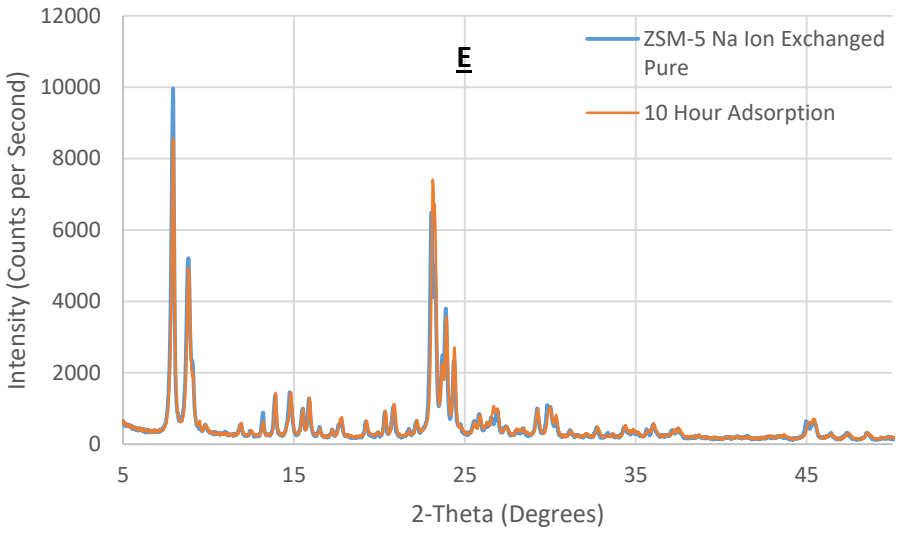
6000
4000
2000
0
5
15
25
35
45


E
ZSM-5 Na Ion Exchanged Pure
10 Hour Adsorption
Intensity (Counts per Second)
2-Theta (Degrees)
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10000
8000
6000
4000
2000
0
5
15
25
35
45

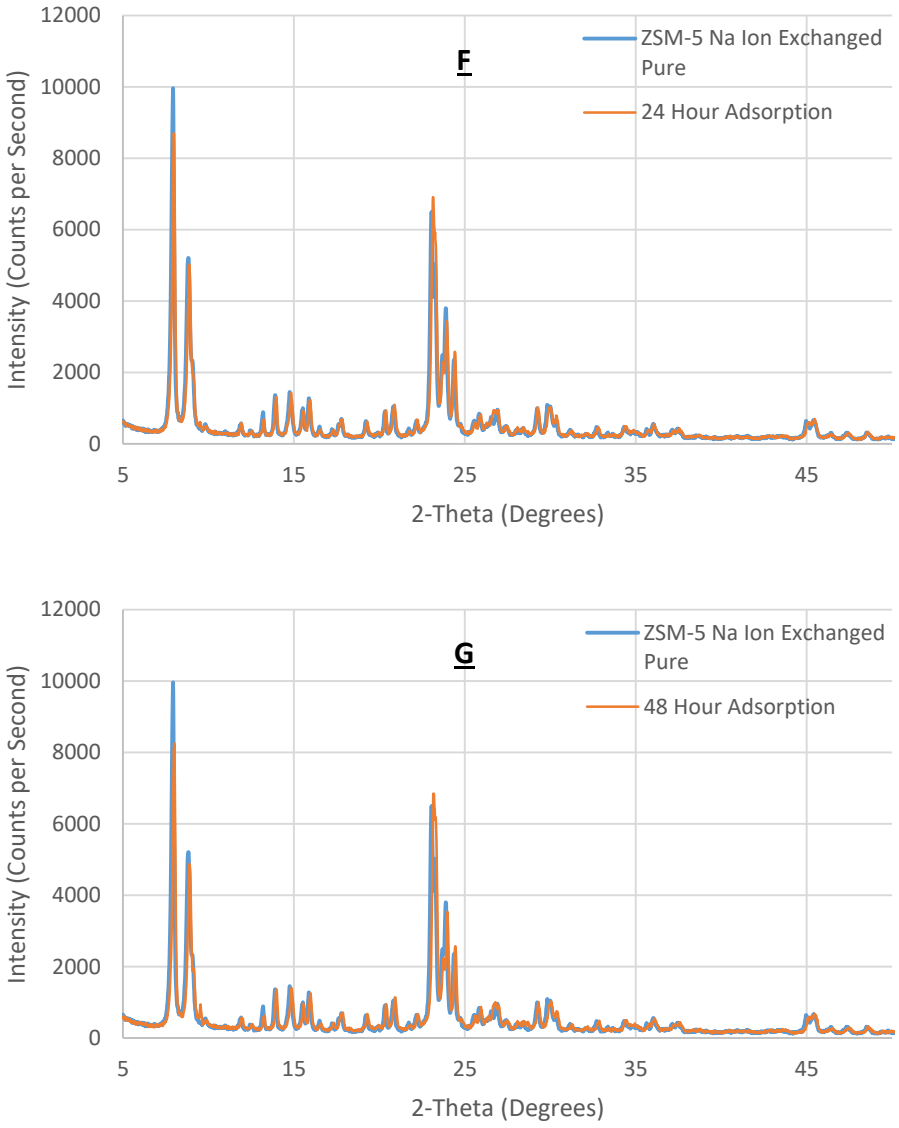


Figure 52. A) Na ion exchanged ZSM-5 30:1 pre-adsorption + Na ion exchanged ZSM-5 30:1 post 2-hour aspirin adsorption. B) Na ion exchanged ZSM-5 30:1 pre-adsorption + Na ion exchanged ZSM-5 30:1 post 4-hour aspirin adsorption. C) Na ion exchanged ZSM-5 30:1 pre-adsorption + Na ion exchanged ZSM-5 30:1 post 6-hour aspirin adsorption. D) Na ion exchanged ZSM-5 30:1 pre-adsorption + Na ion exchanged ZSM-5 30:1 post 8-hour aspirin adsorption. E) Na ion exchanged ZSM-5 30:1 pre-adsorption + Na ion exchanged ZSM-5 30:1 post 10-hour aspirin adsorption. F) Na ion exchanged ZSM-5 30:1 pre-adsorption + Na ion exchanged ZSM-5 30:1 post 24-hour aspirin adsorption. G) Na ion exchanged ZSM-5 30:1 pre-adsorption + Na ion exchanged ZSM-5 30:1 post 48-hour aspirin adsorption.

All seven XRD patterns show minor differences when compared to the original, commercial ZSM-5 30:1. All the patterns have similar forms of change in relative peak intensity in multiple peaks within the range of 5^{o}-23^{o} 2-theta. The biggest

differences are seen in the first two peaks at 7.93^{o} 2-theta and 8.82^{o} 2-theta, with the Na ion exchanged ZSM-5 pre-adsorption having peak intensities of 9961 counts per second and 5208 counts per second respectively, and the peaks at 23.05^{o} 2-theta and 23.88^{o} 2-theta, with the Na ion exchanged ZSM-5 pre-adsorption having peak intensities of 6498 counts per second and 3800 counts per second respectively. Post adsorption these peaks were changed to between 8247-9450 counts per second and 4849-5371 counts per second, with the lowest peaks being produced by the 48-hour adsorption and highest being produced by the 2 and 6 hour adsorptions respectively. For the peaks at 23.05^{o} 2-theta and 23.88^{o} 2-theta the post-adsorption peaks were changed to between 6844-7408 counts per second and 3441-3815 counts per second respectively with the lowest peaks being produced by the 48 and 24 hour adsorptions and the highest being produced by the 10 and 4 hour adsorptions respectively. This change in relative peak intensity indicates that the contents of the unit cell have changed in some way which would indicate that the adsorption of the aspirin has been successful. Another indicator is that the 48-hour adsorption pattern has been noticeably shifted to the right by 0.1010^{o} 2-theta. This shift towards a higher 2-theta value indicates a contraction of the zeolite unit cell is occurring. The zeolite framework has a high degree of flexibility and this peak position shift is a further indication that a species has been adsorbed into the pores of the zeolite, in this case aspirin, though the relatively low shift indicates that this change is negligible.

The HPLC and XRD data indicate that the aspirin has been adsorbed by the Na ion exchanged ZSM-5 30:1 and successfully removed from the solution, though minimally. The data from the XRD patterns were used to determine the cell parameters to see how the cell structure changed to accommodate the adsorbed aspirin. The unit cell parameters for Na ion exchanged ZSM-5 30:1 pre-and post aspirin adsorption were determined using Topas and J-edit and shown in table 38. A Pawley fit was done using a Chebyshev function background and Pseudo-Voight peak shape function, the zero background and unit cell parameters (*a*, *b*, *c*) were refined to determine errors.

Table 38. Lattice parameters of Na ion exchanged ZSM-5 30:1 pre-and post aspirin adsorption with errors included in brackets.

