ADSORPTION OF DOXYCYCLINE AND METHYLENE BLUE ONTO ELECTRIC ARC FURNACE (EAF) STEEL SLAG DERIVED ADSORBENT

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by

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List of Symbols

	Symbol	Unit
A	Arrhenius factor	-
B_T	Constant for Temkin equation	-
C	Boundary layer	-
C_e	Equilibrium concentration of adsorbate	mg/L
C_o	Highest initial adsorbate concentration	mg/L
C_t	Dye concentration at time, t	mg/L
E	Mean free energy	J/mol
E_a	Arrhenius activation energy of adsorption	kJ/mol
k_1	Adsorption rate constant for the pseudo-first-order kinetic	1/hr
k_2	Adsorption rate constant for the pseudo-second-order	g/mg.hr
K_F	Freundlich isotherm constant	mg/g (L/mg$^{1/n}$
K_L	Langmuir adsorption constant	L/mg
W	Mass of adsorbent	g
n_f	Constant for Freundlich isotherm	-
q_e	Amount of adsorbate adsorbed at equilibrium	mg/g
q_m	Adsorption capacity of Langmuir isotherm	mg/g
q_t	Amount of adsorbate adsorbed at time, t	mg/g
R	Universal gas constant	8.314 J/mol K
R^2	Correlation coefficient	-
R_L	Separation factor	-
T	Time	Min
T	Absolute temperature	K
V	Solution volume	L
ΔG^0	Changes in standard Gibbs free energy	kJ/mol
ΔH^0	Changes in standard enthalpy	kJ/mol
ΔS^0	Changes in standard entropy	kJ/mol
λ	Wavelength	Nm

List of Abbreviations

Al_2O_3	Aluminium oxide (Alumina)
DO	Doxycycline
EAF	Electric-Arc Furnace
HCl	Hydrochloric acid
MB	Methylene blue
$NaOH$	Sodium Hydroxide
N_2	Nitrogen gas
rpm	Rotation per minute
SiO_2	Silicon oxide (Silica)
TR	Tetracycline
UV	Ultraviolet
XRD	X-Ray Diffraction

PENJERAPAN DOXYCYCLINE DAN METILENA BIRU MELALUI ELEKTRIK ARKA RELAU(EAR) PENJERAP KELULI SANGA DIPEROLEHI

ABSTRAK

Tujuan penyelidikan ini adalah untuk menilai keupayaan penjerapan zeolit-kaolin dan zeolit untuk menghapuskan Doxycycline, (DO) dan Metilena biru, (MB) daripada larutan akueus. Dalam kajian ini, Elektrik-arka-relau (EAR) keluli sanga yang merupakan sisa industri pembuatan keluli yang digunakan untuk pembentukan zeolit. Nisbah sampel kaolin yang berbeza telah dikaji untuk mendapatkan penjerap yang lebih baik dengan menggunakan 3 jenis farmaseutikal (Tetracycline (TR), Cephalexin (CP) dan (DO)) dan pewarna (MB). Prestasi penjerapan zeolit-kaolin untuk DO dan zeolit untuk penyingkiran metilena biru telah diuji dengan menggunakan kaedah kelompok. Kajian-kajian ini telah memberi tumpuan kepada tiga parameter iaitu kesan kepekatan awal cecair atau larutan dan pewarna ($25 - 400\ mg/L$), suhu ($30\ ℃ - 50\ ℃$) dan pH ($3 - 13$) ke atas penjerapan DO dan MB. Model isoterma Freundlich dan Langmuir telah digunakan pada data penjerapan. Model isoterma Freundlich untuk DO dan MB menunjukkan data penjerapan yang tebaik berbanding model isoterma Langmuir. Untuk penjerapan kinetik, pseudo-tertib kedua membuktikan bahawa proses penjerapan adalah lebih baik daripada pseudo-tertib pertama. Nilai maksimum kapasiti penjerapan zeolit-kaolin untuk DO adalah $188.95, 289.00$ dan $356.70\ \mathrm{mg/g}$ dan $101.75, 120.40$ dan $139.35\ \ \mathrm{mg/g}$ untuk zeolit untuk metilena biru masing-masing pada $30, 40$ dan $50\ ℃$. Berdasarkan keputusan yang diperolehi, ini membuktikan bahawa zeolit-kaolin dan zeolit adalah salah satu penjerap yang memperuntukkan kos yang rendah untuk digunakan sebagai penjerap untuk menyingkirkan farmaseutikal dan pewarna daripada sisa air.

