IRON-MODIFIED COMPOSITE ADSORBENT COATING FOR ACID RED 1

REMOVAL AND ITS REGENERATION FEASIBILITY BY HETEROGENEOUS

FENTON-LIKE PROCESS

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By

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Symbol		Unit
C_o	Initial concentration	mg/L
C_t	Concentration at time t	mg/L
λ_{max}	Maximum wavelength	nm

LIST OF ABBREVIATIONS

AOP   Advanced oxidation process

APE   Acrylic polymer emulsion

AR1   Acid Red 1

Bent   Bentonite

Febent   Iron-modified bentonite

CAC   Composite adsorbents coating

CF   Cotton fabric

EDX   Energy-dispersive X-ray spectroscopy

EPIDMA   Epichlorohydrin-dimethylamine

HP   Hydrogen peroxide

IUPAC   International Union of Pure and Applied Chemistry

R^2 Coefficient of determination

SEM   Scanning electron microscopy

UV   Ultraviolet

UV-Vis   Ultraviolet–visible spectroscopy

LAPISAN PENJERAP KOMPOSIT FERUM TERUBAHSUAI UNTUK PENYINGKIRAN PEWARNA ASID MERAH 1 DAN KEBOLEHLAKSANAAN PEMULIHANNYA OLEH PROSES ALA-FENTON HETEROGEN

ABSTRAK

Penjerapan merupakan teknik yang biasa digunakan dalam rawatan air sisa kerana proses ini adalah murah, mudah dan cekap dalam pengoperasian. Namun, pemulihan penjerap yang terpakai biasanya disekat oleh interaksi yang kuat antara permukaan penjerap dan bahan jerap. Sekiranya, pemulihan dan penggunaan semula penjerap dapat dijalankan bagi beberapa kitaran, penjimatan dari segi ekonomik dapat dicapai. Justeru itu, penyelidikan terkini telah memberi tumpuan kepada kebolehlaksanaan pemulihan lapisan penjerap komposit (CAC) yang dipenuhi oleh (Asid Merah 1) AR1 dengan menggunakan proses ala-Fenton heterogen. Bentonit telah diubahsuaikan dengan ferum untuk menggantikan bentonite bengkak yang digunakan dalam formulasi asal CAC. Hasil kajian menunjukkan bahawa penjerapan AR1 dengan kepekatan awal 50 ppm adalah sangat efesien dan keseimbangan dapat dicapai dalam masa dua jam bagi kedua-dua formulasi, iaitu APE-bent-EPIDMA/CF dan APE-Febent-EPIDMA/CF. Kadar penyingkiran AR1 bagi bentonit yang telah diubahsuaikan dengan ferum adalah lebih tinggi berbanding dengan kadar penyingkiaran AR 1 oleh bentonit bengkak. Kemampuan process Fenton heterogen untuk memulihkan APE-Febent-EPIDMA/CF yang dipenuhi oleh AR1 telah dinilaikan dalam dua keadaan iaitu dengan bantuan sinaran UV dan tanpa sinaran UV (dalam keadaan gelap). Kesan pengaruhan asid dan alkali terhadap desorpsi AR1 juga dikaji dengan menggunakan asid hidrocholik dan natrium hidrosida dengan kemolaran 0.1 M. Kemolaran awal hidrogen peroksida yang digunakan ialah 8.82 mM,. Selepas proses pemulihan dengan bantuan sinaran UV selama 3 jam, APE-Febent-EPIDMA/CF masih boleh mencapai peratus penyingkiran AR1 yang tinggi (>80%), bagi lima kitaran penjerapan. Hasil kajian menunjukkan natrium hidroksida merupakan ajen elusi yang sesuai untuk proses desorpsi AR1 (pewarna anionik) daripada APE-Febent-EPIDMA/CF.

IRON-MODIFIED COMPOSITE ADSORBENT COATING FOR ACID RED 1 REMOVAL AND ITS REGENERATION FEASIBILITY BY HETEROGENEOUS FENTON-LIKE PROCESS

ABSTRACT

Adsorption is widely used technique in wastewater treatment because the process is low cost, ease of operation and efficient. However, regeneration of spent adsorbents is usually restricted by the strong interactions between the surface of adsorbents and adsorbates. It would be very economical if the spent adsorbents can be regenerated and reused for many cycles. Hence, this current research had been focussed on the feasibility of heterogeneous Fenton process to regenerate Acid Red 1 (AR1) loaded composite adsorbent coating (CAC). The iron-modified bentonite was synthesised to replace swelled bentonite in the original formulation of CAC (APE-bent-EPIDMA/CF). The results showed that the adsorption of AR1 with initial concentration of 50 ppm was very efficient and equilibrium was achieved within two hour for both formulations. After modified with iron, the removal rate of AR1 in aqueous solution was higher than that of swelled bentonite. Ability of heterogeneous Fenton process to regenerate the spent APE-Febent-EPIDMA/CF was evaluated under the assistance of UV and without UV (in dark condition). The effect of acid and base on the desorption of AR1 was also studied using 0.1 M of hydrochloric acid (HCl) and 0.1 M sodium hydroxide (NaOH). The initial concentration of hydrogen peroxide used was 8.82 mM. After regeneration process for 3 hours under the UV assistance with addition of 0.1 M NaOH, the APE-Febent-EPIDMA/CF was still able to retain high percentage removal of AR1 (>80%) up to five cycles of adsorption. The findings revealed that sodium hydroxide is a good elution agent to desorb AR1 (anionic dye) from the APE-Febent-EPIDMA/CF coating.

