METAL-ORGANIC FRAMEWORK (MIL-53(Al)) FUNCTIONALIZED MAGNETIC NANOPARTICLES AS A SMART SOLUTION FOR THE REMOVAL OF ANTIBIOTICS

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MR. THILINA RAJEENDRE KATUGAMPALAGE

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE (ENGINEERING AND TECHNOLOGY)
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ENTITLED

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Thesis Title	METAL-ORGANIC FRAMEWORK (MIL-53(Al)) FUNCTIONALIZED MAGNETIC NANOPARTICLES AS A SMART SOLUTION FOR THE REMOVAL OF ANTIBIOTICS
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ABSTRACT

The presence of antibiotics in natural water and soil is causing considerable damage to the ecosystem and it is one of the emerging threats for both humans and animals. The tenacious existence of antibiotic residuals causes ubiquitous progressive environmental issues mainly by developing antimicrobial-resistant in humans and animals for some of the pathogens. Removing residual antibiotics and eradicating the sources of contamination is much needed for the sustainable development of mankind and the ecosystem around.

Multi-functional materials for the removal of antibiotics from waterbodies have fascinated many researchers due to the high demand. Unlike regular adsorbents, smart multifunctional materials can bring easy solutions to the emerging problem. Removal of antibiotics by an adsorbent can give an impermanent solution but leaving the adsorbent in water can be a cause for other substantial passive problems. Current work focused on developing a novel magnetic adsorbent (magnetic@MIL-53(Al)) to remove antibiotics such as oxytetracycline (OTC) present in natural water bodies by adsorption

and degrading them using magnetic induction heating. Surface grafting of metal-organic frameworks (MIL-53(Al)) on polyethylene glycol (PEG) coated magnetic nanoparticle was employed as the method of synthesis. Microwave mediated synthesis protocol was used in synthesizing magnetic nanoparticles. It was a rapid technique in synthesizing magnetic nanoparticles and able to maintain the particle size around 100 nm at all the batch synthesis reactions.

Growing MIL-53(Al) was done at room temperature and successful growth of MIL-53(Al) over magnetic nanoparticles was corroborated via powder diffraction patterns and FT-IR spectrums. Diffractions patterns of the synthesized magnetic@MIL-53(Al) material was similar to that of simulated MIL-53(Al) *ht* and *lt* forms. Thus, the use of an external magnetic field to control magnetic@MIL-53(Al) in aqueous systems makes the process much easier in large scale applications. The overall particle size of magnetic@MIL-53 was maintained to be around 100nm and superparamagnetic properties observed. The basic framework of MIL-53(Al) was maintained during the synthesis of Magnetic MIL-53(Al). The maximum adsorption capacity of the synthesized composite material was 776.5 mg g^{-1}. UV-vis spectroscopy was used to analyze the concentrations of simulated OTC solutions and results show that MNP(PEG)MIL-53(Al) is a suitable smart material for antibiotic adsorption.

Magnetic metal-organic particles were then regenerated several times to determine the reusability by subjecting the particles into magnetic induction heating. Core magnetic particles can be heated using a magnetic induction heater to produce high temperature around the particle to degrade heat-labile OTC molecules. The composite material was regenerated for 10 cycles and found that it can be used over 5 times with significant adsorption capacity.

Keywords: Magnetic Nanoparticles, MOF, Oxytetracycline, Magnetic induction heating

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Mr. Thilina Rajeendre Katugampalage

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LIST OF SYMBOLS/ABBREVIATIONS

Symbols/Abbreviations	Terms
ATR	Attenuated Total Reflectance
FTIR	Fourier-transform infrared spectroscopy
MIL	Matériaux de l'Institut Lavoisier
MNP	Magnetic Nanoparticles
MOF	Metal Organic Framework
MWCNT	Multi-walled carbon nanotubes
NaAC	Sodium Acetate
OTC	Oxytetracycline Hydrochloride
PEG	Polyethylene glycol
SEM	Scanning Electron Microscopy
TC	Tetracycline
TEM	Transmission Electron Microscopy
TGA	Thermogravimetric analysis
UIO	Universitetet i Oslo
VSM	Vibrating-sample magnetometer
XRD	X-ray powder diffraction
ZIF	Zeolitic imidazolate framework

CHAPTER 1
INTRODUCTION

1.1 Background

Antibiotic contaminated groundwater and soil is considered as a source of an emerging threat for both humans and animals due to the tenacious existence of antibiotic residuals in it. The presence of antibiotics in water and soil causes ubiquitous environmental issues due to the progressive development of anti-microbial resistance(Fernando Baquero, Martínez, & Cantón, 2008), especially for pathogenic microorganisms(F. Baquero, Martinez, & Canton, 2008). The use of mainstream broad-spectrum(Luis Campos, Garrido, Méndez, & Lema, 2001) antibiotics in treating aquaculture farms made an enormous impact on the environment by releasing water, contaminated with antibiotics to natural water bodies like rivers, lakes, and streams(Leal, Santos, & Esteves, 2019). Most of these antibiotics have a low degree of biodegradability; and toxic for many organisms including humans, live stocks, and domestic animals(Grenni, Ancona, & Barra Caracciolo, 2018). Tetracyclines are one of the broad-spectrum antibiotics used in various applications mainly in treating humans and animals including aquaculture(I. Chopra & M. Roberts, 2001). Beyond the applications of antibiotics, the lack of knowledge(Pham et al., 2015), availability of antibiotics, and overuse(Martin, Thottathil, & Newman, 2015) might be the hidden roots of this problem.

Removal of such harmful residuals from water is a challenging task that can make a huge impact on protecting the environment. Techniques like membrane separation(Derakhsheshpoor, Homayoonfal, Akbari, & Mehrnia, 2013), adsorption(Mousavi & Janjani, 2018), ozonation(Iakovides et al., 2019), biodegradation(B. Li & Zhang, 2010), and photodegradation(Yuan et al., 2011) had been developed to remove residual antibiotics from water. Oxytetracycline and several other common antibiotics were shown to be heat-labile(Hassani, Lázaro, Pérez, Condón, & Pagán, 2008), using efficient,

smart, and externally maneuverable adsorbents have a high demand to resolve this emerging threat innovatively. Substances that have capabilities in the removal of antibiotics by sorption and also have the accessibility to perform thermal degradation via non-conductive heating might be the easiest solution for the emerging problem.

1.2. Problem statement

Humans produce and consume enormous amount of antibiotics each year than they did the year before. Antibiotics have contributed to the world by serving for public health and curing diseases in livestock farms that might otherwise have killed them. But the antibiotics persists in the environment for a considerably long time after leaching out at the end of human and animal treatment processes. There are numerous problems caused by residual antibiotics present in water and other natural resources. One of the novel studies that measured about 91 rivers in the world including some of the major rivers like Thames, Mekong and Tigris to determine antibiotics present in them. The study reported that antibiotics were found nearly two-thirds of all the rivers.

Using adsorbents in removal of antibiotics is well-known but using them in large scale applications is a challenge. Dispersing adsorbents in water and collecting them back with adsorbed materials is not successful due to the smaller size of adsorbents. When the adsorbents were prepared in the form of larger particles, the adsorption efficiency decreases due to the low surface area. Dispersing nano-sized adsorbent material is an ideal way to effectively remove antibiotics from water. Functionalized magnetic nanoparticles have the ideal properties to overcome all these problems while it can be used as nano-sized particles. Moreover, magnetic induction heating can be deployed in thermal decomposition/degradation of organic drug molecules as an added advantage over conventional adsorbents.

1.3 Objectives of the study

Removal of antibiotics from water is necessary and challenging. It reduces the risk of antibiotic resistance and other problems associated with polluted water and soil. This

study provides a novel smart approach towards resolving the existing problems due to the presence of residual antibiotics in water. Magnetic nanoparticles are one of the key materials that can be synthesized using a simple protocol, which has extreme maneuverability. Metal-organic frameworks (MOFs) are proven to be one of the best materials in drug adsorption. The main purpose of this study is to surface modify magnetic nanoparticles with MOFs to obtain highly efficient and maneuverable material to be used in drug adsorption in water. Moreover, magnetic nanoparticles can be heated using a magnetic induction heating technique to degrade/destroy heat-labile drugs like oxytetracycline. Furthermore, magnetic MOF materials can be used in a wide range of applications and this study might open doors for many research fields which might help to achieve the goal of sustainable development in preserving natural water bodies and soil.

Following objectives are derived to obtain magnetically maneuverable metal-organic frameworks,

1. Microwave mediated solvothermal synthesis of bare magnetic nanoparticles (MNPs) and PEG-coated magnetic nanoparticles (MNP(PEG)) using ferric chloride, ethylene glycol, sodium acetate, and polyethylene glycol as initial materials. Characterization of synthesized materials by various physical techniques.
2. Surface functionalization of PEG-coated magnetic nanoparticle with MOFs and characterization of magnetic MOF to compare and determine the chemistry of pure MOFs with magnetic MOF using X-ray crystallography, FTIR and electron microscopy.
3. Study of drug adsorption capabilities of synthesized smart material and identify the drug adsorption mechanism.
4. Study about the reusability of magnetic MOF material by regenerating it using induction heating technique.

1.4 Scope of the study

The importance of smart materials in drug adsorption is well studied, and highly efficient materials have an enormous demand to be used in maintaining the sustainability of the environment from various industrial and large-scale applications.

Magnetic metal-organic framework (MNP(PEG)MIL-53(Al)) was synthesized using a simple two-step procedure and characterized. Using metal-organic frameworks in drug adsorption is common and well-studied by various researchers but the removal of the metal-organic framework after treatment was challenging. Also, leftover residual MOF nanoparticles can cause various other side effects for both humans and aquaculture. Nano-sized crystals are hard to filter using conventional filtration techniques and it becomes impossible in large scale applications. The scope of the study was to immobilize MOF crystals on a magnetic nanoparticle surface and make use of them while keeping them under control.

Therefore, nanosized magnetic nanoparticles were needed to be synthesized with average particle size around 100nm to obtain superparamagnetic properties in them. Conventional and microwave mediated solvothermal systems were employed in synthesizing magnetic nanoparticles and the outcome of both the techniques was studied. Surface grafting of polymeric material was carried out later to protect the magnetic core from oxidation. Growing MOF using metal ions and organic linkers was deployed at room temperature as a cost-effective simple grafting technique.

Surface chemistry, crystal structure, morphology, surface charge, thermogravimetric analysis, elemental analysis, and adsorption capacities were studied during the research using standard methods. The results were comparatively analyzed with published research articles. Synthesis and drug adsorption performance were studied and the study of other possible applications was not an objective of this study.

CHAPTER 2
REVIEW OF LITERATURE

The objective of this chapter is to elaborate relevant literature about problems related to residual antibiotics in water and the use of adsorbents in removing them. The importance of metal-organic frameworks in drug adsorption has been described in detail with drug adsorption mechanisms concerning different MOF structures. Furthermore, the use of smart materials in drug adsorption and current trends in drug adsorption also discussed in this chapter. There are various techniques developed in the degradation of drug molecules and magnetic induction heating has been described as one of the easiest techniques which can be used along with magnetic nanoparticles in degradation of heat-labile drug by generating hypothermia.

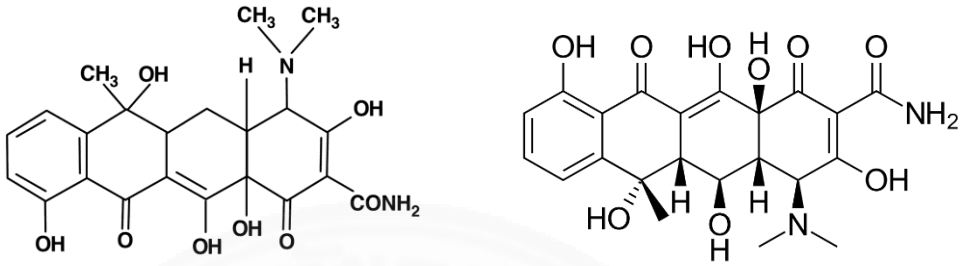
Antibiotics are used for medical purposes for both humans and animals, also they have been used as growth promoters in livestock farming. Tetracyclines, sulfonamides, penicillin, and macrolides are major classes of antibiotics that are used in livestock farming(Landers, Cohen, Wittum, & Larson, 2012; Tian, Khalil, & Bayen, 2017). Various types of food containing antibiotics such as seafood and meat have been consumed and these antibiotics caused many health issues. Antibiotics are administrated to animals typically through animal feed, and antibiotic-treated water is widely used in aquaculture farms. After harvesting livestock, the antibiotics might be released to the neighboring environment such as land and water. These residual antibiotics might get absorbed by other animals and human beings(Sarmah, Meyer, & Boxall, 2006) with their food and drinking water. Residual amounts of antibiotics are detected in various types of food including seafood, meat, milk, and eggs. This can cause various health issues in both humans and animals including anaphylaxis, mild allergies in hypersensitive individuals, and antibiotic resistance. Minnesota pollution control agency in the USA says “antibiotic resistance, one of our most serious health threats that cause at least 2 million illnesses in Americans each year, with 23,000 deaths”(Erickson, Langer, Roth, & Kroening, 2014) also this has become

an emerging public health issue of global concern. Due to the high demand in the meat and seafood industry, it is necessary to use antibiotics to control the spread of diseases among livestock. And preventing the release of antibiotics to the environment has become a challenge with large scale farming and extensive use of water in aquaculture. Using smart materials in capturing residual antibiotics from the environment might help to prevent this problem and smart-nanomaterials can play an important role in *in situ* adsorption and degradation of antibiotics.

2.1 Presence of antibiotics in water

Rapid innovations have developed a large number of antibiotics that benefits the modern way of living, also made a huge impact on it(Gothwal & Shashidhar, 2015). Antibiotics are well known to be used in treating and prevent infectious diseases in both humans and animals causing exponential growth of the market which has grown out of the bounds. Antibiotics can be defined as the chemotherapeutic agents that kill or inhibit the pathogenic microorganisms. Various types of antibiotics can be classified based on their chemical structure, route of administration, action spectrum, and the action mechanism(Etebu & Arikekpar, 2016). Most commonly antibiotics are classified based on their chemical structure named Beta-lactams, Tetracyclines, Quinolones, Macrolides, Aminoglycosides, Sulphonamides, Glycopeptides and Oxazolidinones(Adzitey, 2015; van Hoek et al., 2011). Tetracyclines are a broad-spectrum antibiotic used against a wide range of microorganisms including gram-positive and gram-negative bacteria, chlamydiae, mycoplasmas, rickettsiae, and protozoan parasites. They are extensively used in the prophylaxis and therapy of human & animal infections. Also, it has been given along with animal feed at subtherapeutic levels as growth promoters(Ian Chopra & Marilyn Roberts, 2001). Benjamin Duggar discovered tetracycline in 1945 using a soil bacterium (Streptomyces) and members of this class were named with the suffix '-cycline' due to the presence of four hydrocarbon rings (Figure 2.1). Members of this class of antibiotics are grouped based on the method of synthesis. First-generation antibiotics like Tetracycline, Chlortetecycline, Oxytetracycline, and Demeclocycline were obtained by biosynthesis,

antibiotic derivatives like Doxycycline, Lymecycline, Meclocycline, Methacycline, Minocycline, and Rolitetracycline which was obtained by semi-synthesis was considered as second generation. Third generation of this class was obtained from total synthesis such as Tigecycline.



