MIGUEL ANTONIO MARTIR BRION

DEVELOPMENT OF AN IRON OXIDE NANOPARTICLE-ACTIVATED CARBON ADSORBENT FOR WATER TREATMENT OF COMMON HUMAN PHARMACEUTICAL CHEMICALS

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DEVELOPMENT OF AN IRON OXIDE NANOPARTICLE-ACTIVATED CARBON ADSORBENT FOR WATER TREATMENT OF COMMON HUMAN PHARMACEUTICAL CHEMICALS

Miguel Antonio M. Brion

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Work supervised by

Margarida Ribau Teixeira
José António Moreira

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DECLARATION OF AUTHORSHIP AND COPYRIGHT

I declare that I am the author of this work which is original. The work cites other authors and works, which are adequately referred to in the text and are listed in the references section.

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Miguel Antonio M. Brion

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ABSTRACT

In recent years, there was a big market growth in the pharmaceutical industry (World Health Organization, 2011). As a result, there has also been an increase in pharmaceutical pollutants present in the environment (Weber et al, 2014). These emerging pharmaceutical pollutants are common human pharmaceutical compounds (HPCs) such as ibuprofen (IBU), paracetamol (PAR), acetylsalicylic acid (ASA), and amoxicillin (AMOX). When consumed, the unmetabolized drugs and their metabolites reach the environment through human excretion. Because they are biologically active, a small amount can be a source of possible problems for aquatic creatures (Bacsi et al, 2016). Because some pharmaceutical components are very recalcitrant to common wastewater treatment techniques, new wastewater treatment processes are being explored (Ghafoori et al, 2014). A new composite adsorbent material is created in order to address the separation difficulty and the limited adsorption of other adsorbents. The aim of this research is to synthesize a magnetic activated carbon adsorbent (PACMAG) that combines the adsorbing capabilities of powdered activated carbon (PAC) and the magnetic properties of iron oxide nanoparticles (FeNPs).

The FeNPs, were synthesized by co-precipitation in a basic medium which resulted in a quantitative yield, the afforded particles have a positive zeta potential and a point of zero charge between pH 8 and 9. These were then embedded in powdered activated carbon in order to produce PACMAG with 103 ± 5 % yield. PACMAG was first tested for its adsorption capacity in various HPCs, namely IBU, PAR, and ASA. The adsorption ability of PACMAG was assessed from isotherms of 24 hours. The adsorption of IBU by PACMAG, which was the chosen model compound for aromatic analgesics was further optimized. Several adsorption isotherms were determined by varying the amount of adsorbent and drug present in the system. The behavior of IBU was compared with AMOX, a non-aromatic antibiotic. Based on the behavior of both HPCs (IBU and AMOX) in the presence of PACMAG, the optimum parameters for the adsorption are 120 min adsorption time for 15 mg/L drug concentration, and 300 mg/L PAC content in the adsorbent. This resulted in a 92.22 ± 0.08 % and in a 79.90 ± 0.05 % removal for IBU and AMOX respectively. In the same conditions, IBU and AMOX adsorption was tested using the wastewater (WW) from Estação de Tratamento de Águas Residuais (ETAR) as solvent. In wastewater, a decreases in drug adsorption to 49.52 ± 0.15 % and 26.54 ± 0.01% IBU and AMOX, respectively, was observed. This is due to the presence of other organic molecules in the system that compete for the adsorption sites. By increasing the PAC content of the adsorbent to 1000 mg/L, which was done for AMOX, the percent

removal can be increased up to 76.720 ± 0.001 %. Finally, PACMAG can be regenerated using the Fenton reaction. The regenerated PACMAG removed 53.840 ± 0.004% of AMOX in an AMOX-WW mixture. Based on the sedimentation test, PAGMAG is more time efficient because it requires 5 minutes at the presence of a magnet to settle, and separate the particles from the water supply.

The results of this work can contribute for the improvement of water treatment processes particularly in the removing of HPCs. Being nowadays, this kind of compounds is a growing problem in water treatment.

Keywords: Magnetic Activated Carbon, Magnetite Nanoparticle, Activated Carbon, Water Treatment Analysis, Human Pharmaceutical Compounds, Adsorption

RESUMO

Nas últimas décadas assistiu-se a um enorme crescimento da Industria Farmacêutica (World Health Organization, 2011), o que levou a um aumento exponencial da quantidade e do número de compostos de origem farmacêutica que se podem encontrar no ambiente (Weber et al, 2014). Este novo tipo de poluentes designados por *"human pharmaceutical compounds"* (HPCs), como o ibuprofen (IBU), o paracetamol (PAR), o ácido acetilsalicílico (ASA), ou a amoxicilina (AMOX).

Quando consumidos, tanto as drogas não metabolizadas como os seus metabolitos são libertados no ambiente por via das excreções. Sendo as drogas, e, ou os seus metabolitos biologicamente ativos, mesmo uma pequena quantidade dos mesmos pode ter impacto sobre os seres presentes nos meios aquáticos (Bacsi et al, 2016). Sendo alguns destes compostos particularmente resistentes aos tratamentos comummente usados no processamento das águas residuais, tal tem levado à procura de novos processos de tratamento de águas residuais (Ghafoori et al, 2014).

Neste trabalho mostramos os resultados obtidos com um novo material compósito criado de modo a maximizar a adsorção e a facilitar o processo de separação e regeneração do adsorvente. Assim damos conta da síntese do um adsorvente de carvão ativado com propriedades magnéticas (PACMAG), este material combina a capacidade de adsorção do carvão ativado pulverizado (PAC) e as propriedades magnéticas de nanopartículas de óxido de ferro (FeNPs). As nanopartículas de óxido de ferro (FeNPs) foram sintetizadas por coprecipitação em meio básico, por este método foi possível obter nanopartículas com um rendimento quantitativo, mostrando estas um potencial zeta positivo, e uma ponto de carga zero a pH entre 8 e 9. Estas partículas forma posteriormente embutidas em carvão ativado pulverizado, resultando o novo material PACMAG.

Foi testada a capacidade de adsorção de diversos HPC, nomeadamente o IBU, o PAR e o ASA, pelo PACMAG. Foram realizadas isotérmicas ao longo de 24 horas. O IBU foi escolhido como composto modelo para os analgésicos aromáticos, tendo sido as condições otimizadas para este composto. O comportamento do IBU foi comparado com o da AMOX, um antibiótico não aromático. De acordo com os resultados obtidos para estes dois fármacos foi determinado que, para concentrações de 15 mg/L de droga, o tempo de contacto necessário é de 120 minutos, e que o conteúdo em PAC ótimo, do adsorvente, é de 300 mg/L. Nestas condições observou-se uma remoção de 92,22 ± 0,08 % e de 79,90 ± 0,05 % para o IBU e a AMOX respetivamente.

Em condições idênticas, foram repetidos, os testes de adsorção do IBU e da AMOX, usando água residual (WW) de uma Estação de Tratamento de Águas Residuais (ETAR) como solvente. Nestas condições observou-se uma diminuição da quantidade de droga adsorvida para 49,52 ± 0,15 % e 26,54 ± 0,01% para o IBU e para a AMOX, respetivamente. Tal deve-se à presença de outras moléculas orgânicas que competem com os fármacos em estudo pelos sítios de adsorção. Aumentando a quantidade de PAC no adsorvente para 1000 mg/L, o que foi feito para o caso da AMOX, a remoção aumenta para 76,720 ± 0,001%.

Finalmente mostra-se que o PACMAG pode ser regenerado usando a reação de Fenton. O PACMAG regenerado removeu 53,840 ± 0,004% de AMOX de uma solução AMOX-WW. De acordo com os testes de sedimentação o PACMAG necessita de apenas 5 minutos para na presença de um campo magnético sedimentar, de modo a permitir a sua separação da água tratada.

Os resultados deste trabalho são uma contribuição para a melhoria dos processos de tratamento de águas residuais, em particular na remoção de HPC compostos cada vez mais prevalentes nas águas a tratar.

Palavras Chave: Carvão Ativado com Propriedade Magnéticas, Nanopartículas de Magnetite, Carvão Ativado, Tratamento de Águas, *Human Pharmaceutical Compounds*, Adsorção

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LIST OF ACRONYMS

EPPP:	Environmental Persistent Pharmaceutical Pollutants
HPCs:	Human Pharmaceutical Compounds
ETAR:	Estação de Tratamento de águas residuais
IBU:	Ibuprofen
AMOX:	Amoxicillin
PAR:	Paracetamol/ Acetaminophen
ASA:	Acetyl Salicylic Acid/ Aspirin
WWTPs:	Wastewater treatment plants
NPs:	Nanoparticles
FeNPs:	Iron Oxide Nanoparticles
PAC:	Powdered Activated Carbon
PACMAG/MAC:	Magnetic Activated Carbon
UV-VIS:	Ultraviolet-Visible Spectrophotometry
λ_{max}:	Wavelength of maximum absorption
HCl:	Hydrochloric acid
H_2O_2:	Hydrogen Peroxide
$FeCl{\cdot}6H_2O$:	Iron (III) chloride 6-hydrate
Na_2SO_4:	Sodium sulfate
NH_3:	Ammonia
$AgNO_3$:	Silver Nitrate
NaCl:	Sodium Chloride
NaOH:	Sodium Hydroxide
$C_7H_6O_3$:	Salicylic acid
$C_4H_6O_3$:	Acetic Anhydride
Fe_3O_4:	Magnetite
Fe_2O_3:	Maghemite
EPA:	Environmental Protection Agency
WHO:	World Health Organization
FDA:	Food and Drug Administration
SAICM:	Strategic Approach to International Chemical Management
EU:	European Union
IE:	Industrial Effluents
RS:	River Sediments
GW:	Ground Water
SW:	Surface Water
ZP:	Zeta Potential
TOC:	Total Organic Carbon
COD:	Chemical Oxygen Demand
DOC:	Dissolved Organic Carbon
m/m:	mass FeNPs per mass PAC
DW:	Deionized Water
WW:	Wastewater

OBJECTIVES OF THE RESEARCH

For the past 2 years, there was a US$150 billion increase in global pharmaceutical demand due to increasing global public consumption (World Health Organization, 2011). Once consumed these unmetabolized drugs and their metabolites are normally excreted in urine and feces which end up in wastewater treatment plants (WWTPs). Wastewater treatment plants can remove some of these pharmaceutical contaminants, but not all are removed. Some pharmaceutical components are very recalcitrant or persistent and the usual wastewater treatment processes are inefficient in their removal (Ghafoori et al, 2014). As a result, these contaminants are discharged in water bodies and present in sludges, contaminating the environment. Even though their concentration is low, these drugs and their metabolites are bioactive which can affect aquatic species.

In order to address this problem, a new wastewater treatment process must be optimized or developed. Adsorption through activated carbon is promising in the removal of these contaminants from wastewater (WW). Powdered activated carbon (PAC) is an excellent adsorbent, but it requires an additional filtration step in order to separate it from the effluent (Borghi and Fabbri, 2013). On the other hand, studies had shown that iron oxide nanoparticles (FeNPs) have big surface area, due to its small size, and can be magnetically separated (Stefusova et al, 2012). However, these nanoparticles have a natural tendency to aggregate in aqueous solutions, decreasing their adsorption capacity (Atta et al, 2015). Thus, work must be done in trying to maximize the adsorption capacity of the PAC, and the magnetic property of FeNPs to increase PAC and pharmaceutical removal.

The aim of this research is to develop a composite magnetic activated carbon adsorbent (PACMAG) which can remove pharmaceuticals (like e.g. IBU, PAR, ASA, and AMOX) from wastewater (WW).

The main objective of this study was obtained by achieving the following steps:

- Synthesis and characterization of the FeNPs based on particle size and zeta potential in varying pH and ion concentrations
- Synthesis of PACMAG using the FeNPs and PAC

- Analyze FeNPs and PACMAG kinetics in various aqueous drug solutions (IBU, PAR, ASA, and AMOX)
- Determine PACMAG isotherms in various aqueous drug solutions (IBU and AMOX),
- Compare the sedimentation of PACMAG using various sedimentation set-ups (with and without a magnetic force for 5 minutes, without a magnetic force for 30 min),
- Determine the adsorption capacity of PACMAG to remove IBU or AMOX in WW,
- Perform preliminary tests on the regeneration of PACMAG.

1 INTRODUCTION

1.1 Pharmaceutical Contaminants in Water

Currently the pharmaceutical industry is gaining advancement in the global market. Since 2014, 90 new human pharmaceutical compounds (HPCs) have been approved by the Food and Drug Administration (FDA) (CEN RSS, 2016). According to the World Health Organization (WHO), in just 2 years (2013-2015) the global pharmaceutical sales would increase by US$ 150 billion, amounting to a total of US$ 900 billion (World Health Organization, 2011). There is a big demand for pharmaceuticals annually which is based on the global public consumption of medicines. Contrary to the increase in innovation, the pharmaceutical companies currently spend one-third of all sales revenue on marketing strategies and not on research and development. As a result, many of these new drugs move in the global market not due to their ability to transform lives, rather, to gain profit according to the Chemical Engineering News (C&EN) (CEN RSS, 2016)

As an indirect effect of the high consumption of these HPCs, studies showed that they would eventually reach different environmental sinks (Shalini et al, 2010). According to the Strategic Approach to International Chemical Management (SAICM), there had been an emerging issue of pharmaceuticals in the environment resulting to the term environmental persistent pharmaceutical pollutants (EPPP) (SAICM, 2016). EPPP are defined as compounds that have not been studied before and are not currently covered by existing water-quality regulations. This includes the pharmaceutical residues and metabolites with potential of contaminating the environment (water, soil, organisms) (EUR-Lex, 2016). Table 1.1 depicts the number of EPPP found in aquatic environment in numerous countries. It also shows the variety of drugs that can be an EPPP namely analgesics, estrogens and antibiotics. Most of the EPPP are common drugs such as IBU, ASA, and PAR (Weber et al, 2014). Because of the amount of these HPCs that are being used by the public, they can eventually be problematic (Geissen et.al, 2015).

Table 1.1: Emerging contaminants detected in European ground waters and surface waters water treatment or other pint sources (Weber et.al, 2014)

Pharmaceutical	Therapy Group	Number of countries worldwide in which pharmaceuticals have been found in the aquatic environment
Diclofenac	Analgesics	50
Carbamazepine	Antiepileptic drugs	48
Ibuprofen	Analgesics	47
Sulfamethoxazole	Antibiotics	47
Naproxen	Analgesics	45
Estrone	Estrogens	35
17-β-Estradiol	Estrogens	34
17-α-Ethinylestradiol	Estrogens	31
Trimethoprim	Antibiotics	29
Paracetamol	Analgesics	29
Clofibric acid	Lipid-lowering drugs	23
Ciprofloxacin	Antibiotics	20
Ofloxacin	Antibiotics	16
Estriol	Estrogens	15
Norfloxacin	Antibiotics	15
Acetylsalicylic acid	Analgesics	15

To give a more vivid scope of the prevalence of EPPP contamination in water, Figure 1.1 shows that the problem has been present all over the world. This problem is not just present in developing countries in Africa and Asia. They also affect countries in Europe and America (Weber et.al, 2014). According with Lapworth et al (2012), the pharmaceutical concentrations found in aquatic environment were considerably low to cause acute effects. But, it could bring major concerns in the future because of their high consumption and production.

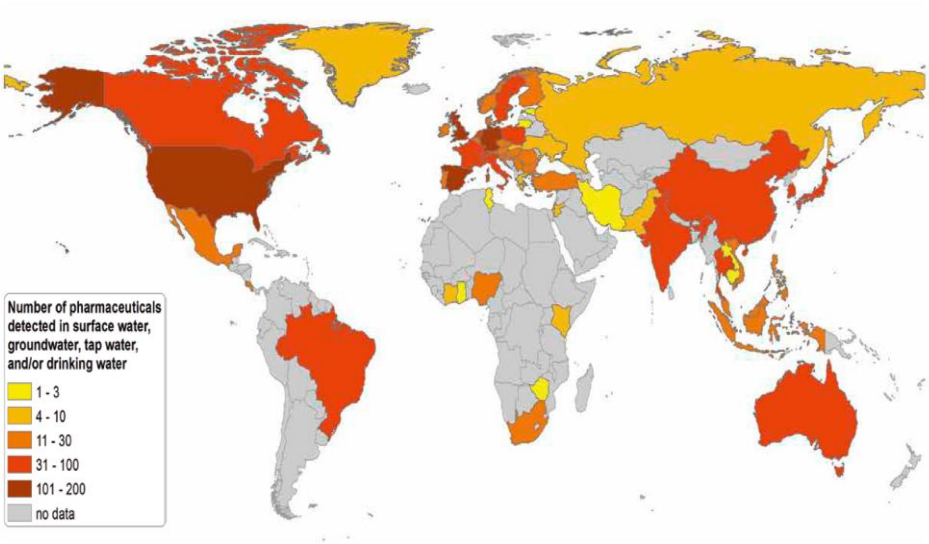


Figure 1.1: Global occurrence of pharmaceuticals that have been found in the environment in all UN regional groups (Weber et.al, 2014)

An example of HPCs contamination in the environment was observed in the northwest of France. According to Mompelat et al (2011), among the 20 HPCs that were being monitored, 16 had been quantified in both surface and drinking water. Their concentration was found to be 22% above the limit of quantification for surface water, and 14 % for drinking water. The HPCs found in surface and drinking waters included psychostimulants, non-steroidal anti-inflammatory drugs, iodinated contrast media, and anxiolytic drugs (Mompelat et al, 2011). Studies in the removal of HPCs and its metabolites from drinking water by activated carbon adsorption, oxidation by ozone, or disinfection by chlorine have been done. Some HPCs are resistant to these treatment. Also specific processes in removing HPCs are expensive, time consuming, and produces by-products of greater concern (Borghi and Fabbri, 2013).

Often these recalcitrant pharmaceutical compounds were retained in both the effluent and solid sludge as either the unmetabolized parent drug and/or metabolites (Ghafoori et al, 2014). This was supported by Murdoch (2015) such that when the contaminated effluents were released or reused as irrigation or the sludge was used as fertilizer, they could contaminate plants and leak to possible source of drinking water. An example is carbamazepine, an anti-epileptic drug, which could not be removed by secondary wastewater treatment. This drug with its metabolites were detected in treated water and crops like pepper, collard, lettuce, radish and tomato (Murdoch, 2015). It was discovered that certain areas in Spain had its soil and water contaminated with carbamazepine, lamotrigine (anticonvulsant), sildenafil (active component of Viagra), sulfapyridine (antibiotic), and metoprolol (beta-blocker) due to the recycling of effluents and sludges for agricultural purposes (Rodriguez-Navas, 2013).

EPPP are continuously entering into aquatic environment, directly or indirectly (Swedish Association of the Pharmaceutical Industry AB, 2004). There are 3 different routes at which these HPCs reach the environment. They can be introduced by improper disposal of unused HPCs, by leaks in the manufacturing process, and by human and animal wastes which reach the water supply through the sewage system or leaching in the soil (Swedish Association of the Pharmaceutical Industry AB, 2004).

According to Stuart et al (2012), there were hospital facilities disposing their unused medical products improperly by throwing untreated drugs or flushing them with water. Also, agricultural usage such as veterinary medicines were sometimes thrown in the soil and these medicines leached through bodies of water. It was detected that in the early 1990's there were

HPCs discharges in the environment by manufacturing plants (Larsson, 2014). But, little attention was given to it because of the limited analytical devices that could measure such reduce concentrations (Larsson, 2014). The problem was ignored only until evidences of the feminization of fish due to the presence of oestrogens from manufacturing plants were found (Larsson, 2014). Larsson et al (2007) recorded a high emission of HPCs from drug manufacturers in Patancheru, India. It was noted that the concentration of ciprofloxacin, a broad spectrum antibiotic, reached 31 mg/L, which was 1 million times more that the regular level found in other areas and was very toxic for organisms. At this concentration, the total release of these drug was 44 kg per day, which was sufficient to treat 44,000 inhabitants (Larsson, 2014). Aside from India, other Asian countries like Korea, Taiwan and China exhibited high concentrations of HPCs leakage from manufacturing companies (Cui et al, 2006). In China, 51 ng/L of ethinyloestradiol was detected in a river, which affected the reproduction of aquatic vertebrates (Cui et al, 2006). There were reports in the USA and Europe of manufacturing companies releasing high concentrations (mg/L) of HPCs in the environment as well (Larsson, 2014).

It is presented in Table 1.2 the different HPCs that were detected in the environment due to improper disposal and manufacturing leakage. Globally, large amounts of HPCs appeared in different environmental mediums in the past 16 years and most of them had high concentrations ranging in the milligrams per liter range. Drugs ranged from antibiotics, anti-inflammatories, analgesics, hormones, antivirals, and anti-depressants.

Table 1.2: Studies on the industrial effluents (IE), river sediments (RS), soil, ground water (GW) and surface water (SW) where presence of HPCs are detected

Country	**HPCs detected**	**Drug type**	**Matrices: Drug Concentration**	**Year**	**Reference**
China	oxytetracycline	Antibiotic	IE: 1065 mg/L	1988	Qiting and Xiheng, 1988
India	Salicylic acid	Anti-inflammatory	IE: 2270 mg/L	1993	Bisarya and Patil, 1993

Denmark	Sulfonamide intermediates and metabolites	Antibiotics,	GW: Sulfaguanidine (1.6 mg/L)	1995	Holm et al, 1995
Germany	Phenazone and metabolites	Analgesic	GW: Phenazone (3.95 μg/L) TW: Phenazone (0.4 μg/L)	2002	Reddersen et al, 2002
Germany	Phenazone and metabolites	Analgesic	GW: Phenazone (2.5 μg/L) TW: Phenazone (0.25 μg/L)	2004	Zühlke et al, 2004
Switzerland	Venlafaxine	Antidepressant	SW: 0.8 μg/L	2004	Amt für Umwelt und Energie Basel-Stadt, 2004
Norway	Bacitracin	Antibiotic	IE: 250 kg/ discharge	2005	Norwegian Environment Agency, 2005
China	Oestrogenic sex steroids	Hormones	IE: Ethinyloestradiol (51 ng/L)	2006	Cui et al, 2006
India	Various drugs including fluoroquinolone	Various	IE: Ciprofloxacin (31mg/L)	2007	Larsson et al, 2007
China	Oxytetracycline	Antibiotic	IE: 19.5 mg/L SW: 712 μg/L	2008	Li et al, 2008
Taiwan	Various drugs	Various	SW: Diclofenac (27 μg/L)	2008	Lin et al, 2008
Croatia	Sulfonamide	Antibiotic	IE: Sulfaguanidine (>1.1 mg/L)	2008	Babic et al, 2007

China	Penicillin and metabolites	Antibiotic	IE: Penilloic acid (44 mg/L) SW: Penilloic acid (11.6 mg/L)	2008	Li et al, 2008
Taiwan	Various drugs	Various	IE: Sulfametoxazle (1.34 mg/L) Ibuprofen (1.5 mg/L)	2009	Lin and Tsai, 2009
India	Various drugs including fluoroquinolone	Various	IE: Ciprofloxacin (14mg/L) GW: Cetirizine (28 µg/L) SW: Ciprofloxacin (6.5 mg/L)	2009	Fick et al, 2009
Switzerland	Oseltamivir	Antiviral	SW: 160 ng/L	2010	Prasse et al, 2010
USA	Metaxalone	Relaxant	IE: 3.8 mg/L	2010	Phillips et al, 2010
India	Fluoroquinolone	Antibiotic	RS: Ciprofloxacin (914 mg/kg of organic material)	2011	Kristiansson et al, 2011
Korea	Lincomycin	Antibiotic	IE: 43.9 mg/L	2011	Sim et al, 2011
Israel	Venlafaxine and metabolites	Antidepressant	IE: Venlafaxine (11.2 µg/L)	2012	Gasser et al, 2012
Israel	Carbamazepine and venlafaxine	Various	IE: Venlafaxine (11.7 µ/L)	2013	Lester et al, 2013
Pakistan	Various antibiotics	Antibiotic	SW: Sulfamethoxazole (49 µg/L)	2013	Khan et al, 2013

India	Fluoroquinolone	Antibiotic	GW: Ciprofloxacin (770 ng/L) Soil: Ciprofloxacin (7.2 μg/g of organic matter)	2014	Rutgersson et al, 2014
Spain	Venlafaxine	Antidepressant	IE: 2.6 μg/L	2014	Collado et al, 2014

Aside from the improper disposal and manufacturing leakage, a more common source of contamination is through human and animal excreted products. HPCs are bioactive compounds primarily designed and prescribed to have specific biological effects on the human body. Depending on their metabolization, HPCs can be excreted from the human body as unmetabolized parent compounds and/or metabolites in urine and/or feces (Mompelat et al, 2011). These body wastes containing the unmetabolized drug and its metabolites are discharged in houses and enter in WWTP. Some examples of the HPCs found are ibuprofen, gemfibrozil, paracetamol, triclosan, aspirin, naproxen, ampicillin, amoxicillin, nicotine, oesterone bisphenol A (Stuart et al, 2012). These HPCs usually range from a concentration of 10 to 1000 ng/L (Lapworth et al, 2012).