CHAPTER ONE

INTRODUCTION

1.1   Textile Industry in Malaysia

Over the decades, Malaysia has embarked on her export-oriented industrialization journey especially in textiles and textile product industry due to its increasing demand in the world market. In 2016, the textiles and textile product industry was the tenth largest export earner with RM13.9 billion, contributing approximately 1.8% to Malaysia's total exports of manufactured goods. Currently, the top three export markets for Malaysian textile and apparel are United States, Turkey, and Japan. The United States remains the largest export market for Malaysian textiles products, contributing for over 18% of the industry's total textile and apparel exports every year (Malaysian Investment Development Authority, 2017). Moreover, with the new TPP market, Malaysia will eliminate import taxes on 79.2% of U.S. textiles and apparel exports immediately (Yarnsandfibers News Bureau, 2016).

The Deputy International Trade and Industry Minister, Datuk Ahmad Maslan reported that the world demand for textile and apparel is expected to further increase to $160 billion (RM641.2 billion) by the end of 2018. The growth is mainly driven by the increasing demand in the global market for high quality textiles and clothing from Malaysia, as well as the rising purchasing power in major importing countries (Nick, 2017). Besides, Ahmad also reviewed that, 970 garment and textile factories were registered with the ministry, of which over 400 are into making ready-made garments, 80 are into making thread and 108 are into manufacturing knitted fabric (Yarnsandfibers News Bureau, 2016, Azuna Hasbullah and Rahman, 2016). Hence, the

position of Malaysia as one of the developing country in the textile and clothing industry is strengthened. Today, Malaysia is well-known for quality, reliability and prompt delivery of a myriad and ever changing range of fashionable apparel and textile items.

1.2   Environment Impact of Textile Effluent

Indeed, textile industry have brought numerous benefits to our country, but also act like a double-edged sword. The development of the textile industries has left a large footprint on the environment in which dyes used in different processes in their production lines might escape to the water bodies nearby. Figure 1.1 shows the major sources of dye effluent released from the textile industry in Malaysia with the Johor state on top of the rank (28.6%), followed by Pulau Pinang with the discrepancy of 0.4%. Each textile industry manufacturer in Malaysia bear his own responsibility to have wastewater treatment facilities to deal with the wastewater produced and the treated effluents are usually disposed to a drain instead of a centralized treatment system (Pang and Abdullah, 2013). With the aim of reducing water pollution problems, it is compulsory to remove the colour and chemical compounds from the wastewater in order to meet the legislative requirement. Unfortunately, yet some of them still fail to meet the disposal limits set by the Department of Environment Malaysia as listed in Environmental Quality (Sewage and Industrial Effluents) Regulations 1979.

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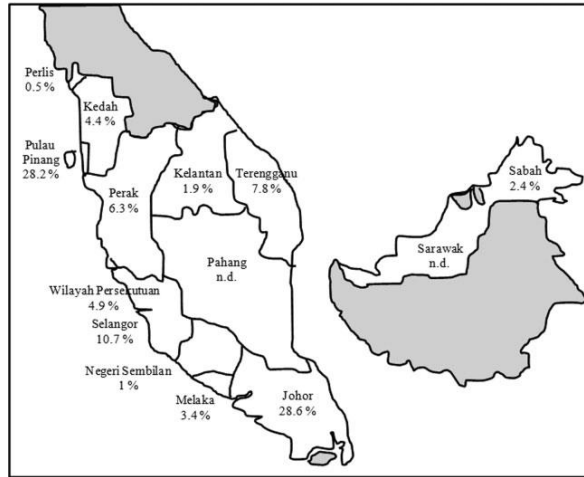
Figure 1.1: The percentage of textile wastewater discharged from the different states in Malaysia, contributing to water pollution (Pang and Abdullah, 2013)

According to previous estimation, 2% of dyes are directly discharged in aqueous waste matters (Kausar et al., 2018). It was also estimated that approximately 10%-15% of total dyes used were lost during the dyeing processes and released into wastewater because of the low levels low dye-fiber fixation (Sahinkaya, 2017). Different classes of dye will have respective fixation degree or affinity on different types of substrate, as shown in Table 1.1 below.

Table 1.1: Fixation degree of different classes of dyes on different substrates and percentage loss of dyes in textile effluent (Kausar et al., 2018)

Dye class	Substrate type	Fixation degree (%)	Loss in effluent (%)
Direct	Cellulose	70–95	5–30
Acid	Polyamide	80–95	5–20
Base	Acrylic	95–100	0–5
Reactive	Cellulose	50–90	10–50
Disperse	Polyester	90–100	0–10

The dyes present in the wastewater are non-biodegradable due to their complex structures and high molecular weight (Wang et al., 2014). Discharge of these kind of wastewaters into the aquatic environment causes serious damage to the environment by indirectly blocking sunlight due to their intense colour and by decreasing the

oxygenation capacity of the surface water (Thabet and El-Zomrawy, 2016). Their visibility is obvious even at low concentrations (<1 mg L^{-1}) and causes the resultant undesirable colour to a water body. In addition, textile effluent usually have high level of chemical oxygen demand (COD), biological oxygen demand (BOD), acidity, chlorides, sulphates, phenolic compounds, and various heavy metals (Verma, 2008). Discharge of these dyes in to hydrosphere affects the people who may use these effluents for daily living purposes such as washing, bathing and drinking. Therefore, effective pre-treatment of these contaminants is very crucial before biological treatment of the wastewater.