(a) (b)

Figure 2.1 Chemical structure of Tetracycline(a) and Oxytetracycline(b)

2.2 Excessive use of oxytetracycline in livestock farming

Among all the types of tetracyclines, oxytetracycline (OTC) is one of the most used antibiotics in aquaculture(Leal et al., 2019). It is highly active and produced by a fermentation method with the use of *Streptomyces rimosus*. The cationic form of this drug was commercialized as oxytetracycline hydrochloride as a water-soluble product. Due to the expansion of intensive aquaculture, fish consumption has increased in recent years. The appearance of pathogenic microorganisms is one of the main problems in intensive aquaculture which leads to the administration of antibiotics like OTC into the water systems. Regardless of its wide usage, the minute number of data available on the amounts of used in aquaculture based on geometrical locations. Furthermore, available information about the usage of OTC is outdated, making it extremely difficult to find a solution to remove OTC from water. Oxytetracycline is administrated mainly for the treatment of fish bacterial diseases caused by *Aeromonas salmonicida, Aeromonas hydrophila, Pseudomonas, Lactococcus garvieae,* and *Vibrio anguillarum*(Sapkota et al., 2008). Dosage of the drug depends on several factors, for instance, type of disease, age type of aquaculture farm, and other favorable natural conditions. As an antibiotic that helps in treating diseases caused by both gram-negative and gram-positive bacteria; it is capable of

diffuse through pores in the cell membranes of gram-negative bacteria with the help of its hydrophilicity. Also, it acts as an inhibitor of protein synthesis by reacting with mRNA (messenger RNA) complex. Medicated feed, bath treatment, and injection are the most common drug administration techniques practiced widely in large scale fish farming. Mostly, OTC is unmetabolized or poorly metabolized in fish and unchanged drug molecules expelled into the water with urine and feces.

Oxytetracycline has characteristic pKa values at pK_{a1} < pH <3.57, pK_{a2} >7.49 and pK_{a3}>pH >8.9, making it cationic, zwitterionic and anionic respectively. The overall charge of the drug molecule becomes negative at higher pH values than pK_{a2} and it attracts to reactive species due to the higher electron density on the ring structure(Jiao, Zheng, Yin, Wang, & Chen, 2008). Zwitterionic characteristics exhibited between pH 3.57 to 7.49 might cause aggregation of drug molecules via intermolecular interactions(Leal et al., 2019).

2.3 Thermostability of oxytetracycline

Antibiotics are widely used in livestock farming as a therapeutic and growth-enhancing agent. Early studies were focused on destroying antibiotics in food by cooking them and subjecting them to extreme heat. Mostly the experiments were evaluated by studying microbial activity on food samples after heat treatment. This technique does not highlight the degradation kinetics about these antibiotics. The ultimate concern of these projects was to reduce residual amounts of antibiotics in food and it does not discuss the residual antibiotics present in the surrounding environment. Later, researchers could study the residual amounts of antibiotics with the help of chromatography techniques.

According to the study carried out by Mounir Hassani et.al about the thermostability of tetracyclines, the low temperature-long-time treatments (conventional sterilization) may degrade 98% of the initial concentration of doxycycline, tetracycline, and oxytetracycline to negligible amounts (theoretically <0.01%). Therefore, the most effective way of degrading tetracycline is conventional sterilization which was done at 121 °C for 20 minutes. Also, their study reported the effect of ultra-high temperature (UHT)

treatment of contaminated food samples which degraded the initial concentration of tetracyclines to 20-40%.

2.4 Conventional techniques used in the removal of oxytetracycline

Practical and efficient methods of removing tetracycline from water have become an important research focus. Various techniques have been researched in the removal of tetracyclines from water including coagulation(Choi, Kim, & Kim, 2008; W. Yang, Wu, Zhang, Jiang, & Feng, 2015), ozonation(Gomes, Costa, Quinta-Ferreira, & Martins, 2017; S. Li et al., 2015), photocatalytic degradation(Galedari, Mehdipour Ghazi, & Rashid Mirmasoomi, 2019; B. Gao et al., 2018), ion exchange(Q. Li et al., 2019; T. Wang et al., 2017), liquid membrane separation(Liu et al., 2017; Pan et al., 2015), reverse osmosis(W. Li, Wang, Xiao, & Dong, 2009), and adsorption(Y. Gao et al., 2012).

Coagulation technique can be used effectively in the removal of antibiotics and it has several advantages such as easy maintenance and operation, adjustable operating time, effective performance; but due to the chemical sludge management problems, the technique is restricted(Homem & Santos, 2011). Ozonation is also an effective technique in the removal of antibiotics and most other residual organic matter by strong oxidation. High consumption of electricity makes it an expensive technique and it has the potential in making toxic substances/by-products make in much more complicated in use for industrial applications(K. Li, Yediler, Yang, Schulte-Hostede, & Wong, 2008). Also, as a laboratory technique, photocatalytic oxidation is capable of removing residual antibiotics. Even though this technique provides faster reactions with substances, low-cost operations, and free from secondary by-products; it cannot be used in larger-scale applications due to narrow application range, complicated reactors, poor photocatalyst reusability, and high energy consumption(Belhouchet, Hamdi, Chenchouni, & Bessekhouad, 2019; B. Gao et al., 2018). Adsorption technique has taken the attention in removing tetracyclines due to its simplicity, ease of operation, high efficiency, relatively low cost, and no high toxicity by-products(Bangari & Sinha, 2019).

2.5 Metal-organic frameworks (MOFs)

Metal-organic frameworks (MOFs) are a group of compounds, either metal ions or clusters, coordinated with organic ligands to form one or multi-dimensional structures(Leus, Muylaert, Van Speybroeck, Marin, & Van Der Voort, 2010). The first research work on metal-organic frameworks was published in 1965 which attracted many of the scientists at the time(Czaja, Trukhan, & Müller, 2009). The basic structure metal-organic frameworks are constructed with metal oxo clusters connected by organic ligands: a metal ion or cluster of metal ions and an organic chelating linker connecting two metal components.

Metal-organic frameworks are usually porous and have a high surface area(Cook, Zheng, & Stang, 2013; "Introduction to Metal–Organic Frameworks," 2012; Xuan, Zhu, Liu, & Cui, 2012). The pore size varies a few nanometers(Verma, Baig, Nadagouda, & Varma, 2017; Zhou & Kitagawa, 2014) making it a perfect substance mainly for adsorption and separation(Ahmed & Jhung, 2014; Burtch, Jasuja, & Walton, 2014; Haohan Wu, Gong, Olson, & Li, 2012). High surface area and porous nature made MOFs a useful material for storage, separation, or conversion of molecules based on the dimension. Commonly, MOFs are similar to the co-ordination polymers but with more specific 2D/3D crystalline networks with pores in the structure. Thus, metal-organic frameworks (MOFs) also called porous coordination polymers. Recent achievements in the field of metal-organic frameworks have synthesized more complex MOFs with nano and mesoscale(Furukawa, Reboul, Diring, Sumida, & Kitagawa, 2014) with enhancing properties.

2.5.1 Primary building units of metal-organic frameworks

The porous 3D structure of metal-organic frameworks is composed of linking metal ions(connectors) with organic polymer ligands. Thus, the organic ligands and metal ions are the primary building units in the formation of metal-organic frameworks. Alkaline-earth metal ions(Platero Prats et al., 2010; L. M. Yang, Vajeeston, Ravindran, Fjellvåg, & Tilset, 2011), alkali metal ions(Soni, Bajpai, & Arora, 2018), first-row transition metal ions(Nguyen et al., 2019; Hui Wu, Zhou, & Yildirim, 2009) and rare earth metal ions(Serre,

Millange, Marrot, & Férey, 2002) are used as metal connectors in the synthesis of metal-organic frameworks. Metal ion precursors are used in the form of nitrates, acetates, sulfates, chlorides, and oxides for the preparation of MOFs in most of the synthesis routes. Metal ions or nodes of the structure are connected by organic linkers generally contain functional groups like carboxylates, phosphates, amines, sulfonates, and nitriles that are capable of forming coordination bonds (Figure 2.2). For the formation of crystal structure of the framework the organic ligands have minimum two or more functional groups.

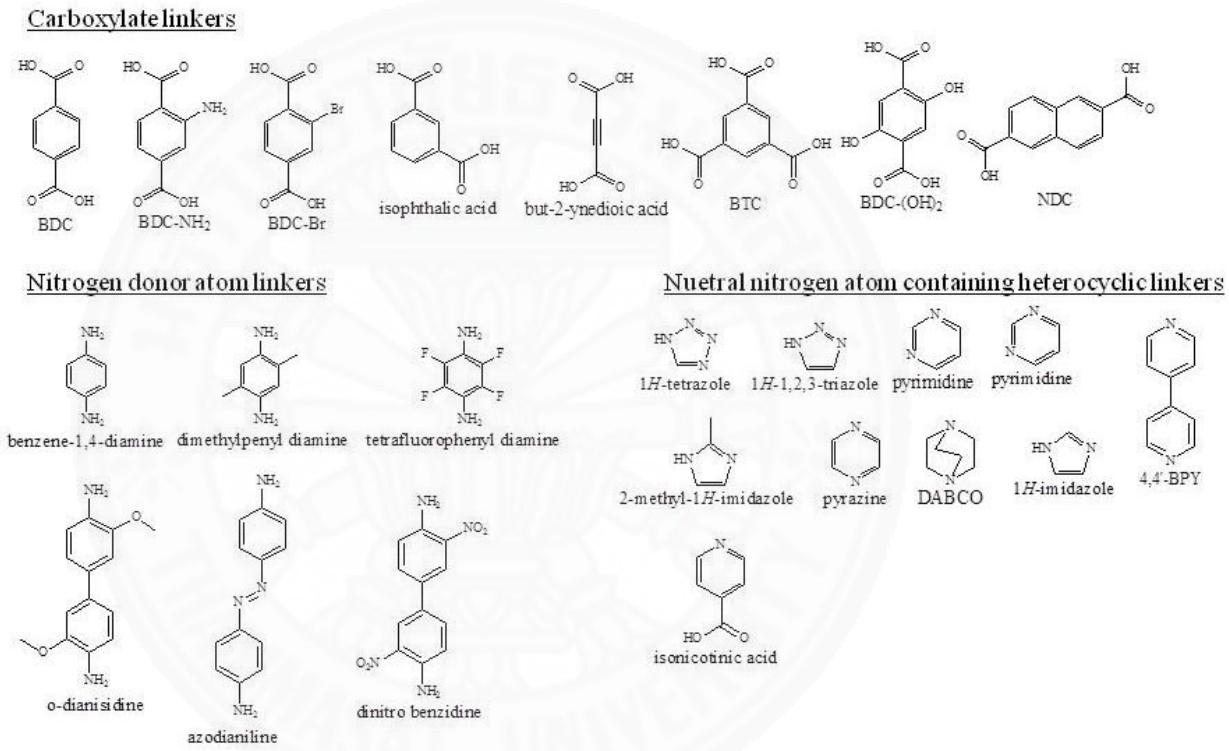


Figure 2.2: Some organic linkers used in the synthesis of MOFs(Soni et al., 2018)

2.6 Adsorption of organic substances by metal-organic frameworks

2.6.1 Overview of metal-organic frameworks on adsorbing organic substances

Porous materials and their applications have increasing attention and significant progress has been made by synthesizing various types of materials. Metal-organic frameworks (MOFs) are one of the promising materials that have been developed during the last few decades. MOFs have taken the attention of researchers due to their high porosity, surface properties, and miscellaneous functionalities, large surface area, tailor-made pore structure, and diverse topology especially to be used in many applications. Compared with activated carbons, zeolites, or other porous materials, many MOFs possess a wide range of window opening/pore cavity and different functionalities, which enable them to accept several types of compounds inside their cavities. MOFs has shown promising applications in a variety of fields, such as gas separation and storage(J.-R. Li, Kuppler, & Zhou, 2009; Murray, Dincă, & Long, 2009), nanocarriers in drug delivery(Al Haydar, Abid, Sunderland, & Wang, 2017), catalysis, luminescence(Allendorf, Bauer, Bhakta, & Houk, 2009), and they offer tremendous potential in adsorbing organic pollutants by adsorption(Kostakis & Tibbetts, 2020; Nguyen et al., 2019; K. Yang, Xue, Sun, Yue, & Lin, 2013; Zha, Yin, Baltzegar, & Zhang, 2019). Several types of MOFs such as UiO-67(Zr)(Zhu et al., 2015), MOF-235(Haque, Jun, & Jhung, 2011), MIL-101(Cr)(Hu et al., 2017b), MOF-74(Abedini, Shariati, & Khosravi-Nikou, 2020), MIL-53(Fe)(Yılmaz, Sert, & Atalay, 2016), ZIF-8, and MIL-53(Al)(Amirilargani et al., 2019; Isaeva et al., 2019; Patil et al., 2011; Saifutdinov, Isaeva, Alexandrov, & Kustov, 2015; M. Wang, Zhang, Zhou, & Chen, 2016) have been employed for the removal of organic pollutants from aqueous atmospheres.

Xiangyang Z. et.al has used zirconium-based UIO-67(Zr) was used for effective adsorption and enhanced removal of organophosphorus pesticides from water(Zhu et al., 2015). Enamul H. et.al has used MOF-235 in removing methyl orange and methylene blue from the water via adsorption. Moreover, they have reported that ion terephthalate can adsorb a very large amount of methyl orange and methylene blue. The work concludes by saying the metal-organic frameworks can be used in the removal of dye materials even if

they do not adsorb gases(Haque et al., 2011). Based on the study conducted by Tianding H. et.al the antibiotic, oxytetracycline can be adsorbed from water by using amino-functionalized MIL-101(Cr). Furthermore, they have studied the regeneration capabilities of MOF by washing them with hydrochloric acid with several successful regeneration cycles. The overall study deliberates about the functionalization and regeneration of MOF materials(Hu et al., 2017b).

The metal-organic frameworks designated as MIL-*n* (Materials of Institute Lavoisier) are mostly used for gas adsorption studies. Among these materials, a conspicuous characteristic of MIL-53(Al) is its extraordinary thermal stability up to 500 °C compared to the other MIL materials, which are stable below 400 °C. Furthermore, the cell volume of MIL-53(Al or Cr) can adjust reversibly to optimize the interactions between adsorbate and framework with no evidence of bond breaking. The study carried out by Dinesh V. et. al concludes saying, MIL-53(Al) is an appropriate adsorbent in the removal of nitrobenzene from the aqueous solutions(Patil et al., 2011).

The study carried out by Mohammad A. et. al demonstrates that NH_2-MIL-53(Al) modified α-alumina membranes can be used in adsorbing organic dyes from organic solvents. The MIL-53(Al) and NH_2-MIL53(Al) modified membranes show high adsorption and easy release of bound Rose Bengal dye and high methanol solvent permeability(Amirilargani et al., 2019).