Gavrilescu et al (2015) observed that the occurrence and concentrations of HPCs in water varied with the local of sampling, the time at which they were obtained, and the efficiency of the treatment plant in removing these contaminants. In general, the concentration of HPCs in water during summer was higher compared to its concentration during winter because precipitation was more frequent in winter causing a natural dilution (Nam et al, 2014). While in terms of location, the frequency and probability at which HPCs could be detected was higher at sources near urban areas than in agricultural or undeveloped areas. But, this did not mean that the HPCs concentration was greater because other factors such as natural attenuation, chemical and physical property of the HPCs could also affect it (Fram and Belitz, 2011).

Trembley et al (2011) referred that there were 156 new EPPPs that could cause environmental concerns. These new EPPPS included analgesics, antibiotics (AMOX) and antibacterial drugs

(ciprofloxacin, erythromycin, tetracycline, sulfamethoxazole), contrast media (lopromide, iopamidol), prescription drugs (benzodiazepines, salbutamol, carbamazepine), and generic medicines (IBU, PAR, ASA). Aside from this, steroids and hormones namely androgens (testosterone, androstenedione), estrogens (estrone, estriol, estradiol), xenoestrogens (ethynilestradiol, diethylstilbestrol), and anti-inflammatory drugs could cause great concern as well (Tremblay et al, 2011). Table 1.3 shows the 4 HPCs studied in this research are among the top 20 most commonly used. As a result, they have a high probability to be present in most water systems

Table 1.3: Top 20 used EPPPs which appear in influents and effluents of typical New Zealand wastewater of urban origin (Tremblay et al, 2011)

Rank	Common Chemical name	Treatment Condition
1	Paracetamol	Analgesic / Antipyretic
2	Aspirin	Analgesic / Anti-platelet
3	Simvastatin	Cholesterol and cardiovascular control
4	Omeprazole	Dyspepsia, peptic ulcer disease
5	Amoxycillin	Broad spectrum antibiotic
6	Metoprolol succinate	β- blocker for blood pressure control
7	Amoxycillin clauvulanate	Broad spectrum antibiotic
8	Salbutamol	Asthma (inhaled)
9	Diclofenac sodium	Analgesic/ Anti-inflammatory
10	Cilazapril	ACE inhibitor
11	Zopiclone	Hypnotic
12	Ibuprofen	Analgesic
13	Prednisone	Steroid
14	Flucloxacillin	Antibiotic
15	Quinapril	ACE inhibitor
16	Bendrofluazide	Diuretic
17	Feldopine	Calcium channel blocker
18	Alendronate sodium	Osteoporosis
19	Metformin	Type II diabetes
20	Fluticasone	Asthma (inhaled)

These 4 HPCs were also the most produced and consumed medicines in Germany, a leading country in the chemical industry (Figure 1.2) (Küster and Adler, 2014).

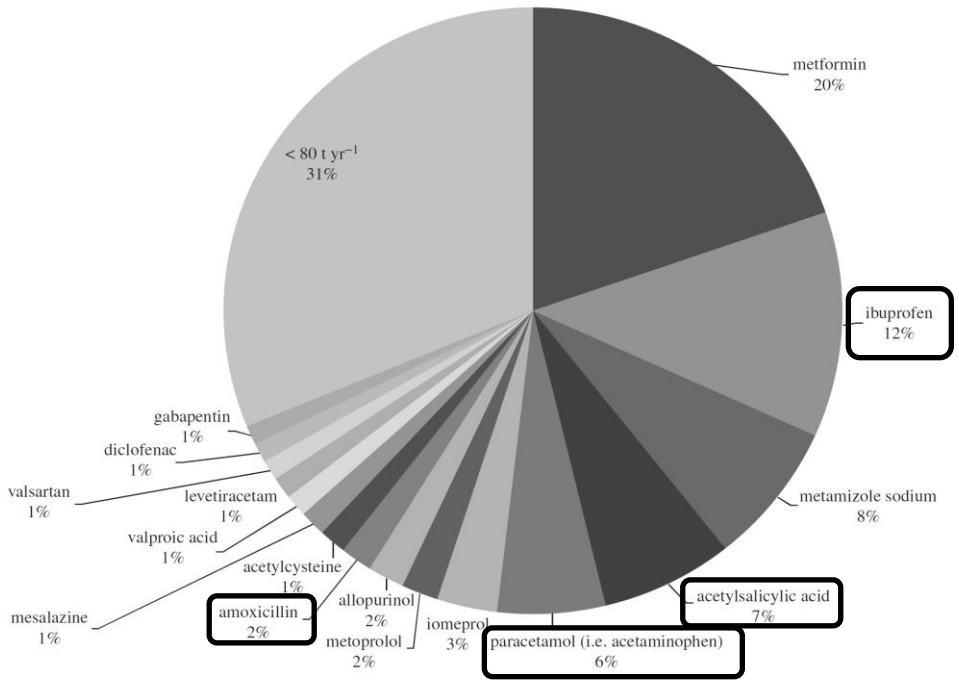


Figure 1.2: Most selling environmentally relevant HPCs in Germany in 2012 and HPCs with an annual consumption of more than 80 tons (Küster and Adler, 2014).

1.2 Common Human Pharmaceutical Compounds

According to the WHO model list of essential medicines (World Health Organization, 2013), these drugs are considered the most important medications needed in a basic health system, which makes them very available. In addition, IBU, PAR and ASA can be purchased as a generic medicine without the need of a prescription (World Health Organization, 2013)

1.2.1 Ibuprofen

Ibuprofen (IBU) (Figure 1.3) is a non-prescription medicine, nonsteroidal, anti-inflammatory drug which is used primarily to treat minor pain, fever, and inflammation (Rainsford, 2009).

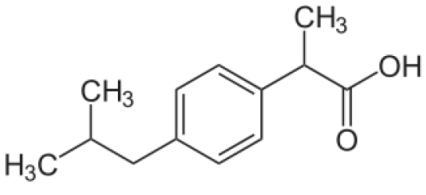


Figure 1.3: Chemical structure of Ibuprofen

It works by inhibiting the synthesis of prostaglandin which is the reason of inflammation (Rainsford, 2009). It was derived from propionic acid by a team led by Stewart Adams in 1961 as a safer alternative to aspirin. It was later on patented in the same year (Halford et al, 2012).

Between 2002 and 2012, the consumption of IBU in Germany increased from 250 t up to 975 t (Küster and Adler, 2014). Currently, globally, roughly 16, 500 t of IBU are produced and consumed by the public (FDA, 2015). Because of this, it has often been found in water ways excreted by humans because of incomplete metabolization. Rainsford (2009) referred that 77 % up to 85 % of ingested ibuprofen were excreted in the form of urine by the body. Based on the study of Bacsi et al (2016), when these body wastes reached the environment, IBU in the wastes could promote growth of unicellular cynobacteria because the organism was not greatly affected by the changes in the chlorophyll-a content which the drug normally attacked. The number of functional groups in the cyanobacteria samples composed of *Synechococcus elongates*, *Microcystis aeruginosa*, and *Cylindrospermopsis raciborskii*, did not change drastically unlike in eukaryotic algae. On the other hand, the presence of IBU affected the chlorophyll-a content of natural eukaryotic algae such as the *Cryptomonas ovata*, flagellated green alga *Haematococcus pluvialis*, and the non-motile green alga *Desmodesmus communis*, thus, limiting its growth (Bacsi et al, 2016). Also, IBU contamination also inhibited the growth of aquatic plants (Boxall, 2004).

Several environmental studies conducted all over the world resulted in the presence of ibuprofen at varying concentrations. In the United States roughly 139 streams contain IBU, 9.5 % of these streams contained an IBU concentration between 0.018 μg/L and 2.11 μg/L (Kolpin et al, 2002). Also, 1.35 μg/L of IBU penetrated the drinking water system of the country (Kolpin et al, 2002). It was estimated that after 5 years, the concentration of IBU in these streams would increase by 1.0 μg/L (Kolpin et al, 2002). In Germany, the sewage effluents had an average IBU concentration of 0.22 μg/L(Küster and Adler, 2014). In general, IBU has a detection frequency of above 50% which makes it more probable than any other HPCs in the market (Küster and Adler, 2014).

1.2.2 Acetylsalicylic Acid

Acetylsalicylic acid (ASA) (Figure 1.4) also known as aspirin is a white, acidic, odorless solid used to address some illnesses such as fever, inflammation and body pains or cramps. It is a stable molecule and is non-reactive in dry air (Schriks et al, 2010). But, it can hydrolyze in

moist air and dissolve in water (Schriks et al, 2010). It is considered as a nonsteroidal anti-inflammatory drug. But unlike most drugs of its kind, the salicylates of aspirin affect the enzyme in an irreversible manner (Burke et al, 2006). It was discovered in 1853 by Charles Frederic Gerhardt wherein he was able to prepare the first ASA (Mahdi et al, 2006). But before it was synthetically made, the active ingredient of ASA namely salicylic acid was already being obtained from the extracts of the willow bark and spiraea plants which Hippocrates used to alleviate pains and fevers (Mahdi et al, 2006). Because "Aspirin" was being used for many years by manufacturing chemists, Bayer lost its trademark in 1918 (Cheng, 2007).Today, aspirin is a generic word in several countries. But Aspirin with a capital "A" remains to be a registered trademark of Bayer in over 80 countries (Cheng, 2007).

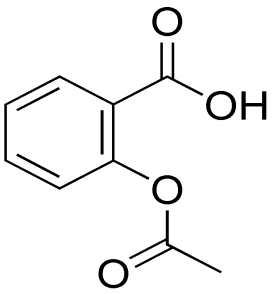


Figure 1.4: Chemical structure of Acetylsalicylic Acid

Because ASA is one of the most common drugs used, the mass production of it can cause environmental issues. On average, more than 50,000 tons or 100 billion tablets of ASA are manufactured each year which leads to a high energy consumption and waste production (Schriks et al, 2010). According to Schriks et al (2010), ASA could be biodegraded at specific concentrations, and could be toxic to some organisms such as fishes and their embryos (*Leuciscus idus* > 100 mg/L) and daphnia (168 mg/L). Though these concentrations are high with regard to pharmaceutical contamination, it can still occur because ASA is widely consumed all over the world.

1.2.3 Paracetamol

Paracetamol (PAR) is also known as acetaminophen (Figure 1.5). It is a non-opioid analgesic and antipyretic which is often used for a large variety of mild to moderate illnesses (Silverman et al, 1992). Aside from a tablet form which can be taken orally, it has rectal formulation and intravenous formulation as well (Silverman et al, 1992). It was discovered in 1877 by Harmon

Northrop Morse via the reduction of p-nitrophenol with tin in glacial acetic acid (Silverman et al, 1992). But it was only in 1887, 10 years after it was discovered, that it was administered to actual patients by Joseph von Mering who was a clinical pharmacologist (Bertolini et al, 2006). It is a non-prescription drug which comes in different forms. Due to its popularity, patents on PAR have long been expired and generic version of the drug is widely available (Thakkar and Billa, 2013).

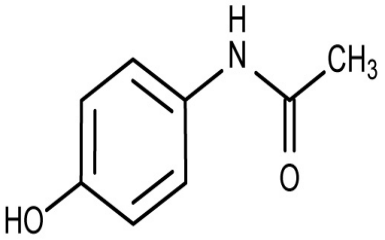


Figure 1.5: Chemical structure of Paracetamol

Because it is often used, PAR and its metabolites (paracetamol glucuronide and p-aminophenol) are also present in the environment when secreted by the body. Its presence was confirmed in rivers having a concentration between 1.63 μg/L and 3.67 μg/L (Nam et al, 2014). It could be biodegraded and be used as a carbon source for *Pseudomonas aeruginosa* strain HJ1012 (Hug et al, 2014). The strain metabolized the drug into *p*-aminophenol. Aside from this, PAR could efficiently adsorbed onto sediments which would be further degraded by other microbial organisms. Even though there are many ways in degrading PAR, it is still recognized as a pseudo-persistent contaminant because of the amount of people using the drug worldwide. In 2009, roughly 3.2 billion tablets each year were consumed by each country in the western world (Bartelt-Hunt et al, 2009). Currently, the annual production and consumption of PAR is approximately 25 billion tablets (Dal Pan, 2015). It is pseudo-persistent because the probability of PAR being present in the environment versus to the rate it can be removed by physicochemical or microbial processes is higher (Kummerer, 2009). Thus, it has a continuous environmental presence but little information about its environmental behavior is known (Küster and Adler, 2014). Though PAR is non-toxic, has a low environmental effect, and non-bio accumulating, it is still considered to be an EPPP because of its high prevalence in most environmental mediums (Küster and Adler, 2014).

1.2.4 Amoxicillin

Amoxicillin (AMOX) (Figure 1.6) is a β-lactam based antibiotic and is one of the many popular antibiotics that is used by both humans and animals (Yasser and Nabila, 2015). On the average, the annual consumption and production of AMOX is roughly 60,000 t (Yasser and Nabila, 2015). As a result, it has a high potential to reach the environment (Kaur et al, 2011). It is a solid substance that is very stable under normal conditions. Amoxicillin was discovered in 1960s as one of the semisynthetic derivatives of 6-aminopenicilanic acid developed in Beecham, England (Ravina, 2014). It entered the market in 1972 after ampicillin (Ravina, 2014). The patent for amoxicillin expired. Currently, its preparations are marketed under many trade names and have several synonyms across the world (Ravina, 2014). AMOX was one of the common antibiotics used with roughly 80 tons of purchases in Germany during 2012 (Küster and Adler, 2014).

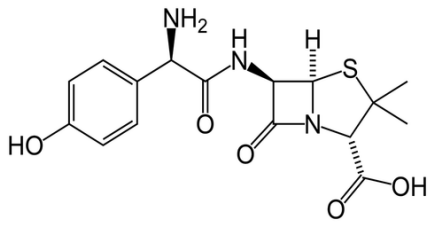


Figure 1.6: Chemical structure of Amoxicillin

According to Kaur et al (2011), unlike other drug contamination which were caused by human secretions, antibiotic contamination was mainly caused by animal husbandry industries. When animals were ill, they were treated with antibiotics whenever necessary. Typical to a normal organism, not all of the compound could be metabolized by the body. Thus they would be released in the environment through animal waste (Kaur et al, 2011). These animal wastes were mixed with soil and used as soil fertilizers for crops, composting, and vermiculture (Moradi, 2015). As a result, these antibiotics leach through the soil and reach bodies of water.

Because it is an antimicrobial drug, amoxicillin has a high toxicity hazard when it comes to aquatic organisms (Yasser and Nabila, 2015). Organisms constantly exposed to this drug can eventually produce immunity and resistance. Based on the overall risk assessment of amoxicillin, 60% of the parent compound is not metabolized by the body (Boxall, 2012).

1.3 Wastewater Treatment Plants

In order to address the increasing concern on pharmaceutical contamination particularly the common HPCs such as IBU, PAR, ASA and AMOX, several wastewater treatment processes can be used before WW is released into the environment. Wastewater treatment plants (WWTPs) uses techniques to eliminate potential pathogens and solid impurities (undissolved substances, easily degradable organic substances, persistent organic substances, plant nutrients, heavy metals, and salts), and restore as much as possible the natural quality of water before it is released in the environment (Murdoch, 2015) (Donau Carbon GmbH, 2014).

1.3.1 Common Decontaminating Techniques

WWTPs follow increasing levels of WW treatment. Preliminary treatment has the objective of the removal of coarse solids and other large materials often found in raw wastewater (AWWA, 2000). Removal of these materials is necessary to enhance the operation and maintenance of subsequent treatment units. Primary treatment involves the removal of organic and inorganic solids by sedimentation, and the removal of materials that will float (scum) by skimming (AWWA, 2000). Secondary treatment is the further treatment of the effluent coming from primary treatment. Its objective is to remove biodegradable dissolved and colloidal organic matter and suspended solids, using aerobic biological treatment processes (AWWA, 2000) Aerobic and anaerobic biological treatments are some of the treatments often used. In some WWTPs, tertiary and/or advanced wastewater treatment are employed when specific wastewater constituents which cannot be removed by secondary treatment must be removed (like nitrogen, phosphorus, additional suspended solids, refractory organics, heavy metals, dissolved solids, emerging contaminants) (World Health Organization, 2011). Because advanced treatment usually follows high-rate secondary treatment, it is sometimes referred to as tertiary treatment (Pescod, 1992). However, advanced treatment processes are sometimes combined with primary or secondary treatment (E.g., chemical addition to primary clarifiers or aeration basins to remove phosphorus) or used in place of secondary treatment (e.g., overland flow treatment or primary effluent) (Pescod, 1992), or used separately (E.G., chemical and or ultraviolet light techniques (Murdoch, 2015)). At the end of the treatment process, WWTPs produce a treated effluent and a treated sludge. The treated effluent is discharged into surface waters and reused as irrigation water. Sludges are disposed in landfills, incineration or used as soil fertilizers (Murdoch, 2015). Table 1.4 presents the common processes used in WW treatment.

Table 1.4: Conventional and advanced wastewater treatment processes and their expected range of removal efficiency for pharmaceuticals (World Health Organization, 2011)

Treatment process	Removal range (%)	Water source	Areas studied	Reference
Conventional wastewater treatment processes				
Activated sludge	11–99	Raw sewage	Australia	Watkinson, Murby & Costanzo (2007)
	7–100	Primary settled sewage	Europe, Japan	DWI (2007)
	< 20–80	Primary settled sewage	France	Gabet-Giraud et al. (2010)
	–193–86[a]	Primary settled sewage	Europe	Vieno, Tuhkanen & Kronberg (2007)
	8–98	Not specified	Brazil, Europe, Japan	Ziylan & Ince (2011)
Biological filtration	6–71	Primary settled sewage	Europe	DWI (2007)
Primary settling	3–45	Not specified	Brazil, Europe, Japan	Ziylan & Ince (2011)
Coagulation, filtration and settling	5–36	Not specified		
Sand filtration	0–99	Activated sludge effluent		
Advanced wastewater treatment processes				
Ozonation	1–99	Activated sludge effluent	Brazil, Europe, Japan	Ziylan & Ince (2011)
	86–100	Secondary effluent	France	Gabet-Giraud et al. (2010)
Ozonation/ ultrasound and sonocatalysis	23–45	Not specified	Europe, India, Japan, Turkey, USA	Ziylan & Ince (2011)
Ozonation and catalytic ozonation	>9–100			
UV irradiation	29	Not specified	Brazil, Europe, Japan	Ziylan & Ince (2011)
Photolysis (UV/ hydrogen peroxide)	52–100	Not specified	Europe, India, Japan, Turkey, USA	Ziylan & Ince (2011)
Dark and light Fenton	80–100			
UV/TiO_2	> 95			
Biomembrane	23–99	Treated effluent	Brazil, Europe, Japan	Ziylan & Ince (2011)
Microfiltration and reverse osmosis	91–100	Secondary treated effluent	Australia	Watkinson, Murby & Costanzo (2007)
Reverse osmosis	62–97	Secondary treated effluent	France	Gabet-Giraud et al. (2010)
Ultrasound	24–100	Not specified	Europe, India, Japan, Turkey, USA	Ziylan & Ince (2011)

1.3.2 Activated Carbon

PAC is a non-graphite form of carbon, which is widely used in water/wastewater treatment (Tolga et al, 2014). PAC can be manufactured by carbonizing and activating various raw materials such as pine wood, coconut shell, coal, eucalyptus, peat, saw dust, rice husk and lignite (Rashed, 2013). In the carbonization process, most of the non-carbon elements like hydrogen and oxygen are first removed in the form of gas by heating the raw material at high temperatures (Tan and Hameed, 2010). The release of these elements is responsible in developing the internal pores of the PAC (Tan and Hameed, 2010). After which, the PAC is activated through chemical activation. In this process, it increases the number and dimension of the pores which increases the internal surface area (Enz et al, 2006). There are different types

of pores present in PAC namely micro pore, meso pore and macro pore (Figure 1.7) (Enz et al, 2006). The macro pores (25 nm < pore radius) are where the contaminants can enter (Enz et al, 2006). The meso pores (1 nm < pore radius < 25 nm) act as the hallways or the corridors where the contaminants are transported (Enz et al, 2006). When the contaminants reach the micro pores (pore radius < 1nm), they start to adhere to the internal surfaces and adsorb within the PAC through intermolecular forces (Enz et al, 2006). The strength of the intermolecular forces in PAC are either weak or strong interactions (Sivasankar, 2008). A weak interaction (<40 kJ/mol) is the same as the interactions between molecules in liquids and allow for what is known as physical adsorption or physisorption (Sivasankar, 2008). Strong interactions (>40 kJ/mol) are similar to the interaction between atoms within a molecule like covalent bonds and allow for chemical adsorption or chemisorption (Sivasankar, 2008). In chemisorption the molecule may be broken down and the fragmented molecule attaches on the surface of the adsorbent, this process is known as dissociative chemisorption (Sivasankar, 2008). Unlike in physisorption where the adsorbed molecule remains intact (Sivasankar, 2008). Because of the varying molecular size and interaction forces, adsorption is not constant. The smaller the molecular size of the contaminant, the deeper it can diffuse into the pores of PAC (Enz et al, 2006). Thus, PAC can adsorb more contaminants with a smaller molecular size. At the same time, the finer the PAC, the more accessible are its surface to contaminants leading to a faster the rate of adsorption (Sivasankar, 2008). The carbon adsorption process is controlled by the diameter of the pores in PAC and by the diffusion rate of organic molecules through the pores. The rate of adsorption is a function of the molecular weight and the molecular size of the organics (Upadhyayula et al, 2009).

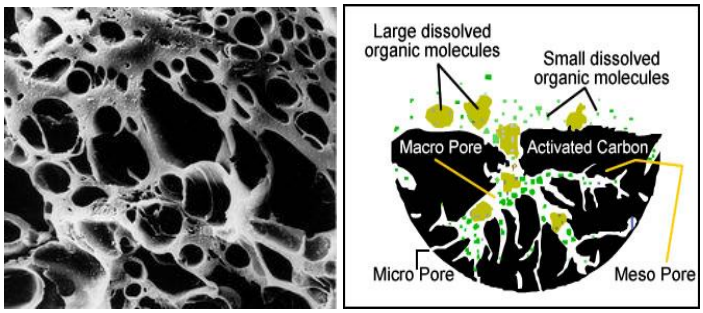


Figure 1.7: Pore structure and type of pores present in activated carbon (Begg Cousland, 2016)

Activated carbon can be used either in powdered (PAC) or granular (GAC) forms and is widely used to remove bio-resistant organic materials due to its simplicity in design, operation, regeneration, and cost (Ghafoori et al, 2014). PAC is used in combination with other treatment processes. Due to its high efficiency, the activated carbon is usually used in the last treatment step to remove the most difficult impurities like pharmaceutical micropollutants (Donau Carbon GmbH, 2014). PAC adsorption in WWTPs is done by adding activated carbon, letting it mix with WW and allowing it to settle for a specific amount of time. In GAC adsorption WW passes through carbon packed columns or carbon filter bed. (Donau Carbon GmbH, 2014).