1.3   Problem Statement

Although the low-cost adsorbents are able to provide high removal of dyes, the regeneration methods of these adsorbents are still not well-developed. Limited studies were carried out especially on the regeneration of bentonite. Regeneration is essential to recover the adsorption capacity to provide maximum cycles of usage instead of disposal after the first usage. By regenerating the adsorbents, wastes could be reduced, thus saving a lots from the aspect of economy and resources. Bentonite can adsorb many types of dyes, however, its desorption and regeneration viability are relatively low. This might be due to formation of strong chemical bonding between the adsorbed dyes and the bentonite surface (Mckay et al., 1987). Consequently, reusability of spent bentonite decreases, reducing its possibility to be recycled. This current work aims to modify the bentonite before being introduced into composite adsorbents coating so as to increase its regeneration and recycle viability. Dyes are able to be adsorbed to the bentonite surface as well as degraded successfully if the modification technique is working well.

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Undoubtedly, the success of this research will bring the recyclable composite adsorbent coating to light.

1.4   Research Objectives

The objectives for this research are as follows:

i)   To modify the formulation of composite adsorbents coating (CAC) with iron modified bentonite.

ii)   To assess the performance of the modified CAC in removal of Acid Red 1 (AR1) dye.

iii)   To evaluate the reusability of spent composite adsorbents coating (CAC) using AR1 dye.

iv)   To verify the ability of heterogeneous Fenton process in regenerating the iron modified CAC.

1.5   Scope of Study

The current study focused on the development of thin adsorbent coating layer for the application of dye removal from wastewater and its reusability. This research work consisted of four major investigation sequences. There are consisted of (1) the preparation of composite adsorbent coatings (APE-bent-EPIDMA/CF) and iron modified composite adsorbent coating (APE-Febent-EPIDMA/CF); (2) the identification of composite adsorbent coating performance through batch adsorption study (3) the determination of reusability of the modified composite adsorbent coating by evaluating the effects of UV light and acid and base; and (4) the characterization of composite adsorbent coating.

Research work started with the investigation and preparation of composite adsorbents coating from swelled bentonite, collectively known as APE-bent-EPIDMA/CF. Bentonite has been selected as the adsorbent due to its good adsorption capacity and low cost. Cationic polymer, EPIDMA, with the concentration of 2 wt% was added into the coating to modify the net negative surface charge of the bentonite to net positive, for the application of anionic dye adsorption. Later, the pristine bentonite was modified with the mixture solution of 2M iron nitrate and sodium carbonate (molar ratio of 0.75:1 for Na^+/Fe^{3+}) to increase its iron content for Fenton process. After the modification process, the iron-modified bentonite was introduced into the coating, collectively known as APE-Febent-EPIDMA/CF

Batch adsorption studies were carried under the room conditions to identify the performance of AR1 removal by both types of coating (APE-bent-EPIDMA/CF and APE-Febent-EPIDMA/CF). In this section, the modification of pristine bentonite with iron was investigated whether the research should be opted for it. Also, the role of EPIDMA in the coating for AR1 removal was also studied. The step-by-step AR1 removal mechanism was proposed at the end of this section.

Regeneration of spent APE-Febent-EPIDMA/CF was carried by using 8.82mM hydrogen peroxide. Reusability and life span of the APE-Febent-EPIDMA/CF was determined that how many cycles the coating can undergo until its maximum capacity. Effects of UV light and acid and base on the regeneration process of the coating were studied under this section. The significance of UV light and suitable elution agent for AR1 were then identified.

In the last section, characterization of both types of coatings such as surface morphology and elemental content were carried out with the aid of Scanning electrons microscope (SEM) and Energy-dispersive X-ray spectroscope (EDX).

1.6   Organization of the Thesis

This dissertation outlines the construction of the thesis, together with the general descriptions of each component. This thesis comprises of five chapters, presenting all the details and findings of the research.

Chapter One (Introduction) firstly present on the development, position as well as the importance of textile industry in Malaysia. However, the main focus in this chapter is about the adverse effect of textile effluent on the environment as well as the society. The problem statement and significance of the research are highlighted in this chapter. Besides, the research objectives together with scope of study to be covered are elaborated in detail. The organization of thesis is discussed in the last section of this chapter.

Chapter Two (Literature Review) gives the retrospective view of the literature from previous studies and researches, especially on the textile dye and its methods of removal. Firstly, this chapter reviews the classification of dye and their characteristics as well as applications. As counteract to the problems caused by the textile wastewater pollution, various methods of dye removal has been discussed in term of their advantages and disadvantages to obtain the best solution for this issue. Besides, a brief explanation on the adsorption kinetic, and types of adsorption will be covered. Then, the next section gives some reviews on the adsorbent being investigated and used by previous researchers. Finally, the theory dye degradation process is presented in this chapter.

Chapter Three (Materials and Methods) covers the experimental and methodology applied through this research work. The first section of this chapter presents the overall experimental flowchart in this work. Next, details on chemicals, materials and equipment used to achieve the objectives of this study are outlined. In the

last section of this chapter, the procedures of coating preparation, bentonite modification, batch adsorption and regeneration are discussed in detail.

Chapter Four (Results and Discussion) displays the experimental results together with the respective discussion. This is the core section throughout the study in which all research findings and results will be analysed, tabulated and extensively discussed and elaborated. The results and discussions cover the characterization of the composite adsorbents coating, decolourization of Acid Red 1 and the reusability of the spent modified adsorbents coating. Two parameters, namely effect of UV light and effect of acid and base were also studied under the section of reusability of composite adsorbents coating.