ADSORPTION OF DOXYCYCLINE AND METHYLENE BLUE ONTO ELECTRIC ARC FURNACE (EAF) STEEL SLAG DERIVED ADSORBENT

ABSTRACT

The aim of this work was to evaluate the adsorption capability of zeolite-kaolin and zeolite to remove Doxycycline, (DO) and Methylene blue, (MB) from aqueous solution. In this study, Electric-arc-furnace (EAF) steel slag which is a waste of steel making industry are used for formation of synthetic zeolite. Different kaolin ratios sample has been studied in order to obtain a better adsorbent by using 3 types of pharmaceuticals (Tetracycline (TR), Cephalexin (CP) and (DO)) and dye (MB). The adsorption performance of zeolite-kaolin for DO and zeolite for MB removal were tested by using a batch method. These studies had focussed on three parameters which are effects of initial concentration of pharmaceutical and dye solution ($25 \text{ to } 400 \text{ mg/L}$), temperature ($30°\text{C} \text{ to } 50°\text{C}$) and pH ($3 \text{ to } 13$) on the adsorption of DO and MB. Freundlich and Langmuir isotherms were applied on the adsorption data showed that data are best fitted with Freundlich isotherm model for DO and MB solution. For adsorption kinetic, Pseudo-second-order kinetics proved that the adsorption process are much better than pseudo-first-order kinetics. The maximum adsorption capacity values of the zeolite-kaolin composite for DO were $188.95, 289.00 \text{ and } 356.70 \text{ mg/g}$ and the adsorption capacity values of the zeolite composite for MB were $101.75, 120.40 \text{ and } 139.35 \text{ mg/g}$ at $30, 40 \text{ and } 50°\text{C}$, respectively. Based on the result obtained, it can be proved that the zeolite-kaolin and zeolite composite could provide basis for more low-cost composite to be used as adsorbents for pharmaceutical and dye removal.

CHAPTER ONE

INTRODUCTION

1.1 PHARMACEUTICAL POLLUTANTS

1.1.1 DOXYCYCLINE

Pharmaceutical industry play an important role in discovers, develops, produces, and markets drugs or pharmaceutical drugs for use as medications. They are subject to a variety of laws and regulations that govern the patenting, testing, safety, efficacy and marketing of drugs. They are also making a research to make a new drugs as a cure for some diseases. Drugs are released into the market after studies and clinical testing. The US Food and Drug Administration, FDA has the authority to decide about the administration of drugs to humans. The discovery of a variety of pharmaceutical substances (such as antidepressants, antibiotics, antihistamines, analgesics and other medicines) are found in surface, ground, and drinking waters. Mompelat et al. (2009) said that it is raising concern about the potentially adverse environmental consequences of these contaminants (Lladó et al., 2016). The presence of these pharmaceuticals will threaten the life of aquatic plants and animals in the water. Thus, it will contribute to water pollution and effect the environment. Basically in market, TR, DO, CP and paracetamol are the most used by consumer. In this study, DO has been chosen as pharmaceutical waste. DO is a TR antibiotic. It fights bacteria in the body. Doxycycline is used to treat many different bacterial infections, such as urinary tract infections, acne, gonorrhea, and chlamydia, periodontitis (gum disease), and others.

1.1.2 SOURCES OF PHARMACEUTICAL POLLUTANTS

The sources of pharmaceutical pollutants are obviously from pharmaceutical industry. During the manufacturing and maintenance operations, some of the pharmaceutical residue along with wastewater will flow from the process as an effluent. Pharmaceutical pollutants also will be existed during the cleaning of the pharmaceutical tanks. Those kinds of pharmaceutical pollutants need to be treated first before discharge to near stream or rivers. Pharmaceutical wastewater also can enter environment by landfills leachate. Landfill leachate can contain trace amounts of pharmaceuticals as well. Often this leachate is sent to the same wastewater treatment systems that receive residential wastewater.

1.1.3 EFFECTS OF PHARMACEUTICAL POLLUTANTS

Pharmaceuticals are being used at an increasing rate, and end up in wastewater through excretion and disposal. They also end up in the effluent water of wastewater treatment plants because they are not specifically designed for pharmaceutical removal. The presence of pharmaceutical in rivers is responsible for the causes of skin cancer and other related skin problems which might cause fatal.

Researchers suspect that hormones and pharmaceutical compounds in the water may be responsible for effects on aquatic life including feminization of male fish, sluggish activity or reduced appetite. In addition, pharmaceutical use in the general population is growing, so more unwanted drugs are generated creating increased environmental concerns. In 2005 the average prescription rate in Washington was 8.5 prescriptions per capital per year. The value keep increasing year by year and create a concern on handling all those kinds of wastes (Robert J. Blendon, 1990).

1.2 DYE POLLUTANTS

1.2.1 METHYLENE BLUE

Beside pharmaceutical industry, various industries such as textiles, cosmetics, plastics and paper industries are using synthetic dyes in their production to apply colour to their finished products. A significant amount of dyes are commonly present in the effluents as a wastes of these industries and need to be treated first before discharged into the environment. Torane et al. (2010) reported that MB is one of the most commonly used azo dyes in industry (Fu et al., 2010). Torane et al. (2010) also mentioned that MB is a cationic dye, is most commonly used as the colouring agent for cotton, wool and silk. It is also used as a staining agent to make certain body fluids and tissues easier to view during surgery and diagnostic examinations. The medical applications of MB also include the treatment of methaemoglobinemia and cyanide poisoning (Shakoor and Nasar, 2016).