Studies showed that activated carbon could remove organic substances and colorants, reduce the amount of trace substances like chemicals and pharmaceutical, and decrease the residual chemical oxygen demand in a WWTP (Donau Carbon GmbH, 2014). Based on the study of Ghafoori et al (2014), approximately 1.07 kg of carbon/L of pharmaceutical WW were required to remove 320 mg of carbon/L of effluent TOC, since the activated carbon followed the Langmuir isotherm which meant that only a monolayer, homogeneous adsorption could occur.

1.4 Iron Nanoparticles

Nanoparticles (NPs) can help in water treatment (Carlos et al, 2013). A common type of NP being used in different applications like water treatment and biological applications is nano-iron oxide due to its size, abundancy, and magnetic property (Ambashta et al, 2010).

Iron is a common transition metal because of its many applications (Huber, 2005). It is used as structural backbone of infrastructure as well as other construction applications (Huber, 2005). However, iron is not as common in the nanoscale unlike its oxide (Huber, 2005). Iron oxide nanoparticles (FeNPs) are stable unlike plain nano-iron, which is pyrophoric making it difficult to study (Huber, 2005). But, both are very magnetic and have catalytic properties, which can be applied in removing contaminants from bodies of water such as inorganic metals (Huber, 2005).

FeNPs have a diameter between 1 to 100 nm and can be observed in two forms namely magnetite (Fe_3O_4) and its oxidized form maghemite (Fe_2O_3), which are stable (Tang and Lo, 2013). FeNPs are used for magnetic data storage, biosensing, and drug-delivery because of their stability and significantly high surface area to volume ratio (Blaney, 2007). FeNPs exhibit high magnetic property even at sizes between 2 to 20 nm (Scott et al, 2011). They display super

paramagnetism which provides an additional stability (Scott et al, 2011). It is also biocompatible and non-toxic (Scott et al, 2011). In Table 1.5, the different synthesis techniques that can be applied to produce FeNPs are shown.

Table 1.5: Techniques used to synthesize FeNPs

Technique	Particle Characteristic	References
High-temperature decomposition of organic precursors	Monodisperse, crystalline structure, uniform size	Scott et al, 2011
Microemulsion or Reverse Micelle	Monodisperse, well-ordered, uniform size,	Blaney, 2007
Co-precipitation: Ferrous hydroxide suspension	Uniform size	Blaney, 2007 ; Mascolo et al, 2013
Co-precipitation: Ageing stoichiometric mixtures	Uniform size	Blaney, 2007 ; Mascolo et al, 2013
Copolymer Templates	Structurally stable, uniform size	Blaney, 2007

Based on Scott et al (2014), FeNPs could be made by high-temperature decomposition of organic precursors (iron carboxylate salts) in the presence of hot organic surfactants (xylenes and sodium dodecylbenezensulfonate). This technique could be used in creating FeNPs for biomedical application like magnetic resonance imaging, and magnetorelaxometry (Scott et al 2014).

According to Blaney (2007), showed microemulsion or the reverse micelle technique which was a stable isotropic dispersion of 2 immiscible liquids with nanosized domains of one or both liquids. This could be done in a water-in-oil system at the presence of an amphiphilic surfactant. The presence of the surfactant lowered the surface tension between the 2 immiscible liquids (Blaney, 2007). As a result, the water nanodroplets acted as nanoreactors where the nanoparticles could be synthesized. Because these nanodroplets acted as carriers of the FeNPs, the size of the FeNPs depended on the size of the nanodroplets. As such, if one desired to change the size of the FeNPs, one should change the size of the nanodroplets (Blaney, 2007).

FeNPs could also be made by co-precipitation using a ferrous hydroxide suspension which was partially oxidized by an oxidizing agent. This was done by reacting iron (III) salt with a base

and a mild oxidant such as nitrate ions. Another process was by co-precipitation which consisted of ageing stoichiometric mixtures of iron (II) and iron (III) hydroxides in aqueous media at a basic pH between 8 to14. The ratio of iron (III) to iron (II) was 2:1 and the environment should be non-oxidizing. The problem with this technique was the susceptibility of the particles to oxidation. As a result, it could easily transform the magnetite into maghemite (Mascolo et al, 2013). In both co-precipitation techniques, the size of the FeNPs could be controlled by adjusting the pH, ionic strength, temperature, nature of the salts used, and the concentration ratio of iron (II) to iron (III) (Mascolo et al, 2013).

The last technique is by co-polymer templates. According to the study of Blaney (2007), co-polymer uses ion exchange resins such as micro-scale styrene beads with divinylbenzene crosslinking. These resins were mesoporous (2-50 nm in diameter) containing negatively charged sulfonic groups which could exhibit cation exchange. When these templates were immersed into the solution of strong positive electrolytes like ferrous iron, the metal loads attached to the sulfonic groups on the mesopores. These mesopores then acted as nanoreactors (Blaney, 2007).

Once synthesized several modifications can be done to FeNPs depending on the desired application. According to Blaney (2007), FeNPs could be coated with a monolayer coat of polymer. By doing so, hydrophobic, organic ligand-coated FeNPs were converted into water-soluble, bio-accessible FeNPs. Because of this coating, the FeNPs were stable at high pH values, and temperatures making them untampered when attaching to other molecules. Aside from coating it with a polymer, biocompatible coatings could also be used such as polysaccharides like dextran and lipid molecules (Blaney, 2007). Innovation in using FeNPs as oil spill collectors are also being done. Atta et al (2015), showed that FeNPs could be oxidized by air and could aggregate in aqueous solutions because of anisotropic dipolar attraction. To prevent aggregation without affecting the magnetic capabilities of the particle, the surface of FeNPs were modified by functionalizing the particles with amidoxime (Atta et al, 2015). Amidoxime is an amphoteric naturally produced molecule found in rosin gum. The acidic and basic sites on amidoxime could prevent aggregation of FeNP particles with each other and could attach to hydrophobic molecules (Atta et al, 2015). The coating process is presented on Figure 1.8. Because the particles were in a basic medium, the hydroxyl (-OH) groups surrounded the FeNPs and bonds to the carboxylic group of amidoxime. Creating a

functionalized particle which contained nitrogen (basic sites), carboxylic groups (acidic sites) and carbon-hydrogen groups (hydrophobic sites) (Atta et al, 2015).

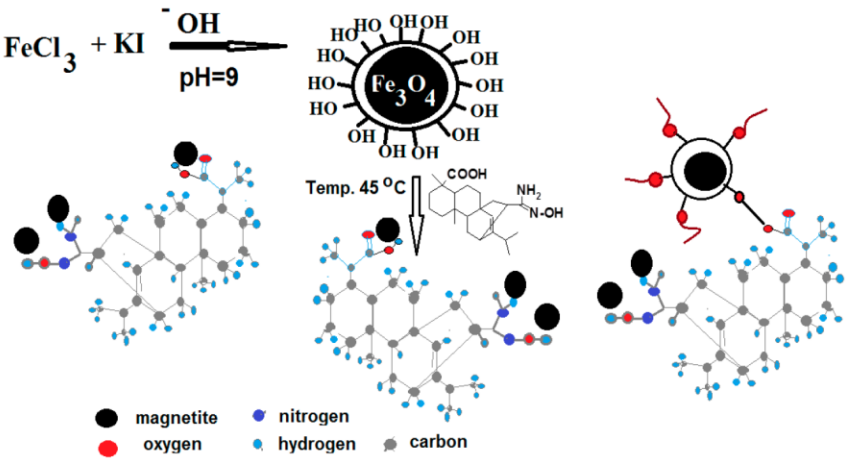


Figure 1.8: Synthesis of FeNPs coated with amidoxime (Atta et al, 2015)

In the study of Atta et al (2015), uncoated FeNPs had a removal efficiency that ranged from 10 % to 45 %. This was far from the removal efficiency of amidoxime coated FeNPs which ranged from 70 % to 95 % because the particles were less aggregated with each other exposing more binding sites for the hydrophobic oil particles (Atta et al, 2015).

Aside from being an oil spill collector, FeNPs are predominantly used in decontaminating WW with heavy metal contamination by applying a magnetic force (Carlos et al, 2013). In the study of Carlos et al (2013), the heavy metals adsorbed by FeNPs are Arsenic (V), Lead (II), Mercury (II), Copper (II), Cadmium (II) and Chromium (II). All of which have a removal of above 95%. This is supported by the study of D'Couto (2008), which analyzed the removal of heavy metals like arsenic and lead in wastewater.

Based on the study of Stefusova et al (2012), High Gradient Magnetic Separation was used to remove heavy metals from WW. In this process a magnetic field across a column with a ferromagnetic matrix was applied (Stefusova et al, 2012). This matrix acted as a magnetic filter such that when a magnetic force was applied, the magnetic filling in the column produced a large field gradient trapping the FeNPs that were mixed with the contaminated water (Stefusova et al, 2012). This process is depicted in Figure 1.9.

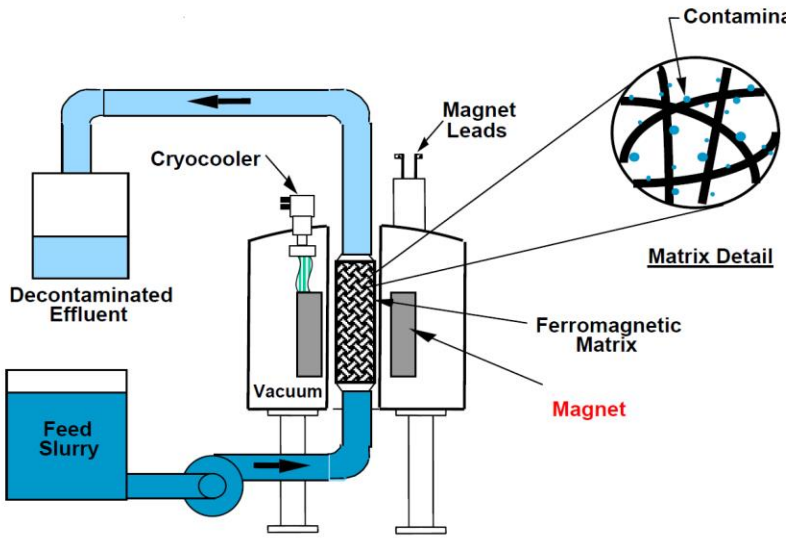


Figure 1.9: Schematic diagram of magnetic separation in wastewater (Stefusova et al, 2012)

1.5 Magnetic Activated Carbon

Though both PAC and FeNPs are being explored and researched on as possible tools in decontaminating WW from pharmaceuticals, there are several drawbacks from using these process. It is known that activated carbon is excellent and versatile adsorbents. But the lack of magnetic property in PAC makes them removable by mechanical filtration or sedimentation (Broghi and Fabbri, 2013). The additional removal step of PAC makes it time and cost inefficient (Borghi and Fabbri, 2013). On the other hand, solely using FeNPs without any coating or functionalization in decontaminating water can be disadvantageous, since it naturally aggregate in aqueous solutions limiting its adsorption capacity (Atta et al, 2015). Also, the preparation of FeNPs with or without coating requires several steps, specific chemicals and procedures that can be costly (Atta et al, 2015). Thus, an efficient way of exploiting the capabilities of PAC and FeNPs is by creating a composite adsorbent.

Magnetic Activated Carbon (PACMAG) is a magnetic adsorbent that has the adsorption capacity of PAC, and the magnetic property of FeNPs. By creating a composite adsorbent, one can increase the particles' surface area which eventually increases the adsorption capacity for contaminants (Kahani et al, 2007). It also makes the particle capable of adsorbing hydrophobic contaminants without functionalize or coating it with another chemical. The presence of the FeNPs will make it easy to remove from the water by using an external magnetic field (Oliveira et al, 2002). According to Safarik et al (2012), magnetic activated carbon (MAC/PACMAG)

have been used by WWTPs to remove various organic and inorganic contaminants ranging from humic substances, dyes, oils, mercury, arsenic and phosphates, depicted in Table 1.6.

Table 1.6: Application of MAC for the separation of organic and inorganic compounds (Safarik et al, 2012)

Type of MAC	Separated organic compound
Almond shells	2,4,6-Trinitrophenol from water; 97% desorption achieved by methanol and hot water
Orange peel	Naphthalene and p-nitrotoluene
Commercial	Methylene blue from river water; maximum adsorption capacity was 47.62 mg g^{-1}
Hydro-thermal process	Methyl orange from water; maximum adsorption capacity was 44.65 mg g^{-1}
Coconut shell	Humic substances
Bitumine	Methylene blue; maximum adsorption capacity was 229.5 mg g^{-1}
Commercial	Adsorption of methylene blue by activated carbon/cobalt ferrite/alginate composite beads
Chezacarb B	Water soluble organic dyes from aqueous solutions
Chezacarb B	Crystal violet and safranin O; magnetic solid-phase extraction used for preconcentration
Palm shells	Oil from palm oil mill effluent
Commercial (Norit)	Imidacloprid from water
Phenolic resin	Methylene orange from water; maximum adsorption capacity was 0.16 mg m^{-2}
Coconut shell	Methyl orange from water; regeneration by hydrogen peroxide performed
Rice husk	Methylene blue from water, maximum adsorption capacity was 321 mg g^{-1}
Commercial	Malachite green from water; maximum adsorption capacity was 89.29 mg g^{-1}
Type of MAC	**Separated inorganic compound**
Coconut shell	Mercury; maximum adsorption capacity was 38.3 mg g^{-1}. Hg desorption can be performed by heating
Bituminous coal	Mercury(II) from water
Commercial	Arsenic(V) removal from contaminated water with MAC coated with bacteria or biopolymers
Coconut or fruit pit	Gold from cyanide leach liquor or cyanide pulp
Orange peel	Phosphate from wastewater

A common application of magnetic activated carbon was aurocyanide separation. It was used to adsorb and separate gold from alkaline cyanide solutions by mixing a magnetic precursor with a carbon source and treating the mixture under controlled conditions. The small particle size of PACMAG allowed rapid adsorption of gold, and its magnetic character enabled recovery by magnetic separation leading to 99 % efficiency (Tolga, et al, 2014).

Aside from aurocyanide separation, PACMAG are used in WWTP to remove endocrine disruptors in the environment. Based on the study of Borghi and Fabbri (2013), the two endocrine disruptors, 4-octylphenol and 4-n-nonylphenol, were 95 $\pm$ 5% until 97 $\pm$ 1% removed from WW using 0.1 - 0.5 g/L of PACMAG. This was done by allowing the contaminated water to pass through a magnetic filtration tube filled with stainless steel spheres at the presence of an external magnetic field. By doing so, the generated magnetic force was able to capture and withhold the adsorbent against the drag force of the surrounding fluid.

2 EXPERIMENTAL PART

2.1 Materials and Methods

2.1.1 Chemicals

The chemicals used in the synthesis of FeNPs were: iron (III) chloride 6-hydrate ($FeCl_3 \cdot 6H_2O$) (Panreac Applichem, Barcelona, Spain)**,** hydrochloric acid (HCl) (VWR International, Pennsylvania, USA), sodium sulfate (Na_2SO_4) (Fisher Scientific International, Inc., Pittsburgh, USA), ammonia (NH_3) (Panreac Applichem, Bareclona, Spain) and deionized water (ELIX Millipore Iberico, S.A.U., Madrid, Spain). Silver nitrate ($AgNO_3$) (Aldrich Chemistry, Steinheim, Germany) was used to assess the presence and absence of chloride anion in the system after particle washing.

Solutions of sodium chloride (NaCl) (Merck, Darmstadt, Germany) were used to adjust the ionic strength when measuring the zeta potential of the particles. Hydrochloric acid (HCl) and sodium hydroxide solutions (NaOH) (Merck, Darmstadt, Germany) solutions were used to adjust the pH of the solutions.

Powdered activated carbon (PAC) was obtained from Águas do Algarve, S.A. which was used in the synthesis of the PACMAG. For the adsorption experiments, DW, and WW (Águas do Algarve, S.A.) were mixed with Ibuprofen (IBU) (Jose M. Vaz Pereira, S.A., Lisboa, Portugal), Paracetamol (PAR) (Jose M. Vaz Pereira, S.A., Lisboa, Portugal), Amoxicillin (AMOX) (Atral Cipan, Castanheira do Ribatejo, Portugal) and Acetylsalicylic Acid (ASA). The ASA was synthesized in the laboratory using salicylic acid ($C_7H_6O_3$) (Marques & Barroso Lda., Braga, Portugal) and acetic anhydride ($C_4H_6O_3$) (Merck, Darmstadt, Germany) based on the standard procedure obtained from literature (Royal Society of Chemistry, 2003).

For the regeneration of magnetic activated carbon (PACMAG), hydrogen peroxide (H_2O_2) (Fisher Scientific International, Inc., Pittsburgh, USA) and hydrochloric acid (HCl) were used.

2.2 Instrumentation

2.2.1 Zetasizer

The size and zeta potential (ZP) of the synthesized FeNP were measured using a Zetasizer Nano Series Nano-Z590 (Malvern Instruments, Malvern, United Kingdom).

2.2.2 Ultraviolet-Visible Spectroscopy (UV-Vis)

An UV 300 UV-Visible Spectrometer (Spectronic Unicam, Cambridge, UK) was used to determine the amount of drugs present in the water. The samples were tested against a blank which was DW. The amount of drug present in the sample was determined at the wavelength of maximum absorption (λ_{max}) shown in Table 2.1, using the molar absorption coefficient experimentally obtained.

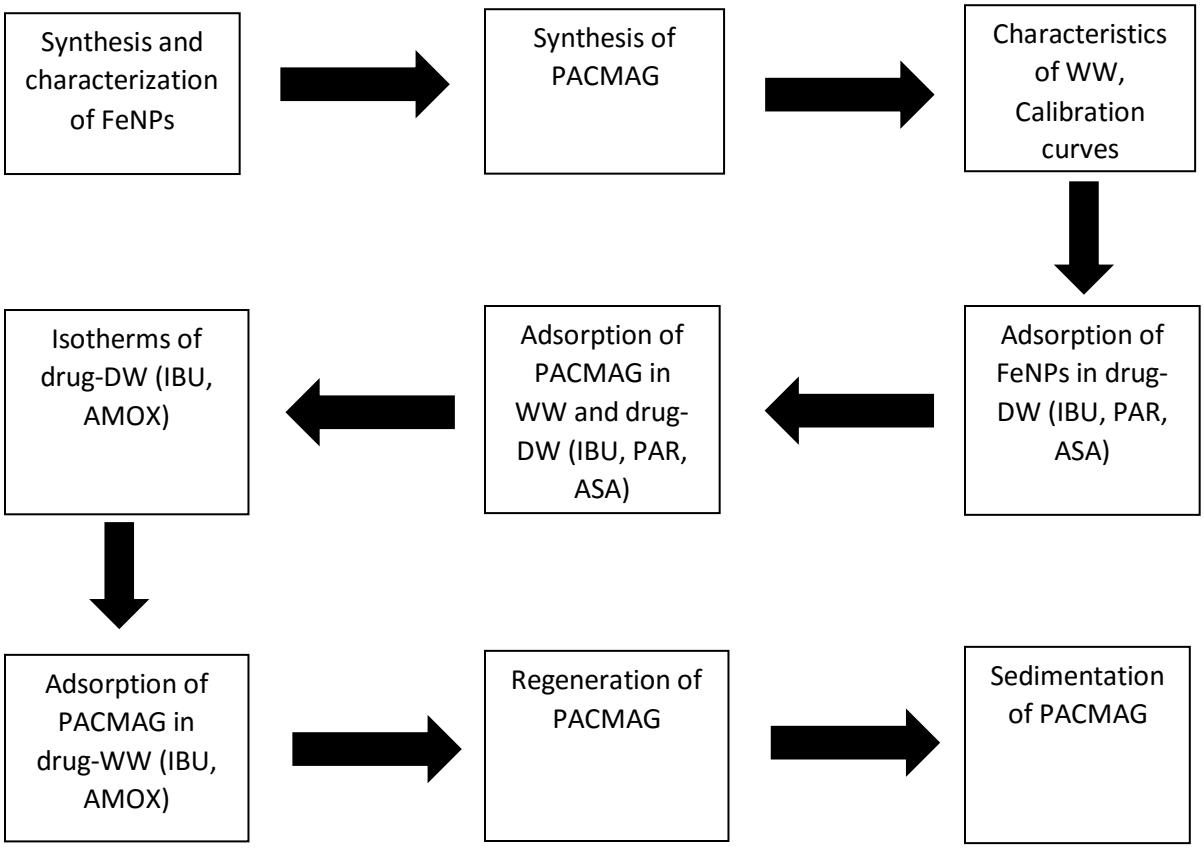
Table 2.1: Pharmaceutical Drugs and its corresponding λ_{max}.

Pharmaceutical Drugs	λ_{max} (nm)
Ibuprofen (IBU)	221
Acetyl Salacylic Acid (ASA)	228
Paracetamol (PAR)	243
Amoxicillin (AMOX)	228

2.2.3 Other Equipment and Materials

IKA RCT classic magnetic stirrer (IKA, Staufen, Germany) was used to ensure homogeneity of the solutions. All masses were measured using a Mettler AE-240 analytical balance (Mettler Toledo, Ohio, U.S.A.). The VWR Ultrasonic Cleaner sonicator (VWR, Pennsylvania, U.S.A.) was used to ensure complete dispersion of FeNPs in the solvent. All adsorption experiments were done using the Edmund Bűhler GmbH linear shaker (Edmund Bűhler GmbH, Hechingen, Germany). Hermle Z300 centrifuge (Hermle Labortechnik GmbH, Wehingen, Germany) was used in settling the FeNPs. The amount of total organic carbon (TOC) was determined after adsorption using the TOC-5000A Total Organic Carbon Analyzer (Shimadzu, Kyoto, Japan). In this research, the TOC content present in the system after adsorption was measured as a confirmatory test. In the characterization of the WW, the turbidity and the conductivity of the water were analyzed using Hach 2100N Turbidimeter (Hach Company, Colorado, USA) and a Crison Conductimeter GLP 32 (Crison Instruments, SA, Barcelona, Spain) respectively.

2.3 General Experimental Flow



2.4 Synthesis of adsorbent particles

2.4.1 Synthesis and Characterization of FeNPs

FeNPs were synthesized following an adaptation of the method first described by Qu et al (1995). In a 150 mL beaker, 16.22 g of $FeCl_3 \cdot 6H_2O$ was dissolved in 30 mL of 2M HCl under constant stirring for 30 minutes. Then, 30 mL of distilled water have been added. In a separate beaker, 2.52 g of Na_2SO_4 was dissolved in 20 mL of distilled water. The Na_2SO_4 solution was added to the $FeCl_3$ solution under constant stirring for 30 min at 250 rpm. After that and, also under constant stirring, the $FeCl_3$-Na_2SO_4 solution was added to a solution previously made by mixing 670 mL of distilled water with 50.8 mL of 25% NH_3. The reaction was allowed to take place for 30 min at 250 rpm. The particles were magnetically separated and the supernatant was decanted.

The FeNPs were pre-washed with distilled water and then with150 mL of 0.1M HCl. To adjust the pH to 5-7 and to remove all the ammonium chloride, the particles were washed several times with distilled water until the supernatant is negative to the anion chloride test. This test consisted in the addition of silver nitrate, being the presence of chloride anions signed by the

formation of $AgCl_2$ precipitate. Finally, the particles were washed with ethanol. In each wash, the particles were allowed to settle and magnetically separated. The pH of the supernatant was measured and then decanted. After the ethanol washing, the particles were air dried for several days. The mass of the product was obtained and the percent yield was computed.

A solution of 0.0100g of FeNP in 100 mL of a 0.1M NaCl solution and another with the same amount of FeNP in 100mL of a 0.01M NaCl solution were made, the homogeneity of the solutions were achieved by sonication for at least 15 minutes. The pH and zeta potential of the unsonicated and sonicated FeNPs mixtures have been measured. The pH of the mixtures were adjusted using 3.5 M HCl and 1 M NaOH based on the desired pH. Once the pH was adjusted, the pH, ZP, and size of the particles have been measured.