Contact Time with Paracetamol Solution (Hours)	**RWP**	***a*** **(Å)**	***b*** **(Å)**	***c*** **(Å)**
0	7.228	20.13230(3)	19.92958(2)	13.42249(2)
2	7.438	20.11644(4)	19.93599(2)	13.42100(3)
4	8.100	20.09623(4)	19.92594(3)	13.41213(3)
6	7.566	20.10042(4)	19.93219(3)	13.41678(3)
8	7.954	20.09909(5)	19.93214(3)	13.41026(3)
10	7.053	20.08977(4)	19.93816(3)	13.41048(3)
24	7.260	20.11195(4)	19.94062(3)	13.41836(3)
48	7.925	20.11052(4)	19.93882(3)	13.41660(3)

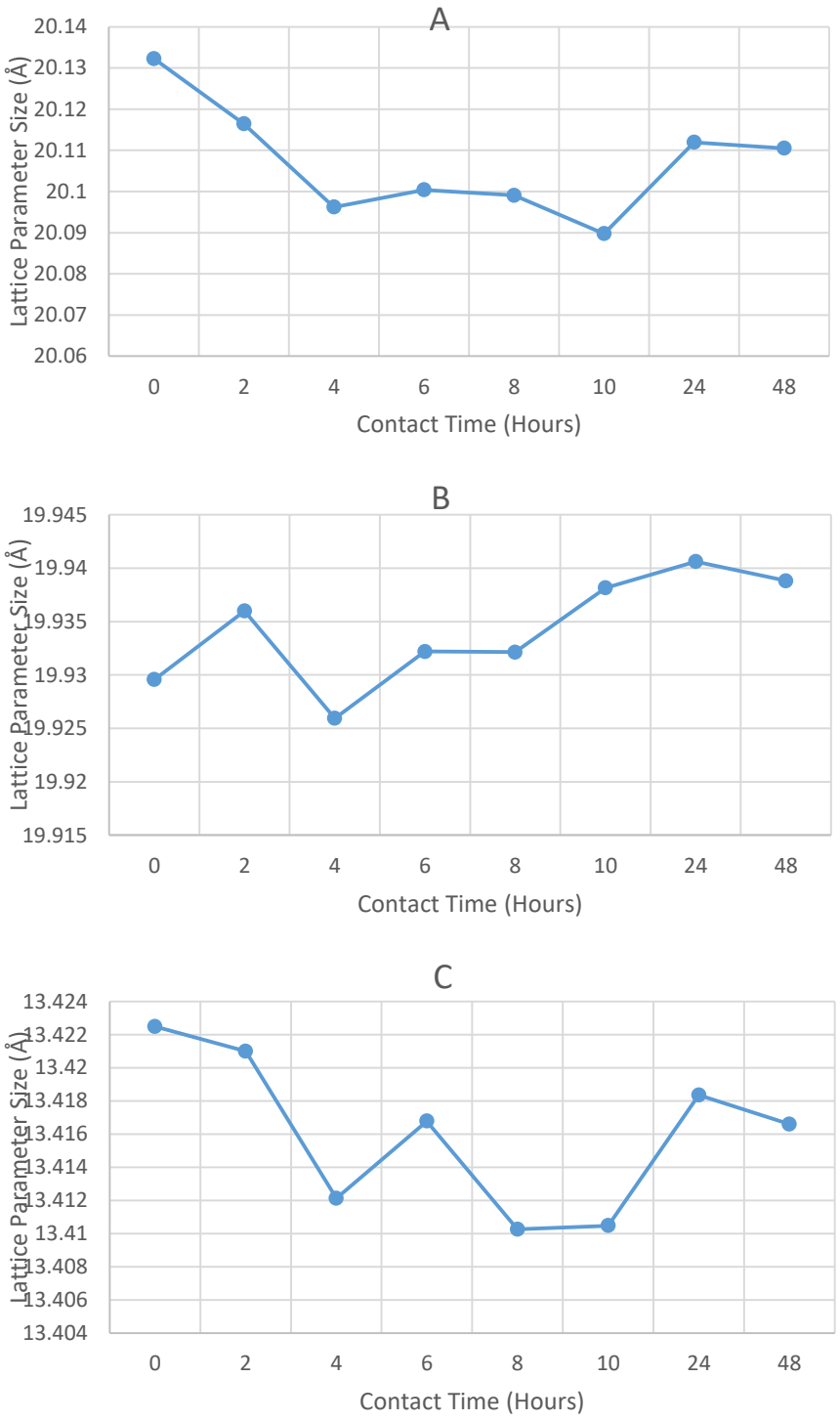


Figure 53. A) Change in lattice parameter *a* against Na ion exchanged ZSM-5 30:1 contact time with aspirin. B) Change in lattice parameter *b* against Na ion exchanged ZSM-5 30:1 contact time with aspirin. C) Change in lattice parameter *c* against Na ion exchanged ZSM-5 30:1 contact time with aspirin.

Figure 53 shows the change in the lattice parameters of ZSM-5 pre-and post paracetamol adsorption with lattice parameters *a* and *c* following a similar path to

one another while parameter *b* changes halfway. Parameters *a* and *c* decrease in size from 0-4 hours, increase in size from 4-6 hours and then decreasing in size from 6-10 hours, though parameter *c* increases from 8-10 hours. They both increase in size from 10-24 hours before a final decrease in size from 24-48 hours. Parameter *b* follows a similar path but does derivate at certain points. It increases in size from 0-2 hours and 8-10 hours rather than decrease. Comparing these changes to the changes in concentration adsorbed shows some inconsistencies. The highest concentration adsorbed was at 24 hours, with 9.02% of the concentration being adsorbed. This is reflected in the increase in lattice parameter size from 10-24 hours with parameter *a* increasing by 0.11%, parameter *b* by 0.1% and parameter *c* by 0.06%. This increase would indicate that the lattice parameter size and concentration adsorbed are directly proportional to one another but all three parameters decrease in size from 2-4 hours when there is an increase in concentration adsorbed within this range. The concentration adsorbed is increased by 0.49% whereas there is a reduction in the size of lattice parameter *a* by 0.10%, lattice parameter *b* by 0.05% and lattice parameter *c* by 0.07%. This indicates that the changes in lattice parameters' sizes are not related to the changes in concentration adsorbed and therefore the lattice parameters do not change to accommodate the aspirin that is adsorbed.

From this we can conclude that Na ion exchanged ZSM-5 30:1 would be an inappropriate compound for the removal of aspirin from aqueous solution, as the concentration of aspirin it can remove from solution is much to low when compared commercial ZSM-5 30:1 ammonium and commercial ZSM-5 200-400:1 ammonium. This reduction in affinity after changing the charge balancing cation to sodium indicates that the charge balancing cation influences aspirin's affinity for ZSM-5. Taken in conjunction with the increase in affinity for ZSM-5 200-400:1 seems to indicate that it was more likely that this increase was due to the increase in its hydrophobicity rather than the reduction of the number of charge balancing cations present. Overall using Na ion exchanged ZSM-5 30:1 to remove aspirin from aqueous solution is not viable though as the amount you would remove against time spent would not be cost effective.

7. Results and Discussion – Adsorptions of Reduced Paracetamol Concentrations Using Commercial ZSM-5 Ammonium 30:1

7.1 Introduction

The data presented in this chapter has been taken from the adsorptions of paracetamol with the reduced concentrations of 0.0025M and 0.00125M, a half and a quarter of the original adsorptions, by commercial ZSM-5 30:1. The ZSM-5 used for the experiments in this chapter has a Si:Al ratio of 30:1 and its charge balancing cation is ammonium.

7.2 – Paracetamol 0.0025M

The previous paracetamol HPLC calibration curve's equation was used to calculate the concentration of the paracetamol left in the solution after the adsorptions. Table 39 shows the HPLC data produced by the adsorption reactions between 2 and 48 hours. Included are the concentration of the drug left in solution, the concentration of the drug that was adsorbed and the percentage of the overall concentration that was adsorbed. A plot showing concentration adsorbed by the zeolite against contact time is presented in figure 54.

Table 39. HPLC results for the 0.0025M paracetamol adsorptions by commercial ZSM-5 ammonium 30:1.