1.2.2 SOURCES OF DYE POLLUTANT

As mentioned earlier, there are several of industries producing a dye pollutant. However, textile industry is one of the major field producing a high volume of wastewater containing a dye pollutant. Dye are used as a colouring agent that has an affinity to the substrate to which it is being applied. The dye is usually used in an aqueous solution and a mordant are require to improve the fastness of the dye on the fibre. By forming covalent bond by physical adsorption, dye can adhere to compatible surfaces by solution

1.2.3 EFFECTS OF DYE POLLUTANT

Even textile industry play an important role in production of yarn, cloth and clothing, however it producing a by-product, dyes pollutant which having various bad effects on human and aquatic life when released into the environment. Kumar et al. (2011) stated that dyes can be toxic and the biodegradation process is slow and complex, releasing possible carcinogenic products. Additionally, the turbidity levels within discharge streams increases, hindering the ability of fish and other organisms to locate food and reducing photosynthetic activity (Torane et al., 2010).

1.3 PROBLEM STATEMENT

Pharmaceuticals plants generate a large amount of wastes during manufacturing, housekeeping and maintenance operations. Rashed (2013) reported that it is recognized that pharmaceutical wastes (pollutants) reach the environment and can be considered as environmental pollution. Previous study showed in Australia, Brazil, England, Germany, Greece and Italy, more than 80 compounds, pharmaceuticals and drugs metabolites, have been detected in the aquatic environment. The pharmaceutical industry play an important role in discovers, develops, produces, and markets drugs or pharmaceutical drugs for use as medications. There are many types of pharmaceuticals in the market such as Doxycycline (DO), Tetracycline (TR) and many others have been detected in wastewater treatment plant effluents, surface water, ground water, and drinking water. Different classes of drug have been recorded as pharmaceutical pollutants such as analgesics, antibiotics and many others. As for MB which act as dye, is one of the major issue especially in textile industry waste. The textile industry is primarily concerned with the design and production of yarn, cloth, clothing, and their distribution. However, the waste does not undergo a proper treatment before discharge to the environment. The traditional methods for removing dyes in effluent can be divided into three main categories which are physical, chemical and biological treatment. Chemical treatment of dye wastewater with a coagulating or flocculating agent is one of the robust ways to remove colour but this process is not good for highly soluble dyes. On the other hand, biological treatment is incapable of removing dyes from effluent on a continuous basis due to low biodegradability of the dyes, less flexibility in design and operation, larger land area requirement and longer times required for decolourisation-fermentation processes. Physical treatment such as ion exchange, reverse osmosis, precipitation, coagulation and adsorption techniques are widely used. However, most of these processes are costly and lead to generation of sludge or formation of by-products. Among the physical methods, adsorption is one of the effective method to remove pollutants from water. It has become well-established technique to remove pollutants. Adsorption method, which is simple and relatively cost effective, has been widely used. In the past few years, conversely adsorption processes do not add undesirable by-products and have been found to be superior to other technique for drinking water treatment plants in terms of simplicity of design and operation, and insensitivity of toxic substances (Tong et al., 2010). Activated carbon is broadly employed to remove wastewater pollutants. However, commercial activated carbon is expensive. Among all the bio waste materials, steel slag which is one of the industry waste are treated under EAF contains approximately 40% SiO_2 and 6% Al_2O_3. Both of these components are essential constituents for zeolite formation and has many applications in various filed based on its chemical and physical properties. Besides that steel slag also available in abundant and does not required high cost. It has removal capabilities for certain toxic pollutants from water such as dyes, pharmaceuticals and many others. Usually, adsorbents used are carbonaceous materials (activated carbon), clay, siliceous adsorbents and polymeric materials. Most important by using EAF steel slag waste, a safe and good environmental condition can be maintained since waste produced by industry are recycle and reused for other application. In this work, the potential of EAF steel slag derived adsorbent for removal of DO and MB are yet to be investigated.

1.4 OBJECTIVES

The aim of this project is to investigate the efficiency of synthetic zeolite in removing some contaminants from fresh water bodies hence making the water safe for consumption and contribute to the reduction of water pollution. The specific objectives include:

1. To prepare and characterize zeolite based adsorbent by using X-Ray Diffraction (XRD) test as adsorbent from EAF steel slag for the adsorption of DO and MB.
2. To investigate the adsorption capacity of the prepared adsorbent for DO and MB and the effect of initial concentrations, solution pH and operating temperature were studied.
3. To establish the adsorption isotherms, kinetics and thermodynamics for the adsorption process.

1.5 ORGANIZATION OF THESIS

There are five different chapters in this thesis and every chapter has different content and explanation.

Chapter one explains about the definition of pharmaceutical and dye pollutants, sources of the pollutants and effects to the environment. Besides that, synthetic zeolite act as selected adsorbent are presented. Other than that, this chapter also shows about problem statement, research objectives and organization of thesis.

Chapter two discuss about the literature review of this study**.** This chapter also displays about current related study to the conventional and advance method of removal pharmaceutical and dye pollutants. An insight into pharmaceuticals and dyes, discussion on adsorption process, natural and synthetic zeolite are elaborated. Moreover, the isotherm models, kinetic models and thermodynamic parameters determination are included as well.