2.4.2 Synthesis and Characterization of PACMAG

PACMAG were synthesized following an adaptation of the method first described by Kahani et al (2007). In a 50 mL beaker, 0.1500 g of FeNPs were added to 15 mL of deionized water (DW) and sonicated for 15 minutes, 0.5000 g of PAC was added to the sonicated FeNPs, and the mixture was stirred for 15 minutes. The particles of PACMAG were allowed to settle in the presence of a magnet for 10 minutes and then decanted. The PACMAG was washed 4 times with 10mL of DW, decanting the liquid in the presence of a magnet after each wash. The particles were allowed to air dry for 2 days.

2.5 Characterization of Wastewater (WW)

The pH, conductivity, turbidity, DOC and TOC of the WW were measured using a pH meter, conductimeter, turbidimeter, Total Organic Carbon Analyzer respectively. This was done for each batch of the WW to ensure similarity between batches.

2.6 Calibration Curves

In order to determine the unknown concentration of the treated samples, calibration curves for each drug (IBU, PAR, ASA, and AMOX) were created at known concentrations (5 mg/L, 10 mg/L, 20 mg/L, and 30 mg/L). The absorbance of the solutions was measured at the λ_{max} (Table 2.1) of the corresponding drug. The correlation between the known concentration of the sample and the measured absorbance was used to develop the calibration curve for each drug.

2.7 Adsorption Tests

2.7.1 Kinetics Measurements

Four types of experiments, described in Table 2.2, were performed. A specific amount of adsorbent was mixed with 100 mL of contaminated water sample. This mixtures were placed on a linear shaker at a speed of 150 mpm. Fifteen milliliters, 15 mL, of liquid sample was taken at specific times (0 min, 15 min, 40 min, 80 min, 120 min, 160 min, 24 hours) in order to follow the adsorption process. The obtained sample was allowed to settle for 5 minutes at the presence of the magnet and the particles were magnetically separated.

Depending on the adsorbent being analyzed, an additional separation technique was done for comparison purposes. After magnetic separation, 5 mL of supernatant was centrifuged for 15 minutes at 4000 rpm.

Both the pH and absorbance values of the samples were measured.

Table 2.2: Parameters for each case (Adsorbent type, Amount of adsorbent, Type of contaminated sample, separation technique performed)

Adsorbent type	Amount of adsorbent	Type of contaminated water sample	Separation technique
Unsonicated FeNPs	0.1 g	30 mg/L (IBU, PAR, ASA) drug –DW solution	Magnetic separation, Magnet-centrifuge
Sonicated FeNPs	10 mL of 1% (m/m) FeNPs – DW mixture	30 mg/L (IBU, PAR, ASA) drug –DW solution	Magnetic separation, Magnet-centrifuge
PACMAG	0.1 g	30 mg/L (IBU, PAR, ASA) drug –DW solution	Magnetic separation, Magnet-centrifuge
PACMAG	0.0390 mg	10 mg/L (IBU, AMOX) drug –DW solution	Magnetic separation
PACMAG	0.0390 mg	WW	Magnetic separation

2.7.2 Isotherms of PACMAG

Table 2.3: Amount of PACMAG used in accordance to the expected PAC content present in the particle

Amount of PACMAG (mg PACMAG/30mL solution)	Corresponding PAC content (mg PAC/L solution)
3.9	100
7.8	200
11.7	300
15.6	400
19.5	500
23.4	600
27.3	700
31.2	800
35.1	900
39.0	1000

In the isotherm for varying amounts of PACMAG, 30 mL of contaminated water samples composed of either a 10 mg/L IBU solution, 10 mg/L AMOX solution, or WW, was mixed with varying amounts of PACMAG (100 mg - 800 mg PAC content) (Table 2.3).

While for the second isotherm in which the drug concentration was varied, the optimum amount of PACMAG (11.7 mg), that has been obtained from the first isotherm, was dissolved in 30 mL of the studied drugs, being at five different concentrations (5 mg/L, 15 mg/L, 20 mg/L, 25 mg/L and 30 mg/L).

In both experiments, samples were taken after 2 hours of adsorption, under constant shaking (the linear shaker set to 150 mpm). The obtained sample was allowed to settle for 5 minutes at the presence of the magnet and the particles were magnetically separated. The absorbance of the liquid sample was measured at the λ_{max} (Table 2.1) of the corresponding drug in order to obtain their concentration.

2.7.3 Adsorption of PACMAG in WW Spiked with Drug

Based on the optimum amounts of PACMAG (11.7 mg) and drug concentration (15 mg/L) of IBU or AMOX determined in 2.7.2, the adsorbent was mixed with 30 mL of WW spiked drug (IBU or AMOX). Adsorption took place for 2 hours under constant shaking (the linear shaker set to 150 mpm). The particles were settled for 5 minutes with the presence of a magnet and separated. The absorbance of the liquid sample was measured at the λ_{max} (Table 2.1) of the corresponding drug in order to obtain their concentration.

2.8 Regeneration of PACMAG (Preliminary Test)

PACMAG were regenerated following an adaptation of the method first described by Do et al (2011). Thirty milliliters, 30 mL, of 15 mg/L of a solution of AMOX in wastewater (WW) was mixed with different amounts of PACMAG (300 mg- 1000 mg PAC content) (Table 2.3 in 2.7.2). Adsorption took place for 2 hours under constant shaking (the linear shaker set to 150 mpm). The particles were settled for 5 minutes with the presence of a magnet and separated. The TOC and the absorbance of the liquid sample at 228 nm (Table 2.1) were measured.

The used PACMAG was air dried for 2 days and at 50 ^{o}C for 4 hours. Under the hood, the used PACMAG was mixed with 100 mL of 0.083 M of H_2O_2. This mixture was shaken for 8 hours on a linear shaker set to 250-275 mpm. The pH was maintained at 2.90-3.10 using a 6 M HCl solution during the reaction. After the reaction, the particles were settled for 5 minutes in the presence of a magnet and separated. In the presence of a magnet, the regenerated PACMAG were washed with 20 ml of DW until pH of the supernatant was neutral. The regenerated PACMAG was dried in the oven for 2 days at 50 ^{o}C. The dried regenerated PACMAG was tested again for adsorption in the AMOX-WW mixture.

2.9 Sedimentation Test of PACMAG

Three, 3, samples containing 20 mL of a 10 mg/L IBU solution mixed with 7.8 mg of PACMAG have been allowed to interact for 2 hours under uniform shaking (the linear shaker set to 150 mpm). The first sample was allowed to settle with a magnet for 5 minutes. The second sample was allowed to settle for 5 minutes without a magnet, the third sample was allowed to settle for 30 minutes without a magnet. The amount of IBU was determined from the absorbance at its λ_{ma}.

3 RESULTS AND DISCUSSION

In the present chapter, the obtained results are shown and discussed. Starting in the synthesis and characterization of iron nanoparticles used in the adsorbent. The adsorption ability of the magnetic activated carbon adsorbent (PACMAG) for IBU, ASA, PAR, and AMOX are determined. This adsorbent was also tested in wastewater spiked with IBU and AMOX. Finally, preliminary tests on the regeneration and rate of sedimentation of PACMAG were done.

3.1 Synthesis of Adsorbent Material

3.1.1 Synthesis and Characterization of FeNPs

The FeNPs are synthesized using the co-precipitation technique following an adaptation of the method first described by Qu et al (1999). Initially, a partial reduction of Fe^{3+} to Fe^{2+} by the presence of sulfide in acidic medium takes place in order to obtain a 2:1 proportion of iron ions. The system is then made basic to precipitate out the FeNPs.

The iron and sulfide will react with each other forming a dark red complex, signifying the presence of $[FeSO_3]^+$ (Equation 3.1) (Betterton, 1993) (Millero et al, 1995).

$$Fe^{3+} + SO_4^{2-} \rightarrow [FeSO_3]^+ \qquad \text{Equation 3.1}$$

The reaction continues by reducing iron (III) to iron (II), and oxidizing sulfur (IV) (S^{4+}) to sulfur (VI) (S^{6+}) (Equation 3.2-3.4) (Karraker, 1963) (Millero et al, 1995).

$$SO_3^{2-} + H_2O \rightarrow SO_4^{2-} + 2H^+ + 2e^- \qquad \text{Equation 3.2}$$

$$2Fe^{3+} + 2e^- \rightarrow 2\,Fe^{2+} \qquad \text{Equation 3.3}$$

$$2\,Fe^{3+} + SO_3^{2-} + H_2O \rightarrow 2\,Fe^{2+} + SO_4^{2-} + 2H^+ \qquad \text{Equation 3.4}$$

Based on the reaction stoichiometry (2 Fe^{3+}: 1 SO_3^{2-}) and the amount of Fe^{3+} (one third) that can be reduced, the concentration ratio would be $[Fe^{3+}] / [SO_3^{2-}] = 6$. However, experimental evidences show an optimal concentration ratio of 3 because the solution has not been de-aerated. In the presence of oxygen and iron ions, as catalysts, the sulfide is oxidized (Equation 3.5) (Shen et al, 2009). Finally, the addition of ammonia has caused the production of magnetite (Equation 3.5-3.6) (Shen et al, 2009).

$2SO_3^{2-} + O_2 \rightarrow 2SO_4^{2-}$ Equation 3.5

$2\ Fe^{3+} + Fe^{2+} + 8OH^- \rightarrow Fe_3O_4 + 4H_2O$ Equation 3.6

The FeNPs are obtained in quantitative yield. Comparing to other techniques, the reaction produces a high percent yield (Blaney, 2007). The particles were washed with different solvents (HCl solution, DW, and ethanol).

The point of zero charge is an important property of nanoparticles. It is the pH at which the electrical charge density on the surface of the particle is zero. On the other hand, the isoelectric point is the pH at which the colloidal particle remains stationary in an electrical field. The isoelectric point of magnetite in water at 25 ^oC is 6.5-6.7 (Jiang et al., 2010). Often, the 2 terms are used indistinctly because their differences are considered to be negligible.

In obtaining the isoelectric point, the zeta potential (ZP) of the particle is needed. Zeta potential is the electrokinetic potential in a colloidal dispersion. The zeta potential is the potential difference between the dispersion medium and the stationary layer fluid attached to the dispersed particle. The zeta potential is caused by the net electrical charge contained within the region bounded by the slipping plane, and also depends on the location of that plane. Thus, it is widely used for quantification of the magnitude of the charge. However, zeta potential is not equal to the Stern potential or electric surface potential in the double layer, because these are defined at different locations. Such assumptions of equality should be applied with caution. Nevertheless, zeta potential is often the only available path for characterization of double-layer properties. The zeta potential is a key indicator of the stability of colloidal dispersion. The magnitude of the zeta potential indicates the degree of electrostatic repulsion between adjacent, similarly charged particles in a dispersion. For molecules and particles that are small enough, a high zeta potential will confer stability, i.e., the solution or dispersion will resist aggregation. When the potential is small, attractive forces may exceed this repulsion and the dispersion may break and flocculate. So, colloids with high zeta potential (negative or positive) are electrically stabilized while colloids with low zeta potentials tend to coagulate or flocculate.

A low ZP magnitude promotes clumping because there is no repulsive force that inhibits the FeNPs from aggregating. This is their natural tendency caused by the anisotropic dipolar attraction that exists between particles (Atta et al, 2015).

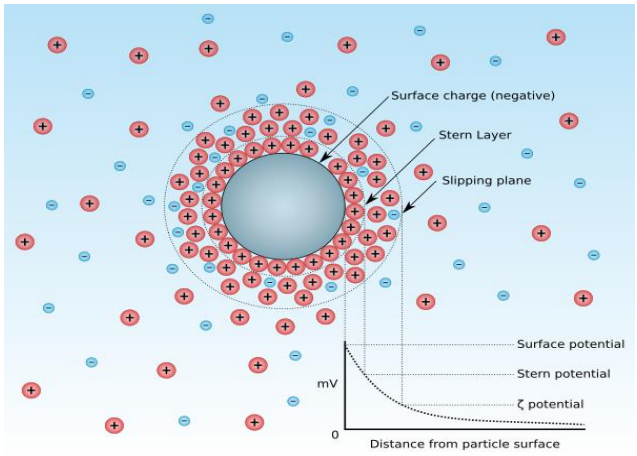


Figure 3.1: Diagram of the 2 layers surrounding the particle

(Malvern Instruments Limited, 2014)

In this work, the ZP are measured before and after sonication (Figure 3.2). Figure 3.2 shows that the ZP of the particles change because of sonication. The unsonicated particles have a low negative ZP compared to the sonicated ones which produced a positive ZP.

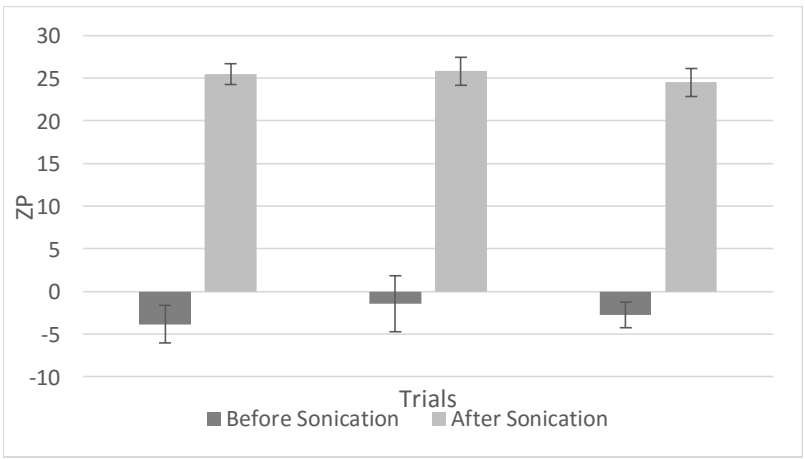


Figure 3.2: Zeta potential of FeNPs before and after sonication

Particles with a low ZP means that they are unstable and colloidal dispersion is low. This was observed when aggregates of unsonicated FeNPs settled at the bottom of the beaker. Because the particles are not colloidally stable, the sample tested were predominantly composed of DW. Because of this, the small amounts of anion such as chlorine caused the slight negative ZP (Jiang et al., 2010). Also, the zetasizer was not able to measure the particle size of the

unsonicated FeNPs because of insufficient amount of FeNPs in the liquid sample. On the other hand, sonication caused the particles to be less aggregated and be more disperse in the colloidal mixture. This resulted in a positive ZP (roughly 25mV) because FeNPs are metallic and are positive (Jiang et al., 2010). Based on Table 3.1, FeNPs have an incipient instability means that it could be in a colloidal state for a certain amount of time (Jiang et al., 2010).

Table 3.1: The stability of particles based on their zeta potential values (Jiang et al., 2010)

Zeta Potential (mV)	Stability behavior of the colloid
0 to (+/-) 10	Rapid Coagulation or flocculation
(+/-) 10 to (+/-) 30	Incipient instability
(+/-) 30 to (+/-) 40	Moderate stability
(+/-) 40 to (+/-) 60	Good stability
More than (+/-) 61	Excellent stability

Size is an important physical property of a particle which is regularly determined by manufacturing industries because it can influence the properties of a material (Table 3.2).

Table 3.2: Direct influence of particle size on the property of the material (Malvern Instruments Limited, 2014)

Property affected by particle size	Examples
Reactivity / Dissolution	Catalysts, tablets
Stability in suspension	Sediments, paints
Efficacy of delivery	Asthma inhalers
Texture and feel	Food ingredients
Appearance	Powder coatings and inks
Ability to flow and handling	Granules
Viscosity	Nasal spray
Packing density and porosity	Ceramics

In this research, the ZP and the size of the particles were measured in the presence of varying pH and ion concentrations (DW, 0.1 M NaCl, and 0.01 M NaCl). Based on the results of the previous experiment, the FeNPs were sonicated before measuring the ZP and size. Figure 3.3 shows that the experimental isoelectric point of the synthesized FeNPs is between pH 8 to 9

which coincided with the isoelectric point obtained by Jiang et al, which was at pH 9 (Jiang et al., 2010).

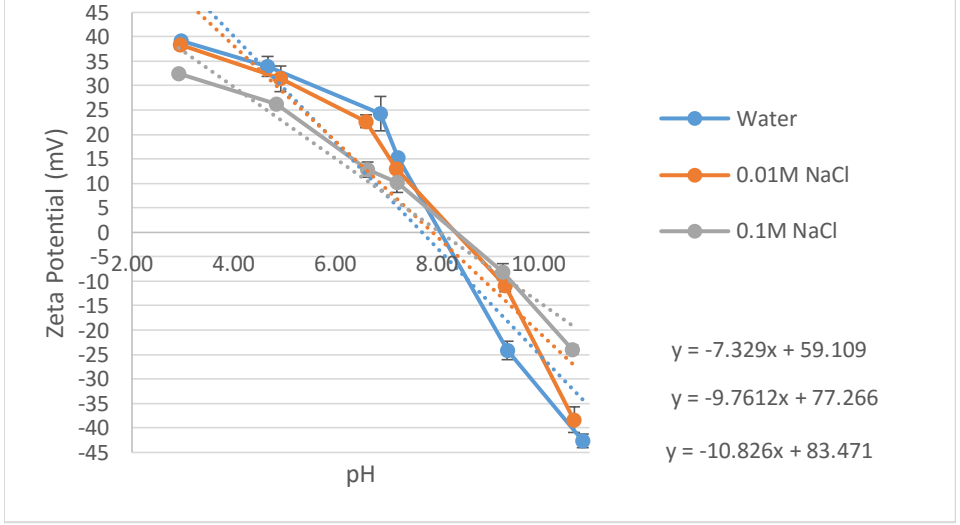


Figure 3.3: Zeta potential of FeNPs in varying ion concentration and pH

Based on the graph, the ZP of FeNPs are affected by the ion concentration in the sample, and by the pH of the sample. The trend line equations show that the absolute value of the slope increases at decreasing ion concentration (0.1 M NaCl until 0 M NaCl = water).

Trend line of 0.1M NaCl: y= -7.329x + 59.109	Equation 3.7
Trend line of 0.01M NaCl: y = -9.7612x + 77.266	Equation 3.8
Trend line of water: y = -10.826x + 83.471	Equation 3.9

The absolute value of the slope changes from 7.329 (0.1 M NaCl) to 10.826 (water) (Equations 3.7, 3.8, 3.9) because the presence of the ions in the mixture cause an unstable distribution of surface charge on the particle. As a result of the change in slope, the ZP range (y-axis) of FeNPs in the 0.1 M NaCl solution is narrower (ZP = $^{+}$33- $^{-}$25) compared to 0.01 M NaCl solution (ZP = $^{+}$38- $^{-}$40) and water (ZP = $^{+}$40- $^{-}$44) because the presence of the ions inhibits colloidal stability and promotes particle aggregation.

Depending on the pH of the mixture, sodium and chloride ions can act as a counter ion (Salgin, S. et al, 2012). Below the point of 0 value, the particles have a positive surface charge, causing chloride anions to act as counter ions. On the other hand, above the point of zero value, the sodium cations are the counter ions because the surface charge of the particles is negative

(Salgin, S. et al, 2012). The counter ions act as a screen, weakening the particles' repulsive forces between each other and promoting aggregation (Salgin, S. et al, 2012). As a result, the ZP is lower and the particles sizes are bigger (AZoNano, 2005). In general, the higher the ion concentration, the more counter ions present which leads to a stronger screening effect (Figure 3.4).

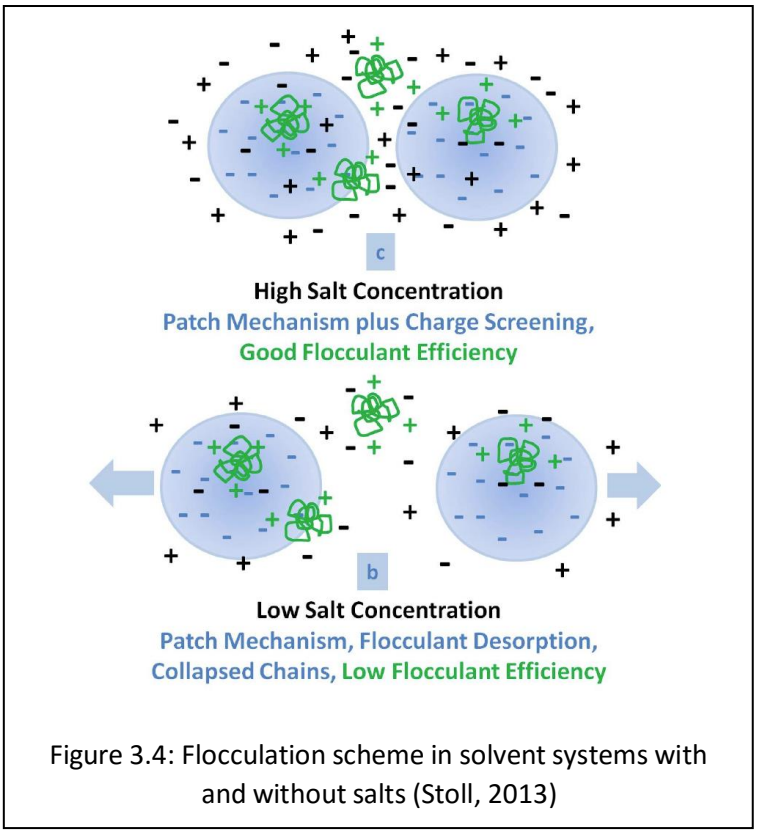


Figure 3.4: Flocculation scheme in solvent systems with and without salts (Stoll, 2013)

The pH of the sample affects the behavior of FeNPs as well. In basic pH, the high hydroxide (OH^-) concentration causes the particles to acquire more negative charge, making the zeta potential to be more negative. While in acidic solutions, the addition of HCl causes an increase in hydronium (H_3O^+) ions leading to the build-up of positive charges (Figure 3.3) (AZoNano, 2005). In both cases, the increase in charges causes an increase in repulsive forces between particles leading to a higher ZP magnitude. While, at neutral pH the zeta potential is positive because even though there are no added hydronium ions, by the presence of the iron in the particles makes the particles' surface to be positive.

The effects on the ZP magnitude is reflected on the stability of the colloidal system and on the particle size. In all three solvent types, the pH values near the point of 0 charge has the biggest particle size because this is when the repulsive force between particles are the weakest (Figure

3.5). Unlike in basic and acidic cases wherein the repulsive force between particles are higher. Also, the absence of counter ions make the particles less aggregated minimizing particle size.

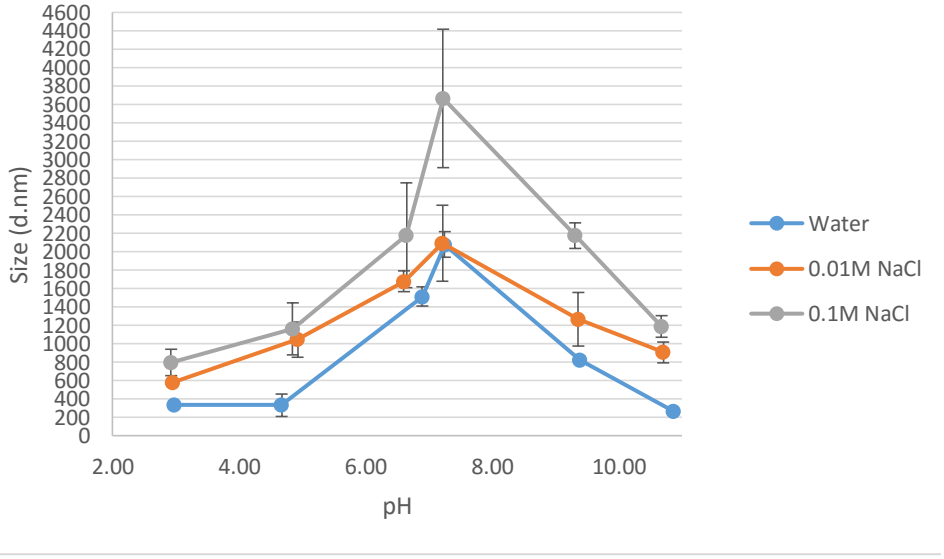


Figure 3.5: Particle size of FeNPs in varying solvent systems and pH

3.1.2 Synthesis and Characterization of PACMAG

Though studies show that FeNPs can be used as adsorbent, its adsorption capacity is minimal due to its natural tendency to aggregate in aqueous medium. On the other hand, PAC is difficult to remove in the water system. Often an additional filtration step is needed which can be time consuming. The new adsorbent material, PACMAG, combines the adsorption capacity of PAC and the magnetic property of FeNPs to address each other's drawbacks. PACMAG were synthesized following an adaptation of the method first described by Kahani et al (2007). Because PAC is highly porous, a possible way of embedding FeNPs is by adsorption which produces quantitative yield (103 ± 5 %). Though some of the adsorption sites of PAC are already occupied by the FeNPs, it can still adsorb a good amount of contaminants. Also, it can be regenerated for multiple usage which is cost efficient. The average percent yield is above 100 % because the particles are not completely dry. Similar with the synthesis of FeNPs, the particles can trap liquid such as DW, which was the liquid used to wash the particles. The presence of DW in PACMAG has no effect on the adsorption experiments because water was used as sample. Its effect on the mass of PACMAG used per experiment is minimal as well because the mass contribution of water versus the mass contribution of PAC and FeNPs is just 7% per mole of PACMAG.