Adsorption of 2,4-dichlorophenoxyacetic acid from aqueous solution is also an important study done by Vera I. et. al. The study shows that microwave-assisted synthesized MIL-53(Al) has a high adsorption capability of 2,4-dichlorophenoxyacetic acid over 300 mg g^{-1}. Also, the study has discussed on physiochemical characteristics of synthesized MIL-53(Al)(Isaeva et al., 2019).

The study on “selective adsorption of aromatic compounds from solutions by the flexible MIL-53(Al)” explains about the adsorption activity of the aromatic compounds under the liquid phase conditions. Moreover, the research explains that the adsorption occurred due to the possible expansion of flexible channels and cavities in the structure by

breathing effect triggered by temperature variation. The selective adsorption of organic compounds shown by MIL-53(Al) is due to the π-π interactions of adsorbate-adsorbent and hydrogen bonding between them. Furthermore, the Bronsted acid sites of the MOF facilitate to develop hydrogen bonds with the adsorbate(Saifutdinov et al., 2015).

Adsorbing dichloromethane and trichloromethane using activated MIL-53(Al) was also an interesting study, carried out by Mingyang W. et.al. The study focusses on activating MIL-53(Al) by removing the trapped, unreacted ligand and solvents from the molecule to produce pure MIL-53(Al) with emptied pores. Furthermore, the adsorption experiment showed that MIL-53(Al) synthesized by the work had a higher dichloromethane vapor adsorption capacity and it is higher than that of traditional activation carbon. The activation of MIL-53(Al) was done by three main techniques. They are, immersing samples in methanol for 10 hours, heating the samples from room temperature to 603K with a heating rate of 60K/h, and combining the above two methods which are solvent extraction followed by heating(M. Wang et al., 2016).

The published research study proves that MIL-53(Al) is a promising adsorbent material in adsorbing organic substances from both aqueous and solvent mediums. Also, the material is highly stable even at elevated temperatures when compared with other conventional adsorbents. MIL-53(Al) is a flawless adsorbent material for adsorbing organic drug molecules from aqueous mediums.

2.6.2 Adsorption of oxytetracycline by metal-organic frameworks

The work carried out using MIL-101 in adsorption of OTC was successful with an adsorption capacity of 115.34 mg g^{-1}. Hydrochloric acid and hydrofluoric acid has been used as two different mineralizers during the synthesis. Structural changes of MIL-101 has been studied considering the influences of HCl and HF. The MIL-101(HCl) which has high crystallinity over MIL-101(HF) has demonstrated good adsorption capabilities with remarkably fast OTC adsorption. The adsorption of OTC onto MIL-101(HCL) occurs mainly by π-π interactions and acid-alkaline interactions(Hu et al., 2016).

ZIF-8 also was used as an adsorbent for tetracyclines dissolved in water, mainly to remove OTC. ZOF-8 (Zeolite Imidazole Framework-8) has been synthesized using $Zn(NO_3)_2.6H_2O$ and 2-methylimidazole ($C_4H_6N_2$) dissolving each in methanol and mixing thoroughly at room temperature. After the material characterization, adsorption studies have been carried out using tetracycline (TC) and oxytetracycline (OTC). The adsorption kinetics was reported as pseudo-second-order and adsorption isotherm studies demonstrated that the adsorption capacity of ZIF-8 for TC is about 303.0 mg g^{-1} and 312.5 mg g^{-1} for OTC. The reported adsorption of OTC and TC onto ZIF-8 is spontaneous and endothermic which was driven by entropy. The mechanism of adsorption has occurred mainly by π-π interactions. Furthermore, ZIF-8 was more efficient at lower concentrations of tetracyclines and that makes it an interesting material(N. Li, Zhou, Jin, Owens, & Chen, 2019).

The use of metal-organic frameworks incorporated composite materials also shows promising properties especially when they are fused with 2D layer materials. Multiwalled carbon nanotubes were successfully incorporated with MIL-53(Fe) and used in adsorb different tetracyclines from aqueous solutions. The study reported that the adsorption capacity of composite materials is much higher than their original forms which are MWCNTs and MIL-53(Fe). Even in this study, the adsorption mechanism was explained as π-π adsorbate-adsorbent interactions. Furthermore, the study reported that the adsorption mechanisms were attributed to pore/size-selective adsorption and influence by ions of the metal-organic framework. The adsorption capacity was reported as 352.59 mg g^{-1} where the adsorption isotherms were better fitted with the Langmuir model. (Xiong et al., 2018)

Table 2.1 Metal-organic frameworks in OTC adsorption from aqueous solutions

	Material	Adsorption capacity (mg g^{-1})	Reference
1	MIL-101	123.3	(Hu et al., 2016)
2	ZIF-8	312.50	(N. Li et al., 2019)
3	MWCNT/MIL-53(Fe)	325.59	(Xiong et al., 2018)

Numerous types of metal-organic frameworks have been deployed in adsorbing various types of organic substances from aqueous solutions but the recovery of adsorbents remains challenging. Ultra-small MOF crystals are difficult to recover from aqueous solutions after adsorption and using them as larger beads might reduce efficiency. Furthermore, the removal of antibiotics should not harm the environment by discharging MOF substances into nature. The maneuverability of small particles of MOFs in aqueous solutions can improve its applications. Using MOF/MNP composites can provide magnetic properties into the adsorbents that can be used in recovery and solvent-free regenerating process.

2.7 Induction Heating of Magnetic Nanoparticles

Since tetracycline is widely used in the prevention and treatment of infectious diseases, residual amounts are commonly detected in food. Thermo stability of these antibiotics is well studied and boiling food for more than 30 minutes was widely practiced in degrading these antibiotics. It is a practically and economically challenging task to remove antibiotics from polluted water and boiling a large amount of water before releasing it to the environment. The use of adsorbents in the removal of antibiotics makes it easier and effective in large scale applications. Remotely controllable smart adsorbents play an important role in collecting and condensing antibiotics from large pools of water and degrading them by techniques like magnetic induction heating.

As a convenient and flexible method, induction heating can increase the local temperature of a magnetic nanoparticle by delivering high-strength magnetic fields. This technique has gained considerable interest in the biomedical field. Magnetic nanoparticles can transform electromagnetic energy to heat upon the excitation with an AC field and the heat generated can be utilized in applications like degradation of organic substances, destroying cancer cells, etc. Three mechanisms explain the incidence of magnetic hyperthermia. They are,

(1) Eddy current heating due to the effects of induction from the application of an alternating pulsed magnetic field

(2) Relaxation and hysteretic losses of the magnetic NPs

(3) Frictional heating induced by the interaction between the NPS and the surrounding medium,

Among these principles, induction heating generates heat in magnetic nanoparticles mainly by eddy current loss and hysteretic losses. Microscopic eddy currents originate from the interactions between the walls of the magnetic domains and the microstructure during the magnetization of the sample(Xiang et al., 2019).

Magnetic nanoparticles, which possess several unique characteristics including biocompatibility and superparamagnetic properties, are widely applied in the biomedical field and several other industrial applications. They can be rapidly heated upon exposure to an AC magnetic field and, unlike conventional heating techniques, the heat generated by induction heating is uniformly spread through the material(Etheridge et al., 2014; Schildkopf et al., 2010). High-frequency induction heating does not involve any physical contact due to the internal generation of heat within the microscopic magnetic nanoparticle. The movement of current inside the coil produces a very strong, and fast varying magnetic field around the coil. This magnetic field generates a flow of current in the magnetic nanoparticles. The combination of the coil and magnetic nanoparticles works as a transformer, where the coil works as the primary being fed with electrical energy and magnetic nanoparticles work as the secondary. The current flow through magnetic nanoparticles is called eddy currents in this phenomenon.

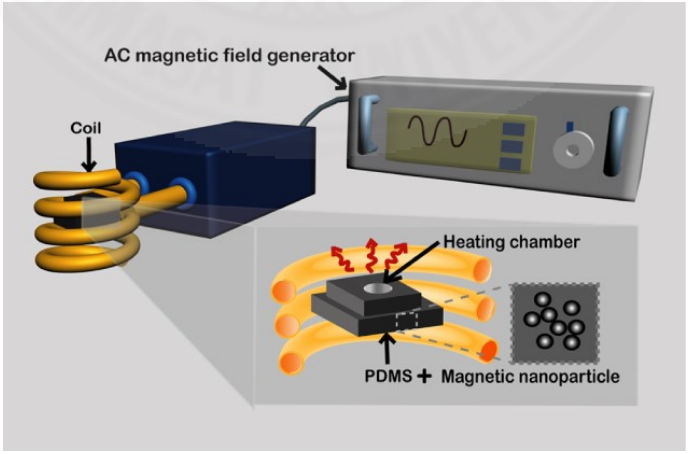


Figure 2.3 Schematic drawing of induction heating based on the magnetic nanoparticles

Induction heating can be controlled by influencing the frequency of the electrical current supplied. Considering the physical and chemical properties like dimension, type of material, the desired depth of penetration, the desired frequency range can be determined. The penetration of heat can be changed with the changes of the electric frequency in the primary coil. As the frequency is increased, the penetration of heat is decreased. Low-frequency induction heating is suitable for larger objects which ranges from 500 Hz to 10 kHz, while high-frequency induction heating ranging from 100kHz to 2MHz is suitable for smaller microscopic materials. Frequencies above 100 kHz create comparatively high energy heat that is suitable for the rapid heating of smaller objects or the surface of the larger materials. Extensive cycles of heating at low frequency are required when deeper penetration of heat is required. The most transfer of energy during the process of induction heating is at high frequency when the depth of current penetration is low.

2.8 Magnetic metal-organic framework composites

Magnetic nanoparticle arbitrated applications have gained substantial attention due to its compatibility, rapidity, high selectivity, and especially the maneuverability of nanoparticles using an external magnetic field(Lohe et al., 2011). Particularly, the high selective properties arise in magnetic separation applications mainly when it is used as a complex composite material(Aguilar-Arteaga, Rodriguez, & Barrado, 2010). Mostly in the field of separation studies, functionalized magnetic nanoparticles with several groups are used for the isolation and preconcentration of analytes(Huo & Yan, 2012; X.-l. Zhang, Niu, Li, Shi, & Cai, 2011). Furthermore, considering the unique properties of metal-organic frameworks, functionalizing magnetic nanoparticles with MOFs can provide interesting and significant materials for many applications. Using pure metal-organic frameworks in aqueous systems for adsorption might lead to several other problems when it has to be removed from aqueous solutions and it might be left in the water as another organic pollutant even though MOFs are good adsorbents. Combining high porous adsorbent with highly maneuverable magnetic nanoparticles can provide composite materials that have

both the magnetic properties along with the properties of MOFs. Various approaches have been developed to stabilize magnetic nanoparticles with MOFs. Considering the synthesis of MNP/MOF can be classified into four main approaches. They are,

1. Introducing MOF into a solution with a metal precursor to synthesize MNPs within the MOF or outer surface of MOF. Also, solid-state mixing of MOF with metal precursors can be categorized under this.
2. Introducing a dispersion of magnetic nanoparticles into a MOF synthesis reaction solution to obtain the outer surface of MNPs incorporated with MOFs. The compatibility of reactants is well-thought-out in these types of reactions and the solvent mixing sequence should be considered to obtain a particle with a core magnetic material.
3. Step-by-step synthetic processes of magnetic nanoparticles and MOFs to obtain for a sandwich-like structured MOF/MNPs/MOFs.
4. Simultaneous formation of the components to synthesize MNP/MOF composites(Q. Yang, Xu, & Jiang, 2017).

The most appropriate technique to synthesize MOF encapsulated MNP is introducing pre-synthesized MNPs as seeds or nucleation centers into MOF starting materials. This allows MOF to grow or assemble around MNPs to produce MNPs@MOF composites. This is also called a “bottle-around-ship” method which requires a binder on the surface of magnetic nanoparticles to begin the MOF growth and anchor heterogeneous growth of MOF. This also avoids homogenous nucleation of metal-organic framework crystals. There are two substantial advantages to this strategy. They are,

(1) Pre-controllable size, shape, and composition of MNPs in the composite by changing the concentrations of reactants and reaction conditions.

(2) Possible formation of MNP@MOF core-shell structure.

Despite that, the presence of magnetic nanoparticles in the MOF synthesis system sometimes causes problems in the successive MOF formation by disturbing the bond formation between the metal ion and organic ligand. Due to this reason, not all the MOF materials can be used in encapsulating magnetic nanoparticles by this technique. Currently, MIL-101, MIL-53(Fe), ZIF-8 and UiO series based magnetic@MOF have been reported. Mostly a polymer encapsulated magnetic nanoparticles are used in this kind of synthesis, where the polymer acts as the binder between MNP and MOF. Not only the polymer coating act as a binder but also it helps in protecting the magnetic core from extreme conditions. Not all the polymers are compatible with most of MOF materials and the technique is limited to certain MOF materials(Q. Yang et al., 2017).

Guihuan C. et. al successfully demonstrated the synthesis of Fe_3O_4@ZIF-8 and the morphology of magnetic MOF composite could be controlled by changing reaction temperature, time, and dosage of reactants. The study has conducted using 2-methylimidazole (2-MeIM) to surface modify magnetic nanoparticles before introducing them to the ZIF-8 reaction system. According to the published paper particle size around 180nm of Fe_3O_4@ZIF-8 has a good dispersibility with a larger surface area(Chen et al., 2018). Furthermore, Lu et al. reported a sophisticated strategy permitting a variety of magnetic nanoparticles to be encapsulated into ZIF-8 in a well-controlled manner. Magnetic nanoparticles were surface modified with surfactant PVP before encapsulation. This technique was further optimized and MNPs with various sizes, shapes, and compositions were able to well disperse inside the porous ZIF-8 matrix. The spatial distribution of modified magnetic nanoparticles was controlled by changing the addition sequence(Lu et al., 2012). This strategy was successful and various other nanoparticles also could be encapsulated into ZIF-8 matrices, such as Au, Pt, Pd, Ag NCs, polystyrene spheres, Fe_3O_4, CdTe, CdSe, b-FeOOH nanorods, NaYF4 rods, and NaYF4 NPs(Jiang, Xue, Liu, Chen, & Xing, 2016; Ohhashi et al., 2015). This technique has a limitation that it can only encapsulate MNPs in ZIFs composed with N-donor ligands. Encapsulation of PVP-capped MNPs could be done with a good dispersion when the MOF particles constructed with carboxylate linkers(W. Zhang et al., 2014)

CHAPTER 3

MATERIALS AND METHODS

3.1 Materials

$FeCl_3.6H_2O$, n,n-Diméthylformamide, anhydrous sodium acetate, and anhydrous sodium hydroxide pellets, was purchased from Carlo Erba Reagents. Poly(ethylene glycol) (2000 Mw), $Al(NO_3)_3.9H_2O$ and terephthalic acid were purchased from Sigma-Aldrich. Commercial oxytetracycline hydrochloride solution (200 mg ml-1) was purchased from phenix pharmaceuticals NV, Belgium.