Chapter Five (Conclusion and Recommendations) gives overall conclusion based on the research findings and results. Last but not least, recommendations for future improvement were given at the end of this chapter.

CHAPTER TWO

LITERATURE REVIEW

2.1   Textile Dyes

Colorants are additive substances that can cause variation in colour or visible light absorption, and can be divided into two categories: dyes and pigments. Typically, pigments are insoluble and have no chemical affinity for the substrate to be coloured. On the other hand, dye are soluble or partially soluble organic coloured compounds suspended in a medium (Rajeshwar et al., 2008). Dye molecules can connect themselves to substrate surfaces or fabrics to impart colour. The majority of dyes are complex organic molecules which have high resistance towards the action of detergents (Yagub et al., 2014). Dye molecules can absorb electromagnetic radiation, but differ in the specific wavelengths absorbed. Typically, dyes absorbs only some wavelengths in the visible light spectrum (400–800 nm), thus giving coloured property (Rangabhashiyam et al., 2013).

Basically, dye molecules comprise of two key functional groups. The first one is chromophores (NR_2, NHR, NH_2, COOH, and OH) which is responsible for giving the colour characteristics of dye; The another one is auxochromes (N_2, NO and NO_2), playing role as supplement the chromophore as well as render the solubility of dye molecule in water and give enhanced affinity and attachment toward the fibers (Gupta and Suhas, 2009). Dyes are mainly classified based on their structure, source, colour and method of application in colour index (C.I.), which has been continuously edited since 1924 (Rauf et al., 2011).

Dyes can be classified according to where they are derived, either natural or synthetic sources. Natural dyes can be extracted from sources including plants, animals

and minerals. Since the last 5000 years, natural dyes were used mostly in textile dyeing industry. For instances, the natural dyes used include jackfruit, onion, eucalyptus, turmeric and henna. However, due to the growing of population and industrial activities, people are shifting their paces from natural dyes because of the massive industrial demand. Hence, natural dyes' application nowadays is mostly found in the food industry (Ngulube et al., 2017). In 1856, with Perkin's historic discovery of the first synthetic dye, mauveine, that dyes were manufactured synthetically and on a large scale (Gupta and Suhas, 2009). Consequently, the discovery of synthetic dyes have supressed the uses of natural dyes in the 19th century almost completely, especially in the fabrics and textile industry. The synthetic dyes can be produced in large scale and can be utilized in various industries such leather, paper, food, cosmetics, agricultural research, pharmaceuticals, electroplating, and distillation (Natarajan et al., 2017).

Based on the general structure, the synthetic dyes can be further divided into three categories: anionic dyes (direct, acid and reactive dyes), cationic dyes (basic dyes) and non-ionic dyes (disperse and vat dyes) (Huang et al., 2017). Cationic dyes carry a positive charge in their molecule, furthermore it is water soluble and yield coloured cations in solution. Meanwhile, anionic dyes depend on a negative ion and it is soluble in water (Salleh et al., 2011). Figure 2.1 displays the classification of dyes based on their chemical constitution.

Most of the organic dyes used in textile industry are azo dyes, representing for over 70% of annual dyes consumption. They have the azo group (-N= N-) as chromophore, associated with aromatic systems containing groups such as -OH and -SO_3H (Florenza et al., 2014). Azo dyes are not biodegradable by aerobic treatment processes. Furthermore, azo compound included in these dyes can reduce to or anaerobically degrade and regenerate aromatic amines, which were reported to generate

possible carcinogens and mutagens to fatally harm human health. These compounds can also bio-accumulate in the food chain leading to negative impact on the ecosystem (Fosso-Kankeu et al., 2017, Huang et al., 2017). Besides, even at just 1.0 mg/L of dye concentration in drinking water, it could impart a significant colour, making it unsuitable for human consumption (Adegoke and Bello, 2015).

Acidic dyes are named so as they are normally applied to the nitrogenous fibers or fabrics in which the dyeing process is conducted in inorganic or organic acid solutions (Ajmal et al., 2014). It is mainly used for nylon, wool, leather, silk and others. According to the chemical structure, acidic dyes can be divided into azo type, triphenylmethane type, anthraquinone type, anthracene oxygen type and nitroso type pyrazolone type. Examples of acidic dyes are Acid Red 1, Acid Red 14, Acid Red 27, Acid Green 25 and Acid Blue 119 (Chemicalbook) (Chakraborty, 2010). Table 2.1 shows the different applications of dye based on their chemical nature.
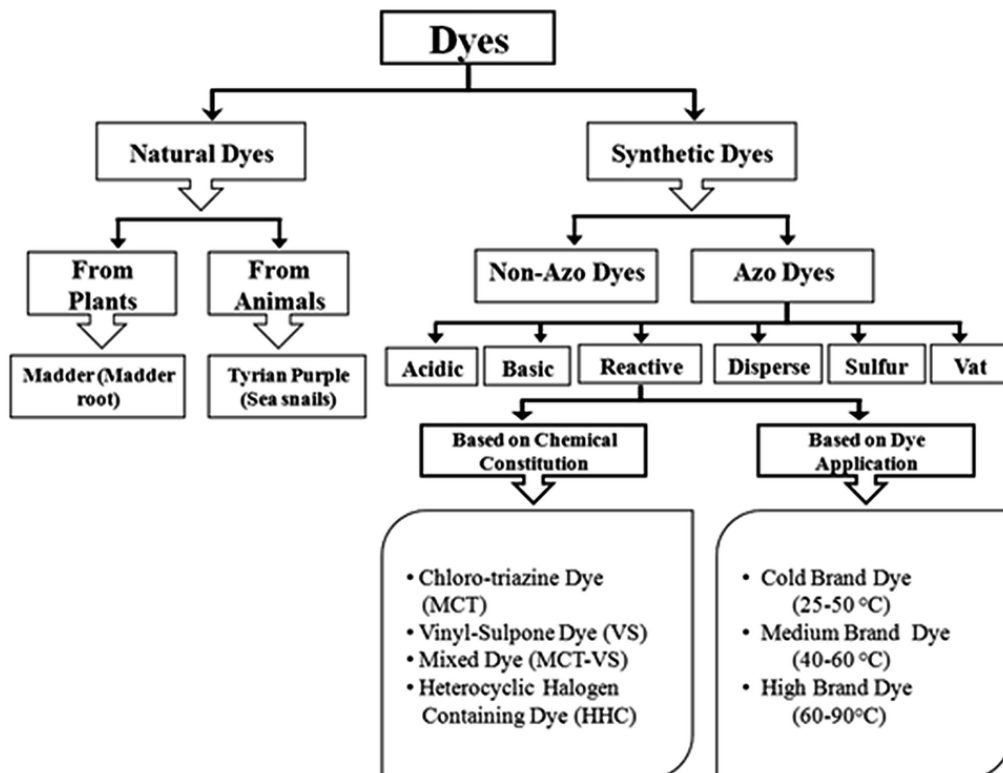