3.2 Characterization of Wastewater (WW)

Because the particles were also tested in actual WW, water from the Estação de Tratamento de Águas Residuais of Águas do Algarve, SA was obtained and characterized. A problem with using WW in adsorption experiments is that its components are unknown, and the amount of contaminants vary depending on when the wastewater has been collected. Thus, it is important to monitor the pH, conductivity, turbidity, dissolve organic carbon (DOC), and total organic carbon (TOC) of the batches of WW used in order to minimize variations in the results (Table 3.3).

Table 3.3: Properties of WW

Property	Average	
pH	7.71 ± 0.04	
Conductivity ((μs/cm)	1293 ± 16	
Turbidity	1.70 ± 0.03	
DOC (ppm)	Batch 1	7.89 ± 0.06
	Batch 2	7.34 ± 0.13
	Batch 3	8.63 ± 0.39
TOC (PP)	Batch 1	9.73 ± 0.14
	Batch 2	8.79 ± 0.05
	Batch 3	9.05 ± 0.40

The isotherms using WW as sample were measured, for a 24 hour time period, as well in order to confirm if PACMAG can adsorb contaminants that interfere with the signal measured by UV-VIS at the λ_{max} of IBU (221 nm) and AMOX (228 nm). Considering the presence of unknown contaminants in WW, competition between those contaminants and the monitored drugs can occur. By determining the isotherms of contaminants dissolved in WW adsorption on PACMAG (300 mg/L PAC content), the minimum time for maximum contaminant removal can be determined. Figure 3.12 shows the minimal decrease in the absorbance values for both λ_{max} is after 120 minutes. So 120 min (2 h) is the minimum amount of adsorption time needed by PACMAG in WW (Figure 3.5). This minimum decrease in adsorption after 120 minutes is because the adsorption capacity of PACMAG is slowly being reached. There is a decreasing amount of available adsorption sites because PACMAG follows the Langmuir isotherm, similar with PAC (Tan and Hameed, 2010). Langmuir isotherm assumes a monomolecular isotherm behavior which contains fixed individual sites that equally adsorbs a molecule

forming a monolayer with the thickness of the adsorbed molecule (Tan and Hameed, 2010). Thus, once an adsorption site is occupied by a contaminant, another contaminant cannot occupy the same space. This is why after 300 mg/L of PAC content, the graph flattens out (Figure 3.6).

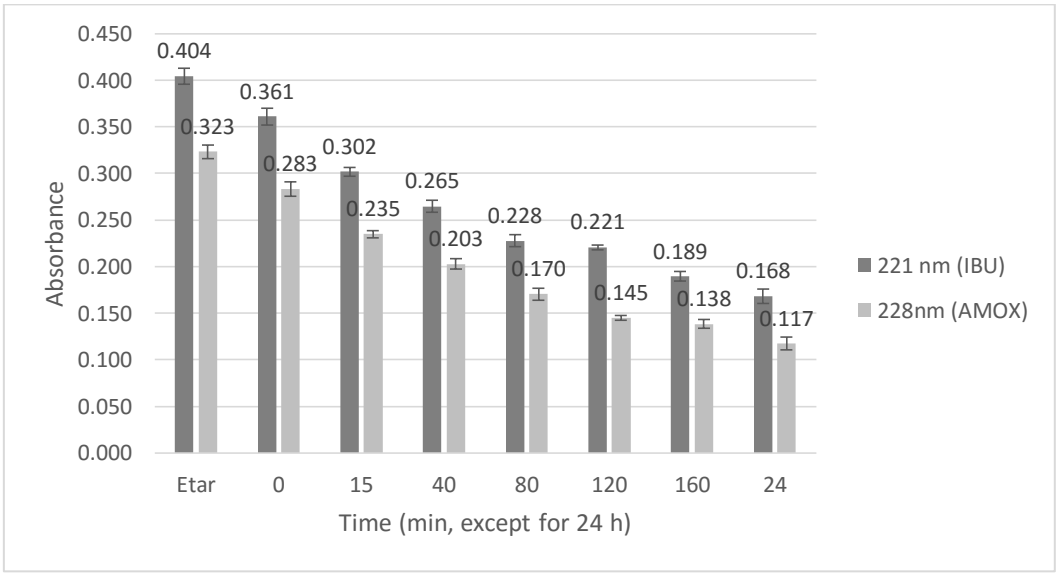


Figure 3.6: Absorbance of wastewater water in the presence of PACMAG at 221 nm for IBU and at 228 nm for AMOX in a 24 hour adsorption period

The isotherm of WW in the presence of varying amounts of PACMAG (100 mg/L PAC - 600 mg/L PAC content) is performed to determine the optimum amount of PACMAG that can adsorb a maximum amount of contaminant. Figure 3.7 shows that beyond 300 mg/L of PAC content there is no drastic change in the absorbance of WW at both wavelengths. This PAC content amount is used as the minimum amount of PACMAG needed to remove IBU or AMOX in WW (Figure 3.7). The minimal decrease of absorbance after 300 mg/L PAC content is because of the insufficient amount of contaminants left in the water that can be adsorbed. As a result, the percent removal of IBU and AMOX had a minimal increase after 300 mg/L PAC presented in Figure 3.8.

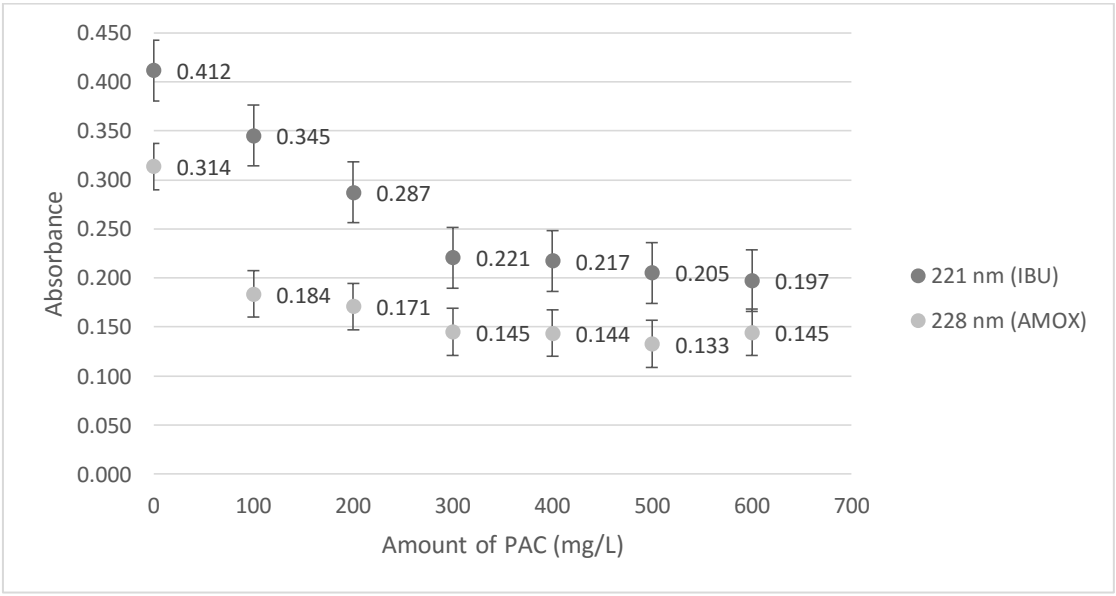


Figure 3.7: Isotherm of the absorbance of wastewater water in the presence of varying amounts of PAC content in PACMAG at 221 nm for IBU and at 228 nm for AMOX

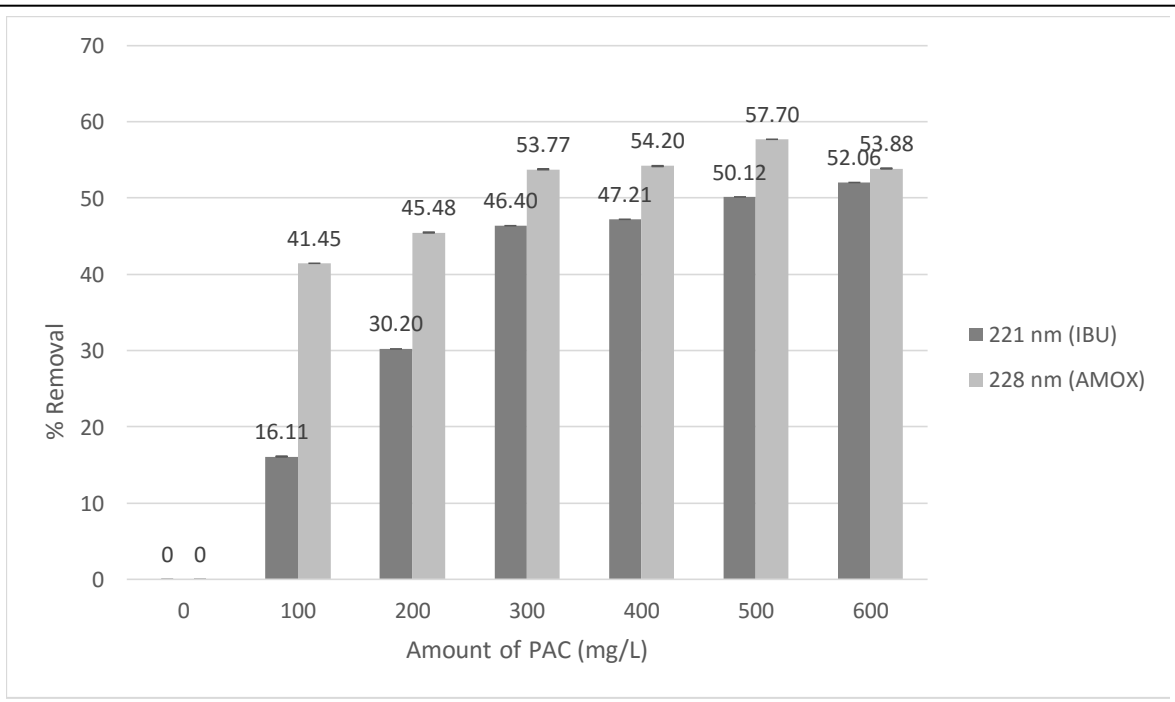


Figure 3.8: Absorbance of wastewater water in the presence of varying amounts of PAC content

3.3 Calibration Curves

Calibration curves were established for each type of aqueous drug solution using the UV-Vis absorption at their respective λ_{max}. The calibration curves for each type of drug are shown in Figure 3.9. All calibration curves are considered to be an accurate form of detection for their respective drug with a concentration of 30 mg/L and below. These were used to calculate for the experimental drug concentration after adsorption based on their absorbance values.

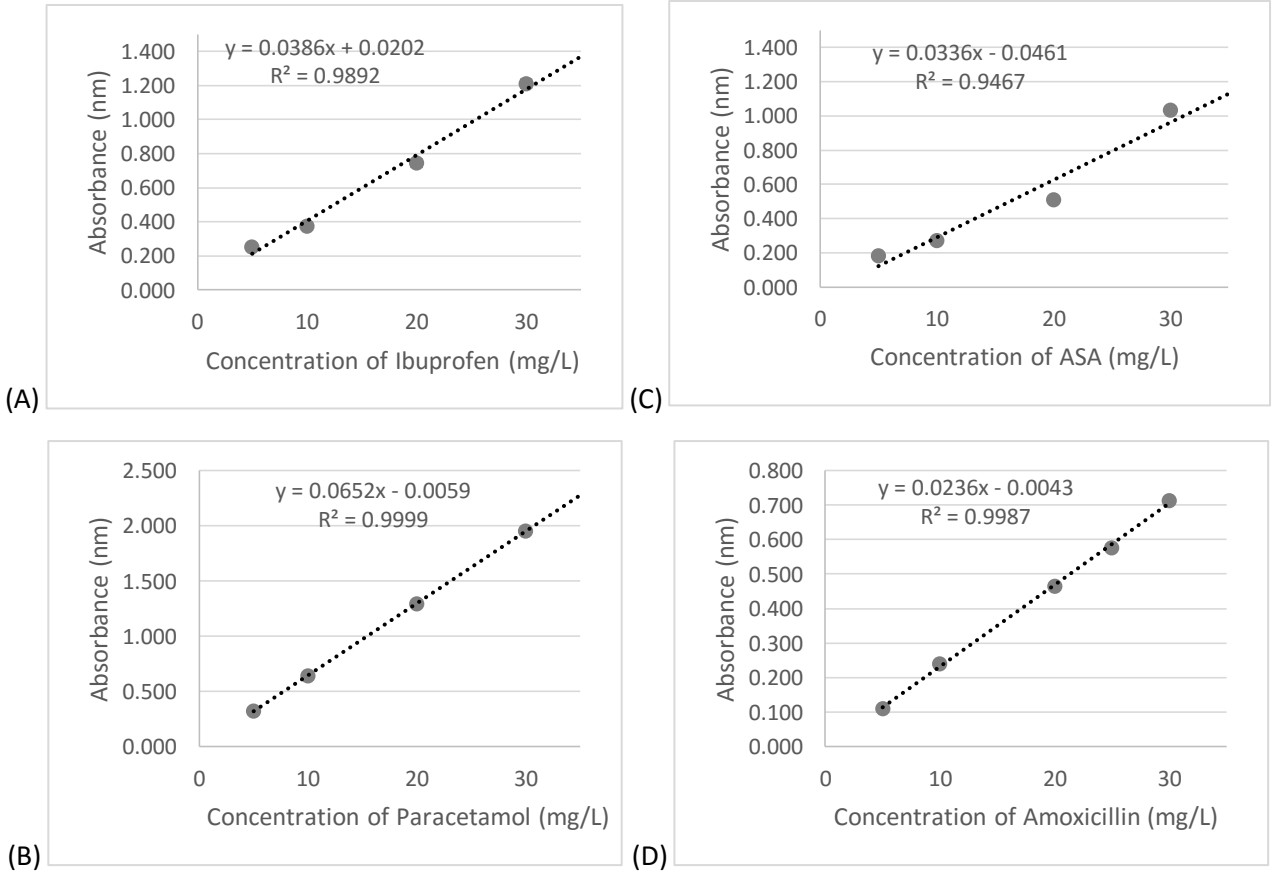


Figure 3.9: Calibration curves of (A) IBU, (B) PAR, (C) ASA, and (D) AMOX

3.4 Adsorption Test of FeNP

Adsorption is one of the common techniques applied in WWTPs used in removing particulates and chemical contaminants. Adsorption involves the binding of particles on a surface which involves intermolecular forces of attraction. But not all types of material can be used as adsorbent. The common industrial adsorbent are activated carbon, silica gel, and alumina because these materials have a big surface area per unit weight. In this research, adsorption is often used to assess the efficiency of FeNPs and PACMAG as adsorbents in removing IBU,

PAR, ASA, and AMOX in water. 4 different experimental set-ups were performed and studied which are depicted in Table 3.4.

Table 3.4: Experimental set-ups for drug adsorption of either FeNPs or PACMAG

Adsorbent type	Amount of adsorbent	Type of contaminated water sample	Separation technique
Unsonicated FeNPs	0.1 g	30 mg/L (IBU, PAR, ASA) drug –DW solution	Magnetic separation, Magnet-centrifuge
Sonicated FeNPs	10 mL of 1% (m/m) FeNPs – DW mixture	30 mg/L (IBU, PAR, ASA) drug –DW solution	Magnetic separation, Magnet-centrifuge
PACMAG	0.1 g	30 mg/L (IBU, PAR, ASA) drug –DW solution	Magnetic separation, Magnet-centrifuge
PACMAG	0.0390 mg	10 mg/L (IBU, AMOX) drug –DW solution	Magnetic separation
PACMAG	0.0390 mg	WW	Magnetic separation

3.4.1 Kinetics Measurements of IBU, PAR, ASA in FeNPs

The adsorption capacity of FeNP is tested by changing its form through sonication, and by varying the separation technique of the adsorbent before UV-Vis analysis. There is a minimal decrease in the absorbance values of the samples after adsorption with unsonicated FeNPs. Though samples that are separated by a combination of magnet and centrifuge are lower in absorbance values than the magnetically separated samples, the amount of drugs removed of both techniques are very small (Figure 3.10, Figure 3.11).

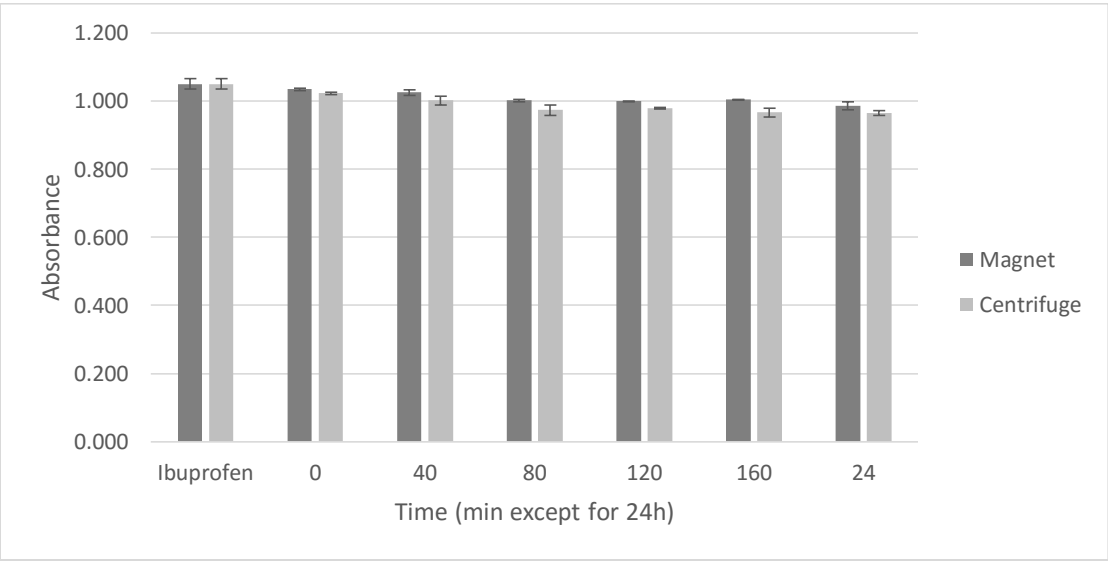


Figure 3.10: Absorbance measurements of IBU samples in the kinetic experiment of unsonicated FeNPs

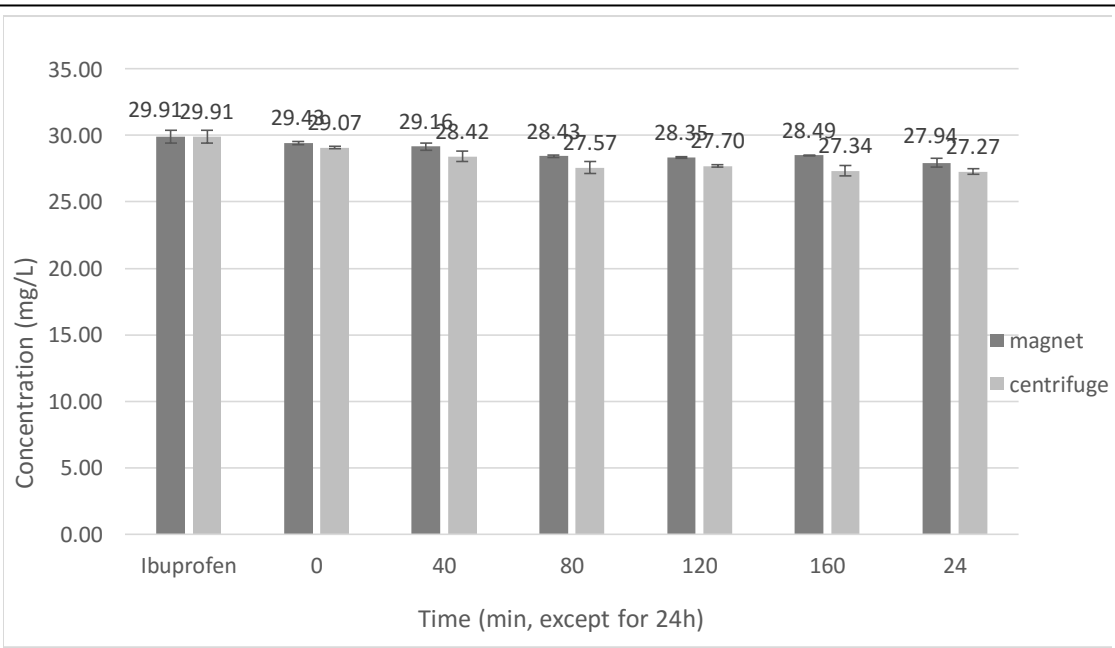


Figure 3.11: Concentration of IBU samples in the kinetic experiment of unsonicated FeNPs

The same trend is observed in the sonicated FeNPs. The samples that were separated with a combination of magnet and centrifuge had lower absorbance measurements, resulting to lower drug concentration (Figure 3.12). Comparing the two treatments on FeNPs, sonication increases the capacity of the FeNPs to adsorb contaminants because the particles are smaller compared to the unsonicated FeNPs. The sonicated FeNPs are more dispersed in a colloidal system and not aggregated leading to a bigger surface area and more available adsorption sites.