3.2 Methodology

3.2.1 Microwave-assisted synthesis of Magnetic nanoparticles

Microwave-assisted solvothermal synthesis(Huang et al., 2010) of MNPs was used in this study to obtain nano-magnetic particles. The technique is less time consuming compared with the conventional solvothermal technique that needs 8 hours of reaction time. 1.35g of $FeCl_3$.6H2O was dissolved in 40ml of ethylene glycol until a clear solution. Then, 3.6g of sodium acetate (NaAc) was added into the solution and dissolved well and stirred for 30-60 minutes till it becomes a yellow cloudy solution. The solution was transferred into 100ml Teflon lined microwave autoclave and conducted the reaction at 200 °C using the flexiWAVE microwave synthesis platform (Milestone®). The microwave reactor was programmed to heat the polar ethylene glycol solvent from room temperature to 200 °C in 10 minutes and maintained the temperature for another 30 minutes. The maximum power of the microwave was set to 1000W. Teflon lined autoclave was allowed to cool down after the reaction without taking it out from the microwave synthesis platform. The internal temperature of the reaction chamber was monitors using the optic fiber dip-probe and external display unit of the machine. MNPs were washed with an excessive amount of DI water to remove residual sodium acetate and ethylene glycol. Synthesized magnetic nanoparticles were dried at 60 °C overnight in a vacuum oven. Besides, to obtain PEG-coated magnetic nanoparticles, 1g of polyethylene glycol (MW 2000) was added to

the above-mentioned reaction mixture after sodium acetate dissolved completely in Fe^{3+} ethylene glycol solution.

3.2.2 Functionalization of PEG-MNP with MIL-53(Al) complex at room temperature

Room temperature synthesis of MIL-53(Al) was reported earlier by Manuel et.al(Sánchez-Sánchez et al., 2015) and, the procedure was slightly modified in the current work. All synthesis was carried out at room temperature (23 °C) in water as the only solvent. 1.32g of terephthalic acid was dissolved in a NaOH solution (0.64g of NaOH in 14.5ml DI water) and allowed the acid to deprotonate and dissolve in water. Meanwhile, 6.0021g of $Al(NO_3)_3$ was dissolved in 14.5ml of DI water. Two different clear aqueous solutions of the metal salt and a solution of the organic linker H_2BDC (terephthalic acid) were mixed vigorously for several minutes at room temperature and gently stirred for 24 hours. Terephthalic acid was deprotonated by dissolving in an aqueous solution containing a stoichiometric amount of NaOH in it. It is necessary to deprotonate the functional groups of the organic linker involved in the formation of the MOF materials. Creamy white color sample was washed after the synthesis process by excessive amount of water. Nano-crystalline MIL-53(Al) particles were separated from water by centrifugation and dried after washing with water at 70° C. The resultant powder was grounded well, dispersed in 250ml of DMF, and heated at 100°C for 12h to remove trapped terephthalic acid within the structure of MIL-53(Al).

Similar procedure was followed to prepare MIL-53(Al) coated magnetic nanoparticles and the only change was to add PEGylated Fe_3O_4 into the reaction system. MNP(PEG) was physically mixed with metal ion solution by ultrasonication before incubating in the solution containing deprotonated terephthalic acid. The reaction was carried out for 24h and the obtained MIL-53(Al) and MIL-53(Al) coated Fe_3O_4 particles were separated by centrifugation. Magnetic separation of magnetic MIL-53(Al) wasn't successful due to the slurry-like product formation. The solid substance was washed several times with DI water and dried in a vacuum oven for 24h to remove the residual

water. The resultant powder was grounded well, dispersed in 250ml of DMF, and heated at 100°C for 12h to remove trapped terephthalic acid within the structure of MIL-53(Al). The resultant solid sample was collected using an external magnet, washed with an excessive amount of methanol to remove the residual solvent. The final product was again separated from methanol using an external magnet, dried at 70 °C overnight, and labeled as MNP(PEG)MIL-53(Al).

3.3 Adsorption experiments

All the experiments were conducted in the dark to prevent the possible photo-degradation of oxytetracycline. A stock solution was prepared by diluting 200 mg ml^{-1} commercial oxytetracycline solution with deionized water and further diluted to obtain the desired concentrations (100 - 550 mg L^{-1}). All adsorbents were dried overnight under vacuum at 70 °C before the adsorption experiments. The exact amount of adsorbent was weighed using an analytical balance, mixed with the known concentrations of OTC solutions, and experiments were triplicated. Adsorbent containing OTC solutions was shaken at 50 r.p.m. using the Heidolph duomax 1030 rocking platform shaker. After the pre-determined time, the adsorbents were separated using a strong magnet, and supernatants were analyzed using Thermo Fisher scientific GENESYS™ 10S UV-Vis Spectrophotometer. The adsorbed amount of OTC (qt) was calculated using Eq. 1

$$q_t = \frac{(C_0 - C_t)}{M} \times V \qquad \text{(eq.1)}$$

Adsorption capacity represents by q_t (mg g^{-1}); initial and final concentrations were represented by C_0 and C_t (mg L^{-1}) respectively. The initial volume of the OTC solution represents by V (L) where M (g) denotes the mass of the adsorbents.

3.3.1 Adsorption kinetics

Adsorption kinetics were studied by adding 100mg of MNP(PEG)MIL-53(Al) into 80 mg L^{-1} OTC solution and continuously stirred using a platform shaker at 50 r.p.m. The concentration of the adsorbate was calculated by measuring the UV-vis spectrum at pre-determined time intervals ranging from 0 to 300 minutes. Separation of adsorbent from

adsorbate was performed by placing the solution on a strong magnet before extracting OTC samples for analysis.

3.3.2 Adsorption isotherms

Adsorption isotherm experiments were conducted using known concentrations of OTC solutions prepared by diluting the stock solution. An equal amount of adsorbate was incubated in each OTC samples where the concentration of adsorbate was maintained at 1 mg ml^{-1} to analyze both adsorption capacity and regeneration capabilities. A series of experiments were conducted and each experiment was triplicated.

3.3.3 Effect of pH on adsorption capacity

The effect of pH on adsorption behavior was studied by carrying out the experiments at different pH values ranging from 2-12. The single batch reaction was carried out by incubating 10ml of 80 mg L^{-1} OTC solution with 2mg of MNP(PEG)MIL-53(Al). A solution of 0.1 mmol/L HCl and NaOH was used to adjust the pH of samples. UV absorbance of initial OTC at different pH was measured to determine the changes in the UV absorbance spectrum since OTC shows anionic, cationic, and zwitterionic behavior depending upon solution pH. Adsorption experiment was allowed for 12h to ensure firm equilibrium and residual OTC was measured after magnetically separating the adsorbent.

3.4 Regeneration of materials by magnetic induction heating

Regeneration of MNP(PEG)MIL-53(Al) was carried out using a high-frequency induction heater at 650kHz for several minutes. Samples were incubated with known concentrations of OTC for a sufficient time until the equilibrium and separated using an external magnetic field. The supernatant was decanted, analyzed to determine the remaining OTC concentration and the separated wet magnetic slurry was subjected to induction heating while the temperature was monitored using an optic fiber probe temperature sensor. Induction heating was conducted till the temperature of the slurry increases up to 70° C. Regenerated MNP(PEG)MIL-53(Al) samples were washed once

using DI water, re-incubated in a solution of OTC, and this process was carried out for 9 regeneration cycles. Samples were handled carefully to avoid material loss and they were able to separate using an external magnet in less than 2 minutes.

3.5 Material Characterization

Powder diffraction patterns of synthesized materials were carried out by a Bruker D8 advance using Cu-Kα radiation under 40kv and 40mA with a step size of 0.02. A Thermo Scientific Nicolet iS5 FTIR/ATR was used to determine the functional groups of PEG-coated magnetic nanoparticles, pristine MIL-53(Al) and MNP(PEG)MIL-53(Al). Surface morphologies were examined using field emission scanning electron microscope (Hitachi FE-SEM SU8030) and transmission electron microscope (Jeol, JEM-2100 Plus). Thermal gravimetric analysis was conducted (Metler-Toledo simultaneous thermal analysis TGA/DSC 3+) to determine the thermal stability and characteristic weight loss of magnetic nanoparticles, pristine MIL-53(Al) and the composite magnetic MIL-53(Al)RT. Half a crucible of each sample was heated from 25 °C - 900 °C at a heating rate of 10 °C/min under a nitrogen flow of 50 ml min^{-1}. UV-Vis spectrums were collected using Thermo scientific Genesys 10s spectrophotometer in the range from 190 to 500 nm at ambient conditions.

CHAPTER 4
RESULTS AND DISCUSSION

4.1 Material Characterizations

4.1.1 Morphological analysis of functionalized magnetic materials

TEM and SEM images were studied to identify the shape and surface morphonology from bare MNP to MNP(PEG)MIL-53(Al) and the overall particles are in the range of 100-150nm in size. Bare MNPs and PEG-coated MNPs were smaller when compared with the final MNP(PEG)MIL-53(Al) particles and the surface morphology was also changed from smooth to rough. The MNP(PEG)MIL-53(Al) composite has a fuzzy-like surface due to the surface grafting. EDS elemental analysis confirmed the presence of aluminum in the final composite signifying the formation of MIL-53(Al) in it.

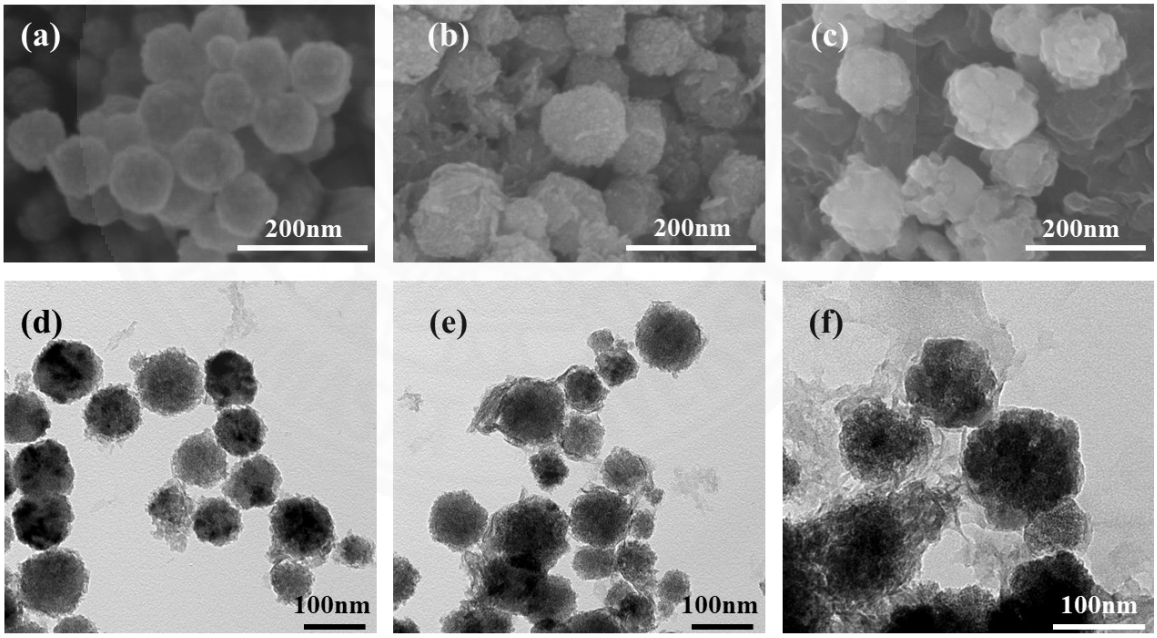


Figure 4.1 Morphological analysis of functionalized nanoparticles. SEM image of microwave synthesized bare MNP (Fe_3O_4) (a), MNP-PEG(b), and MNP(PEG)MIL-53(Al) (c). Transmission electron microscopic images (TEM) of Bare MNP(Fe_3O_4) (d), MNP-PEG (e) and MNP(PEG)MIL-53(Al) (f)

4.1.2 X-Ray crystallographic analysis of synthesized materials

XRD patterns were analyzed to recognize the existence of iron oxide and metal-organic framework in the final nanocomposite by studying crystal structures. Figure 4.1(A) shows the XRD patterns of pure Fe_3O_4 which is close to the standard XRD pattern of crystalline magnetite (JCPDS Card #19-629)(Gong & Lin, 2003; Rajan et al., 2014; L. Zhang, He, & Gu, 2006). Six characteristic peaks were observed at 30.0°, 35.4°, 43.0°, 53.3°,56.9° and 62.5° which can be indexed as 220, 311, 400, 422, 511 and 440 as face-centered cubic Fe_3O_4.

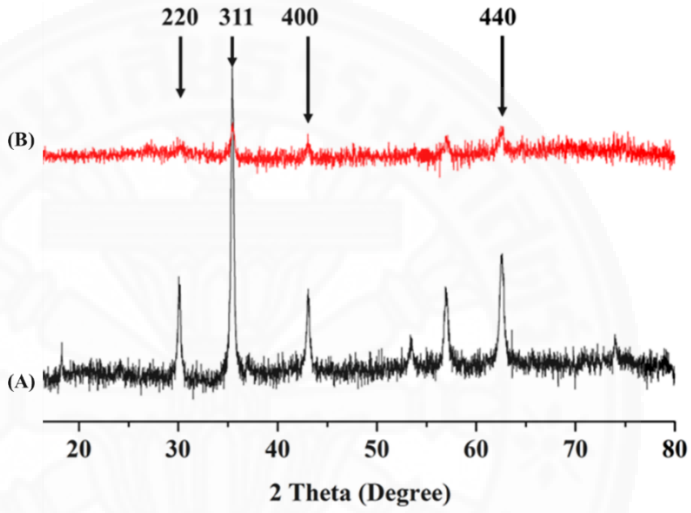


Figure 4.2 X-ray diffraction pattern of (A) Bare MNP, (B) MNP(PEG)

Crystalline nature of the magnetic Fe_3O_4 nanoparticles confirmed by the high intensity of peaks wherein PEGylated magnetic (Fe_3O_4(PEG)) nanoparticles, the peak intensities reduced due to coating of amorphous PEG on the surface of Fe_3O_4(Icten, Hosmane, Kose, & Zumreoglu-Karan, 2017; Panwar, Kumar, Bansal, Ray, & Jain, 2015). XRD patterns of surface-functionalized magnetic nanocrystals can be indexed into pure Fe_3O_4, signifying that functionalization does not cause any structural changes in the magnetic core in both MNP(PEG)(Icten et al., 2017) and MNP(PEG)MIL-53(Al) nanocomposites. Characteristic peaks for Fe_3O_4 was observed in the XRD patterns of MNP(PEG)MIL-53(Al) nanocomposite are at 30.1°, 35.4°, 43.1°, 53.5°,56.9° and 62.5° which can be indexed as 220, 311, 400, 422, 511 and 440.