Chapter three covers materials, equipment and method involves related to this study. Preparation of adsorbent and adsorption experiment procedure also described under this chapter.

Chapter four explains about result of discussion which is cover for selection for an adsorbent, batch adsorption result, isotherm, kinetic and thermodynamic adsorption studies.

Chapter five discuss about conclusion of the whole work and suggestion/recommendation for better improvement.

CHAPTER TWO

LITERATURE REVIEW

2.1 PHARMACEUTICAL POLLUTANTS

Pharmaceuticals are bioactive compound and they are able to cause potential effects on living system. Different classes of pharmaceuticals have found their way to the environment after being used or excreted through wastewater and sewage treatment system. In 2002, 150 pharmaceutical compounds have been monitored in the environment, mainly in aqueous samples which the wastewater treatment enables to remove these pharmaceuticals partially (Rashed, 2013). The amounts of various pharmaceuticals detected in influent of wastewater treatment plants confirmed that many of these substances are not effectively removed by former treatments. Thus, conventional treatment system are unable to totally remove a large amount of the pharmaceutical micro pollutants present in urban wastewaters. More effective and particular treatments are required to reduce the potential impact of these pollutants.

2.1.1 DOXYCYCLINE, DO

In this study, DO has been chosen as a pharmaceutical to be investigated. DO is a tetracycline antibiotic that fights with a bacteria in human body. The major function of DO to treat many different bacterial infections, such as acne, urinary tract infections, intestinal infections, eye infections, gonorrhea, chlamydia, periodontitis (gum disease), and others. Besides that, DO are used to treat blemishes, bumps, and acne-like lesions caused by rosacea. In addition, some DO are used to prevent malaria, to treat anthrax, or to treat infections caused by mites, ticks, or lice.

2.2 DYE POLLUTANTS

Among many different pollutants released from industrial applications, dye are important and should pay more attention due to their environmental impact, especially their toxicity to aquatic life in the water. Dye are an important class of pollutants, and can even be identified easily by the human eye. Gupta and Suhas (2009) and Ghaedi et al. (2012) said that dye are mainly discharged into wastewaters from various industries, such as the dye manufacturing, textile, printing, food, cosmetic, and leather manufacturing industries. Due to the high concentration of dye in wastewater, sunlight are difficult to penetrate. The treatment of wastewater is a difficult to perform since dyes are more stable due to the presence of light and heat. Aysan et al. (2016) mentioned that the removal of dye from wastewater is an extremely important application. Since the wastewater contains a complicated matrices of matrix, a proper treatment should take consideration.

2.2.1 METHYLENE BLUE, MB

In this work, MB has been chosen as a dye to be investigated. MB is commonly used as a colouring agent in textile industry. Figure 2.1 showed chemical structure of MB (Anon., n.d.). Kumar and Kumaran (2005) stated that although MB is not strongly hazardous to an environment, however it can cause some harmful effects where acute exposure to MB will cause increased heart rate, vomiting, shock, cyanosis, jaundice, and quadriplegia and tissue necrosis in humans. Wastewater contains significant amount of MB need to undergo a proper treatment before discharge to river in order to prevent pollution to an environment.

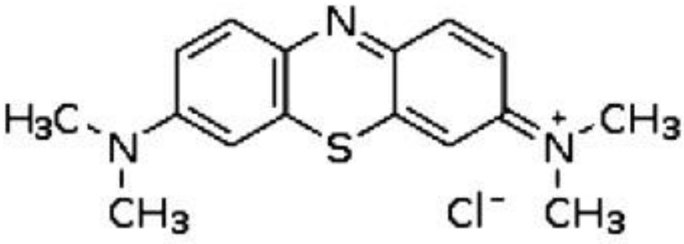

Figure 2.1: Chemical structure of MB

2.3 CONVENTIONAL METHODS FOR ADSORPTION PROCESS

Pharmaceutical and dye pollutants are kinds of waste which are produced from an essential industries. If want to minimize these kinds of pollutants produced by discontinued the industries production, it is not worth because these industries application gain a high demand from human usage like medicine, cloth and many others. There are a lot of method that can be used in order to remove the pollutants from wastewater.

Several different methods are reported in literature data are shown in Table 2.1. The method of removal of pollutants from wastewater can be divided into three categories which are physical, biological and chemical methods.

2.3.1 PHYSICAL METHODS

Physical methods include processes where no addition of any chemical or biological changes are carried out and strictly physical phenomena are used to improve or treat the wastewater. For instances, coarse screening need to carry out to remove any large object from entering the wastewater treatment plant. Physical methods also include membrane-filtration processes (nanofiltration, reverse osmosis, electrodialysis) and adsorption techniques. However, the major disadvantages of the membrane processes is that they have limited lifetime before fouling phenomena tend to occur. Besides that,

Table 2.1: Different technologies for dye removal (Robinson et al., 2001)