Paracetamol Concentration Left in Solution (M)	Peak Area (mVmin)	Contact Time (Hours)	Retention Time (mins)	Height (mV)	Concentration Adsorbed by the Zeolite (M)	% Concentration Adsorbed
0.002409	268.7025	2	3.351	1071.962	0.000091	3.6244
0.002461	274.4252	4	3.447	1159.051	0.000039	1.5718
0.002419	269.7596	6	3.427	1078.407	0.000081	3.2452
0.002464	274.8350	8	3.438	1140.841	0.000036	1.4248
0.002415	269.3480	10	3.425	1097.696	0.000085	3.3928
0.002451	273.3517	24	3.405	1082.383	0.000049	1.9568
0.002447	272.9518	48	3.430	1135.358	0.000053	2.1003

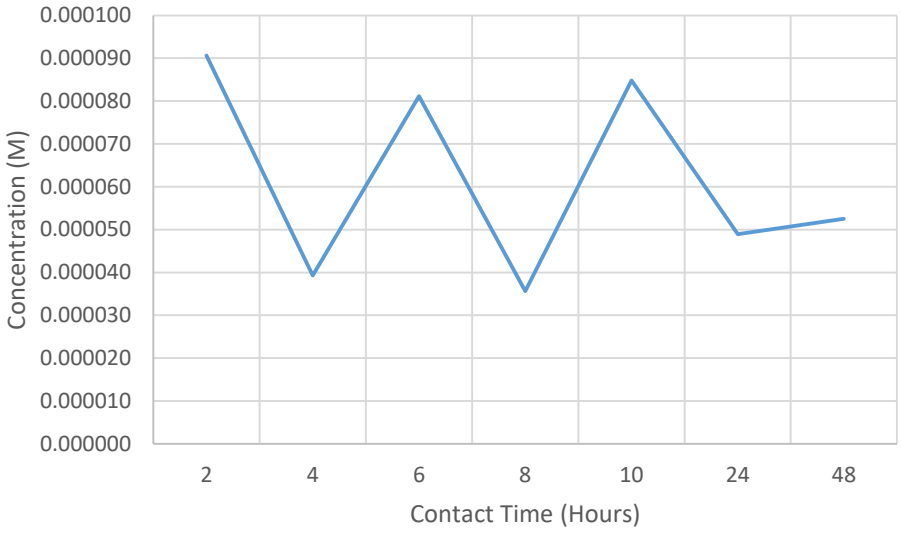
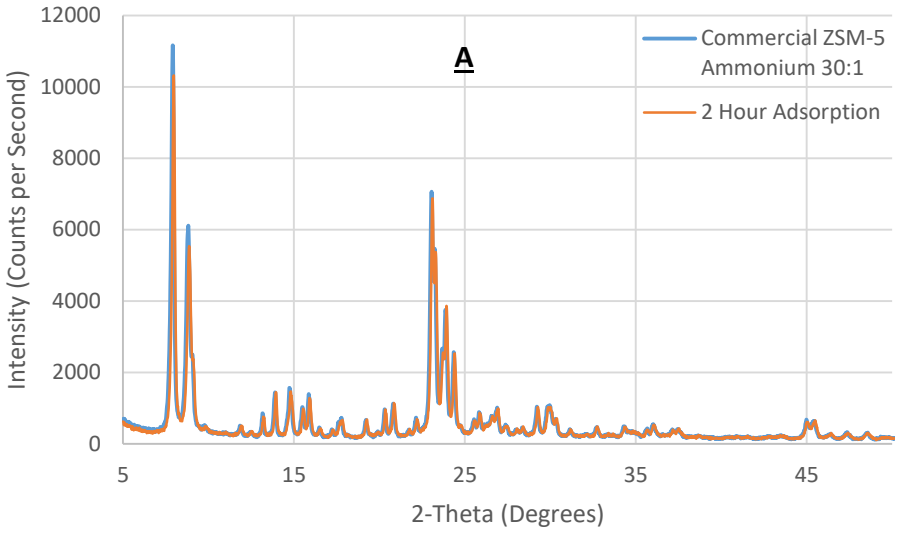
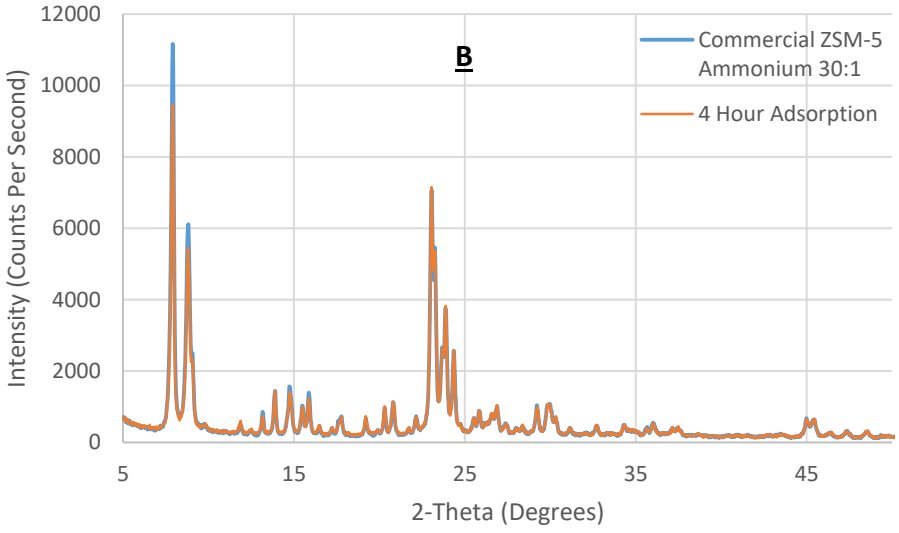


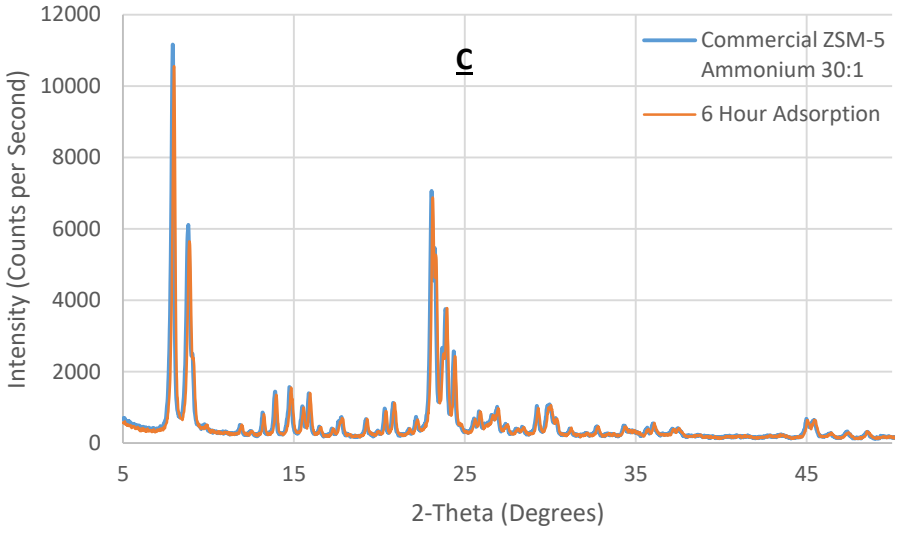
Figure 54. Graph depicting concentration of 0.0025M paracetamol adsorbed by commercial ZSM-5 ammonium 30:1 against contact time.

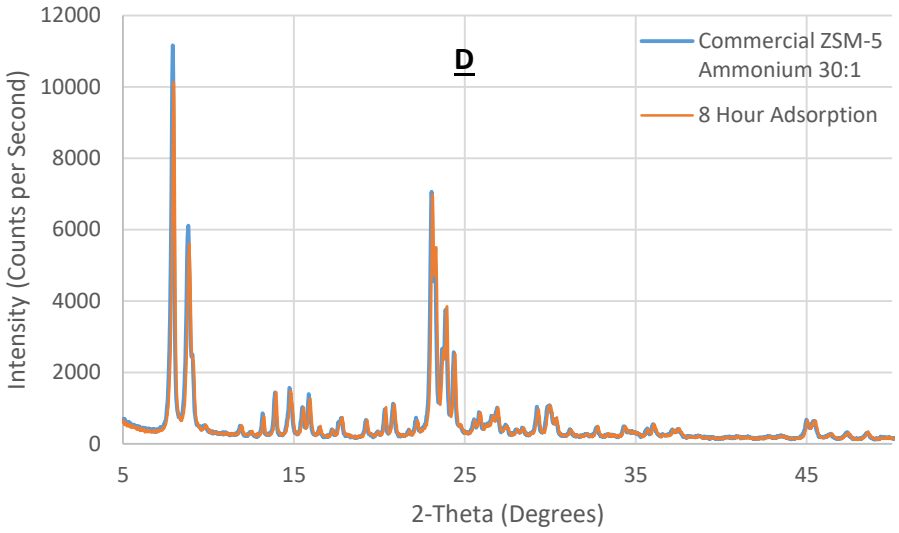
The overall concentration adsorbed is small in comparison to the previous ZSM-5 30:1 paracetamol adsorption, only having a maximum of 0.000091M, 3.62% of the overall concentration. This is much lower than the 0.005M paracetamol ZSM-5 30:1 adsorption which had a maximum adsorption of 0.0032M, 64.39% of its overall concentration. The concentration adsorbed seems to fluctuate within the range of 1.43-3.62%, which would put its equilibrium somewhere in this range though it doesn't reach it. This low amount of concentration adsorbed seems to indicate that commercial ZSM-5 ammonium 30:1's ability to adsorb paracetamol from solution is reduced considerably at lower concentrations making it impractical for the removal of concentrations of this level from wastewater.