Figure 2.1: Flow chart indicating dye classification on the basis of dye chemical constitution (Ajmal et al., 2014)

Table 2.1: Classification and applications of dye based on their chemical nature (Yagub et al., 2014)

Class	Substrate	Method of application	Chemical types
Acid	Wool, nylon, silk, inks, leather and paper.	Generally from neutral to acidic bath.	Anthraquinone, xanthene, azo (including, nitroso, premetallised), nitro, and triphenylmethane.
Basic	Inks, paper, polyacrylonitrile, treated nylon, and polyester	Applied from acidic dye baths.	Hemicyanine, azo, cyanine, diazahemicyanine, azine diphenylmethane, xanthene, triarylmethane, acridine, anthraquinone and oxazine.
Direct	Nylon, rayon, paper, leather and cotton.	Applied from neutral or a little alkaline bath containing additional electrolyte.	Phthalocyanine, azo, oxazine, and stilbene.
Disperse	Polyamide, acrylic polyester, acetate, and plastics	Fine aqueous dispersions often applied by high temperature/pressure or lower temperature carrier methods; dye may be padded on cloth and thermo fixed.	Benzodifuranone, azo, anthraquinone, nitro, and styryl.
Reactive	Wool, cotton, silk and nylon.	Reactive site on dye reacts with functional group on fibre to bind dye covalently under influence of heat and pH.	Anthraquinone, formazan, phthalocyanine, azo, oxazine and basic.
Sulphur	Rayon and cotton.	Aromatic substrate vatted with sodium sulphide and reoxidised to insoluble sulphur-containing products on fibre	Indeterminate structures
Vat	Wool and cotton.	Water-insoluble dyes solubilised by dropping in sodium hydrogen sulphite, then exhausted on reoxidised and fibre.	Indigoids and anthraquinone.

The presence of metals in different dyes plays important role in giving colours and some functional characteristics to the textile. These trace metals include metal complex dyes, dye stripping agents, oxidizing compounds, antifungal, odour-preventive agents and mordant reactive (Tuzen et al., 2008). Table 2.2 summarizes some heavy metal content in different dye classes such as copper, chromium, lead, manganese, cadmium, nickel, and zinc. Discharging of these metals and the persistent dyes structure with toxicity properties may threat and harm human health as well as the ecosystem. Many negative effects from the contacting of dyes with respect to their carcinogenic, genotoxic, mutagenic, and teratogenic properties in animal studies have been reported (Pang and Abdullah, 2013), even at low concentrations in textile products. Table 2.3 shows some potential health effects caused by different classes of dye.

Table 2.2: Common metals in different classes of industrial dye (Pang and Abdullah, 2013, Verma, 2008)

Dye classes	Metals in dyes
Acid dyes	Copper, lead, zinc, chromium, cobalt
Basic dyes	Copper, zinc, lead, chromium
Direct dyes	Copper, lead, zinc, chromium
Mordant dyes	Chromium
Pre-metallized	Cobalt, chromium, copper
Reactive dyes	Copper, chromium, lead
Vat dyes	None
Disperse dyes	None

Table 2.3: Different classes textile dyes and their health effects (Kausar et al., 2018)

Dyes classes	Health effects
Acid	Skin and mucous membrane irritation and burns.
Basic	Carcinogens, allergic skin reactions, allergic dermatitis, skin irritation, mutation and cancer.
Direct	Bladder cancer carcinogen.
Disperse	DNA damage, induction of bladder cancer in humans, splenic sarcomas.
Reactive	Allergic respiratory problem.
Vat	Severe burns, skin and mucous membrane irritation.