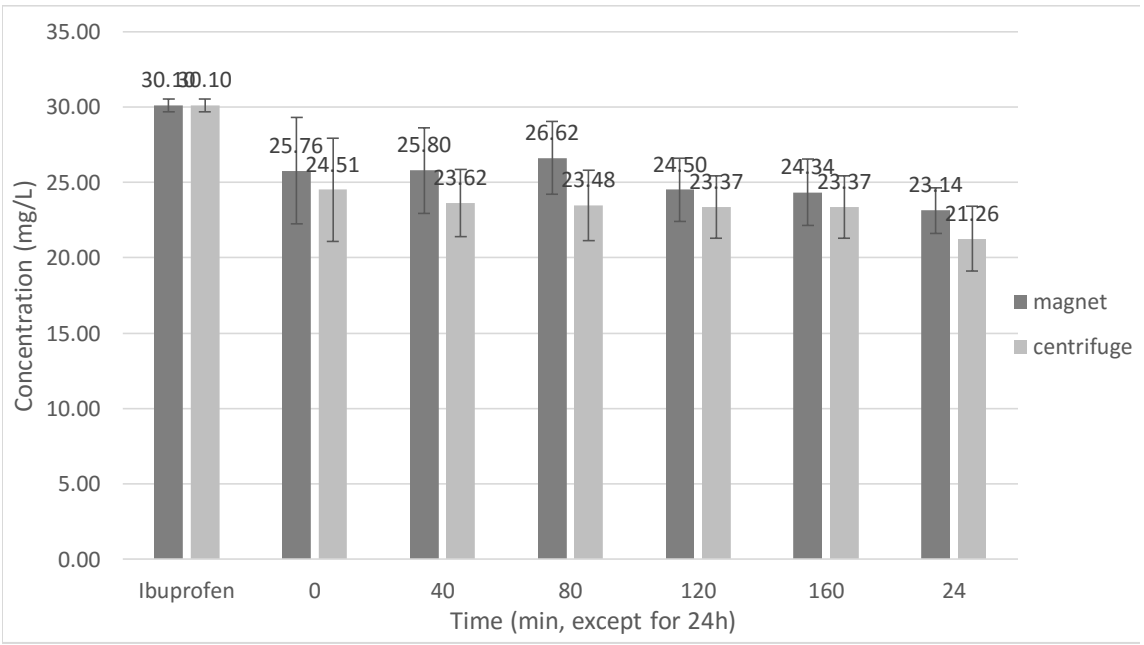
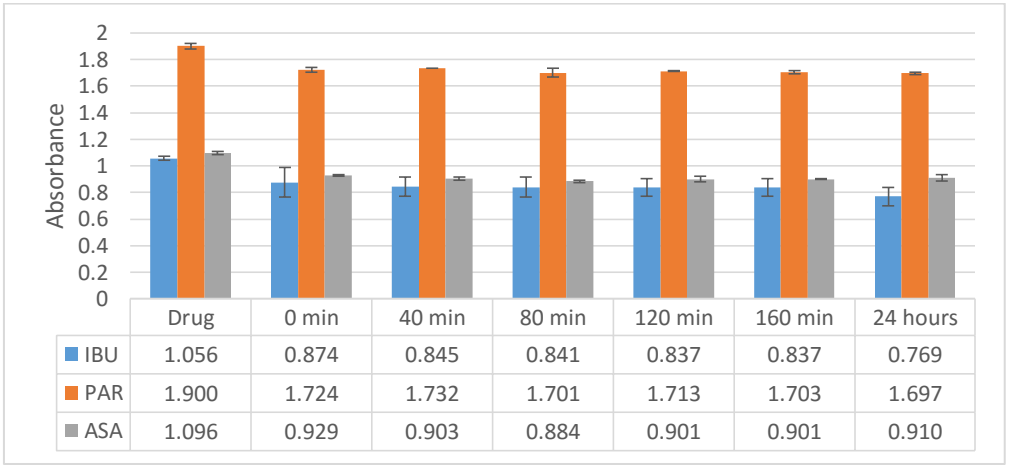


Figure 3.12: Concentration of IBU samples in the kinetic experiment of sonicated FeNPs

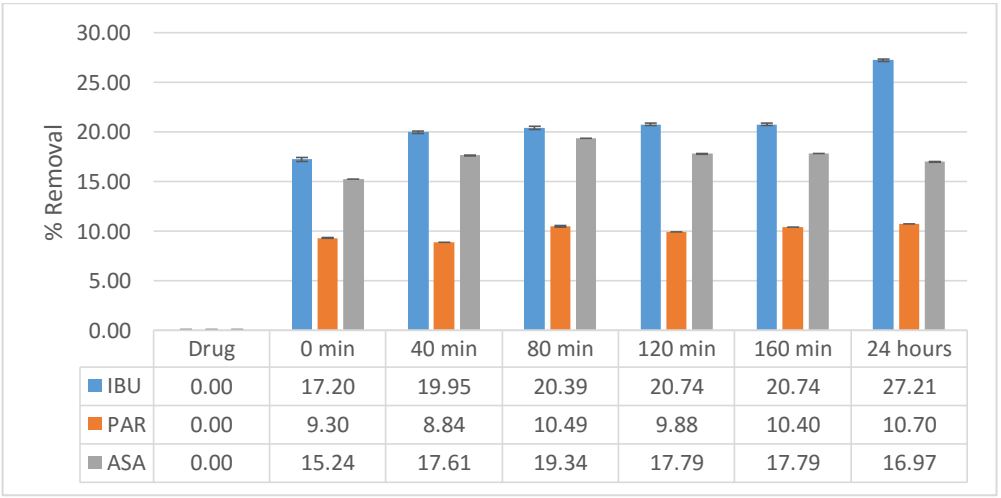
Because sonicated FeNPs and separation using a combination of magnet and centrifuge produced better absorbance results for IBU, similar parameters were applied in the adsorption experiment of ASA and PAR. Because IBU, PAR and ASA have similar molecular structures, it is expected that the adsorption behavior of ASA and PAR will be similar with IBU. Figure 3.13 shows the absorbance values of the three drugs after 24 hours of adsorption on PACMAG (Figure 3.13). Calculating for the amount of drugs adsorbed after 24 hours, it can be said that sonicated FeNPs adsorbed PAR the least, followed by ASA. The drug that is adsorbed the most is IBU which coincides with their respective percent removals (Figure 3.14).

Though all three are partially adsorbed by FeNPs, the adsorption difference are minimal because of the solubility of IBU, PAR and ASA in water. All three drugs have polar functional groups, carboxyl group for IBU and ASA, and a hydroxyl group for PAR, which can interact with water. Also, all three drugs are weak acids causing a decrease in pH, a positive ZP, and a higher colloidal stability. But, because of the presence of the aromatic ring in their structure, these drugs become partially insoluble in water (Shen et al, 2009). The partial insolubility of the HPCs limits the full surface contact between the drugs and FeNPs (Shen et al, 2009). As a result, there is insufficient adsorption, resulting to low percent removal. The maximum percent removal are 27.21 ± 0.14% (IBU), 10.70 ± 0.02% (PAR), and 16.97 ± 0.05% (ASA) (Figure 3.13).



	Drug	0 min	40 min	80 min	120 min	160 min	24 hours
IBU	1.056	0.874	0.845	0.841	0.837	0.837	0.769
PAR	1.900	1.724	1.732	1.701	1.713	1.703	1.697
ASA	1.096	0.929	0.903	0.884	0.901	0.901	0.910

Figure 3.13: Absorbance measurements of the drug samples in the kinetic experiment of sonicated FeNPs using magnetic separation and centrifuge



	Drug	0 min	40 min	80 min	120 min	160 min	24 hours
IBU	0.00	17.20	19.95	20.39	20.74	20.74	27.21
PAR	0.00	9.30	8.84	10.49	9.88	10.40	10.70
ASA	0.00	15.24	17.61	19.34	17.79	17.79	16.97

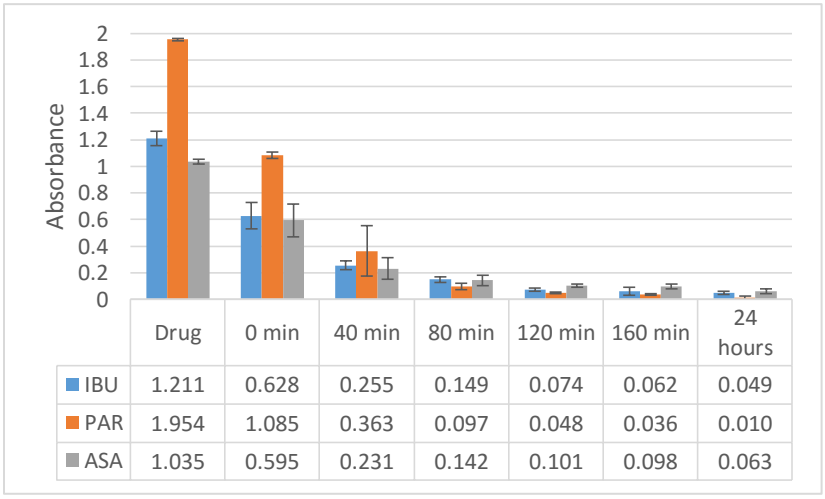
Figure 3.14: Percent removal of the drug samples in the kinetic experiment of sonicated FeNPs using magnetic separation and centrifuge

3.4.2 Kinetics Measurements of IBU, PAR, ASA in PACMAG

The adsorption capacity of PACMAG with IBU, PAR, and ASA is determined in order to compare its efficiency with FeNPs. Figure 3.14 shows the absorbance, sample concentration, and percent removal of all 3 drugs with PACMAG. After 120 min, the adsorption capacity of PACMAG is slowly reaching its limit. The change in the absorbance measurements as time elapses is decreasing because the adsorption sites are slowly being occupied by the contaminants. Among the 3 drugs, PAR is adsorbed the most having a percent removal of 99.47 ± 0.02%, while ASA is adsorbed the least having a percent removal of 93.95 ± 0.02% (Figure 3.15). IBU has a percent removal of 95.93 ±0.01%. As a representative of the analgesic group

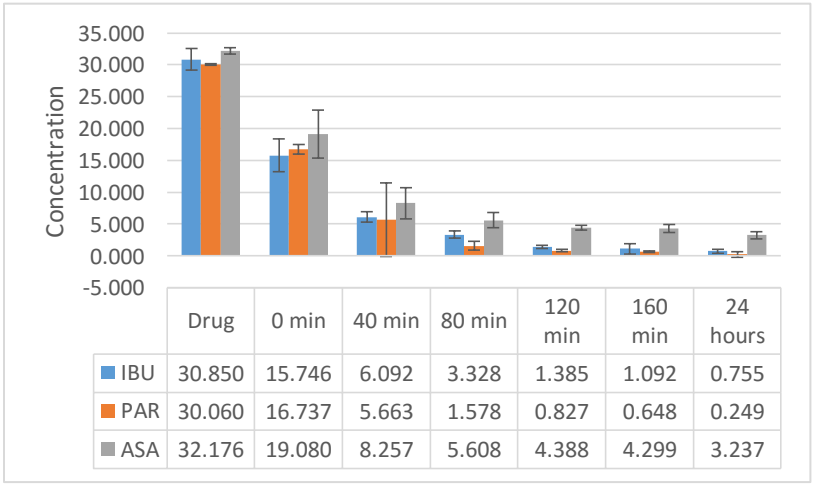
which is prevalently detected in most bodies of water and is vastly produced, IBU was further tested for its adsorption in PACMAG. This was then compared with the behavior of AMOX, a common antibiotic

A)



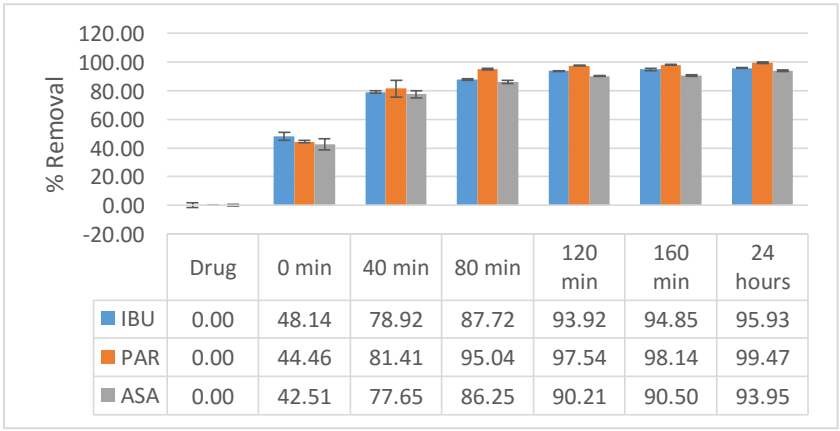
Drug	0 min	40 min	80 min	120 min	160 min	24 hours
IBU	1.211	0.628	0.255	0.149	0.074	0.062	0.049
PAR	1.954	1.085	0.363	0.097	0.048	0.036	0.010
ASA	1.035	0.595	0.231	0.142	0.101	0.098	0.063

B)



Drug	0 min	40 min	80 min	120 min	160 min	24 hours
IBU	30.850	15.746	6.092	3.328	1.385	1.092	0.755
PAR	30.060	16.737	5.663	1.578	0.827	0.648	0.249
ASA	32.176	19.080	8.257	5.608	4.388	4.299	3.237

C)



Drug	0 min	40 min	80 min	120 min	160 min	24 hours
IBU	0.00	48.14	78.92	87.72	93.92	94.85	95.93
PAR	0.00	44.46	81.41	95.04	97.54	98.14	99.47
ASA	0.00	42.51	77.65	86.25	90.21	90.50	93.95

Figure 3.15: Absorbance (A) and concentration (B) of the samples at varying times of adsorption using PACMAG as adsorbent and its corresponding percent removal (C)

To mimic environmental drug concentrations without going lower than the UV-Vis detection limit, the concentration of IBU was lowered to 10 mg/L in the adsorption tests. Figure 3.16 shows that IBU behaves similarly with the previous kinetic experiment which involved a higher IBU concentration. The changes in absorbance measurements beyond 120 minutes of adsorption are minimal which signified that the adsorption capacity of PACMAG is slowly being reached (Figure 3.16).

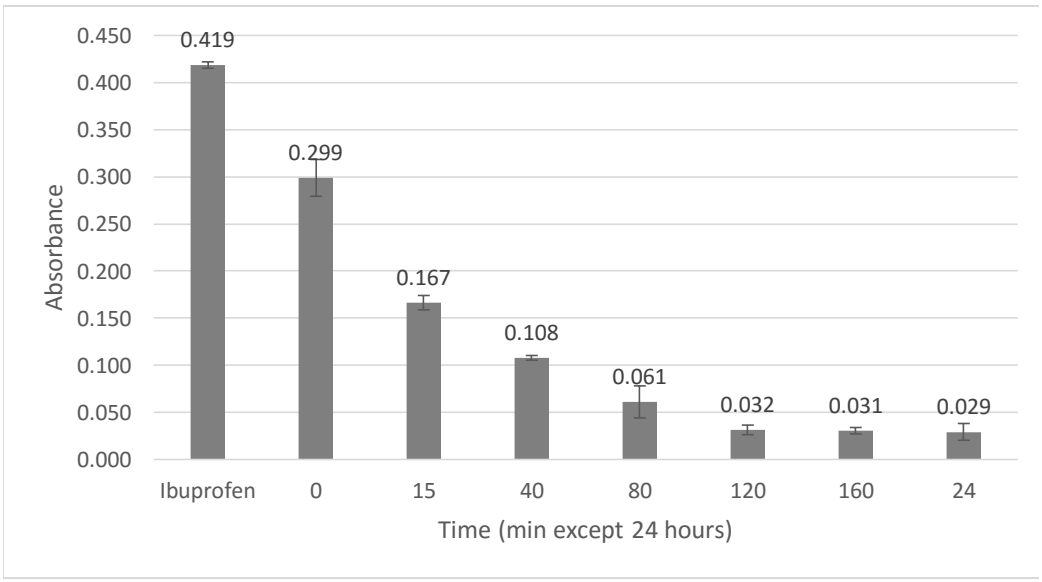
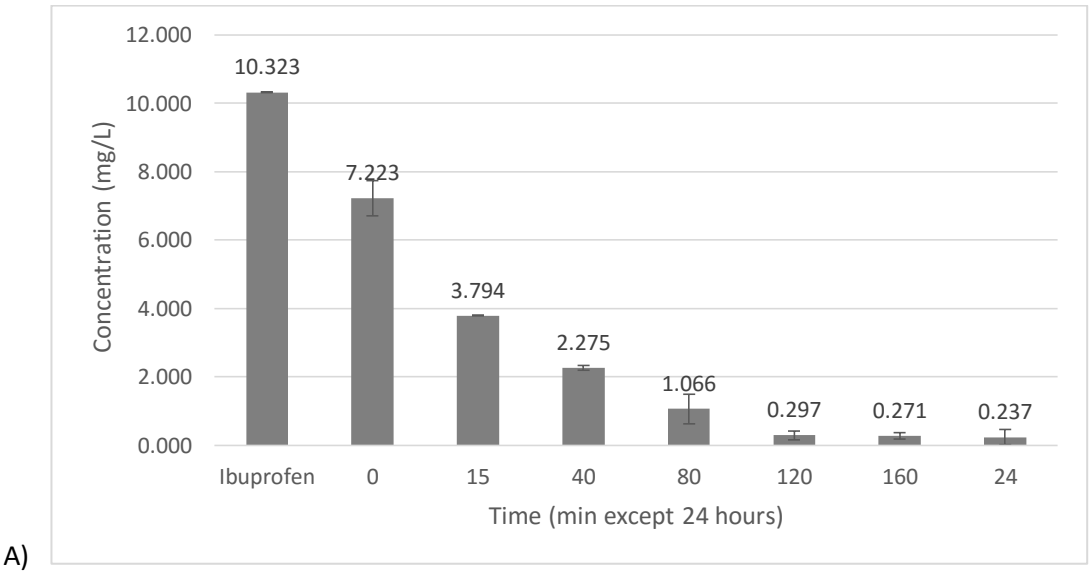
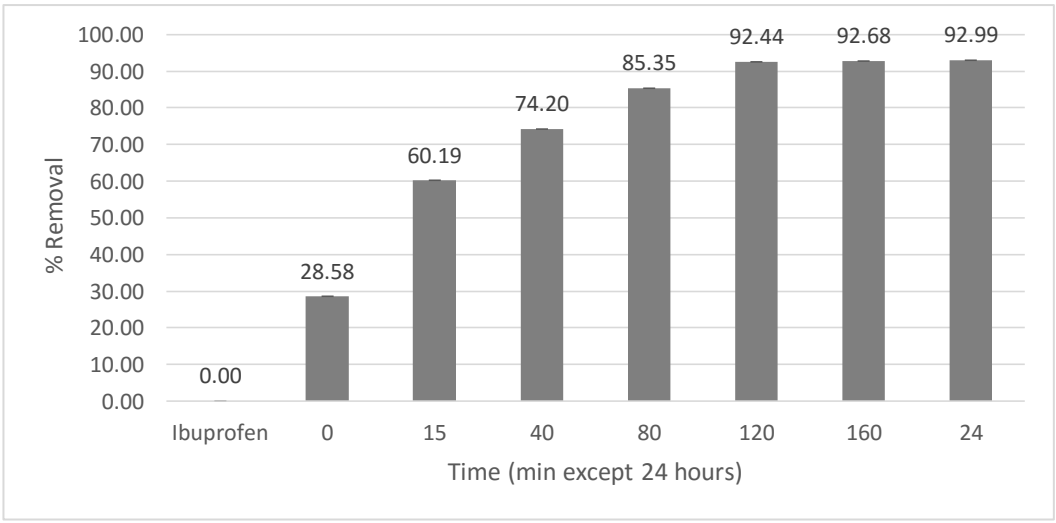


Figure 3.16: Absorbance of IBU at varying times of PACMAG exposure

Based on the gathered data, PACMAG is able to decrease the IBU concentration dramatically after 2 hours of adsorption, from an initial concentration of 10 mg/L to roughly 0.30 mg/L, resulting into a 92.99 ± 0.01 % removal (Figure 3.17 A and B). The high percent removal coincides with the percent removal of 30 mg/L IBU in PACMAG which is 95.93 ± 0.01%. It can be seen as well that adsorption takes place as soon as the PACMAG is placed in the system, resulting into an immediate decrease from the initial concentration. Though previous studies showed that complete removal of IBU was possible with magnetic activated carbon (Stackelberg et al, 2004), this is not applicable with PACMAG because of a decrease in adsorption sites. Some of the pores of PACMAG are already occupied by FeNPs and are not available for adsorption.



A)



B)

Figure 3.17: Concentration (A) of IBU at varying times of PACMAG exposure, Percent removal (B) of IBU at varying times of PACMAG exposure

Aside from IBU and other analgesics, another common drug present in most bodies of water are antibiotics such as sulfamethoxazole, trimethoprim, ciprofloxacin, erythromycin and many more (Baghapour et al, 2014). For this experiment, the antibiotic used was amoxicillin. The kinetics of AMOX in DW was conducted in order to determine the minimum amount of time at which PACMAG could adsorb a significant amount of AMOX (Figure 3.18). To make it comparable with the kinetics of IBU, the same amount of drug and of PACMAG in the previous experiments were used.

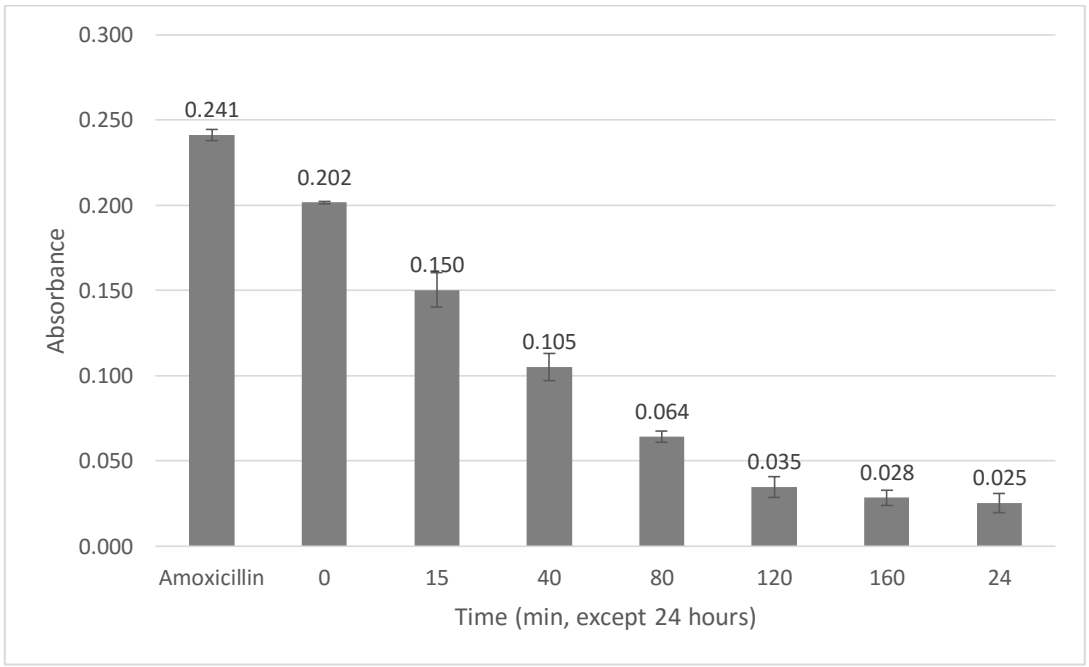
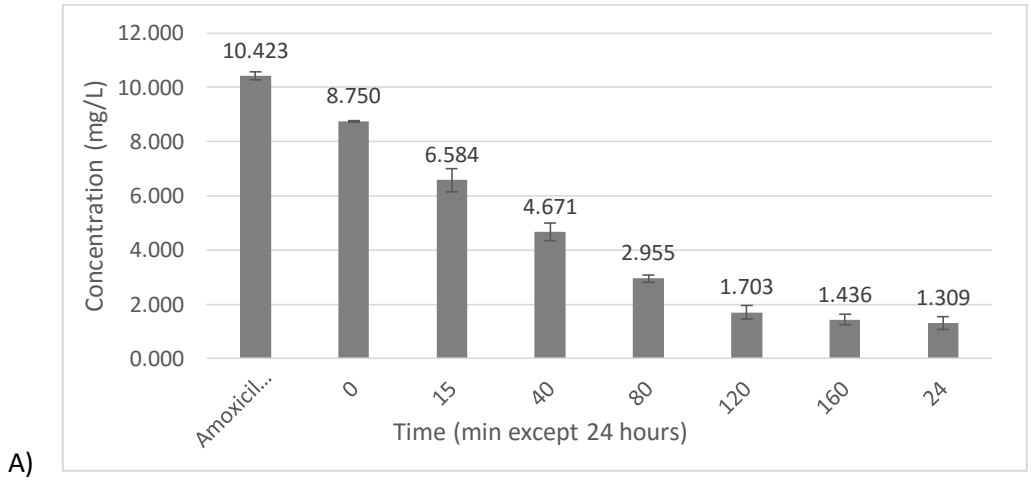
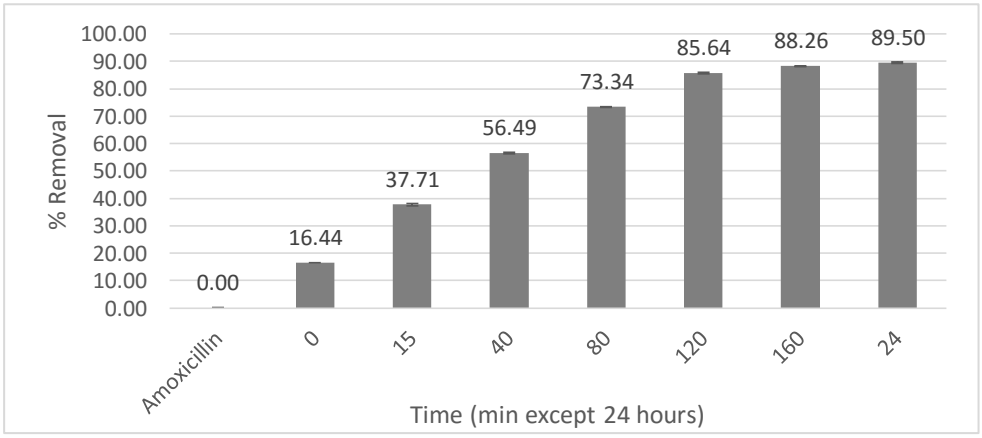


Figure 3.18: Absorbance of AMOX at varying times of PACMAG exposure

As in the case of IBU, PACMAG was able to adsorb AMOX effectively, decreasing the AMOX concentration from 10.4 ± 0.1 mg/L to 1.7 ± 0.3 mg/L in 2 hours (Figure 3.19 A). Also, there is a sudden decrease in AMOX concentration (1.673 mg/L) as soon as PACMAG is placed in the system. It is observed that for times of exposure beyond 120 minutes, the variation of the percent removal values was negligible (Figure 19 B). Similarly with the previous experiments, the adsorption capacity of PACMAG is slowly being reached because the sites of adsorption are limited. Although, the percent removal of IBU is greater than of AMOX, the general removal efficiency of PACMAG to both drugs are high.