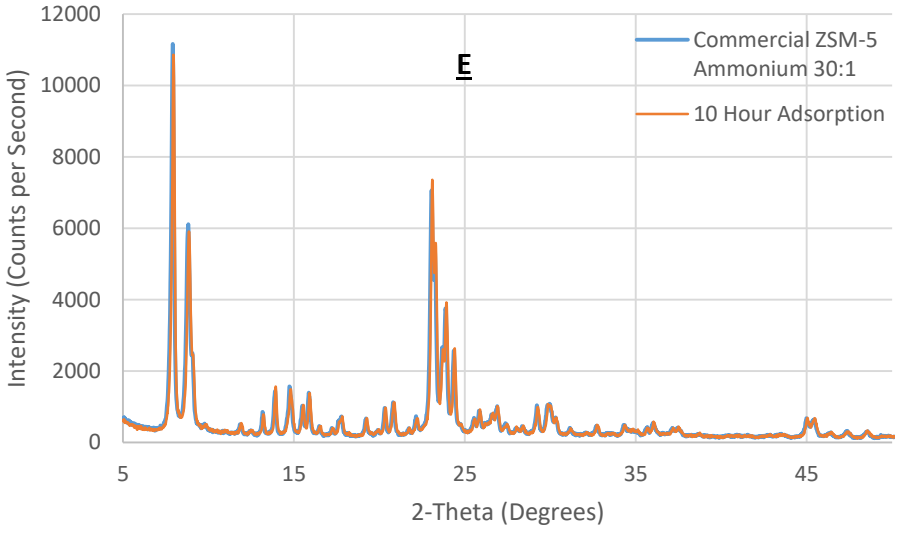
To confirm that the paracetamol has been adsorbed into the pores of ZSM-5 and not absorbed on to the surface of the particles powder XRD was performed on the filtered solid after adsorption had occurred. As a basis, the commercial ZSM-5 ammonium 30:1 XRD pattern is included in figure 8. The diffraction patterns for the post adsorption ZSM-5 is shown in figure 55 with the post adsorption pattern overlaid onto the pre-adsorption pattern.

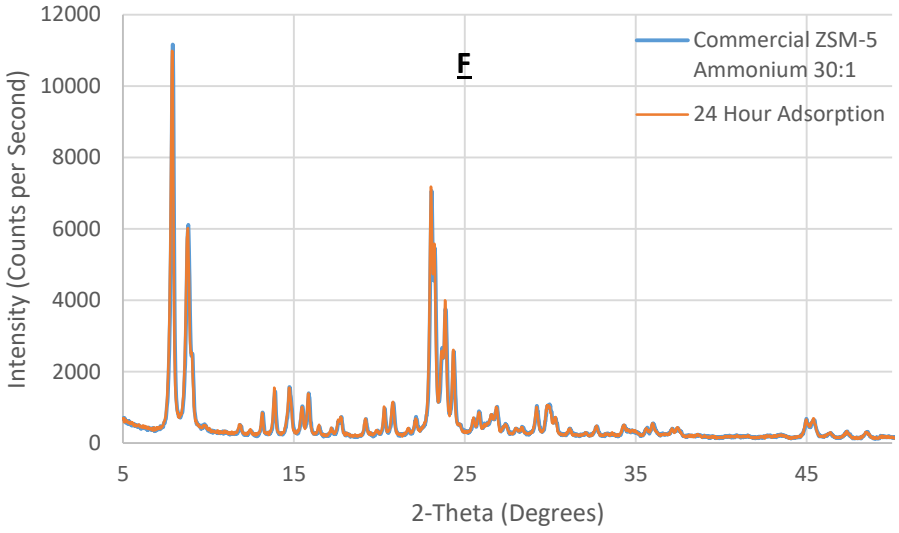

A
Commercial ZSM-5 Ammonium 30:1
2 Hour Adsorption
Intensity (Counts per Second)
2-Theta (Degrees)
12000
10000
8000
6000
4000
2000
0
5
15
25
35
45


B
Commercial ZSM-5 Ammonium 30:1
4 Hour Adsorption
Intensity (Counts Per Second)
2-Theta (Degrees)
12000
10000
8000
6000
4000
2000
0
5
15
25
35
45


C
Commercial ZSM-5 Ammonium 30:1
6 Hour Adsorption
Intensity (Counts per Second)
2-Theta (Degrees)
12000
10000
8000
6000
4000
2000
0
5
15
25
35
45


D
Commercial ZSM-5 Ammonium 30:1
8 Hour Adsorption
Intensity (Counts per Second)
2-Theta (Degrees)
12000
10000
8000
6000
4000
2000
0
5
15
25
35
45


E
Commercial ZSM-5 Ammonium 30:1
10 Hour Adsorption
Intensity (Counts per Second)
2-Theta (Degrees)
12000
10000
8000
6000
4000
2000
0
5
15
25
35
45


F
Commercial ZSM-5 Ammonium 30:1
24 Hour Adsorption
Intensity (Counts per Second)
2-Theta (Degrees)
12000
10000
8000
6000
4000
2000
0
5
15
25
35
45

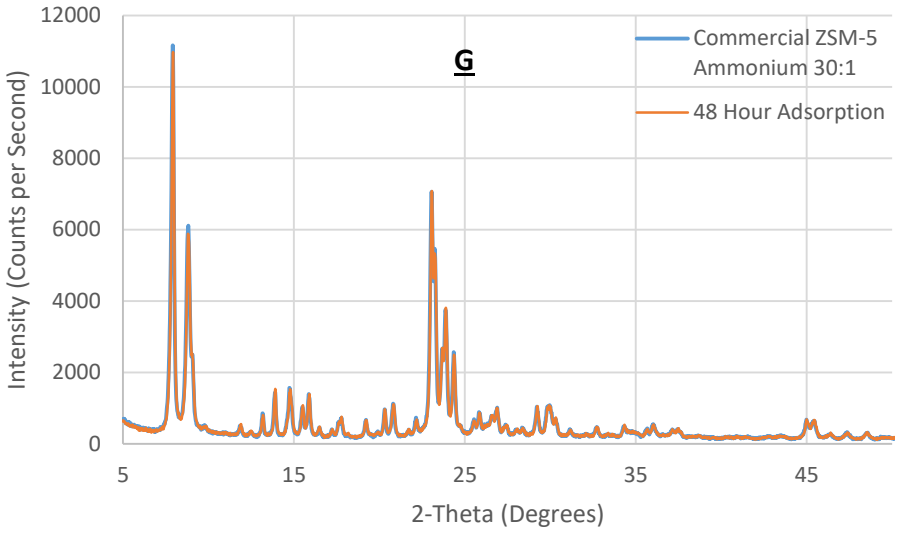


Figure 55. A) Commercial ZSM-5 Ammonium 30:1 + ZSM-5 30:1 post 2 hour 0.0025M paracetamol adsorption. B) Commercial ZSM-5 Ammonium 30:1 + ZSM-5 30:1 post 4 hour 0.0025M paracetamol adsorption. C) Commercial ZSM-5 Ammonium 30:1 + ZSM-5 30:1 post 6 hour 0.0025M paracetamol adsorption. D) Commercial ZSM-5 Ammonium 30:1 + ZSM-5 30:1 post 8 hour 0.0025M paracetamol adsorption. E) Commercial ZSM-5 Ammonium 30:1 + ZSM-5 30:1 post 10 hour 0.0025M paracetamol adsorption. F) Commercial ZSM-5 Ammonium 30:1 + ZSM-5 30:1 post 24 hour 0.0025M paracetamol adsorption. G) Commercial ZSM-5 Ammonium 30:1 + ZSM-5 30:1 post 48 hour 0.0025M paracetamol adsorption.

All seven XRD patterns show some slight differences when compared to the original, commercial ZSM-5. All the patterns have some form of reduction in relative peak intensity in multiple peaks within the range of 5^{o}-23^{o} 2-theta. The most notable differences are seen in the first two peaks at 7.91^{o} 2-theta and 8.82^{o} 2-theta, with the commercial ZSM-5 having peak intensities of 11162 counts per second and 6111 counts per second respectively. Post adsorption these peaks were reduced to between 9460-10985 counts per second and 5448-6019 counts per second with the lowest peaks being produced by the 4-hour adsorption and highest being produced by the 24-hour adsorption. This change in relative peak intensity indicates that the contents of the unit cell have changed in some way which would indicate that the adsorption of the paracetamol has been successful. Another indicator is that the 2, 6 and 8-hour adsorption patterns are shifted to the right by 0.0606^{o} 2-theta. This shift towards a higher 2-theta value indicates a contraction of the zeolite unit cell is occurring. The zeolite framework has a high degree of flexibility and this peak position shift is a further indication that a species has been adsorbed into the pores of the zeolite, in this

case paracetamol, though the relatively low shift indicates that this change is negligible.