Acid Red1 (AR1), also known as Amido Naphthol Red G and Azophloxine, is included in the list of 11 non-biodegradable azo dyes by Environmental Protection Agency (EPA) because of its resistivity towards biological degradation by activated sludge process. Its IUPAC name is Sodium 5-(acetylamino)-4-hydroxy-3-(2-phenyldiazenyl)-2,7-naphthalenedisulfonate, with molecular formula of $C_{18}H_{13}N_3Na_2O_8S_2$ (Thomas et al., 2014). AR1 is very soluble in water, forming a bright red solution. Figure 2.2 shows the chemical structure of AR1.
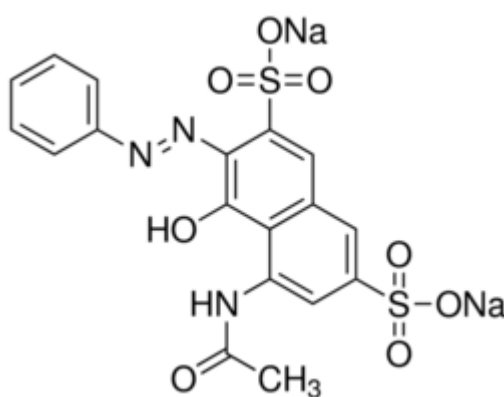
Figure 2.2: Chemical structure of Acid Red 1 (AR1) (Khanna and Rattan, 2017)

2.2   Methods of Textile Dyes Removal

Dye wastewaters can be treated by physical, chemical and biological methods. Currently, some of the physico-chemical methods are used for the treatment of dye wastewaters such as coagulation-flocculation, adsorption, liquid membrane filtration, and oxidation. Nevertheless, each of these treatments has its own advantages and drawbacks (Su et al., 2016). Table 2.4 summarizes the advantages and disadvantages of different dyes removal methods.

Table 2.4: Advantages and disadvantages of dyes removal methods (Adegoke and
Bello, 2015)

Methods	Advantages	Disadvantages
Chemical treatment		
Oxidative process	Simplicity of application	(H_2O_2) agent needs to activate by some means
H_2O_2+Fe (II) salts (Fenton's reagent)	Fenton's reagent is a suitable chemical means	Sludge generation
Ozonation	Does not increase the volume of wastewater and sludge	Short half-life (20 min)
Photochemical	No sludge is produced and foul odours are produced	Formation of by-products
Sodium hypochlorite (NaOCl)	Initiate and accelerates azo bond cleavage	Release of aromatic amines
Electrochemical destruction	No consumption of chemicals and no sludge build up	Relatively high flow rates cause a direct decrease in dye removal
Biological treatments		
Decolourization by white rot fungi	White-rot fungi are able to degrade dyes using enzymes	Enzyme production has also been shown to be unreliable
Other microbial cultures (mixed bacterial)	Decolorized in 24–30 h	Under aerobic conditions azo dyes are not readily metabolized
Adsorption by living/dead microbial biomass	Certain dyes have a particular affinity for binding with microbial species	Not effective for all dyes
Anaerobic textile dye bioremediation systems	Allows azo and other water soluble dyes to be decolorized	Anaerobic breakdown yields methane and hydrogen sulfide
Physical treatments		
Adsorption by activated carbon	Good removal of wide variety of dyes	Very expensive
Membrane filtration	Removes all dye types	Concentrated sludge production
Ion exchange	Regeneration: no adsorbent loss	Not effective for all dyes
Irradiation	Effective oxidation at laboratory scale	Requires a lot of dissolved O_2
Electro-kinetic coagulation	Economically feasible	High sludge production

2.3   Adsorption

Adsorption is a technique involving the transfer of pollutants from the bulk, either in liquid or gaseous phase, to the solid phase (Aljeboree et al., 2017). This phenomenon will cause increase in the concentration of a pollutant in the surface layer of the material in comparison with the bulk phase with respect to unit surface area. The pollutants adsorb on the surface is termed as adsorbate, whereas the material on which the pollutants adsorb to is known as adsorbents (Crini and Badot, 2008).

2.3.1   Adsorption Kinetics

The adsorption kinetics describe the time dependence of adsorption on solid surfaces. With the development of the theory of equilibria of adsorption on heterogeneous solid surfaces, the theory of adsorption/desorption kinetics on the heterogeneous surfaces was also developed. Adsorption kinetics can be determined through four major stages. First stage involves diffusion of molecules from the bulk phase towards the interface space, it is known as external diffusion. Secondly, internal diffusion takes place, in which the diffusion of molecules inside the pores. Then, the process is followed by the diffusion of molecules in the surface phase, named as the surface diffusion and finally adsorption/desorption elementary processes occur. The total rate of the kinetic process is determined by the rate of the slowest process (Dąbrowski, 1999).

2.3.2   Types of Adsorption

The adsorption process can be classified into two main types, namely, physical and chemical adsorption. Physical adsorption, or physisorption is a process in which the adsorbate sticks to the surface of adsorbent through weak intermolecular interactions

such as Van der Waals forces, hydrophobicity, hydrogen bonding, polarity, static interactions, dipole–dipole interactions and Π- Π interactions. This process does not require specific site to occur and the transfer or sharing of electrons. On the other hand, in chemical adsorption or chemisorption, formation of chemical bond through electron exchange facilitates the binding of adsorbate to the surface of the adsorbent (Dąbrowski, 2001). This process is limited to monolayer molecules on the surface and site-specific. Table 2.5 below shows some of the differences between physisorption and chemisorption.