Process	Technology	Advantages	Disadvantages
Conventional treatment process	Coagulation, Flocculation, Biodegradation	Simple, economically feasible	High sludge production, handling and disposal problems
		Economically attractive publicly acceptable treatment	Slow process, necessary to create an optimal favourable environment, maintenance and nutrition requirements
	Adsorption on activated carbons	The most effective adsorbent, great, capacity, produce a high-quality treated effluent	Ineffective against disperse and vat dyes, the regeneration is expensive and results in loss of the adsorbent, non-destructive process
Established recovery processes	Membrane separations	Removes all dye types, produce a high-quality treated effluent	High pressures, expensive, incapable of treating large volumes
	Ion-exchange	No loss of sorbent on regeneration, effective	Economic constraints, not effective for disperse dyes
	Oxidation	Rapid and efficient process	High energy cost, chemicals required
Emerging removal processes	Advanced oxidation process	No sludge production, little or no consumption of chemicals, efficiency for recalcitrant dyes	Economically unfeasible, formation of by-products, technical constraints
	Selective	Economically attractive, regeneration is not necessary, high selectivity	Requires chemical modification, non-destructive process
	Bio-adsorbents Biomass	Low operating cost, good efficiency and selectivity, no toxic effect on micro-organisms	Slow process, performance depends on some external factors (pH and salts)

membrane method required high operation cost since the membrane need to replace at certain time to prevent fouling. According to abundant of literature review from journal, liquid phase adsorption is the most popular and selected methods for the removal of pollutants from wastewater since proper design of the adsorption process tend to produce a high quality treated effluent.

2.3.1.1 ADSORPTION PROCESS

During the last decades, the concerned about the potential public health impact of environmental contaminants originated from industrial, agricultural and human activities has risen from time to time. The waste which are also known as emergent pollutants, include prescription and non-prescription human and veterinary pharmaceutical compounds and personal care products (PPCPs). Adsorption has become well-established technique to remove pollutants. Adsorption method which is also simple and relatively low cost, has been widely used in plant. Salem Attia et al. (2013) said that adsorption process do not add undesirable by-products and have been found to be superior compare to other techniques in terms of simplicity of design and operation, and insensitivity of toxic substances. Adsorption is the most popular method used for removal of trace amount of pollutants from wastewater before discharge to wastewater treatment plant. Other techniques such as reverse osmosis and membrane filtration are used for post-treatment of drinking water. Both method are not applicable due to high cost. Among adsorbents, there are few reports available showed that activated carbon been used as an adsorbent in removing some pharmaceuticals. However, due to high production and maintenance cost plus not being friendly through environment, a bio-waste materials appear to be one of the efficient adsorbent. Since bio-waste are relatively available in abundant, adsorption method by utilizing a bio-waste has been selected as the economical method compare to other methods.

2.3.2 CHEMICAL METHOD

A number of different chemical methods are used such as coagulation or flocculation combined with floatation and filtration, precipitation-flocculation with $Fe(II)/Ca(OH)_2$, electro kinetic coagulation, convectional oxidation methods by oxidizing agent (ozone), irradiation, electro-floatation or electrochemical processes. Although these chemical methods are effective in removal of pollutants from the wastewater but it is not widely used due to the high cost. In addition, chemical method tend to promote a high disposal problem because of the accumulation of the concentrated sludge. Besides that, chemical method also required high electrical energy demand, large consumption of chemical reagents and high operational cost.

2.3.3 BIOLOGICAL METHOD

Biological method are most economical compared to other method. Biological treatment utilize organisms such as bacteria, yeast, algae and fungi to break down organics substance are widely used around the world. Unfortunately, their application is often restricted due to the technical constraints. Bhattacharyya and Sarma (2003) stated that biological treatment is not found to be advantageous as it requires large land area and is constrained by sensitivity toward diurnal variation as well as toxicity of some chemicals, and less flexibility in design and operation. Biological treatments is incapable of removing dyes from effluent on a continuous basis. This is due to the time period of a few days required for decolourisation-fermentation processes (Robinson et al., 2001).

2.4 ADVANCED METHOD

Besides conventional method, advanced method has been proposed as a new approach towards the removal of pollutants from wastewater. Several technologies such as ozonation, advanced oxidation process, membrane filtration and Fenton-based electrochemical oxidation has been introduced. Basically ozonation in wastewater promote the micro pollutants to directly oxidize by O_3 or by hydroxyl radicals ($HO\bullet$) which are formed during ozone decay. By undergo direct reaction, pharmaceutical and dye compounds will react rapidly with O_3 and oxidized, while the rest will be oxidized by $HO\bullet$. When ozone resistant contaminants start to appear, ozone will be transformed to HO radicals and the ozonation turn to advanced oxidation process (Zhang et al., 2016). The purpose of the formation of AOP is to use $HO\bullet$ as a strong oxidant. The advantages of this treatment is to disinfect the final effluent before discharge it. However, even though a lot of research proved that AOPs are an efficient way to degrade synthetic contaminants including pharmaceutical and dye, various intermediate are usually produced during the partial oxidation of complex compounds. Besides that, their toxicity can be worse than the primary contaminants. In addition, Moussavi et al. (2013) stated that AOPs are very expensive and difficult to operate for complete elimination of recalcitrant compounds including antibiotics and dyes.