The HPLC and XRD data indicate that the paracetamol has been adsorbed by the commercial ZSM-5 30:1 and successfully removed from the solution. The data from the XRD patterns were used to determine the cell parameters to see how the cell structure changed to accommodate the adsorbed paracetamol. The unit cell parameters for commercial ZSM-5 30:1 pre-and post paracetamol adsorption were determined using Topas and J-edit and shown in table 40. A Pawley fit was done using a Chebyshev function background and Pseudo-Voight peak shape function, the zero background and unit cell parameters (*a*, *b*, *c*) were refined to determine errors.

Table 40. Lattice parameters of commercial ZSM-5 30:1 pre-and post 0.0025M paracetamol adsorption with errors included in brackets.

Contact Time with Paracetamol Solution (Hours)	**RWP**	***a*** **(Å)**	***b*** **(Å)**	***c*** **(Å)**
0	7.466	20.11848(3)	19.92388(2)	13.41704(2)
2	7.113	20.12973(3)	19.93565(2)	13.42620(2)
4	7.345	20.11167(4)	19.92043(2)	13.41578(2)
6	7.105	20.12197(3)	19.92777(2)	13.41839(2)
8	7.520	20.11178(3)	19.91999(2)	13.41566(2)
10	6.881	20.11458(4)	19.92679(3)	13.42030(3)
24	7.461	20.11642(3)	19.92676(2)	13.42089(2)
48	7.220	20.11410(3)	19.92328(2)	13.41619(2)

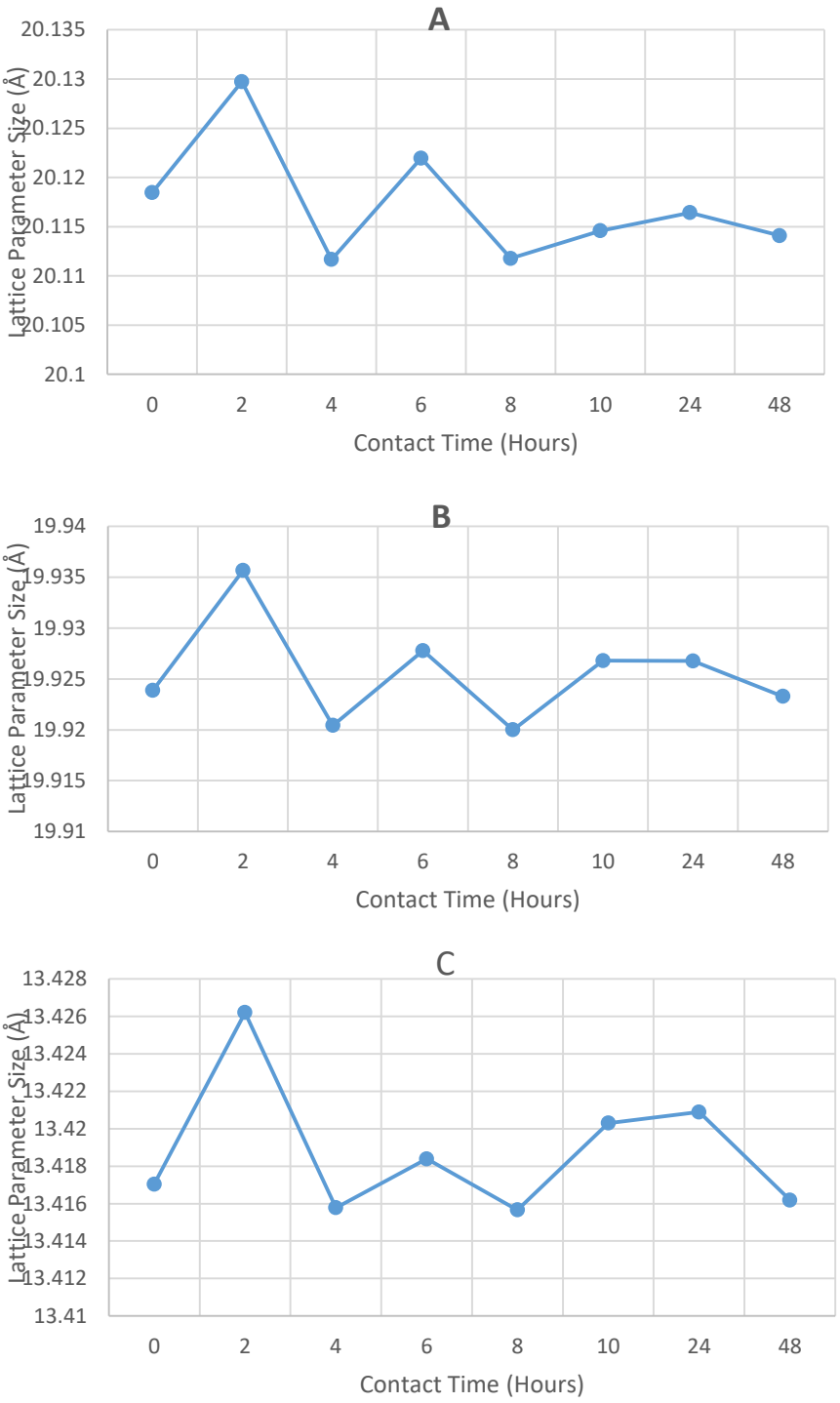


Figure 56. A) Change in lattice parameter *a* against ZSM-5 30:1 contact time with 0.0025M paracetamol. B) Change in lattice parameter *b* against ZSM-5 30:1 contact time with 0.0025M paracetamol. C) Change in lattice parameter *c* against ZSM-5 30:1 contact time with 0.0025M paracetamol.

Figure 56 shows the change in the lattice parameters of ZSM-5 pre-and post paracetamol adsorption and shows all three lattice parameter size changes are related

to each other. All three lattice parameters increase in size from 0-2 hours, reduce in size from 2-4 hours, increase in size from 4-6 hours, reduce in size from 6-8 hours and then increase in size from 8-10 hours. Parameters *a* and *c* both increase in size from 10-24 hours while parameter *b* has a slight reduction before all three reduce in size from 24-48 hours. This pattern seems to match the pattern of the concentration adsorbed, except for parameter *b* at 24 hours. Disregarding this one point, the data indicates that lattice parameter size and concentration adsorbed are directionally proportional to one another. They both share the same position for their maximums, the 2-hour contact time accounting for adsorbing 3.62% of the overall concentration and a 0.06% increase in size for lattice parameters *a* and *b*, and an increase of 0.07% for *c*. This overall directional proportionality indicates that the lattice parameters increased in size to accommodate for the paracetamol to be adsorbed, confirming that paracetamol has been adsorbed.

Commercial ZSM-5 ammonium 30:1 is not a viable compound for the adsorption of 0.0025M paracetamol, though it does remove paracetamol from the solution it doesn't remove enough to make it cost effective or a viable choice for it.

7.3 – Paracetamol 0.00125M

The previous paracetamol HPLC calibration curve's equation was used to calculate the concentration of the paracetamol left in the solution after the adsorptions. Table 41 shows the HPLC data produced by the adsorption reactions between 2 and 48 hours. Included are the concentration of the drug left in solution, the concentration of the drug that was adsorbed and the percentage of the overall concentration that was adsorbed. A plot showing concentration adsorbed by the zeolite against contact time is presented in figure 57.

Table 41. HPLC results for the 0.00125M paracetamol adsorptions by commercial ZSM-5 ammonium 30:1.