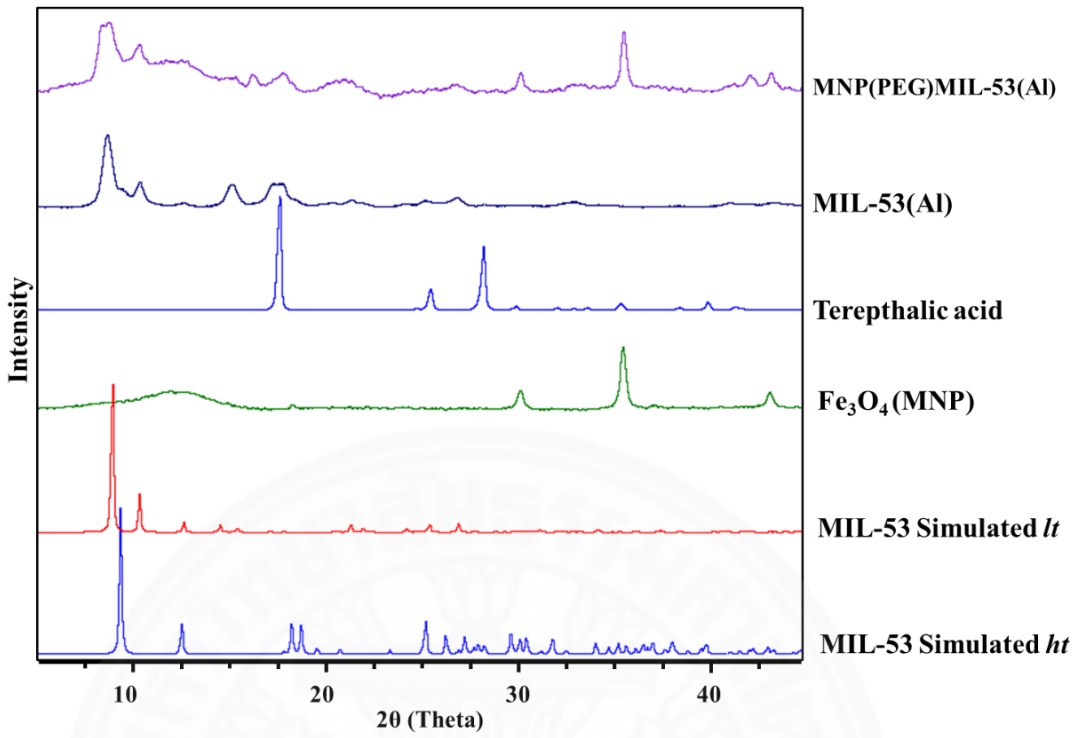


Figure 4.3 X-ray diffraction patterns of (a) MNP(PEG)MIL-53(Al), (b) Pure MIL-53(Al), (c) Terepthalic acid, (d) Bare MNP, (e) MIL-53 Simulated *lt*, (f) MIL-53 Simulated *ht*

Characteristic XRD spectrum of room temperature synthesized MIL-53(Al) was also observed in final composite material which was further comparatively analyzed with simulated XRD patterns of MIL-53(Al)*lt* and MIL-53(Al)*ht*. The XRD pattern of MNP(PEG)MIL-53(Al) depicted a combination of both the MIL-53(Al)*lt* and MIL-53(Al)*ht* phases in its structure. The most intense peaks around 8° - 10° in MNP(PEG)MIL-53(AL) sample might be due to the presence of both the *ht* and *lt* forms of MIL-53(Al) in its structure.

4.1.3 Fourier-transform infrared spectroscopy (FTIR) analysis to identify surface functionalization

FT-IR spectra of all the nanocomposites in the region of 500cm^{-1} to 4000cm^{-1} were used to identify surface-functionalized groups. The characteristic intense band which significantly weakened after surface modification observed in all the magnetic samples

from 600-500cm^{-1} corresponding to the vibration of Fe-O in the Fe_3O_4 lattice(Junejo, Baykal, & Sözeri, 2013; Park, Daksha, Lee, Woo, & Chang, 2008). Absorption bands corresponding to the covalently bound carboxylate group (Figure 4.4 (b)) to the Fe on the surface of the Fe_3O_4 particle were observed at 1575 and 1435.6 cm^{-1}.

The absorption bands observed at 1087 and 3286 cm^{-1}, corresponding to the C-H and O-H vibrations, respectively. Several narrow peaks were observed in the FT-IR spectrum of pure PEG at 1050, 1095, and 1114 cm^{-1}. The most dominant band at 1086 cm^{-1} corresponds to the C-O stretching of PEG in both pure PEG spectrum as well as the spectrum of PEG-coated magnetic nanoparticles(Park et al., 2008). The broad peak at 3438cm^{-1} correspond to the terminal hydroxyl groups of PEG(Chieng, Ibrahim, Yunus, & Hussein, 2013) or the O-H stretching of adsorbed water. The peaks observed at 1438 and 1573.7 cm^{-1} in both bare Fe_3O_4 and PEG-coated Fe_3O_4 corresponding to the carboxylate group from the sodium acetate used in the synthesis bound to the Fe_3O_4 surface. The presence of these absorption bands confirms the existence of PEG in the final product which was further used to incorporate with MIL-53(Al).

After coating with MIL-53(Al), MNP(PEG) MIL-53(Al) shows peaks that are similar to that of the pure MIL-53(Al). The peaks at 1604 and 1509 cm^{-1} corresponds to -COO^- asymmetric stretching while the bands at 1438 and 1412 cm^{-1} are ascribed to -COO^- symmetric stretching. The sharp and intense peak at 1696 cm^{-1} is ascribed to the unreacted carboxylic acid trapped within the porous structure of MIL-53(Al)(Rallapalli et al., 2011). Peaks appeared at 3421 cm^{-1} in MIL-53(Al) and the peak at 3395 cm^{-1} in MNP(PEG)MIL-53(Al) may be attributed to the intermolecular bonded hydroxyl groups and the peak at 3677 cm^{-1} corresponds to the free hydroxyl molecules.

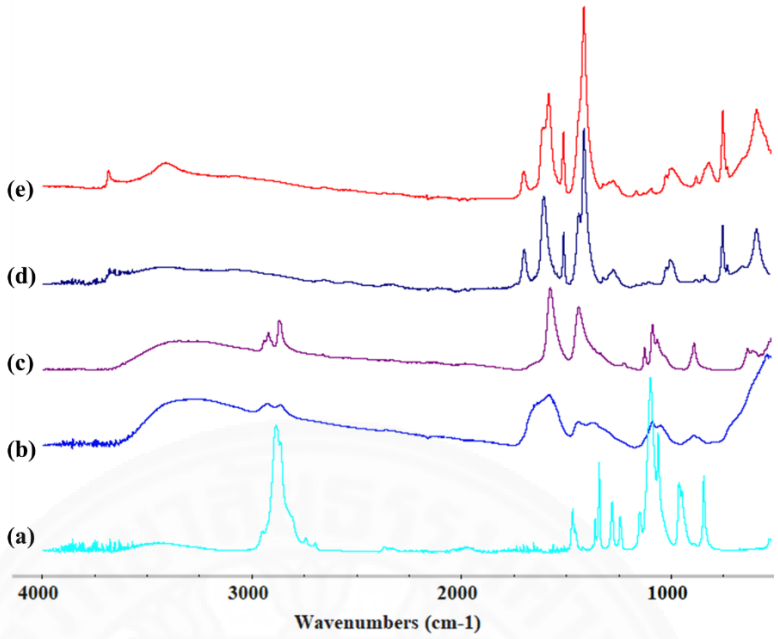


Figure 4.4 FTIR-ATR spectrum of (a) PEG, (b) Bare MNP, (c) MNP(PEG), (d) MIL-53(Al), (e) MNP(PEG)MIL-53(Al)

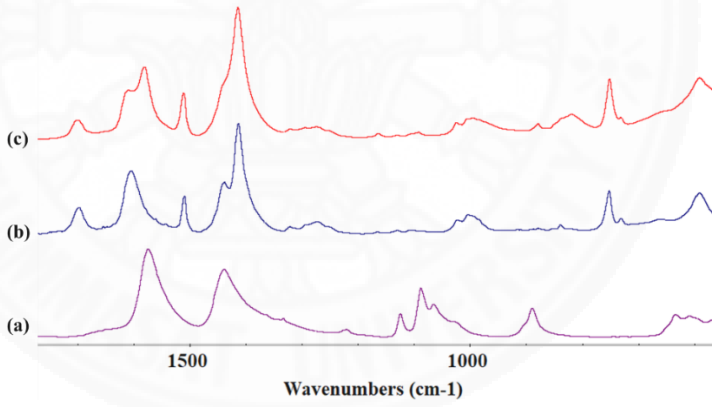


Figure 4.5 FTIR-ATR spectrum of (a)MNP(PEG), (b)MIL-53(Al), (c)MNP(PEG)MIL-53(Al)

4.1.4 Vibrating-sample magnetometer analysis

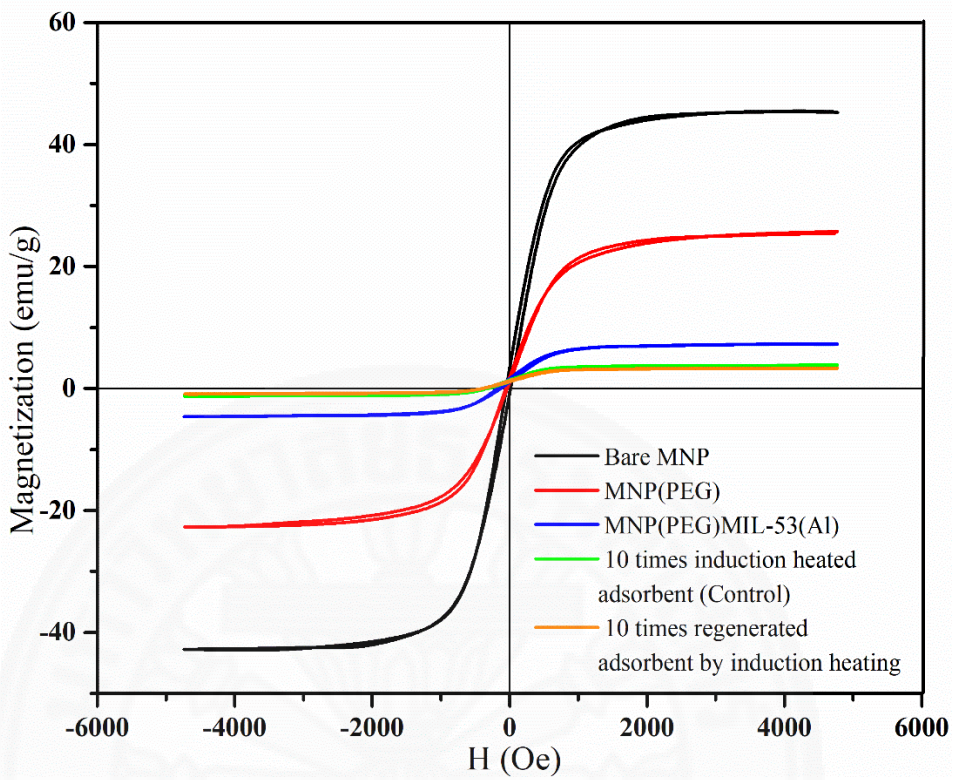


Figure 4.6 VSM hysteresis loops of magnetic nanoparticles after each fabrication process

A representative hysteresis loop taken from VSM analysis at room temperature is shown in figure 4.6. The saturation magnetization value of bare iron oxide (Fe_3O_4) nanoparticles was about 44.21 emu/g while MNP(PEG) and MNP(PEG)MIL-53(Al) was about 24.23emu/g and 5.98emu/g respectively. Saturation magnetization might have decreased due to the presence of coated PEG and MOF materials on the surface of magnetic nanoparticles(Ge et al., 2009). Exhibited magnetic remanence and coercivity of the coated and uncoated particles were nearer to zero demonstrating typical superparamagnetic behavior. Particles remained magnetic even after regenerating for 10 times. This demonstrated that the particle's magnetic core is well-protected and it can withstand high inductive heating temperature without losing its magnetic properties.

4.1.5 Thermogravimetric analysis (TGA) of synthesized materials

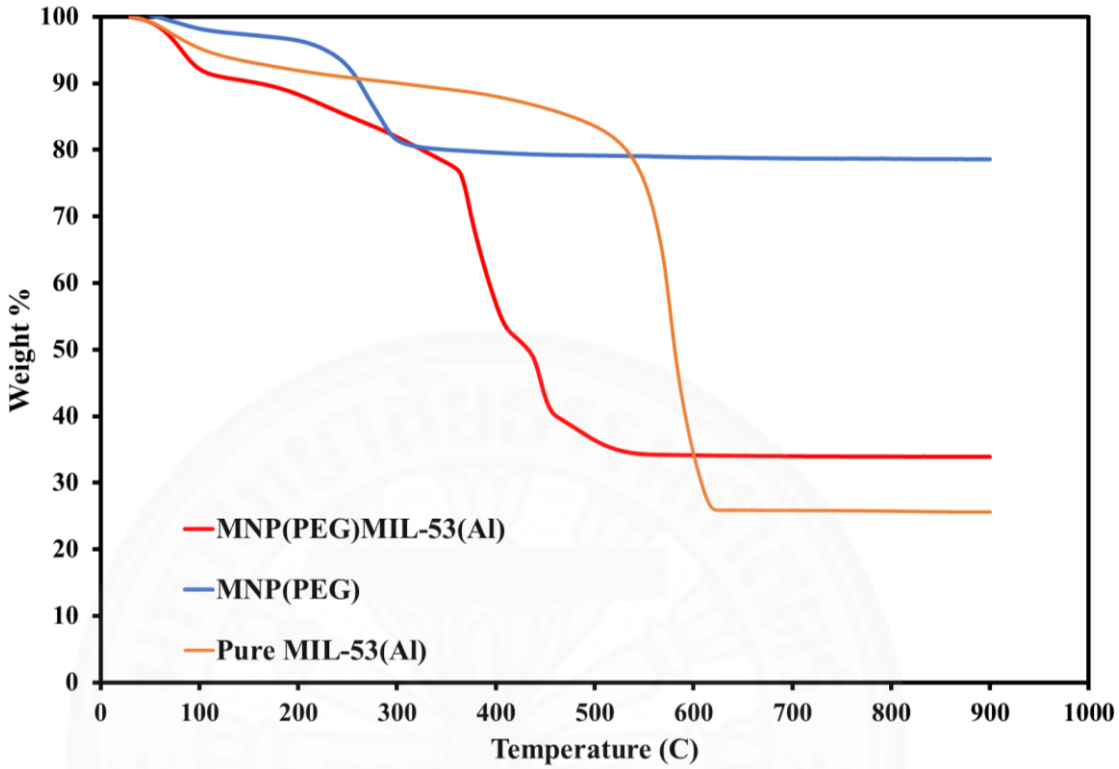


Figure 4.7 Thermogravimetric analysis MNP(PEG)MIL-53(Al) composite

The thermogravimetric analysis (TGA) provides various information about the synthesized composite material. The amount of each component that was used in surface grafting has been studied in comparison with each phase. The final composite material showed 3 major TGA losses from room temperature to 120 °C, 145 – 355 °C, and 355 – 467 °C. The first weight loss of the MNP(PEG)MIL-53(Al) observed in the TGA curve below 120 °C with 9% of loss is associated with the removal of absorbed water from the material. The MNP(PEG) also shows similar initial weight loss due to adsorbed water of about 4%. Further weight loss around 150 – 350 °C in both the MNP(PEG) and MNP(PEG)MIL-53(Al) was attributed to the degradation of the PEG and acetate molecules around the magnetic core. Degradation of PEG over iron oxide particles begins at much lower temperature than pure PEG. This might occur due to the catalysis behavior of iron

oxide particles thus, reducing the degradation temperature.(Karaoğlu, Kavas, Baykal, Toprak, & Sözeri, 2011)

In MNP(PEG) and MNP(PEG)MIL-53(Al), the major weight loss of the final composite material was observed around 360 – 520 °C due to the degradation of MIL-53(Al) structure. In pure MIL-53(Al), the degradation occurs at a higher temperature region around 510-610 °C. The degradation of the MIL-53(Al) in the MNP(PEG)MIL-53(Al) structure occurs at a lower temperature than that of the pure MIL-53(Al). This is probably due to the incomplete crystal growth of the MIL-53(Al) around the MNP(PEG) surface as compared to the pure MIL-53(Al), which seems to have better crystallinity. XRD patterns of pure MIL-53(Al) have a much sharper pattern compared with the composite material which is reflected in figure 4.4. In MNP(PEG)MIL-53(Al), the weight loss in this regions seems to occur in two stages in the region from 360-425 °C and from 425-520 °C, which may be attributed to two species of terephthalic acids in the MIL-53 structure: the loosely bound terephthalic acids and the strongly bound terephthalic acids in the crystalline MIL-53(Al). The loosely bound terephthalic acids seem to degrade at a lower temperature around 360-425° while the terephthalic acid linkers that are strongly bound to the Al3+ in the MIL-53(Al) structure degrade at a slightly higher temperature around 425-520 °C (Sánchez-Sánchez, 2015).