Rivera-Utrilla et al. (2013) reviewed that the removal of pharmaceuticals from wastewater by using activated carbon, advanced oxidation technologies using ozone, UV radiation, gamma radiation and electro-oxidation. In adsorption, carbon activated by phosphorous oxyacids showed high adsorption capacity ($345\ mg/g$) for pharmaceuticals. Advanced oxidation treatments were found as a most effective in removing pollutants from wastewater. Removal efficiency for various pharmaceuticals was $70-100\%$ using gamma radiations, 40-99% using ozone-based advanced oxidation and followed by $20-100\%$ using UV radiations.

While Sirés and Brillas (2012) reviewed that the removal of pharmaceuticals using electrochemical oxidation, Fenton-based electrochemical oxidation and photoelectrocatalysis. Both of them recommended UV radiation method for refractory carboxylic acids produced as secondary by-product during pharmaceuticals decomposition.

Ikehata et al. (2006) reported that the removal of pharmaceuticals pollutants through ozonation and advanced oxidation and recommended that these two methods as a suitable option for removal of pharmaceuticals from wastewater. Based on the research, it can be proved that simple ozonation treatment are sufficient to remove pharmaceuticals containing active functional groups. For instances non-aromatic carbon-carbon rings containing double bonds, amines and activated aromatics rings.

2.5 ZEOLITES

Zeolites are microporous crystalline solids with well-defined structures. Basically, zeolites are crystalline solids structures which are made by silicon, aluminium and oxygen as shown in Figure 2.2 (Chris, n.d.). All of them are then form a framework with cavities and channels inside where cations, water and small molecules may reside. Besides that, they are also are known as molecular sieves. There are two types of zeolites which are natural zeolite and synthetic zeolite. Synthetic zeolite has been introduced due to the available of abundant of raw materials of zeolite formation. Generally, there are 191 unique zeolite frameworks identified and over 40 naturally zeolite frameworks are known.

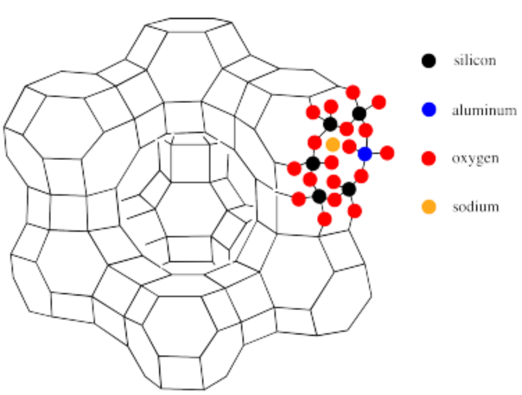

Figure 2.2: Structure of zeolite

Figure 2.3 shows a framework structure of zeolite (Bell, 2001). In 1954, zeolites were introduced as adsorbents for industrial separations and purifications (Peskov, n.d.). Nowadays, zeolites are used in a variety of industry applications due to their unique porous properties. They are widely used in as ion-exchange beds in domestic and commercial water purification, softening and other applications. In addition, zeolites are also widely used in many processes which act as catalysts and adsorbents. Their well-defined pore structure and due to the adjustable acidity make them highly active in many reactions.

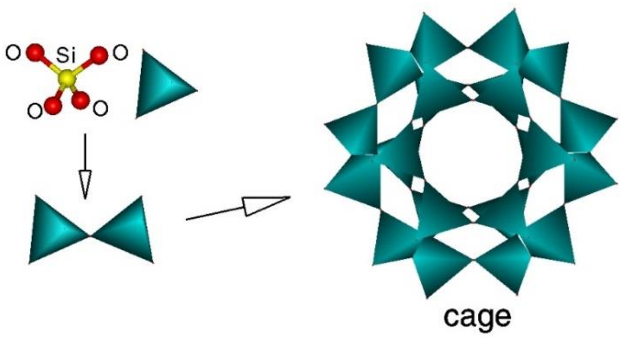

Figure 2.3: Framework structure of zeolite

Zeolites are crystalline alumina silicates with open 3D framework structures which made up of SiO_4 and AlO_4 tetrahedral. They were linked to each other by sharing all the oxygen atoms to form regular intra-crystalline cavities and channels of molecular dimensions. Basically, zeolite's framework are made up of 4 connected network of atoms. These framework are formed in tetrahedral shape, with a silicon atom at the centre and oxygen atoms at the corners. Figure 2.4 shows that they were linked together by their corners to from a rich variety of structures (DuHamel, 2015).

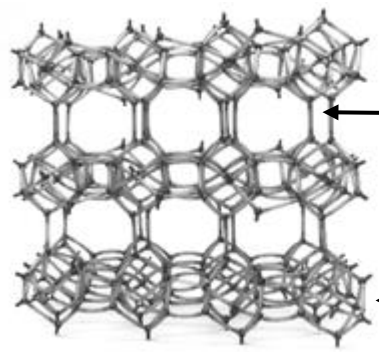

Figure 2.4: Three dimensional cages and channels of zeolite structure

Basically, the framework structure consists of linked cages, cavities or channels as shown in Figure 2.4. All of them should have a big enough space so that a small molecules are allow to enter. For system that have a large voids, it shows the consistent of low specific density of these compounds. In industries application, the voids are interconnected and form long wide channels of various sizes depending on the compound. By the existence of these channels, it allows the resident ions and molecules into and out of the structure easily. Generally, alumina silicate framework is negatively charged and attracts the positive cations that reside in cages in order to compensate negative charge of the framework.