Paracetamol Concentration Left in Solution (M)	Peak Area (mVmin)	Contact Time (Hours)	Retention Time (mins)	Height (mV)	Concentration Adsorbed by the Zeolite (M)	% Concentration Adsorbed
0.00097	108.0052	2	3.350	414.969	0.00028	22.5235
0.00109	121.5950	4	3.430	493.509	0.00016	12.7749
0.00110	122.4508	6	3.430	486.657	0.00015	12.1610
0.00111	124.2864	8	3.425	501.281	0.00014	10.8443
0.00106	118.0431	10	3.423	476.616	0.00019	15.3229
0.00105	116.6749	24	3.401	452.057	0.00020	16.3043
0.00108	120.9125	48	3.421	484.394	0.00017	13.2645

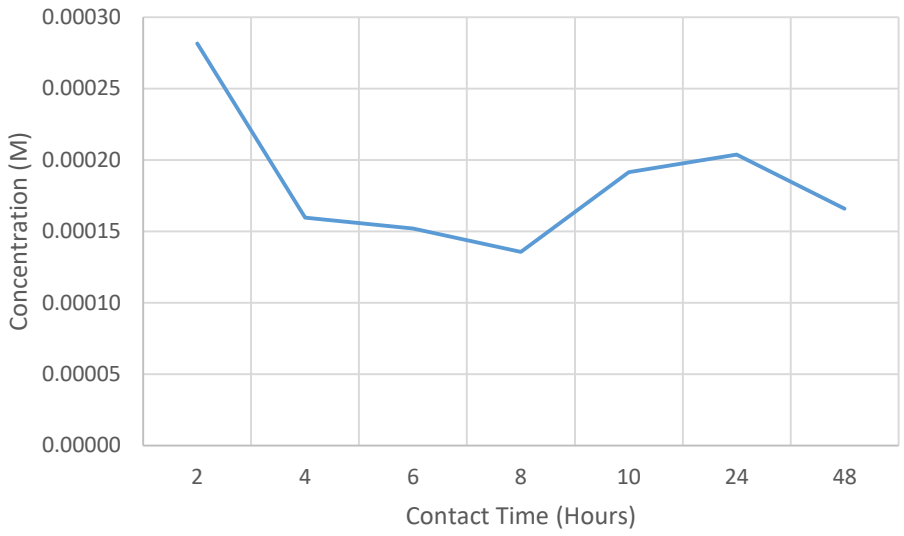
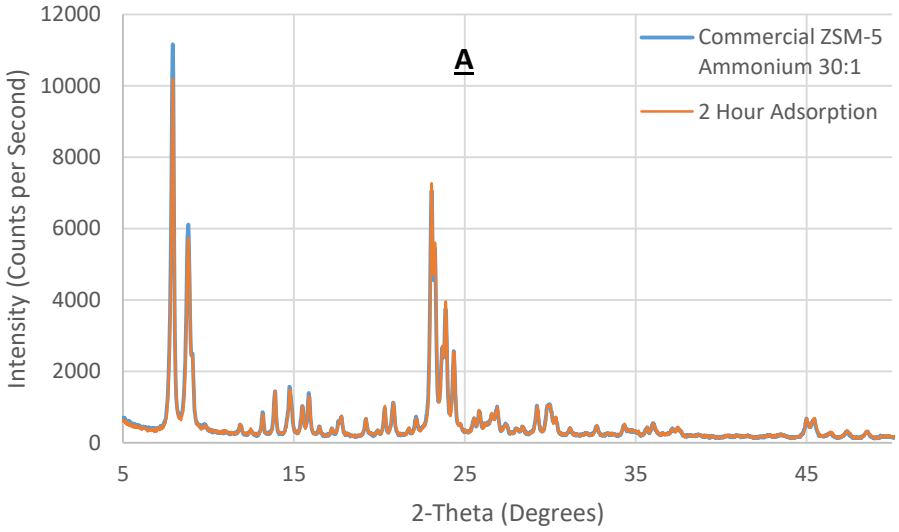


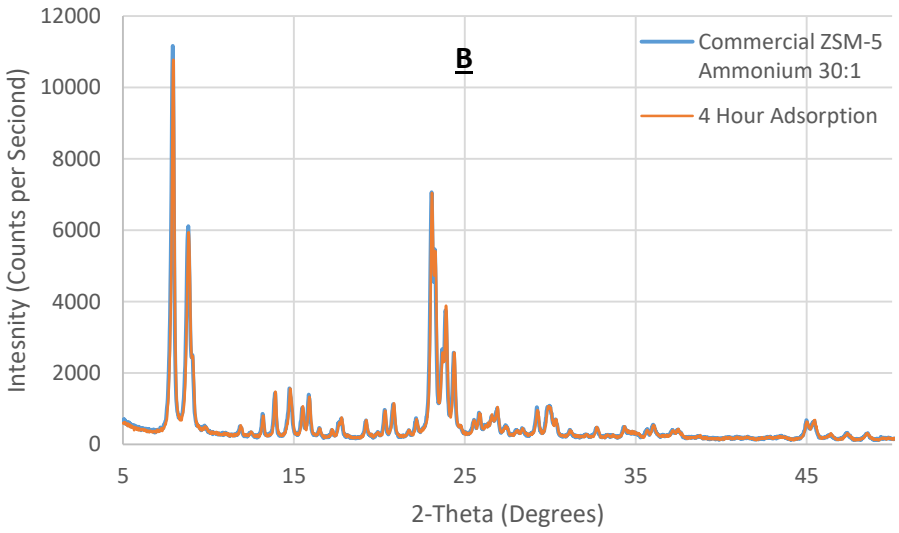
Figure 57. Graph depicting concentration of 0.00125M paracetamol adsorbed by commercial ZSM-5 ammonium 30:1 against contact time.

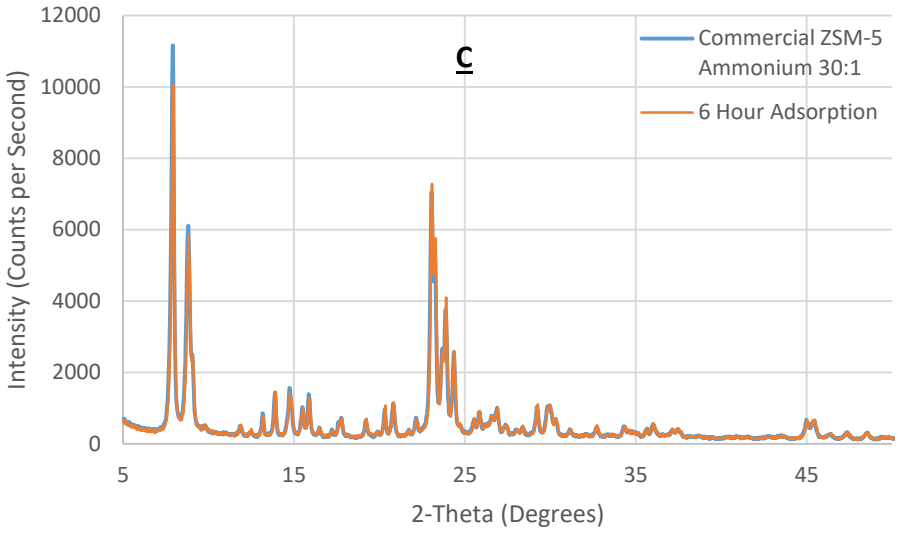
The overall concentration adsorbed is less when compared to the 0.005M commercial ZSM-5 ammonium 30:1 adsorption but higher than its 0.0025M counterpart. This seems inconsistent as an even lower base concentration should lead to a lower amount of concentration adsorbed. This makes sense however when taken in tandem with the ibuprofen lysine HPLC results. Those results produced negative concentrations adsorbed due to a lack of clarity in the HPLC machine producing higher than possible results because the original concentration was so small, 0.002M in that case. If that was happening here also it would make the higher than expected HPLC results make sense, as some of the concentration is being adsorbed though the actual exact amount

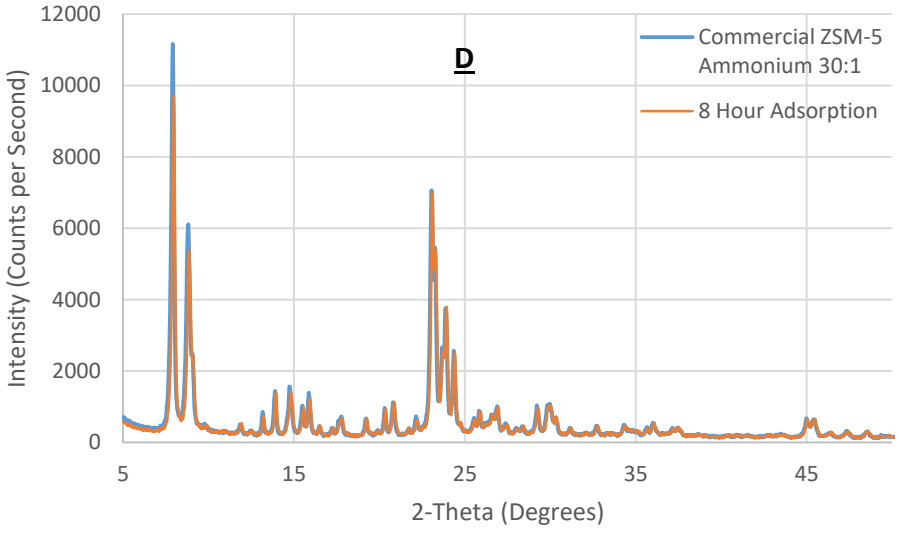
is unknown due to the inaccuracy of the analytical machine. The overall pattern the adsorptions follow will be useful for later analysis though.