Table 2.5: Comparison between physisorption and chemisorption (Ngulube et al., 2017)

Physisorption	Chemisorption
Weak intermolecular forces like van der Waals forces	Strong covalent bonding involving electron exchange
Low enthalpy: $\Delta H < 20$ kJ/mol	High enthalpy: $\Delta H \sim 400$ kJ/mol
Multilayer adsorption	Monomolecular adsorption
This process take places at low temperature, constantly lower than the adsorbate critical temperature	This process take places at high temperatures
Low activation energy	High activation energy
Reversible process	Non-reversible process.
Nonselective surface attachment	Selective surface attachment

2.4   Adsorbent

2.4.1   Activated Carbon

Activated carbon can be prepared using a variety of activation methods, principally chemical and physical activation methods (Heibati et al., 2015) and in some

cases using a combination of both types of methods. Regti et al. (2017) successfully synthesized activated carbon obtained from the nuts of *Persea americana* as a low cost and eco-friendly adsorbent for the removal of basic yellow 28(BY28) from aqueous solution. In works of Islam et al. (2017), it was reported that activated carbon is synthesized from coconut shells through hydrothermal carbonization and NaOH activation for attraction of Methyl Blue. Although activated carbons have gained much attentions as choice adsorbents, their main feedstock for commercial production are expensive materials for many countries, namely wood, coal and coconut shells (Attia et al., 2008).

2.4.2 Agriculture Waste

Recent years, agriculture wastes or food residues have gained much attention from the researchers, as precursors to produce low-cost and renewable adsorbents. Utilization of these wastes as adsorbent will not only help to remove dyes in wastewater, but also reduce the disposing problems of agriculture wastes (Lin et al., 2013, Menya et al., 2018). These wastes include banana peels (Munagapati et al., 2018, Ahmad and Danish, 2018), banana fibers (Abdul Karim et al., 2016), *cucumis sativus* peel (Shakoor and Nasar, 2017), rice husk (Sawasdee et al., 2017), oak acorn peel (Kuppusamy et al., 2017), *citrus limetta* peel (Shakoor and Nasar, 2016), potato plant (Gupta et al., 2016) and almond gum (Bouaziz et al., 2017). It was reported that the adsorption capacities of unmodified agriculture waste are relatively low. Therefore, treatments or modifications on the adsorbents were carried out with the hope to increase their adsorption capacities as well as to prevent secondary pollution by release of some soluble compounds (Zhao *et al.*, 2017). However, some findings revealed that the adsorption capacities of these adsorbents did not improve much after modifications. For

instance, Amela et al. (2012) reported that the maximum values of adsorption capacities for activated banana peel (ABP) was 19.671 mg/g and 18.647mg/g for natural banana peel (NBP) at pH 4-8, 20°C.

2.4.3   Natural Clays

Clays are fine-grained mineral that exist naturally and abundantly on the surface of the earth and pose no harm to the environment. Clays are mainly composed of silica, alumina, weathered rock and water (Olusegun et al., 2018) . Naturally, clay has a property to show plasticity and can harden when dried or fired (Kausar et al., 2018). Upon contacting with water, clay evenly disperses and results in slurry form due to strong attraction of water molecules to clay mineral surfaces. Clay mix with water will form a mud, allowing it to be moulded into desired shape and dried to form a relatively rigid solid. Therefore, this property is applied in the pottery and ceramics industries to produce items like pots, plates, cups, bowls, pipes, and children's toys from clays (Uddin, 2017).

Clays are widely used as adsorbents due to their high adsorption capacity. Their lamellar structure contributes high specific surface areas and possibility to adsorb ions and polar organic molecules on particle external site and in the space between their layers. Surface properties of the clay and the chemical properties of the organic molecules are primary factor in controlling the adsorption and desorption of organic molecules in the clays (Errais et al., 2011). Most of the clay minerals have negatively charged and hydrophilic surface, thus making them more favourable in adsorbing positively charged molecules such as cationic dye. On the contrary, due to this property, its adsorption capacity to anionic dye is very low (Kang et al., 2009, Uddin, 2017).

2.4.3.1 Bentonite

Bentonite, a very rich clay mineral, consists of layers of two tetrahedral silica sheets sandwiching one octahedral alumina sheet. The parallel layers in these structures are held together by weak electrostatic forces and can expand by penetration of polar species between the clay layers. Bentonite has net negative charge due to the isomorphous substitution of Al^{3+} for Si^{4+} in the tetrahedral layer and Mg^{2+} for Al^{3+} in the octahedral layer. This negative charge is compensated by the presence of exchangeable cations such as H^+, Na^+, Ca^{2+}, and Mg^{2+} in the lattice structure, which makes it favours in adsorption of basic (cationic) dyes by cationic exchange mechanism (Ma et al., 2011, Bouberka et al., 2005, Koyuncu, 2008). Due to the loose binding in the lattice structure, these inorganic cations can be substituted for cationic surfactant or hydroxy-metal, producing materials such as organobentonite and illared bentonite (Yan et al., 2015). The world bentonite resource is plentiful with its approximate ultimate reserve of 2.5 billion tons. Bentonite can be found as Ca-bentonite (more than 80% of the ultimate reserve) and Na-bentonite (Lian et al., 2009). Figure 2.3 shows schematic illustration of layered structure of bentonite.
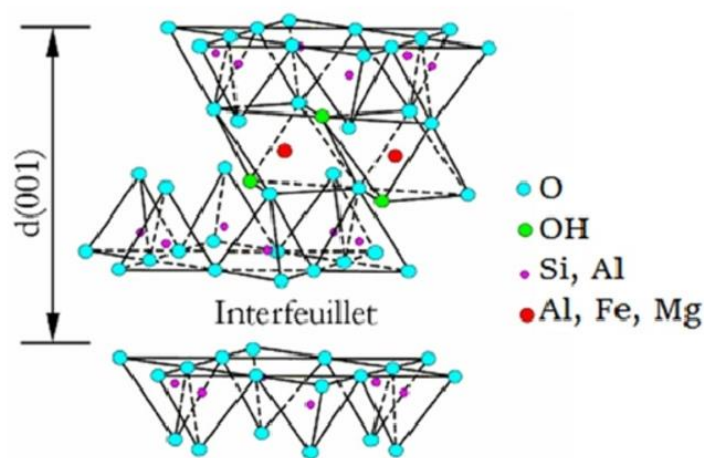