A)



B)

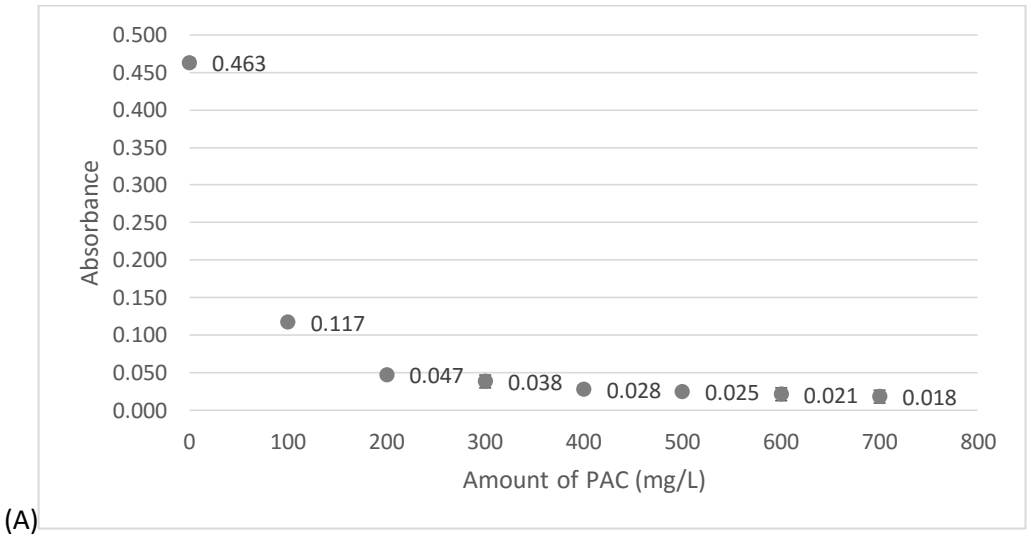
Figure 3.19: Concentration (A) of AMOX at varying times of PACMAG exposure, Percent removal (B) of AMOX at varying times of PACMAG exposure

3.5 Isotherms of PACMAG

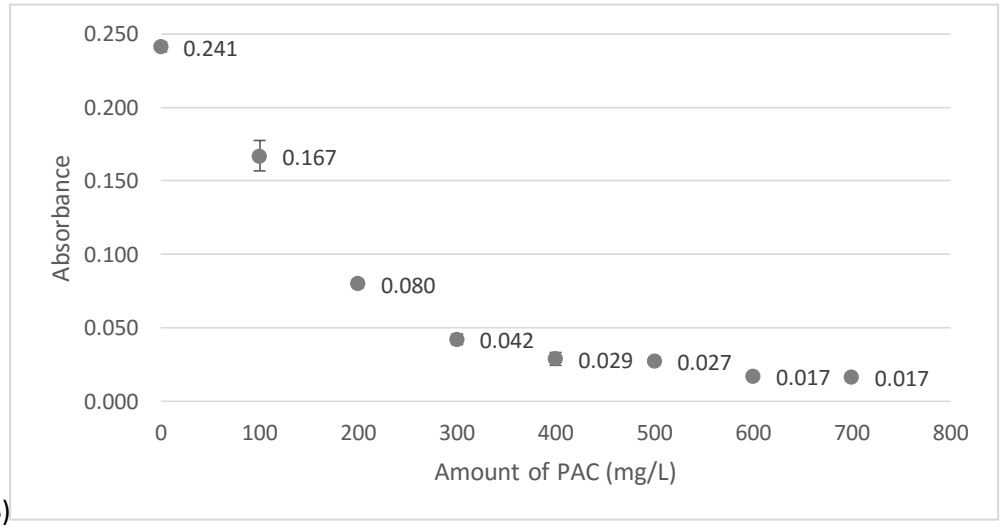
The isotherms for IBU and AMOX solutions were created by varying the amount of PACMAG and by varying the concentration of the drugs. The particles are exposed with the drugs for 120 minutes which is based on the previous experiments.

3.5.1 Varying Amounts of PACMAG

By varying the amount PACMAG, the PAC content also varies. Through this isotherm, one can determine the minimum amount of adsorbent that is needed to remove an acceptable yet sufficient amount of drug from a 10 mg/L starting concentration. By doing so, the material usage is maximized, leading to a more cost effective experiment.



(A)



(B)

Figure 3.20: Isotherm of the absorbance of (A) IBU and (B) AMOX at varying amounts of PAC content in PACMAG

Figure 3.20 shows that the increase in PACMAG increases the amount of IBU or AMOX removed because the increase in PAC content increases the adsorption sites that are available for adsorption. Similar with other figures, the graph flattens out at a specific quantity. In both graphs, beyond 300 mg/L, the difference in the absorbance measurements decreases. This is not caused by the lack of adsorption sites or the limited adsorption capacity of PACMAG. Rather, the amount of drugs that can be adsorbed by the adsorbent is limited. Because the concentration of IBU or AMOX in all set-ups are equal, the amount of PACMAG in a set-up outweighs the amount of drug that could be adsorbed. This is why even though the amount of PAC content is increased by 400 mg/L, from 300 to 700 mg/L, there is only a minimal increase, 4.39 ± 0.23 % (IBU) and 10.49 ± 0.18 % (AMOX), in the percent removal of the contaminant

(Figure 3.21 A and B). Taking into consideration the minimal amount of drugs removed versus the big amount of adsorbent used, 300 mg/L PAC content in PACMAG is the optimum amount of adsorbent that can be used for adsorption. It will be uneconomical to use more materials for a minimal difference.

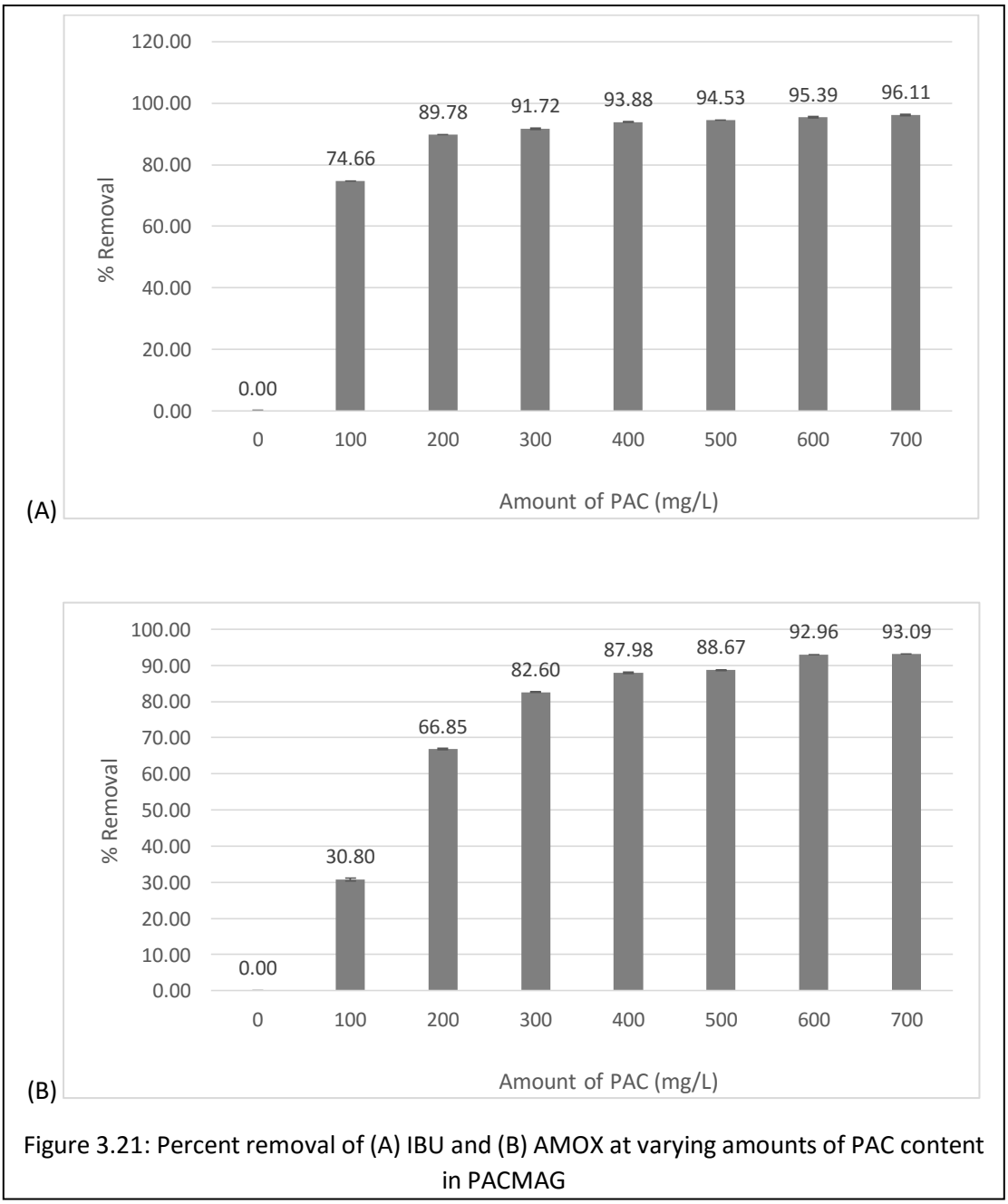


Figure 3.21: Percent removal of (A) IBU and (B) AMOX at varying amounts of PAC content in PACMAG

3.5.2 Varying Concentration of Drug

Using 300 mg/L PAC content, the maximum amount of IBU or AMOX that it can adsorb is determined. This is done by exposing varying concentrations of IBU or AMOX solutions to a

consistent amount of PACMAG. Determining the optimum amount of drugs is important because the adsorption capacity of the adsorbent is maximized. The initial drug concentrations ranges from 5 mg/L - 30 mg/L. Figure 3.22 A and B shows that the absorbance measurements of the IBU and AMOX samples after adsorption are low. The low absorbance trend is evident until 15 mg/L drug concentration.

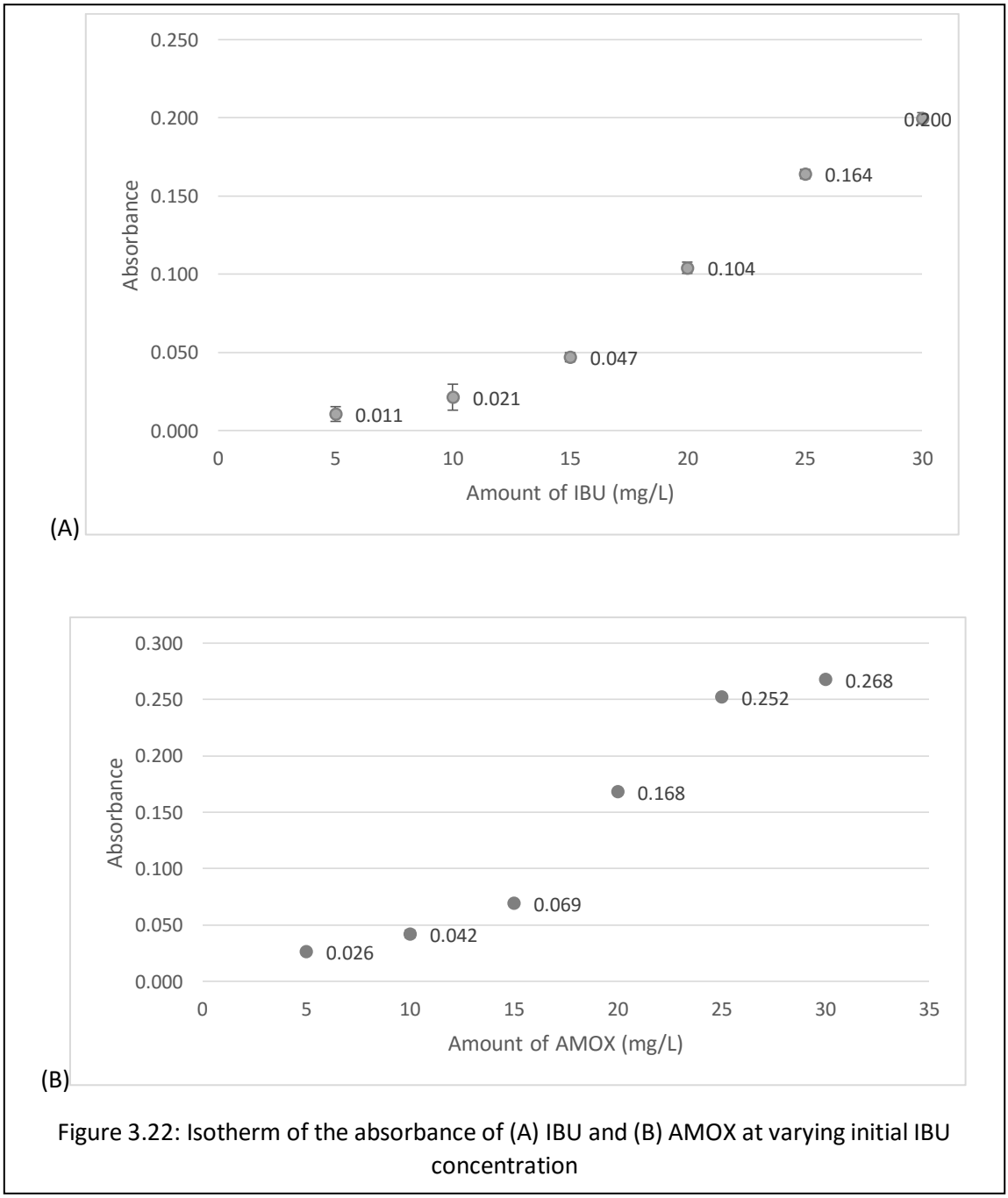


Figure 3.22: Isotherm of the absorbance of (A) IBU and (B) AMOX at varying initial IBU concentration

The absorbance measurements start to drastically increase after 15 mg/L IBU because the adsorption capacity of PACMAG is slowly being reached. Drug saturation occurs when the amount of PACMAG is insufficient to adsorb the drug present in solution. As a result, the

natural tendency is to leave some drugs unadsorbed causing an increase in absorbance value and a decrease in percent removal (Figure 3.23 A and B). It is evident that with only a 5 mg/L increase in drug concentration (15 mg/L to 20 mg/L), the percent removal drastically decreased by 6.19 ± 0.08 % (IBU) and 16.11 ± 0.05 % (AMOX). Unlike between 5 mg/L and 15 mg/L wherein the total difference is 3.60 ± 0.22 % (IBU) and 13.33 ± 0.16% (AMOX). Because of this, the optimum initial drug concentration that PACMAG (300 mg PAC content) can adsorb is 15 mg/L. Any drug concentration below it can be removed efficiently by PACMAG. While any concentration above it can cause a drastic decrease in percent removal.

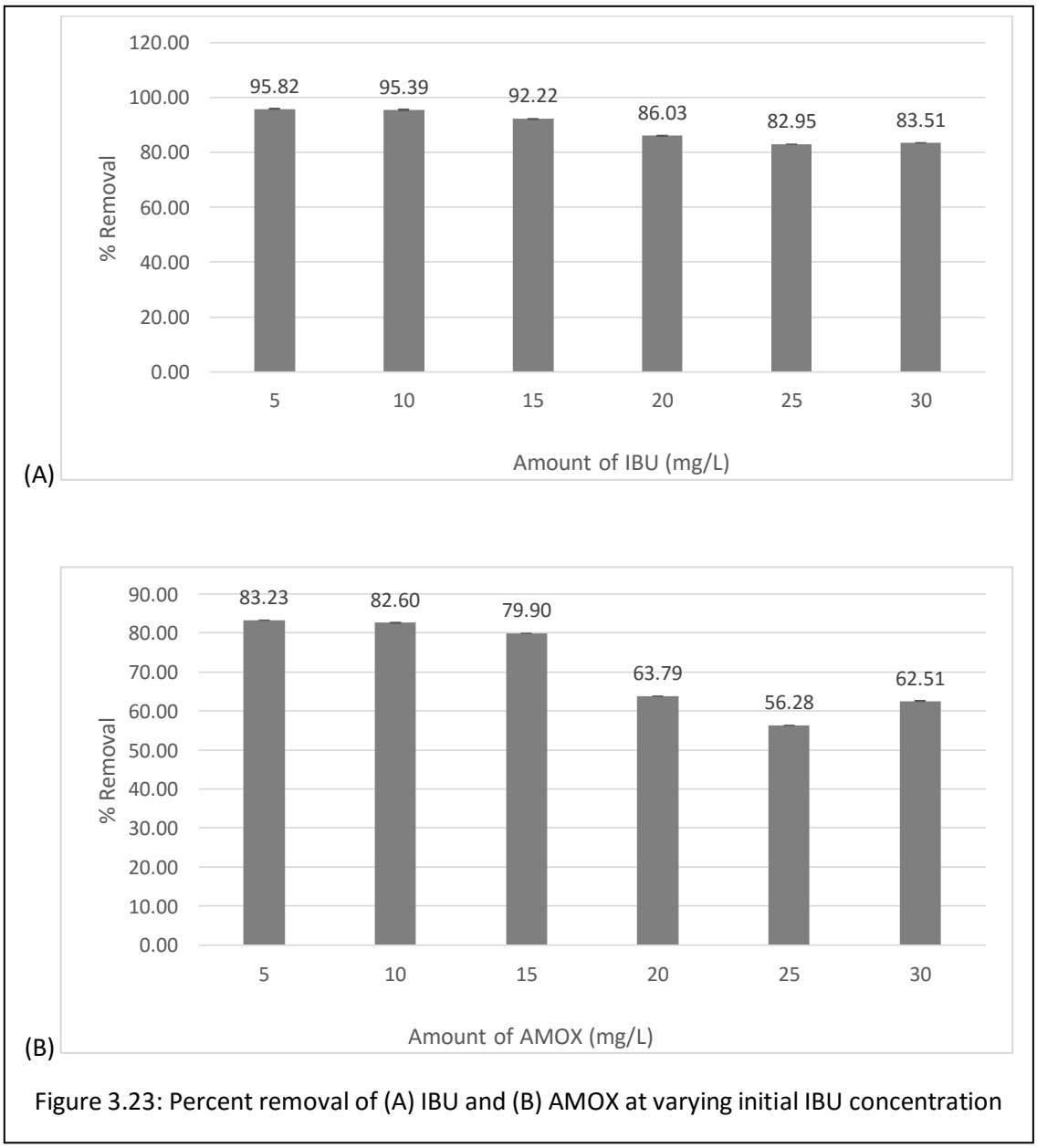


Figure 3.23: Percent removal of (A) IBU and (B) AMOX at varying initial IBU concentration

The slight percent removal decrease in the 25 mg/L AMOX concentration (Figure 3.23 B) is due to the presence of unremoved PACMAG in the sample which blocked the UV-Vis light beam causing it to be undetected by the machine.

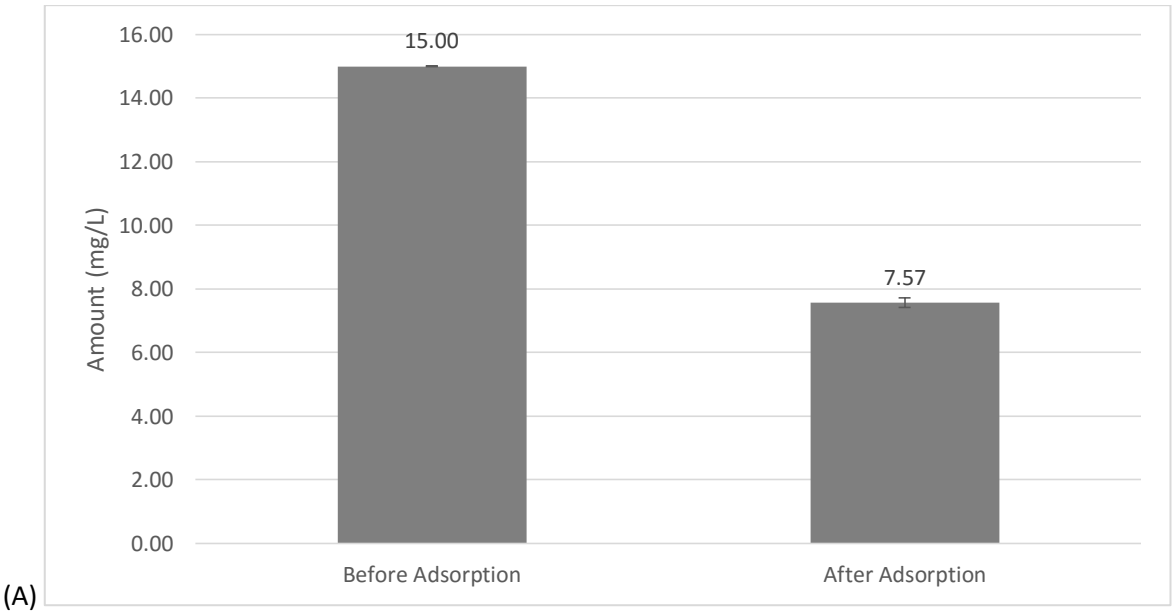
3.6 Adsorption of PACMAG in WW Spiked with Drug

The parameters from the kinetics and the two isotherm experiments of IBU and AMOX, namely 120 min of adsorption exposure, 300 mg/L PAC content in PACMAG, and 15 mg/L drug concentration, are used in the actual adsorption of WW spiked with either IBU or AMOX (IBU- WW, AMOX-WW). Unlike in the previous experiments where the drugs are mixed with DW, WW is more difficult to measure the amount of drug that PACMAG can adsorb. This is because the amount of contaminants within WW are unknown. Thus, the probability of competition between contaminants can occur and affect the adsorption capability of PACMAG. To control variations in the contaminants only a single batch of WW is used in the whole experiment.