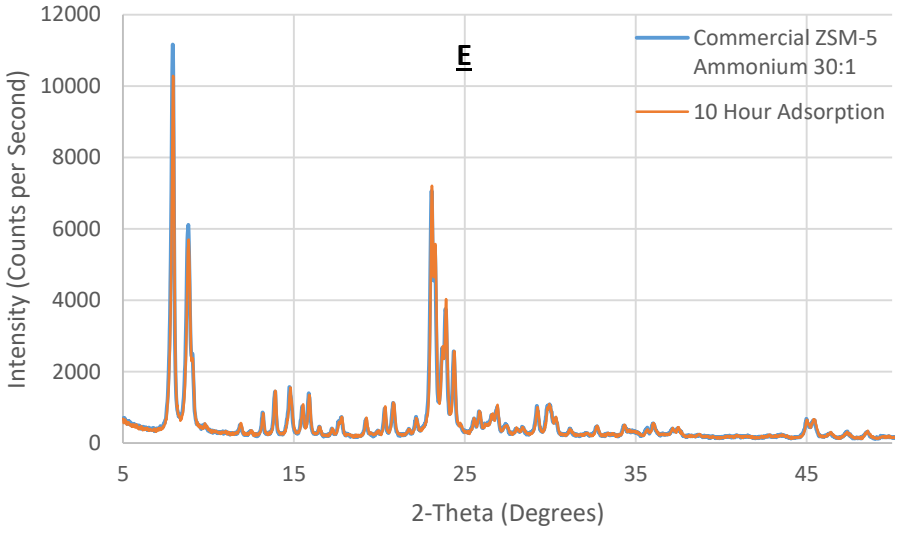
To confirm that the paracetamol has been adsorbed into the pores of ZSM-5 and not absorbed on to the surface of the particles powder XRD was performed on the filtered solid after adsorption had occurred. As a basis, the commercial ZSM-5 ammonium 30:1 XRD pattern is included in figure 8. The diffraction patterns for the post adsorption ZSM-5 is shown in figure 58 with the post adsorption pattern overlaid onto the pre-adsorption pattern.






C
Commercial ZSM-5 Ammonium 30:1
6 Hour Adsorption
Intensity (Counts per Second)
2-Theta (Degrees)
12000
10000
8000
6000
4000
2000
0
5
15
25
35
45


D
Commercial ZSM-5 Ammonium 30:1
8 Hour Adsorption
Intensity (Counts per Second)
2-Theta (Degrees)
12000
10000
8000
6000
4000
2000
0
5
15
25
35
45


E
Commercial ZSM-5 Ammonium 30:1
10 Hour Adsorption
Intensity (Counts per Second)
2-Theta (Degrees)
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10000
8000
6000
4000
2000
0
5
15
25
35
45

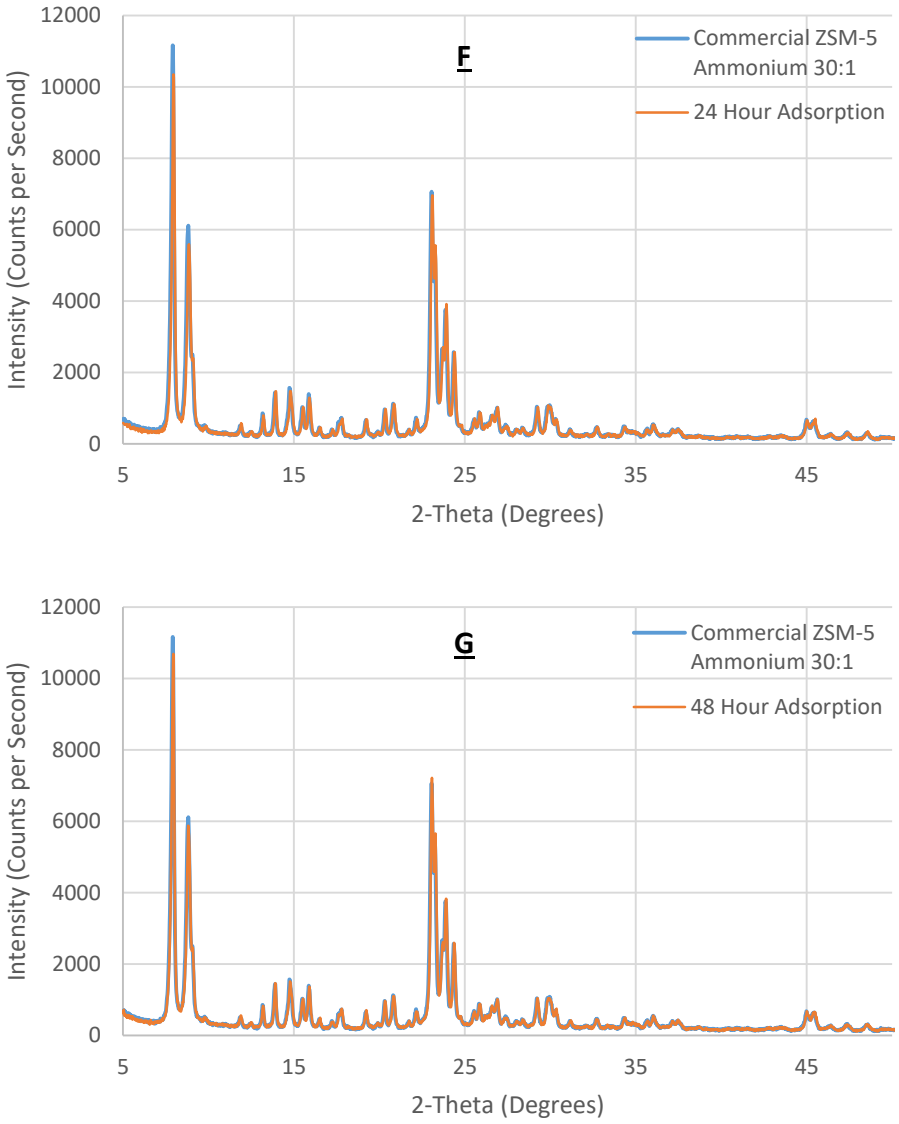

Figure 58. A) Commercial ZSM-5 Ammonium 30:1 + ZSM-5 30:1 post 2 hour 0.00125M paracetamol adsorption. B) Commercial ZSM-5 Ammonium 30:1 + ZSM-5 30:1 post 4 hour 0.00125M paracetamol adsorption. C) Commercial ZSM-5 Ammonium 30:1 + ZSM-5 30:1 post 6 hour 0.00125M paracetamol adsorption. D) Commercial ZSM-5 Ammonium 30:1 + ZSM-5 30:1 post 8 hour 0.00125M paracetamol adsorption. E) Commercial ZSM-5 Ammonium 30:1 + ZSM-5 30:1 post 10 hour 0.00125M paracetamol adsorption. F) Commercial ZSM-5 Ammonium 30:1 + ZSM-5 30:1 post 24 hour 0.00125M paracetamol adsorption. G) Commercial ZSM-5 Ammonium 30:1 + ZSM-5 30:1 post 48 hour 0.00125M paracetamol adsorption.

All seven XRD patterns show some slight differences when compared to the original, commercial ZSM-5. All the patterns have some form of reduction in relative peak intensity in multiple peaks within the range of 5^{o}-23^{o} 2-theta. The most notable differences are seen in the first two peaks at 7.91^{o} 2-theta and 8.82^{o} 2-theta, with the

commercial ZSM-5 having peak intensities of 11162 counts per second and 6111 counts per second respectively. Post adsorption these peaks were reduced to between 9703-10774 counts per second and 5368-5942 counts per second with the lowest peaks being produced by the 8-hour adsorption and highest being produced by the 4-hour adsorption. This change in relative peak intensity indicates that the contents of the unit cell have changed in some way which would indicate that the adsorption of the paracetamol has been successful, though due to small overall differences when compared to other paracetamol adsorptions the amount adsorbed would be very small almost negligible.

The HPLC and XRD data indicate that the paracetamol has been adsorbed by the commercial ZSM-5 30:1 and successfully removed from the solution, though how much has exactly been removed is unknown. The data from the XRD patterns were used to determine the cell parameters to see how the cell structure changed to accommodate the adsorbed paracetamol. The unit cell parameters for commercial ZSM-5 30:1 pre-and post paracetamol adsorption were determined using Topas and J-edit and shown in table 42. A Pawley fit was done using a Chebyshev function background and Pseudo-Voight peak shape function, the zero background and unit cell parameters (*a*, *b*, *c*) were refined to determine errors.

Table 42. Lattice parameters of commercial ZSM-5 30:1 pre-and post 0.00125M paracetamol adsorption with errors included in brackets.