From this TGA results, it may be inferred that the MIL-53(Al) growth near the MNP-PEG surface are probably rather amorphous, or have only partial crystallinity. The MIL-53(Al) layer which is further away from the MNP-PEG may probably have better crystallinity, but probably smaller domains than those in pure MIL-53(Al). This is also observed in the XRD pattern of the MNP(PEG)MIL-53(Al) which was not as sharp as that of the pure MIL-53(Al) synthesized under the same conditions. The rather amorphous MIL-53(Al) growth on the MNP-PEG surface may essentially be beneficial in the high OTC adsorption capacity compared to that of pure MIL-53(Al).

The weight loss (or weight remains) after all the carbonaceous materials have been combusted can also be used to calculate the amount of MIL-53(Al) in the MNP(PEG)MIL-53(Al) composite. Here MNP-PEG has a weight remains of 79%, while the

MNP(PEG)MIL-53(Al) has a weight remains of about 34%. The pure MIL-53(Al) has a weight remains of about 26%. From this, the approximate amount of MIL-53(Al) in the MNP(PEG)MIL-53(Al) composite is calculated to be about 84% in good agreement with that from the VSM measurement which was about 86%.

4.1.6 The growing mechanism of Fe_3O_4 and growing sequence of MIL-53(Al) on MNP-PEG

The mechanism of the growth of Fe_3O_4 clusters can be explained considering the solvent and sodium acetate. Ethylene glycol is an appropriate solvent that can be used in the solvothermal technique and it can be heated using microwave irradiation. Synthesizing Fe_3O_4 particles can be done using ethylene glycol and it has remarkable physical and chemical properties. During the synthesis process, the magnetite was nucleated in ethylene glycol medium under solvothermal conditions. Water generated from metal precursors and sodium acetate was used in forming crystalline Fe_3O_4. Initially, amorphous magnetic particles might have nucleated from highly saturated ethylene glycol medium and aggregated to form grains. Later, these aggregated particles formed nano-sized spherical crystallites. Thus, to minimize the total surface energy, the nano-sized particles might further aggregate randomly forming larger particles and/or grew larger depending on the reaction conditions. Ultimately, the formation of Fe_3O_4 clusters decreases the availability of Fe^{3+}/Fe^{2+} in the reaction system and that causes a slow reaction rate preventing primary crystal to grow larger. The existing magnetic nanoclusters might have an electrostatic repulsion due to the dense existence of carboxylate groups in the medium and on the surface of the crystal. This also leads primary crystals to remain as smaller magnetic clusters. Simultaneously, sodium acetate suppresses the crystal growth of the magnetic nanoclusters by covalently bonding onto the surface of Fe_3O_4.

Synthesis of MIL-53(Al) grafted magnetic nanoparticle was done by pre incubating PEG-coated MNP with metal ion solution before the addition of a terephthalic acid linker. The experimental synthesis sequence was confirmed observing the adsorption capacity of MNP(PEG) by incubating it with both terephthalic acid linker and metal ion solutions. The

initial and final concentration of terephthalic linker was analyzed using UV-Vis absorbance spectrum while Perkin Elmer Optima 8000 ICP-OES was used to determine initial and final concentrations of Al^{3+} solution. No significant change in the concentration of the terephthalic acid solution was observed after incubating with PEG-MNP but a considerable drop of concentration was observed in Al^{3+} solution confirming the adsorption of Al^{3+} onto the surface of PEG-MNP. The growing sequence as depicted in figure 4.8. based on the above experimental results where Al^{3+} adsorbs onto the PEG layer as a precursor to initiate the growth of MIL-53(Al) over the magnetic core.

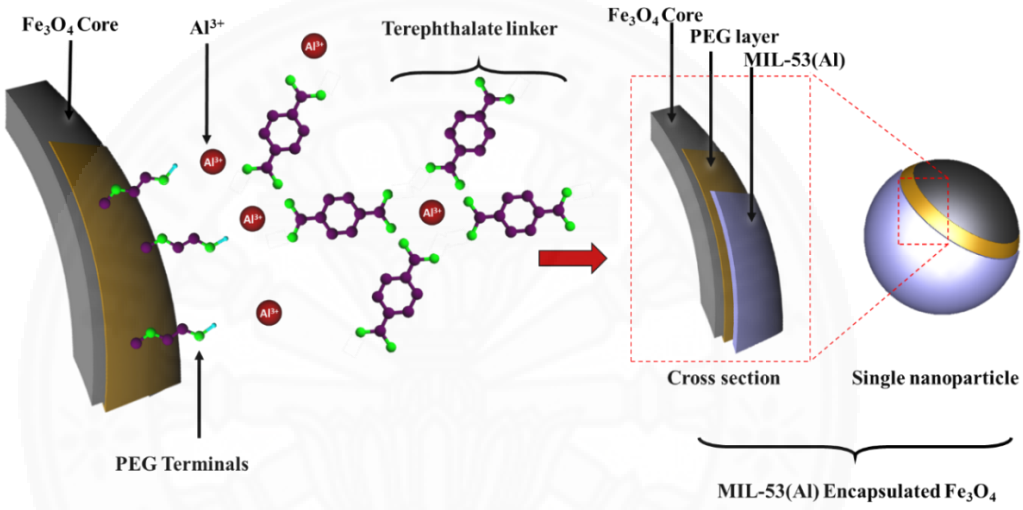


Figure 4.8 Growing mechanism of MIL-53(Al) on the surface of MNP(PEG)

4.2 Experimental Results and discussion

4.2.1 Adsorption kinetics and isotherms.

The adsorption equilibrium curves of oxytetracycline onto MNP(PEG)MIL-53(Al) and pure MIL-53(Al) is depicted in Figure 4.9 (a). Abundant availability of active adsorption sites on the surface of magnetic MIL-53(Al) might cause the increase of the adsorption during the first 10 minutes. A progressive decrease in the rate of adsorption capacity was observed until ~180 minutes, which can be explained because the drug molecules might not occupy on the surface since the specific binding sites are already saturated; and the remaining available sites might not be attractive enough for more

adsorbate molecules to occupy. Equilibrium of adsorption was completed within 180 minutes, making the synthesized MNP(PEG)MIL-53(Al) a rapid adsorbent for oxytetracycline hydrochloride. Thus, 12 h was selected as the time for ensuing all adsorption equilibriums to be well established. The adsorbent was magnetically separated before analyzing the aqueous solution of the adsorbate. Adsorption kinetics was analyzed using about 75 mg L^{-1} diluted OTC solution and the samples were analyzed by UV-vis spectroscopy without further diluting.

Adsorption isotherm was conducted to determine maximum adsorption capacity (Q^0) and the experiments were carried out at ambient conditions. Adsorption isotherm was further analyzed using a typical Langmuir and Freundlich adsorption models(Hu et al., 2017a) to evaluate the adsorption capacity at equilibrium. The Langmuir and Freundlich isotherm equations are described respectively as follows.

$$\mathrm{Qe} = \frac{Q^0 k\ \mathrm{Ce}}{1+kQe} \qquad \text{(eq.2)}$$

$$Qe = K_f(Ce)^{1/n} \qquad \text{(eq.3)}$$

Ce and Q_e denote the concentration and capacity of OTC at the adsorption equilibrium, respectively. Q^0 is the maximal adsorption capacity. *k*, the Langmuir constant (L mg^{-1}), is related to the free energy of adsorption. Adsorption capacity and adsorption intensity correspond to K_f and n respectively in the Freundlich model. The fitting results of the isotherm models are summarized in table 4.1 and found that better fit result was provided by the Langmuir model with high correlation coefficient ($R^2 > 0.9549$) suggesting that the adsorption sites of OTC onto MNP(PEG)MIL-53(Al) are quite homogeneous (Chao et al., 2014; Z. Zhang, Lan, Liu, Li, & Qu, 2015). The calculated maximum adsorption capacity of OTC onto magnetic MIL-53(Al) reached 776.5 mg g^{-1} confirming the high adsorption capabilities of the synthesized material.

Table 4.1 Langmuir and Freundlich isotherm models

	Langmuir			Freundlich		
	Q^0	k	R^2	n	K_f	R^2
MNP(PEG)MIL-53(Al)	776.51	0.0044	0.9549	2.14032	27.61733	0.87427

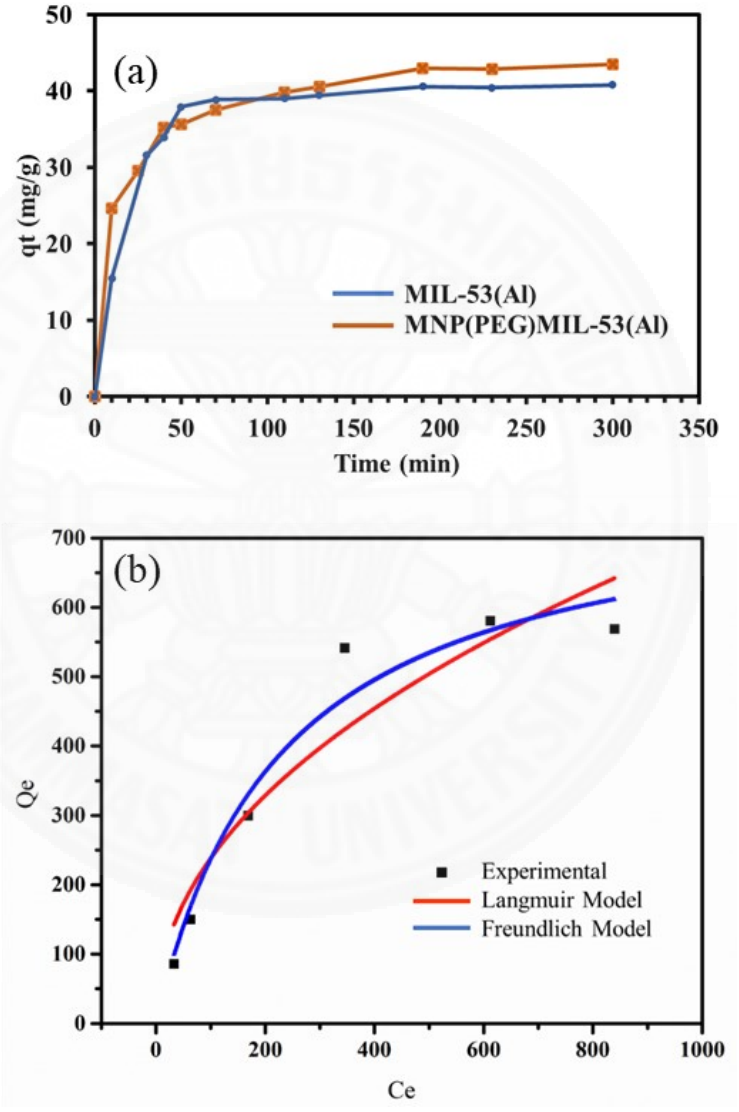


Figure 4.9 Adsorption kinetics of OTC on MNP(PEG)MIL-53(Al) (a), the Adsorption isotherms of OTC on MNP(PEG)MIL-53(Al) (b)

4.2.2 Effect of pH on adsorption of oxytetracycline

Oxytetracycline has the capability of showing different ionic states based on the solution pH values by protonating/deprotonating its active sites (Figueroa, Leonard, & MacKay, 2004). The pH of the solution affects the surface charge of adsorbent, and the liquid-phase adsorption behavior changes with the pH of the solution. Hence, oxytetracycline shows anionic, zwitterion, and cationic behaviors at pH < 3.3, pH between 3.3 and 7.3, and pH > 7.3, respectively (Kulshrestha, Giese, & Aga, 2004). 2 mg of magnetic MIL-53(Al) composite was incubated in 10ml of OTC solution at different pH values ranging from 2-12.

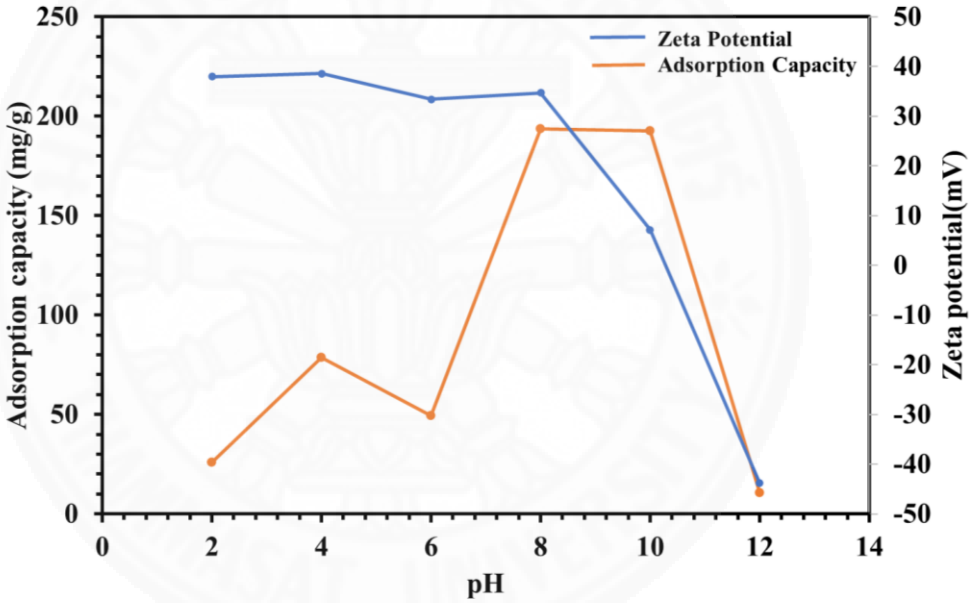


Figure 4.10 The OTC adsorption capacity and zeta potential of MNP(PEG)MIL-53 at different pH values

Adsorption capacities against respected solution pH values are depicted in figure 4.10. At extreme conditions, the adsorption capacity has reduced where the maximum adsorption was obtained from pH 8 to 10. Oxytetracycline becomes anionic above pH 7.3 which also reported in several studies. Figure 4.10 reveals the maximum adsorption capacity occurs at pH 8 which is due to the anionic behavior of oxytetracycline(J. Li, Wu,

Li, Zhu, & Li, 2014) and the positively charged MIL-53(Al). At the optimum pH, the adsorbent (MNP(PEG)MIL-53(Al)) remains positive (+34.7 eV) facilitating the adsorption driven by electrostatic interactions. The effect of pH on adsorption capacity can be broadly divided into three main regions below pH 6, pH 8-10, and pH 10-12.