The general formula representing their structure could be written as follows:

$$Mx_{/n}[(AlO_2)_x(SiO_2)_y] \bullet wH_2O \qquad (2.1)$$

In this general formula, M is the positive counter ion of valence $+n$ which balances the positive charge due to the x (AlO_2-) groups. The ratio y/x represents the 45 Silicon-to-Aluminium ratio and is a parameter of paramount importance to describe the zeolite's properties. The sum $(x + y)$ represent the total number of tetrahedral in a unit cell of the particular zeolite. In general, zeolite can be classified into various family as presented in Table 2.2.

Table 2.2: Family of zeolites (Król and Mikuła, 2017)

Family of zeolites	Minerals	Shape
Analcime	Analcime, pollucite, wairakite, bellbergite, bikitaite, boggsite, brewsterite	Cubic/tetrahedral
Chabazite	Chabazite, willhendersonite, cowlesite,dachiardite, edingtonite, epistilbite, erionite, faujasite, ferrierite	Rhombohedral
Gismondine	Amicite, garronite, gismondine, gobbinsite, gmelinite, gonnardite, goosecreekite	Monoclinic/orthogonal
Harmotome	Harmotome, phillipsite, wellsite	Monoclinic
Heulandite	Clinoptilolite, heulandite, laumontite, levyne, mazzite, merlinoite, montesommaite, mordenite	Monoclinic/orthogonal
Natrolite	Mesolite, natrolite, scolecite, offretite, paranatrolite, paulingite, perlialite	Orthogonal/tetrahedral
Stilbite	Barrerite, stilbite, stellerite, thomsonite, tschernichite, yugawaralite	Monoclinic

2.5.1 NATURAL ZEOLITES

Basically, zeolites formed as crystals in small cavities of basaltic rocks over the years or as volcanic tuffs or glass altered by the interaction with saline water. These natural zeolites are formed in a number of geological environments such as alkaline deserts, lake sediments, ash ponds and marine sediments at relatively low temperature and under natural conditions. They also get crystallized in geologically young metamorphic rocks in mountainous regions.

There are many natural zeolites identified in the previous research. Clinoptilolite, mordenite, phillipsite, chabazite, stilbite, analcime and laumontite are very common forms whereas offretite, paulingite, barrerite and mazzite, are much rarer. Wang and Peng (2010) reviewed that clinoptilolite, popularly known as Clino zeolites is the most abundant natural zeolite and is widely used in the world. The Clinoptilolite has been widely used in agriculture, soil amendment and feed additives because of its higher acid resistant silica content. However, such zeolites are contaminated by other minerals such as Fe^{2+}, SO_4^{2-}, quartz, other zeolites, and amorphous glass making it is not be suitable for several industries applications where uniformity and purity are important.

Natural zeolites are environmentally and economically acceptable aluminosilicate materials since it offers an exceptional ion-exchange and sorption properties. Their effectiveness in different processes depends on their physical and chemical properties. Due to the unique tree-dimensional porous structure of natural zeolites, it has been widely used in many application. Since it consists of excess of the negative charge on the surface of zeolite, natural zeolites belong to the group of cationic exchangers (Margeta et al., 2013).

2.5.2 SYNTHETIC ZEOLITES

Synthetic zeolites means that these zeolites are synthesized by chemical processes, which result in a more uniform and purer state as compared to the natural zeolites. The raw materials used in the formation of synthetic zeolites are pure chemicals rich in silica and alumina, minerals which is usually available as the by-products or wastes of industries. Based on the Si/Al molar ratio in the activated steel slag, zeolites can be classified as “low silica zeolites”, “intermediate silica zeolites” and “high silica zeolites”, as listed in Table 2.3.

Table 2.3: Grades of zeolites (Ilić and Wettstein, 2017)

Zeolite grade	Si/Al molar ratio	Some of the common minerals names and their framework codes
Low silica	≤2	Analcime (ANA), cancrinite (Özcan et al.), Na-X (FAU), natrolite (Margeta et al.), phillipsite(Arya and Philip), sodalite (SOD)
Intermediate silica	2-5	Chabazite (CHA), faujasite (FAU), Mordenite (MOR), Na-Y (FAU)
High silica	≥5	ZSM-5(MFI), zeolite-b (BEA)

2.5.3 COMPARISON OF ADSORBENTS ON ADSORPTION

Various adsorbents such as zeolites and other composites, and their maximum monolayer adsorption capacities for DO and MB uptake are listed in Table 2.4 and 2.5.