Contact Time with Paracetamol Solution (Hours)	**RWP**	***a*** **(Å)**	***b*** **(Å)**	***c*** **(Å)**
0	7.466	20.11848(3)	19.92388(2)	13.41704(2)
2	7.353	20.11611(3)	19.92765(2)	13.42184(2)
4	7.239	20.12049(3)	19.92811(2)	13.42222(2)
6	7.043	20.11800(4)	19.92906(3)	13.42155(3)
8	6.768	20.12637(3)	19.93390(2)	13.42717(2)
10	7.54	20.11106(3)	19.92344(2)	13.41694(2)
24	7.317	20.12267(3)	19.92729(2)	13.42270(2)
48	7.368	20.11206(3)	19.92033(2)	13.41717(2)

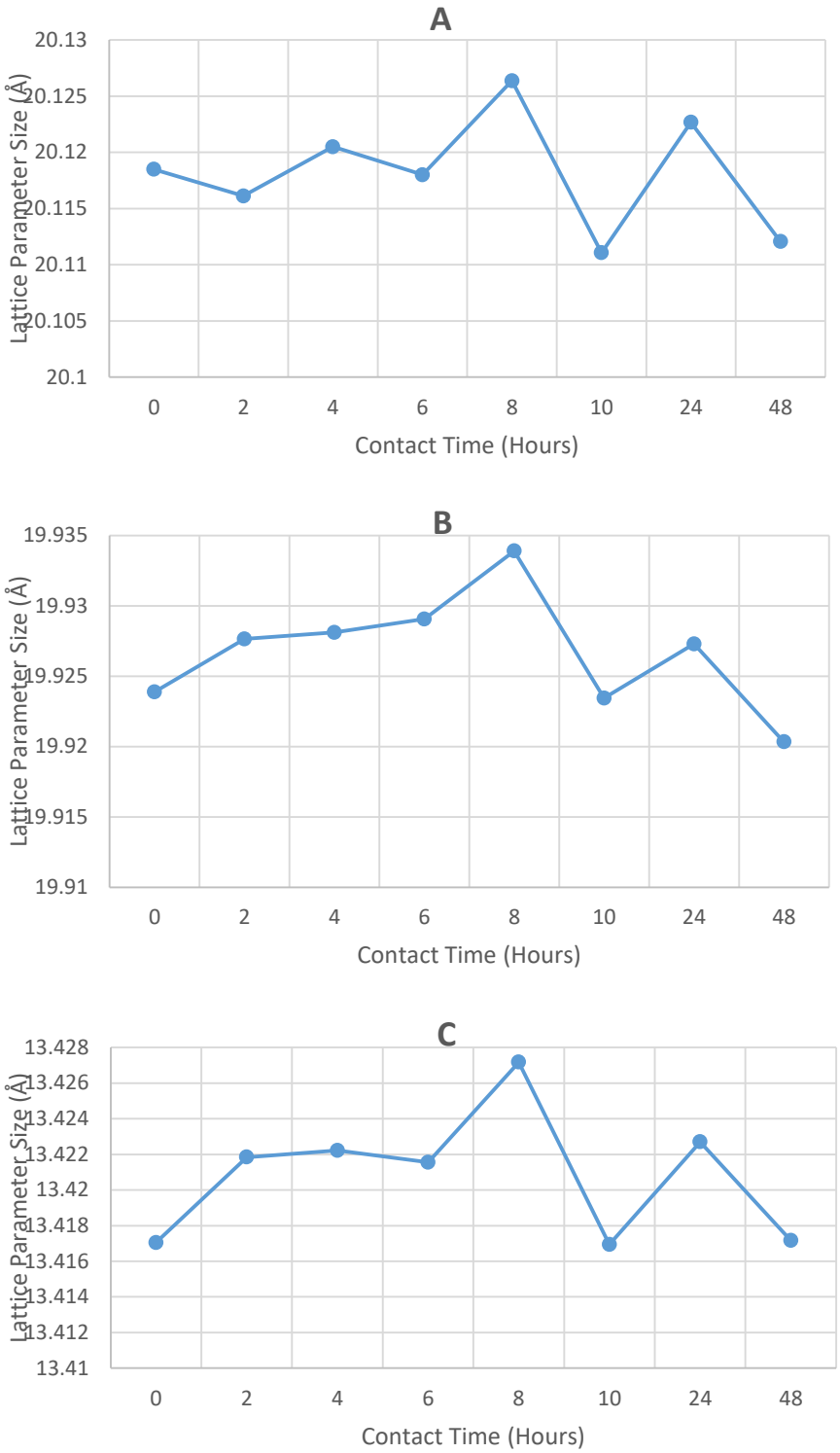

Figure 59. A) Change in lattice parameter *a* against ZSM-5 30:1 contact time with 0.00125M paracetamol. B) Change in lattice parameter *b* against ZSM-5 30:1 contact time with 0.00125M paracetamol. C) Change in lattice parameter *c* against ZSM-5 30:1 contact time with 0.00125M paracetamol.

Figure 59 shows the change in the lattice parameters of ZSM-5 pre-and post paracetamol adsorption and shows all three lattice parameter size changes follow an overall similar pattern. Lattice parameter *a* decreases in size from 0-2 hours while parameters *b* and *c* increases in size at this time. Then all three parameters increase in size from 2-4 hours before parameters *a* and *c* decrease in size while parameter *b* increases in size. After this all three follow the same path, an increase in size from 6-8 hours, a reduction in size from 8-10 hours, an increase in size from 10-24 hours and a final reduction in size 24-48 hours. The maximum concentration adsorption was produced at 2 hours and the minimum at 8 hours. The maximum size of the lattice parameters is produced at 8 hours, this would indicate that the lattice parameter size and concentration adsorbed are inversely proportional but this is not reflected in the rest of the data, the smallest lattice parameter sizes being produced by 13.26% concentration adsorbed, which seems to be in the middle of the pattern rather than the top. This indicates that there is no correlation between ZSM-5 lattice parameter's size and the concentration of paracetamol adsorbed and that the lattice parameters are not changing in size to accommodate the adsorption of paracetamol.

Commercial ZSM-5 ammonium 30:1 is not a viable compound for the adsorption of 0.00125M paracetamol, though it does remove paracetamol from the solution the low base concentration and inaccuracy of the HPLC machine mean that it is not certain how much exactly it did adsorb and so it is not a viable adsorbent and very low concentrations.

8. – Conclusions and Further Research

Commercial ZSM-5 ammonium 30:1 was found to be the optimum form of ZSM-5 investigated for the adsorption of paracetamol from aqueous solution. Eight hours was its optimum contact time for adsorption, accounting for the removal of 64.39% of the paracetamol concentration. The aspect of ZSM-5 that most affected the affinity of paracetamol for ZSM-5 was the charge balancing ammonium cation. A reduction in concentration adsorbed was observed when the charge balancing cation was changed and when the number of charge balancing cations present were reduced by increasing the Si:Al ratio. Commercial ZSM-5 ammonium 30:1 is not appropriate for the removal of lower concentrations of paracetamol as the percentage of concentration adsorbed dropped to a maximum of 3.62% when the batch concentration was halved. Overall commercial ZSM-5 ammonium 30:1 is the most viable form of ZSM-5 investigated for the removal of paracetamol from aqueous solution and therefore it is viable for removing paracetamol from waste water, though further research is required into its use at lower concentrations.

Commercial ZSM-5 ammonium 30:1 was also found to be the optimum form of ZSM-5 investigated for the adsorption of ibuprofen lysine from aqueous solution. At 2 hours, it adsorbed its maximum of 56.82% of the ibuprofen in the solution, making this the optimum contact time for adsorption. Similarly, to paracetamol the aspect of ZSM-5 that most affected the adsorption was the ammonium cation, as a reduction in the concentration adsorbed was observed when the charge balancing cation was changed and when the number of charge balancing cations present were reduced by increasing the Si:Al ratio, these changes leading to almost no ibuprofen lysine getting adsorbed at all. Overall we conclude that, though commercial ZSM-5 ammonium 30:1 is viable for the removal of ibuprofen lysine from solution, its tendency to desorb all the ibuprofen lysine back at certain contact times makes it harder to implement for ibuprofen lysine's removal from waste water.

Commercial ZSM-5 ammonium 200-400:1 was also found to be the optimum form of ZSM-5 investigated for the adsorption of aspirin from aqueous solution. It had an optimum contact time of 48 hours, removing 61.52% of the aspirin from the solution

in this time. Conversely to the other two analgesics it was the hydrophobicity caused by the increase in the Si:Al ratio that had the greatest positive effect on the amount of concentration adsorbed by ZSM-5. This conclusion was arrived at due to the data showing that a decrease in the number of ammonium cations present increased aspirin's affinity for ZSM-5 while the change in charge balancing cation reduced it. This makes commercial ZSM-5 ammonium 200-400:1 viable for the removal of aspirin from aqueous solution and therefore viable for aspirin's removal from waste water.

ZSM-5 overall was found to be an appropriate compound for the removal of the analgesics investigated from aqueous solutions though further research into its affinity for other analgesics and pharmaceutical compounds is required. Similarly, further investigation into the effects of a varied temperature and pH of the system on the affinity of the analgesics investigated would be advisable, as would considering the effects other charge balancing cations, such as calcium and potassium, if reducing the Si:Al ratio of ZSM-5 would have a positive effect on the adsorption of paracetamol and ibuprofen lysine by ZSM-5 and the ability of ZSM-5 to adsorb analgesics from a mixed solution.

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