At lower pH values (< 3.3), the cationic behavior of OTC due to the protonation of OTC while zeta potential of the adsorbent also remains positive may be the reason for the lower adsorption capacity due to electrostatic repulsion. At basic pH values (pH 10-12), OTC shows anionic properties as well as the adsorbent showing negative surface potential resulting also in low adsorption.

In the favorable pH region of pH 8-10, the oxytetracycline becomes negative while the adsorbent remains positive making the electrostatic interactions between adsorbent and adsorbate. Adsorbent shows higher zeta potential value at pH 8 causing the highest adsorption capacity and it gradually decreases when the pH increased up to 10. Meanwhile in all the pH conditions, OTC and adsorbent have π-π interactions between the aromatic structures and can also help the adsorption. The adsorption in the acidic pH region may be due to this π-π interactions.

4.2.3 Regeneration of adsorbent

MOF based adsorbents demonstrate good adsorption capacities and, it is important to reuse materials to make the overall process cost-effective. The reusability of MNP(PEG)MIL-53(Al) was carried out using magnetic induction heating assuming the heat-labile oxytetracycline should degrade at elevated temperature making the magnetic adsorbent available for re-adsorption of the OTC again.

The adsorption capacity was studied up to 10 regeneration cycles and finally, the adsorbent was dried for further analysis. Furthermore, the amount of removed OTC was calculated, plotted along with the adsorption capacity (figure 4.11), and found that the adsorption capacity was significantly good till 5 regeneration cycles and it gradually decreased after. Also, there was a noticeable improvement in adsorption capacity in the 1st regeneration cycle compared to the fresh sample adsorption cycle. An additional

experiment was conducted as a control by re-incubating OTC saturated non-regenerated adsorbents in a fresh OTC solution to determine the adsorption capacity. The non-regenerated adsorbents undergo the same produce of the induction regeneration, except that no heat was given. There was no significant absorption of OTC was observed with non-regenerated adsorbents.

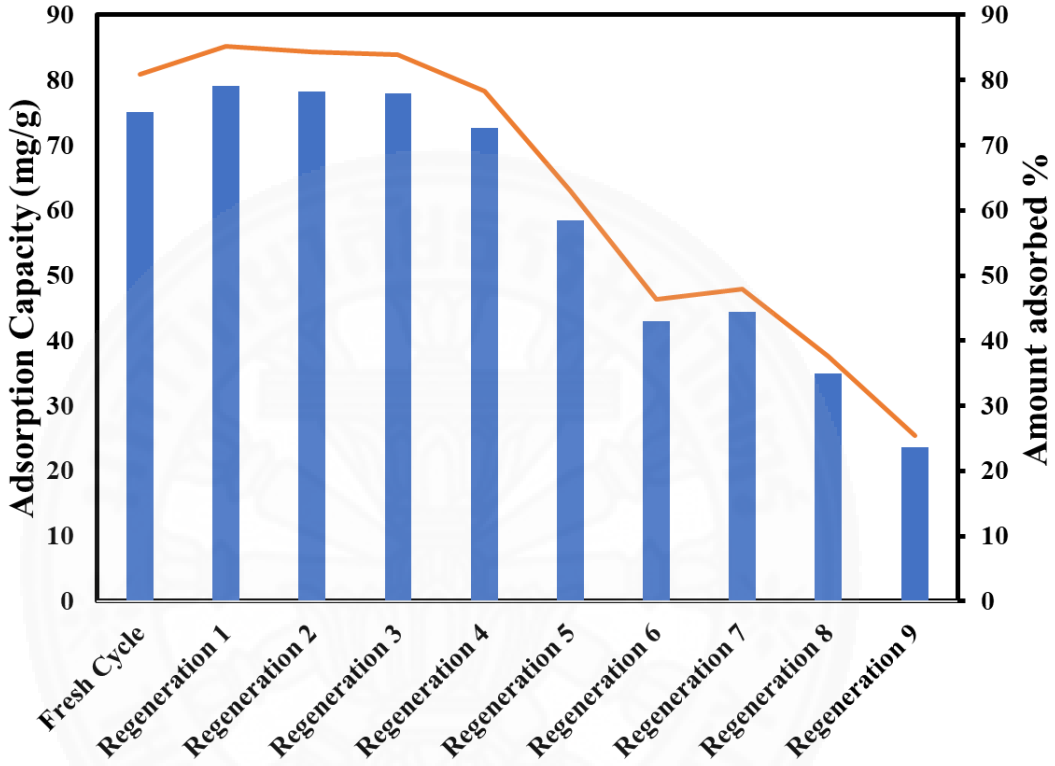


Figure 4.11 Regeneration of MNP(PEG)MIL-53(Al) using magnetic induction heating

X-ray crystallographic analysis was done for the adsorbent material in comparison with a fresh sample and a sample incubated and regenerated similarly without using drugs. XRD spectrum depicted in figure 4.11 shows that the crystallinity of the regenerated adsorbent has reduced a lot after 10 cycles while the crystallinity of the magnetic core remains unchanged. Meanwhile the two control samples (Fresh adsorbent sample and 10 times regenerated sample without using OTC) do not make any structural changes in it. This confirms that the adsorbed drug has strongly attached to the metal-organic framework stricture causing structural changes and reduced crystallinity. It may also explain the very

high adsorption capacity and affinity of the MNP(PEG)MIL-53(Al) for the OTC. In all these samples, the crystallinity of the magnetic core has not changed confirming its stability at induction heating; also, it helps to understand that the magnetic core in the composite material is well protected. This concludes that MNP(PEG)MIL-53(Al) is a reusable material in adsorbing oxytetracycline from water that can be used even in industrial applications.

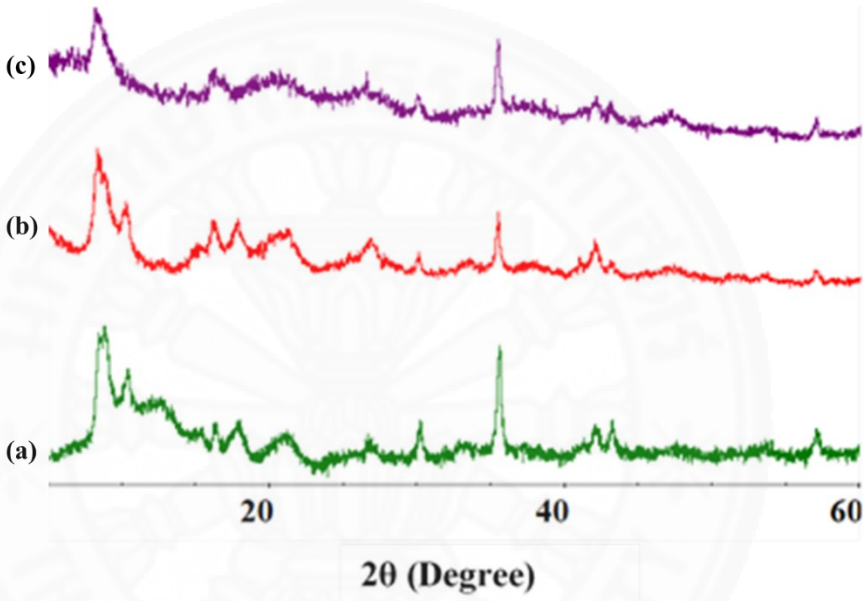


Figure 4.12 X-ray diffraction patterns of magnetic materials after regeneration
(a) Fresh MNP(PEG)MIL-53(Al) sample (Control 1), (b) Heated without adsorbing drug (Control 2), (c) 10 Times Regenerated MNP(PEG)MIL-53(Al)

CHAPTER 5
CONCLUSIONS

Antibiotics are a group of beneficial chemical substances that helps humans to stay away from various pathogenic diseases and to treat domestic and farm animals. Broad-spectrum antibiotic oxytetracycline plays an important role in the modern world. People have created various other problems due to the overuse of various types of antibiotics in recent history. The current work focused on addressing the problem by removing and degrading existing residual amounts of antibiotics in aqueous solutions with the help of smart nanomaterials.

Magnetic nanoparticles are widely studied from the past few decades due to the numerous properties that can be used in various applications. The synthesis of magnetic nanoparticles was performed using a novel microwave synthesis platform. Ethylene glycol was used as the solvent in the synthesis and it also was the reducing agent to produce Fe^{2+} ions from Fe^{3+}. Acetate ions present in the reaction system worked as a capping agent to avoid magnetic nanocrystals to grow larger. Nano-sized magnetic particles were obtained at the end of the synthesis with an average particle size of 100nm. These particles were characterized by various physical techniques like XRD, FTIR, TEM, SEM, and EDS to confirm their crystal structure. XRD analysis had given a clear and intense spectrum similar to Fe_3O_4 which is magnetite. FTIR confirms the existence of PEG on the magnetic particle surface. TEM and SEM confirmed the spherical appearance of the magnetic nanoparticles. Highly porous material that has a high temperature stability was needed to be coated onto the surface of magnetic nanoparticle surface, and MIL-53(Al) was chosen since it is also one of the simplest among various metal-organic frameworks. Also, MIL-53(Al) can be synthesized in room temperature which facilitated the surface coating of MNP without harming it. Immobilizing ultra-small MIL-53(Al) crystals around magnetic nanoparticle extends its application. Having magnetic properties in a nano-sized MIL-53(Al) gives access in controlling the motion of the particles and allowing the particles to be heated via magnetic induction heating.

Physical and chemical properties of MNP(PEG)MIL-53(Al) have been studied in this work and characterization results obtained from FTIR, XRD, TEM, and TGA confirm the formation of MIL-53(Al) around the PEG-coated magnetic nanoparticle. Several experiments were done to determine the growing sequence of metal-organic frameworks encapsulating magnetic nanoparticles. This was examined by comparing the adsorption of Al^{3+} metal ions and deprotonated terephthalic acid onto MNP(PEG) particles. The growing sequence was shown to be the adsorption of Al^{3+} onto MNP(PEG) particles followed by continued growth network of terephthalic acid and Al^{3+} ions.

Adsorption of oxytetracycline from the water was studied with the synthesized material and the maximum adsorption capacity was obtained as 776.5 mg g^{-1}. The adsorption results of the final composite material were similar to that of pure MIL-53(Al). Various materials can adsorb antibiotics based on electrostatic interactions and π-π interactions but most of them cannot be reused. The MNP(PEG)MIL-53(Al) is capable of adsorbing and it is reusable after subjecting it to physical treatments.

The regeneration of the adsorbent was conducted via magnetic induction heating to degrade heat-labile oxytetracycline by increasing the temperature around the magnetic nanoparticle. MNP(PEG)MIL53(Al) was able to regenerate up to five times with substantial performance, confirming that synthesized magnetic MOF as a good adsorbent for oxytetracycline in water. This material can be used in industrial applications and low-cost synthesis protocol makes it cost-effective. This technique might be an appropriate solution for the existing problems caused by residual amounts of antibiotics in water.

Recommendation

1. Synthesis of magnetic nanoparticles can be conducted varying the sodium acetate concentration to control the particle size. Moreover, increasing the reaction time might improve the density of magnetic core and magnetic properties also might increase due to this.
2. Functionalization of magnetic nanoparticles with MIL-53(Al) can be done using other MIL-53(Al) synthesis techniques like microwave-assisted MIL-53(Al) synthesis.
3. MNP(PEG)MIL-53(Al) nanoparticles can be further processed into larger beads using sodium alginate to make it appropriate for industrial use.
4. The photocatalytic activity of composite material can be studied corresponding to the photocatalytic degradation of drugs.
5. The composite material can be used in other important applications like nitrobenzene adsorption and heavy metal adsorption.

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APPENDICES

APPENDIX A

Experimental data

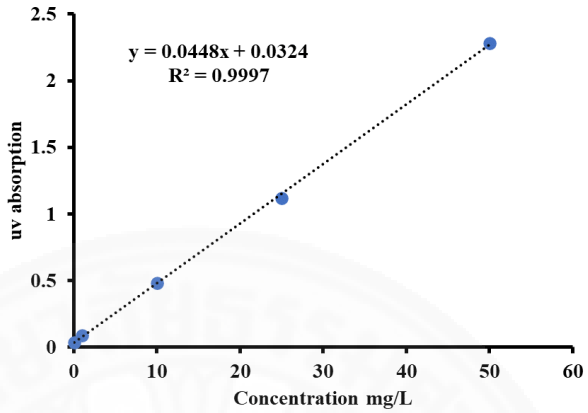


Figure 1. Standard curve for Oxytetracycline

Table 1: Effect of pH on adsorption capacity and zeta potential of MNP(PEG)MIL-53(Al)

pH	Adsorption Capacity	Zeta Potential of Adsorbent
2	25.92	37.96
4	78.8	38.6
6	49.3	33.4
8	193.54	34.73
10	192.62	7.12
12	10.59	-43.8

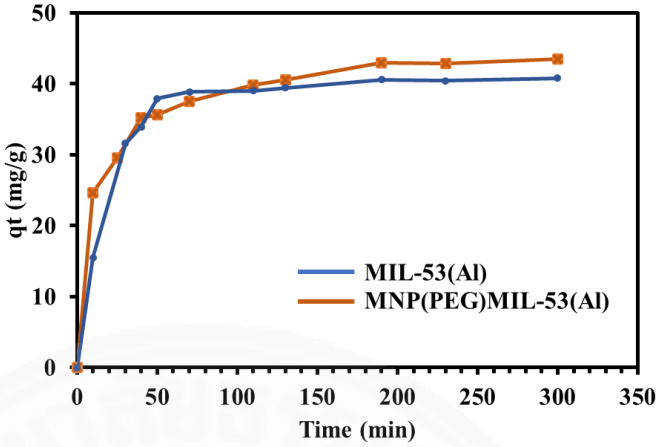


Figure 2: Adsorption equilibrium curves of OTC by MNP(PEG)MIL-53(Al) and pure MIL-53(Al)