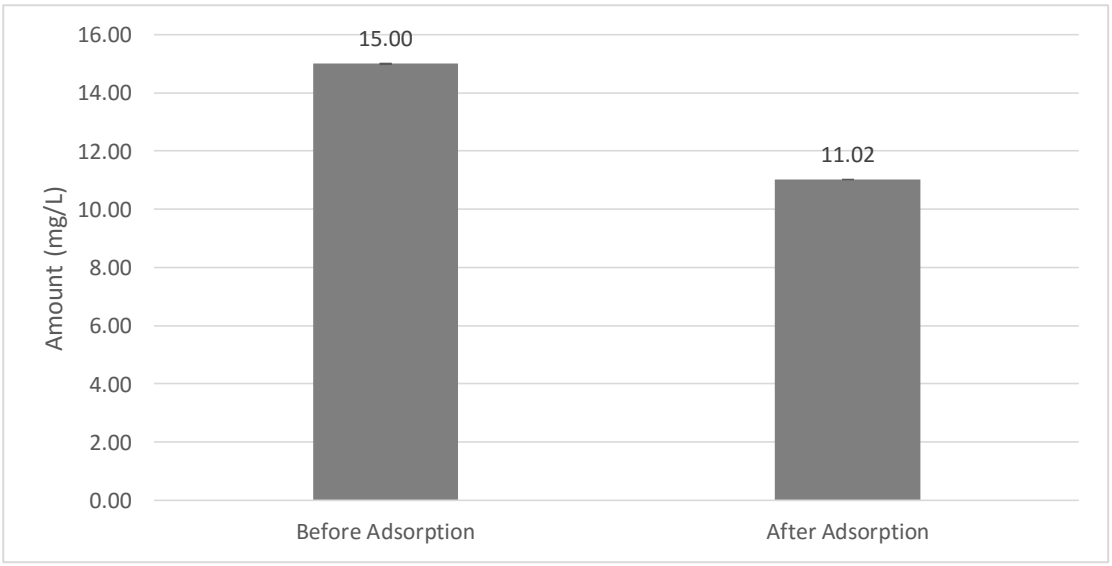
Figure 3.24 A and B shows the amount of drugs in the solution after being exposed with PACMAG for 2 hours. There is a 7.43 ± 0.15 mg/L (IBU) and 3.98 ± 0.01 mg/L (AMOX) decrease in the amount, resulting to a 49.52 ± 0.15% (IBU) and 26.54 ± 0.01% (AMOX) removal. The decrease in percent removal from 92.22 ± 0.08 % (IBU) and 79.90 ± 0.05% (AMOX) in DW is due to the presence of competing unknown contaminants in WW. It has been observed that some unknown contaminants in WW can adsorb at the same λ_{max} of IBU and AMOX. Because of this, it cannot be determined if all of the 49.52 ± 0.15% (IBU) and 26.54 ± 0.01% (AMOX) of contaminants removed are purely IBU and AMOX.

Comparing the adsorption of IBU and AMOX in both DW and WW water, it is evident that PACMAG has a higher percent removal in IBU than in AMOX. This is because certain penicillin-derived compounds such as AMOX are unstable in aqueous solution and behaves differently at varying pH conditions. Depending on the pH, AMOX exists in its zwitterionic form due to the dissociation of the carboxylic group and the protonation of the amine group in its molecular structure (Moradi, 2015). Because the surface of PAC which is the main material of PACMAG is negatively charged, there is a repulsive interaction that exists between the carboxylic group of AMOX and the surface of PACMAG (Mansouri et al, 2015). This limits the amount of AMOX that can be adsorbed. Unlike in IBU, which is a weaker electrolyte than AMOX, the neutral and the protonated form of IBU are more dominant in solution than its

negative form. Because of this, it is easier for IBU to attach on the surface of PACMAG (Mansouri et al, 2015).



(A)



(B)

Figure 3.24: Amount of (A) IBU and (B) AMOX in the drug- WW mixture before and after adsorption

3.7 Regeneration of PACMAG (Preliminary Test)

Because of the low removal of AMOX in WW, AMOX is chosen to be further optimized. AMOX is also used in the regeneration experiment of PACMAG to see if the PACMAG can be recycled. PACMAG has been regenerated by following an adaptation of the method first

described by Do et al (2011). The regeneration experiment makes use of the Fenton reaction wherein hydrogen peroxide (H_2O_2) is used to remove the adsorbed contaminants on the adsorbent with the assistance of a metal catalysts (FeNPs) (Do et al, 2011). The metal catalyst will generate a highly reactive hydroxyl radical (.OH) from the hydrogen peroxide (equation 3.10 and 3.11) (Barbusinski, 2009).

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + .OH + OH^- \qquad \text{Equation 3.10}$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + .OOH + H^+ \qquad \text{Equation 3.11}$$

The hydroxyl radical will react with the contaminants on the PACMAG. The reaction can either be through addition, hydrogen abstraction, electron transfer or radical interaction (Table 3.5).

Table 3.5: Four kinds of reactions by hydroxyl radical (.OH) with pollutants (Muranaka et al, 2010)

Reaction Type	**Example**
Addition	$.OH + C_6H_6 \rightarrow (OH)C_6H_6$
Hydrogen Abstraction	$OH + CH_3OH \rightarrow CH_2OH + H_2O$
Electron Transfer	$.OH + [Fe(CN)^6]^{4-} \rightarrow [Fe(CN)_6]^{3-} + OH^-$
Radical Interaction	$.OH + .OH \rightarrow H_2O_2$

Figure 3.25 compares the absorbance values of the AMOX- WW set-ups that are exposed to the new PACMAG and regenerated PACMAG adsorbent. For the 1000 mg/L PAC content, there is a 0.457 (new PACMAG) and a 0.311 (regenerated PACMAG) decrease in absorbance.

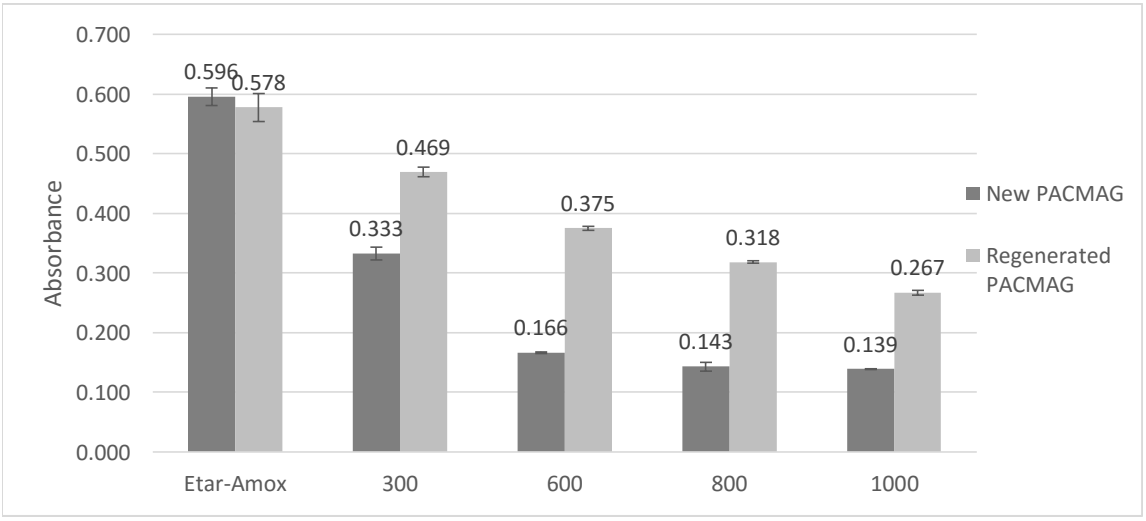


Figure 3.25: Comparison of absorbance of new PACMAG and regenerated PACMAG in the adsorption of AMOX in AMOX- wastewater

Figure 3.26 shows that by increasing the amount of PACMAG to 1000 mg/L PAC content, the percent removal of AMOX can be increased to 76.720 ± 0.001 % from a dismal 44.15 ± 0.01%. At the same time, the particles can be regenerated because the percent removal of the regenerated PACMAG is satisfactory (53.840 ± 0.004%) (Figure 3.26).

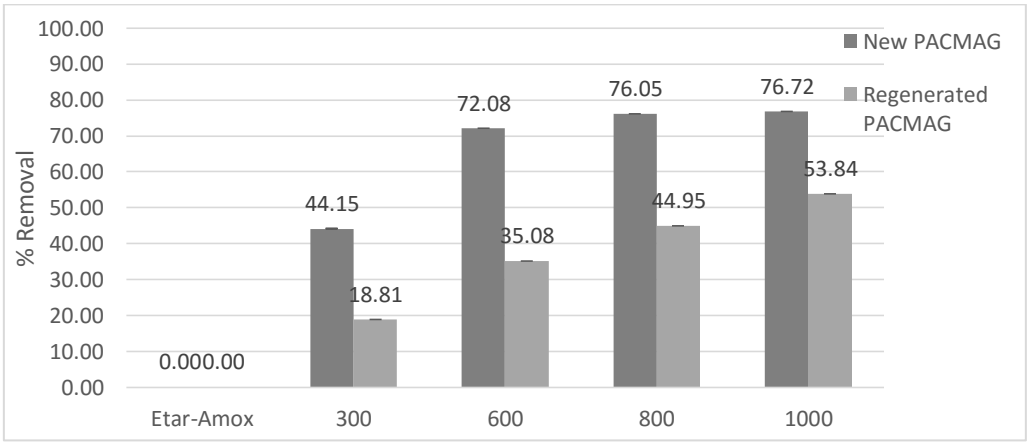


Figure 3.26: Comparison of the percent removal of PACMAG and regenerated PACMAG in the adsorption of AMOX in wastewater -AMOX

Aside from the absorbance and percent removal measurements, the total organic carbon (TOC) of the two adsorbents was measured as a confirmatory test. Figure 3.27 shows that the TOC values of the initial AMOX- WW mixtures are consistent, making them comparable. It can be seen that as the amount of PACMAG (new and regenerated) increases, the TOC concentration decreases because more adsorbent are present to adsorb the organic matter. Also, the higher TOC values of regenerated PACMAG coincides with the fact that it adsorbed a lesser amount of contaminant than the new PACMAG. The regenerated PACMAG have a lower adsorption capacity because its pores are previously occupied.

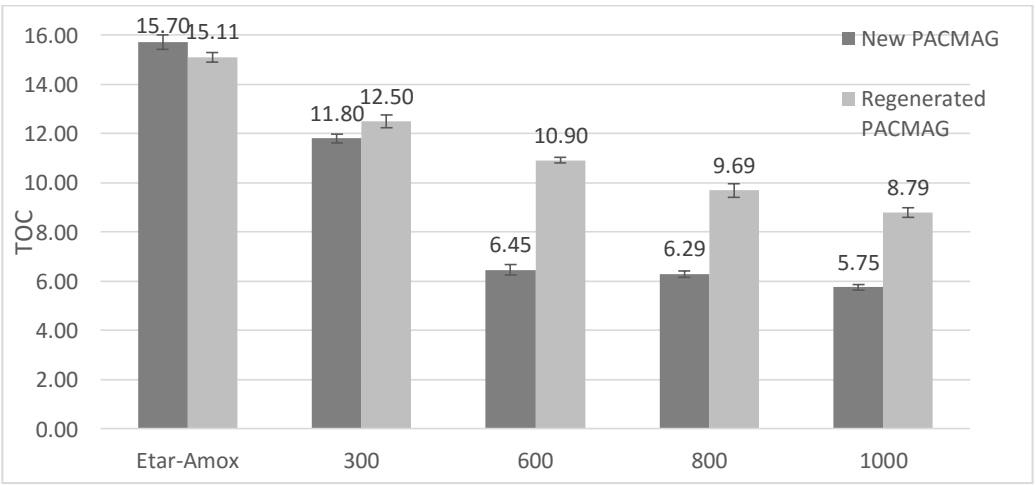


Figure 3.27: Comparison of the total organic carbon (TOC) concentration (ppm) of samples that were exposed to new PACMAG and regenerated PACMAG

3.8 Sedimentation Test of PACMAG

The sedimentation test was done to compare the rate of sedimentation of PACMAG in the presence and absence of a magnetic field. Because some of the pores of PACMAG are occupied by FeNPs, the adsorption capacity of PACMAG is lower than PAC. As such, it is necessary to determine if PACMAG can outperform the commonly used PAC in terms of the rate of sedimentation and time needed for separation. Because PAC takes a longer time to settle down, it cannot be separated from water immediately. Thus, WW treatment facilities tend to use an additional filtration step to remove the PAC. This is an added cost in terms of materials, effort, and time (Borghi and Fabbri, 2013).

The sedimentation experiment composed of 3 different set-ups: 5 min with the presence of a magnetic field, 5 minutes without the presence of a magnet, and 30 minutes without the presence of a magnet (Figure 3.28). Based on the graph, the efficiency of PACMAG in adsorbing IBU is very high because it almost removed most of the IBU in the solution.

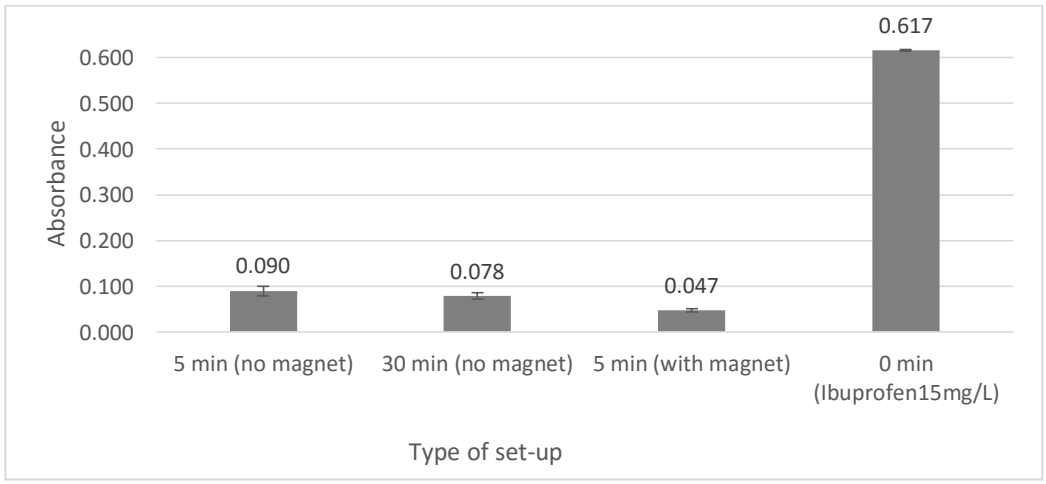
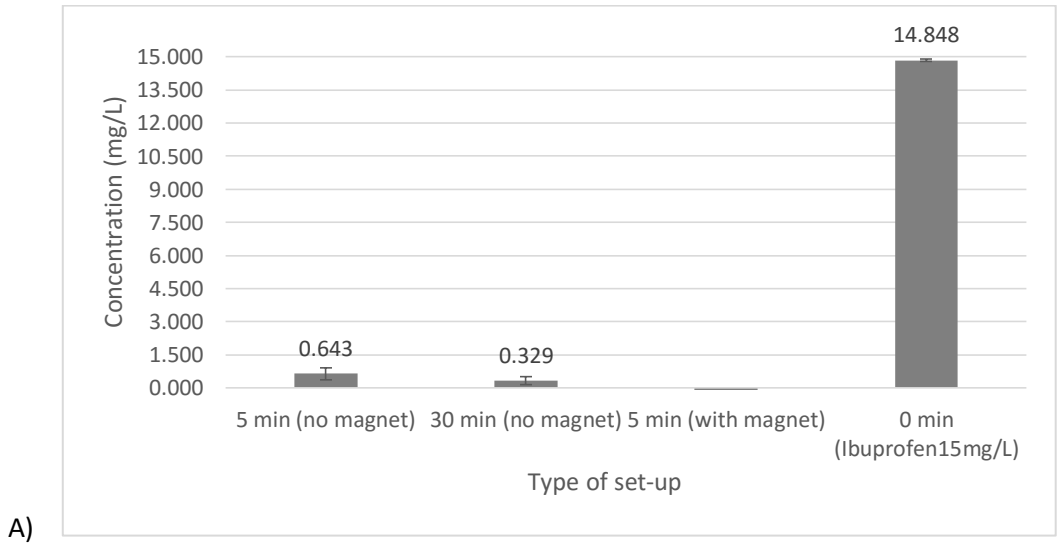
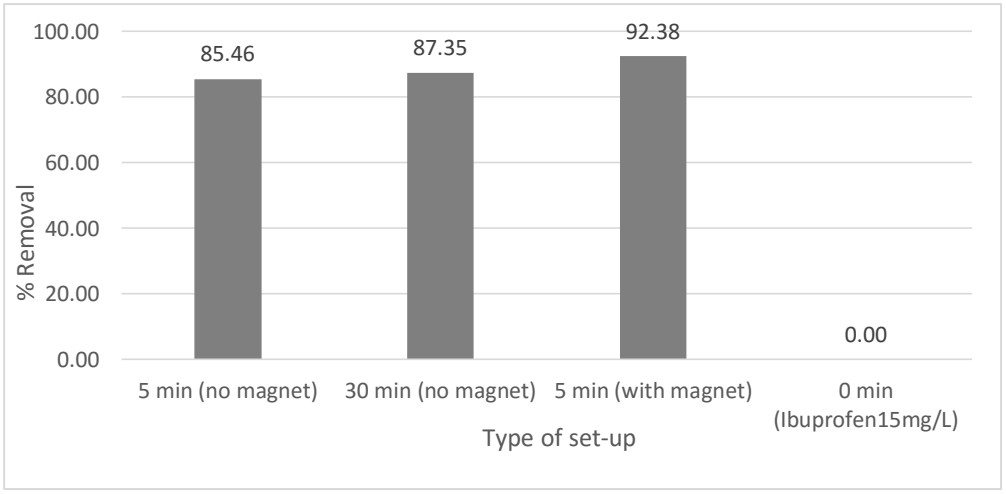


Figure 3.28: Absorbance of IBU in varying sedimentation set-ups

But among the three types of sedimentation set-ups, the set-up of 5 minute sedimentation in the presence of a magnet has the most favorable result, resulting to a negligible final IBU concentration and a 92.38 ± 0.16% removal (Figure 3.29 A and B). This is in accordance with the results obtained by Borghi and Fabbri (2013), where in at the presence of a magnetic field, the amount of contaminants in the samples were lower than those separated without a magnetic field.



A)



B)

Figure 3.29: Concentration (A) of IBU in varying sedimentation set-ups, Percent removal (B) of IBU in varying sedimentation set-ups

Figure 3.30 shows that at 5 minutes with a magnet, most of the PACMAG are already at the bottom of the beaker creating a non-turbid sample. This is supported by the study of Borghi and Fabbri (2013), wherein among the 3 separation techniques, magnetic separation is the least turbid because the adsorbent settled very fast (Figure 3.31).

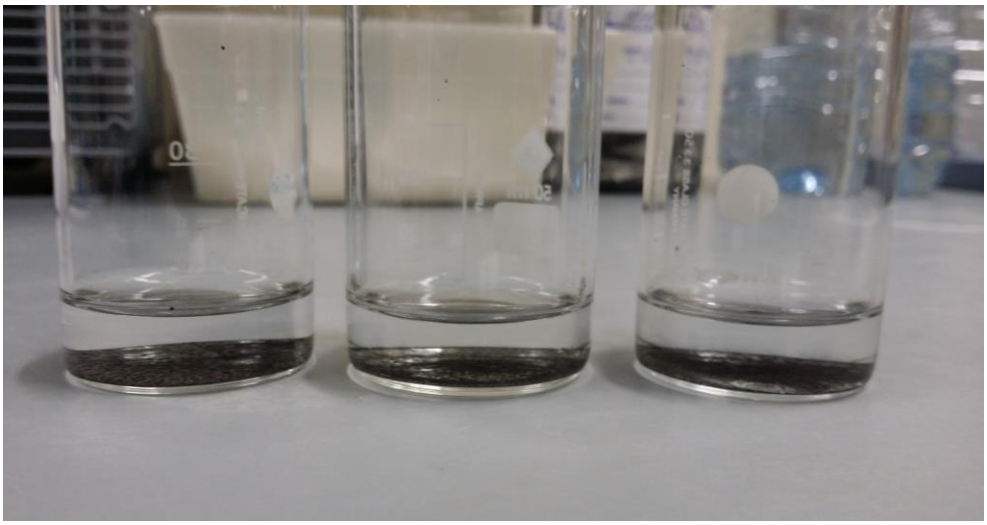


Figure 3.30: Trial 1-3 of the sedimentation of PACMAG with the presence of a magnet after 5 min

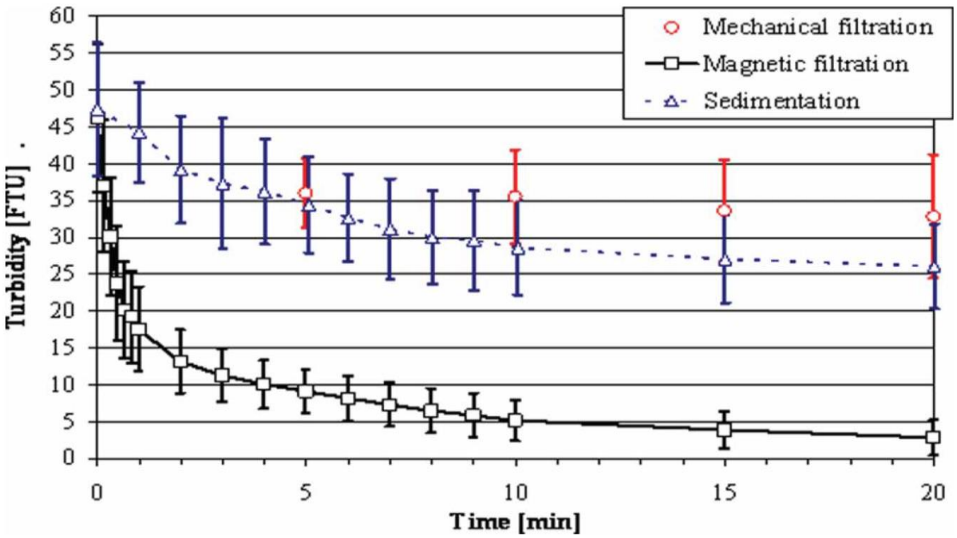


Figure 3.31: Turbidity of the different sedimentation set-ups as time passes (Borghi and Fabbri, 2013)

4 CONCLUSION & RECOMMENDATION

This work was done with an aim of developing a composite magnetic activated carbon adsorbent (PACMAG) which could remove model drugs (IBU, PAR, ASA, and AMOX) from deionized water and wastewater samples. Pharmaceutical drugs are an emerging concern because of their presence in the environment and the inadequacy of WWTPs in removing them. Based on the research done, PACMAG was a more efficient adsorbent than PAC and FeNPs because it had a high adsorption capacity, it could be magnetically separated and regenerated. All of which could minimize the overall water treatment cost.

Based on the objectives presented, the main conclusions of this research work are:

- The synthesis techniques performed in creating the FeNPs and PACMAG were very efficient producing quantitative yields. The synthesized adsorbents had the desired properties: positive ZP and size measurement for FeNPs, and adsorption capacity and magnetic property for PACMAG.
- IBU, PAR or ASA were adsorbed in low amounts by FeNPs, exhibiting a removal of 27.21 ± 0.14 %, 10.70 ± 0.02 % and 16.97 ± 0.05 % respectively. Having an aromatic ring in the molecular structure of the 3 drugs, they are partially insoluble in water. This limited the surface interaction with the adsorbent.
- In DW, PACMAG was able to adsorb the drugs efficiently producing 92.22 ± 0.08 % (IBU), 97.54 ± 0.01 % (PAR), 90.21 ± 0.01 % (ASA), and 79.90 ± 0.05 % (AMOX) removal.
- In WW, PACMAG was able to adsorb IBU and AMOX. But, inhibition by unknown contaminants present in WW was evident. This could have caused the removal to decrease to 49.52 ± 0.15 % and 26.54 ± 0.01 % for IBU and AMOX respectively. This could be optimized by increasing the PAC content to 1000 mg/L, resulting to a 76.720 ± 0.001% removal for AMOX.
- PACMAG with a 1000 mg/L PAC content could be regenerated. The regenerated PACMAG was able to remove 53.84 ± 0.004 % of contaminants. The decrease in removal between the regenerated and new PACMAG was caused by the incomplete oxidation of the contaminants that were previously attached on the surface of the adsorbent.
- PACMAG only required 5 minutes to settle when exposed to a magnetic field

Knowing the potential of PACMAG as an efficient adsorbent for common drugs like IBU, AMOX, PAR and ASA, this experiment can be further improved on by doing the following,

- Optimizing the regeneration experiments,
- Exploring the adsorption of other HPCs like drug metabolites, hormones and endocrine disruptors
- Using other metallic nanoparticles as composite material
- Using other forms of carbon like graphene

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