Table 2.4: Comparison of monolayer adsorption on DO onto various adsorbents

Pollutant	Adsorbent	Temperature (℃)	Maximum monolayer adsorption capacities (mg/g)	References
Doxycycline	Zeolite-kaolin composite from electric-arc-furnace (EAF) steel slag	30	Current study	Current study
	Zeolite composite from electric-arc-furnace (EAF) steel slag	30	Current study	Current study
Flumequine polymer	Kaolinitic clay	25	3.12	Khandal et al. (1991)
Oxytetracycline	Na-kaolinite	25	15.18	Figueroa et al. (2004)
Tetracycline	Na-kaolinite	25	29.00	Figueroa et al. (2004)
	Kaolinite	25	3.80	Li et al. (2010)
	Mesoporous silica	23	44.40	Turku et al. (2007)
Tylosin	Kaolonite	-	6.80	Bewick (1979)

Table 2.5: Comparison of monolayer adsorption on MB onto various adsorbents

Pollutant	Adsorbent	Temperature (℃)	Maximum monolayer adsorption capacities (mg/g)	References
Methylene blue	Zeolite-kaolin composite from electric-arc-furnace (EAF) steel slag	30	Current study	Current study
	Zeolite composite from electric-arc-furnace (EAF) steel slag	30	Current study	Current study
	Z-AC composite from oil palm ash	50	285.71	Khanday et al. (2017)
	Natural zeolite	60	29.18	Han et al. (2009)
	Zeolite NaA	30	64.80	Sapawe et al. (2013)
	Zeolite fly ash (ZFA)	NA	14.30	Shah et al. (2011)
	Chitosan modified zeolite	25	37.04	Xie et al. (2013)
	Biopolymer oak sawdust composite	22	38.46	Gouamid et al. (2013)
	Montmorillonite/$COFe_2O_4$composite	NA	97.75	Ai et al. (2011)
	GO/CA composite	25	181.81	Li et al. (2013)
	$TiO_2/SiO_2/Fe_3O_4$ composite	25	147.00	Zhang et al. (2013)

2.6 CHARACTERIZATION OF ADSORBENT

It is essential to test the adsorbent structure in order to identify the physical and chemical characteristics of the adsorbent. Based on literatures, it stated that the characterization of the structure and surface of the adsorbent is considerable interest for the development of adsorption and separation process.

2.7 ADSORPTION PARAMETERS

There are a few factors with strongly influence the adsorption process. Salem Attia et al. (2013) reported that batch adsorption process was carried out to study the influence of different adsorption parameters such as amount of contact time, solution pH, temperature, biomass loading and initial concentration of adsorbate. In this study, only three parameters will be investigated which are initial pH value of pollutants, initial concentration of pollutants and operating temperature.

2.7.1 INITIAL CONCENTRATION

Initial concentration of pharmaceutical and dye pollutants tend to give strong influence towards adsorption capacity and rate of adsorption. Akhtar et al. (2016) reviewed that initial concentration are able to minimize mass transfer resistance by supplying necessary driving force. Generally, initial concentration of pollutants will increase the adsorption of pharmaceutical and dye onto adsorbent surface such as microporous, mesoporous, negatively or positively charge surface. High concentration of pollutants will promote the accessibility of pores for adsorbate molecules and increases interactions at solid-liquid interface. According to Aksu and Tunç (2005), they observed that there was an increase in adsorption capacity of three adsorbents which are activated carbon, activated sludge and Rhizopus arrhizus by increasing initial concentration of penicillin G from 50 to 1000 mg/L. Besides that, Tian et al. (2006) reported that amount of levofloxacin adsorbed onto polyacrylonitrile filters at initial concentration of

100 mg/L was much more than 5 mg/L. From the research obtained, it can be proved that the higher initial concentration of pollutants, the higher amount of pharmaceuticals adsorbed onto the adsorbent and will also be full or blocked faster.

2.7.2 SOLUTION pH

The pH of the solution play an important role in order to influence on adsorption of pharmaceuticals and dyes especially in case of interactive sorption. Nandi et al. (2009) reported that the pH of the solution changed due to the surface charge of the adsorbent, the degree of ionization of the adsorptive molecule and extent of dissociation of functional groups on the active sites of the adsorbent. Based on the Salem Attia et al. (2013) literature review, it stated that the removal of pollutants was favoured at low pH values. Thus, as pH turns from acidic to basic conditions, these compounds were become less efficient.

2.7.3 TEMPERATURE

Last but not least, temperature is also essential in determining the adsorption capacity of pollutants. Based on the literature review, it stated that the adsorption behaviour of solute onto adsorbent might be endothermic or sometimes exothermic. Basically, high temperature tend to increase molecular activity at boundary layer interface. Then, it may increase the rate of diffusion of solute molecules. In this case, the adsorption are in endothermic condition. Based on Khanday et al. (2017) studied, the adsorption capacity of methylene blue were $143.47\ mg/g$, $199.6\ mg/g$ and $285.71\ mg/g$ at 30°C, 40°C and 50°C. It can be proved that at higher temperature, maximum adsorption capacity were able to achieve. However, Akçay et al. (2009) found that adsorption of flurbiprofen antibiotic decreased when the temperature increase from 25°C to 40°C. Akhtar et al. (2016) mentioned that temperature are essential in modify molecular activity at solid interface, groups of solute and adsorbent species and modify the nature of adsorbent.