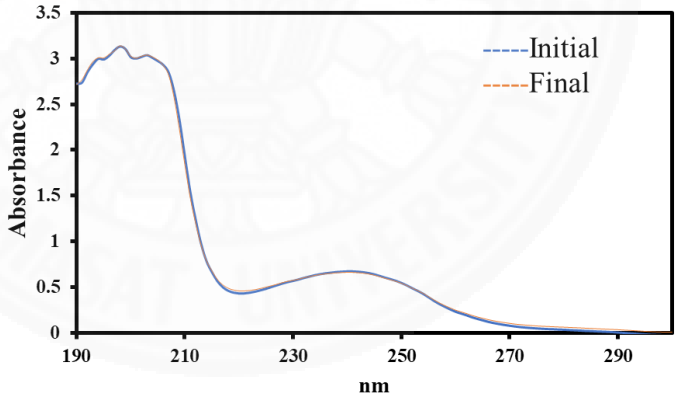


Figure 3: Concentrations of terephthalic acid before(initial) and after(final) incubating with MNP(PEG) (Concentrations were measured using Thermo Fisher scientific GENESYS™ 10S UV-Vis Spectrophotometer)

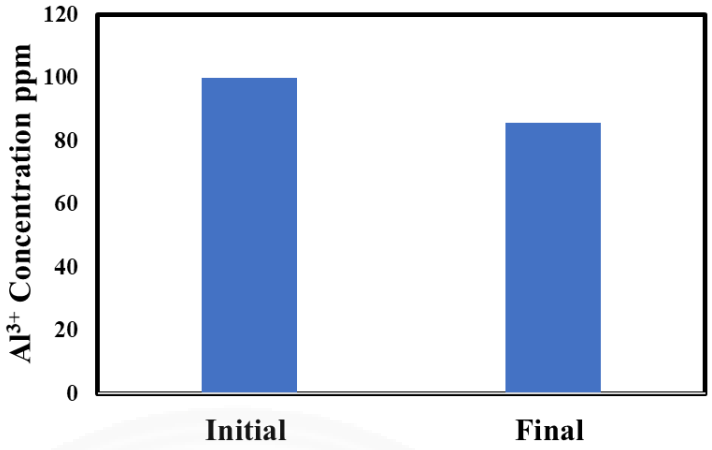


Figure 4: Concentrations of Al^{3+} solution before(initial) and after(final) incubating with MNP(PEG). (Concentrations were measured using Perkin Elmer Optima 8000 ICP-OES)

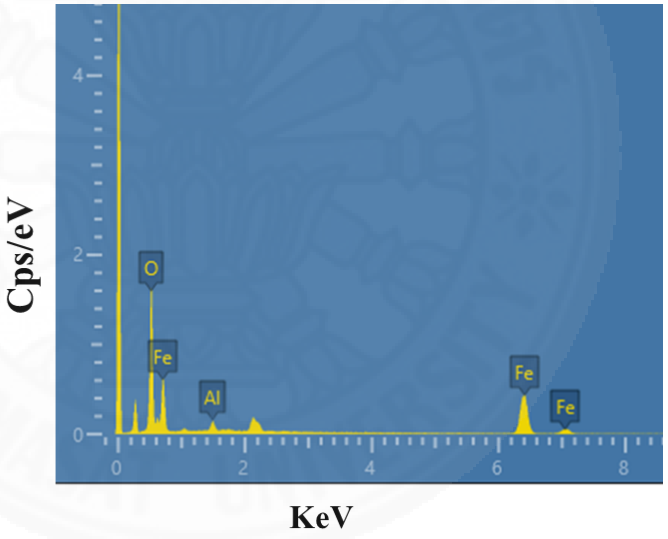


Figure 5: Elemental analysis of MNP(PEG)MIL-53(Al) by SEM-EDS

APPENDIX B

Experimental Setup and Products

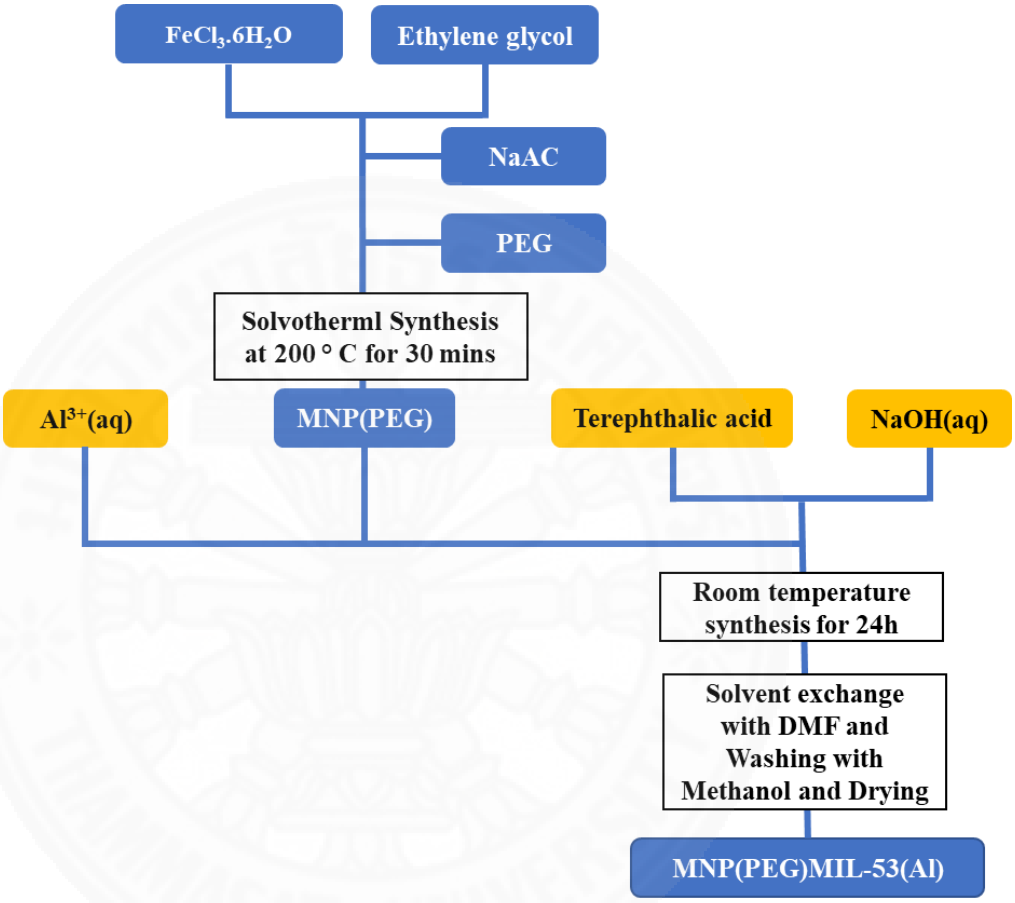


Figure 1: Experimental procedure for the synthesis of MNP(PEG)MIL-53(Al) materials.

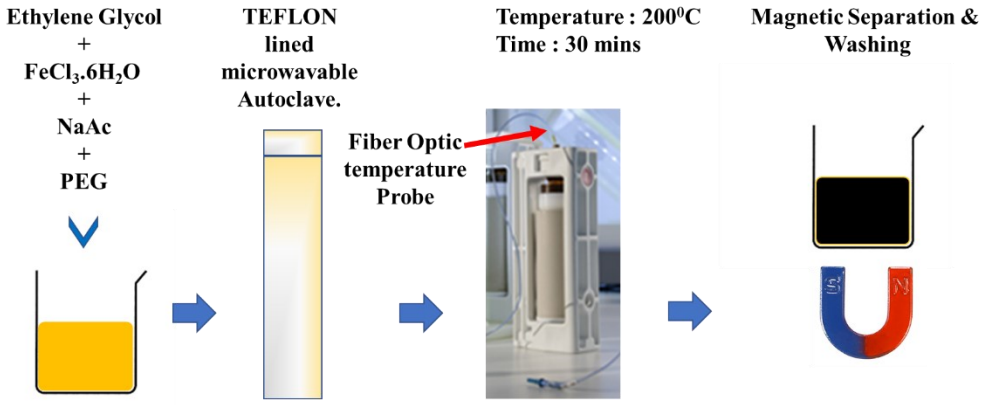


Figure 2: Microwave synthesis of MNP(PEG)

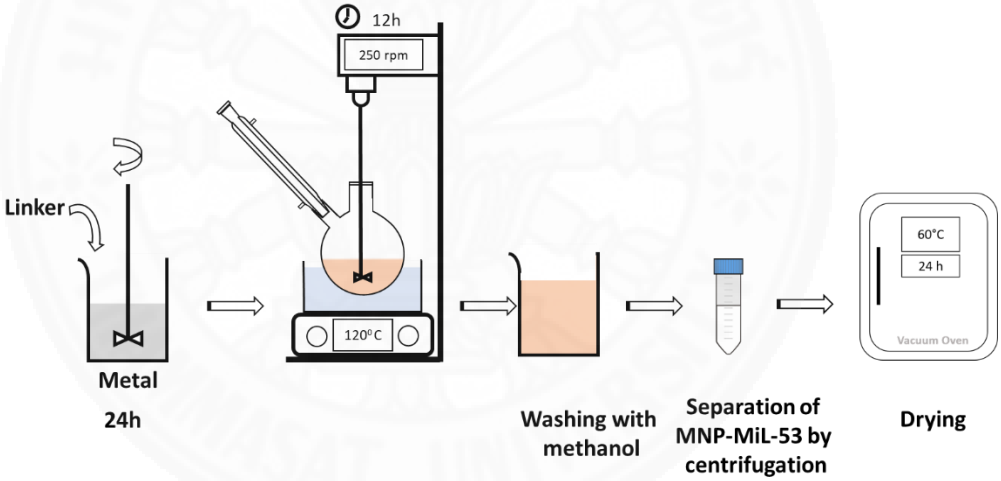


Figure 3: Experimental setup for the room temperature Synthesis of MIL-53(Al)

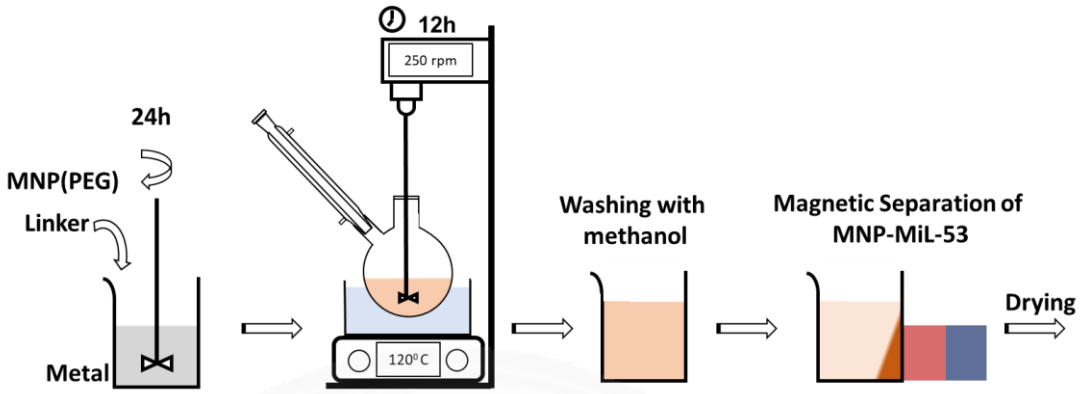
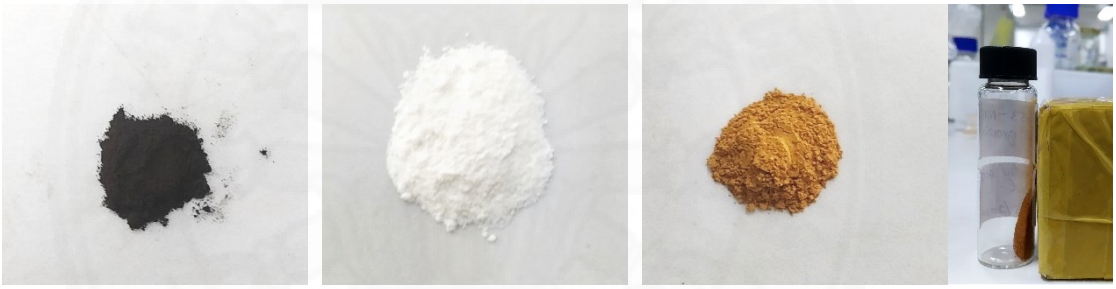


Figure 4: Experimental setup for the room temperature Synthesis of MNP(PEG)MIL



(a) (b) (c)

Figure 5: Products from each synthesis. (a) Bare Fe_3O_4, (b) Pure MIL-53(Al) & (c) MNP(PEG)MIL-53(Al)

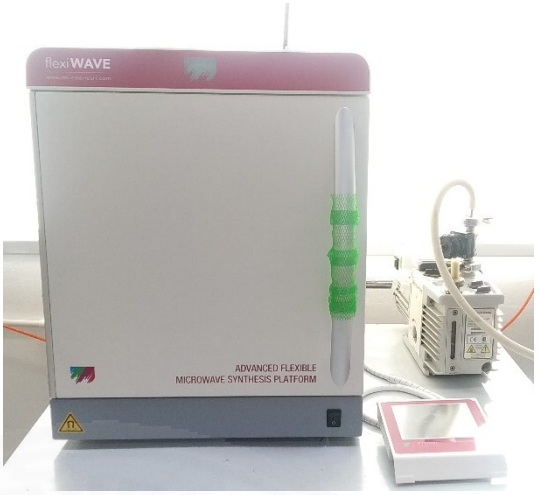


Figure 6: flexiWAVE microwave synthesis platform

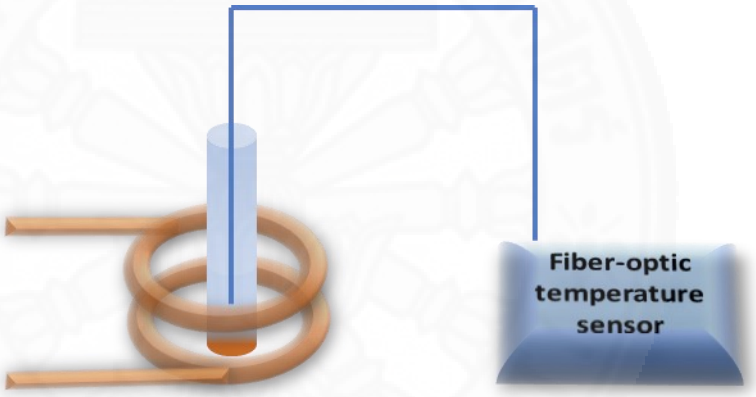


Figure 8: Induction heating and temperature measurement setup

BIOGRAPHY

Name	Mr.Thilina Rajeendre Katugampalage
Date of Birth	September 14, 1990
Education	2015: Bachelor of Science (Biotechnology) University of Mysore, Karnataka, India.
	2019: Master of Science (Engineering and Technology, Chemical Engineering) Sirindhorn International Institute, Thammasat University.
Scholarships	2012: ICCR Scholarship, University of Mysore, India.
	2015: EFS Scholarship, Sirindhorn International Institute of Technology, Thammasat University, Thailand.

Publications

E-Proceeding - MRS Thailand conference 2019

Synthesis and Characterizations of MXene/Magnetic Nanoparticles Composite Loaded Porous PLGA Microspheres.

Conferences and Awards

Best student Oral presentation award - MRS Thailand International conference 2019

Work experience

Teaching assistant/Laboratory Instructor - Fermentation Lab (Subject code - CHS362)

Instructor – Civic Engagement (Subject code - TU100) 1/2019