Figure 2.3: Schematic illustration of layered structure of bentonite (Belbachir and Makhoukhi, 2017)

2.4.3.2 Modified Bentonite

Adsorption power of bentonite is primary determined by its chemical nature and pore structure (Koyuncu, 2008). In many studies, modification is required to alter the clay structure so as to enlarge its surface area, therefore enhancing the adsorption capacities (Uddin, 2017). The adsorption performance of clay minerals and its modified forms also depend strongly on class of dye. Many of natural clay minerals have a high adsorption capacity for binding basic (cationic) dyes but often difficult to remove dyes from other groups or classes of dyes (Belbachir and Makhoukhi, 2017). Therefore, modification of bentonite is essential to increase the range of applicability of bentonite for the adsorption of acidic dyes. This would result changes in physical, chemical and biological properties from the original bentonite (Toor, 2011).

In order to enhance the adsorption capacity, bentonite is modified by several methods, including acid activation, thermal activation, formation of composites Cr(III)-intercalating, aluminum pillaring, surfactant modification , Na^+ exchanging, and layered double hydroxide modification (Shaban et al., 2017, Ma et al., 2011).

For example, bentonite/zeolite-NaP composite, with removal efficiency of methylene blue and Congo red (5 mg/l) up to 94 and 93%, respectively was synthesized through the hydrothermal treatment process (Shaban et al., 2017). Hajjaji and El Arfaoui (2009) evaluated the equilibrium adsorption of Methyl Blue and Zn ions on raw and acid-activated bentonite consisting essentially of montmorillonite.

As we know that the anionic dyes such as acid and reactive dyes are negatively charged, a cationic surfactant is required to modify the surfaces of the bentonite for the anionic dye adsorption. The inorganic cation present in the bentonite could be exchanged by the organic surfactant cation through the ion-exchange mechanism. Thus, the introduction of organic cation changes the bentonite from hydrophilic to

hydrophobic form, in which the product is known as organoclay (Özcan et al., 2007).

For instance, a study was undertaken by (Kang et al., 2009) to modify bentonite with

cationic polyelectrolyte, poly(epicholorohydrin dimethylamine) (EPIDMA). The

performance of EPIDMA/bentonite to remove dyes namely, Direct Fast Scarlet (DFS),

Eosin Y (EY) and Reactive Violet K-3R (K-3R) from single, binary and ternary dye

systems was investigated. Similar research was developed by Li et al. (2009) to adsorb

two reactive dyes, namely, Reactive Blue K-GL and Reactive Yellow K-4G onto the

polyepicholorohydrin-dimethylamine/bentonite (EPIDMA/bentonite). In their works,

the desorption kinetics of two dyes from EPIDMA/bentonite were also studied in NaOH

solution with different concentrations. Their findings showed that the desorption of the

dye is preferred at high NaOH concentration, which give a strong basic medium.

In the works of Azha et al. (2017a), an acrylic based composite adsorbent

coating was developed to eliminate cationic dyes from aqueous solutions with

solid/liquid separation after adsorption treatment. However, both desorption and

regeneration values for all the dyes are less, indicating perhaps, that there is strong

chemical bonding (hydrogen bond) between the dyes and the bentonite clay surface, as

reported by Mckay et al. (1987).

2.5   Fenton Process

Traditional methods for dye wastewater treatment may results in many problem,

thus causing the treatment to become less efficient. In this case, advanced oxidation

processes (AOPs) are widely applied, as these generate highly reactive OH radicals,

which are known as strong and non-selective oxidizers of the organic matter in

wastewater. Among the AOPs is the Fenton process, a mixture of hydrogen peroxide

and iron salt. Fenton process can be either in homogeneous or heterogeneous system

and with or without light assistance (Chen et al., 2009). The Fenton process is based in the ability of Fe(II) to generate hydroxyl radicals from H_2O_2.

$$Fe(II) + H_2O_2 \rightarrow Fe(III) + OH\cdot + OH^- \tag{2.1}$$
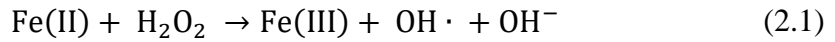
These hydroxyl radicals are highly oxidative and can generate chain reactions with organic matter that leads to the mineralization of contaminants. Fe(II) acts as a catalyst and is regenerated from Fe(III), generating even more radicals.

$$Fe(III) + H_2O_2 \rightarrow Fe(III) - OOH^{2+} + H^+ \tag{2.2}$$

$$Fe(III) - OOH^{2+} \rightarrow Fe(II) + HO_2\cdot \tag{2.3}$$
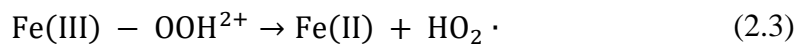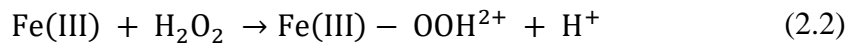
In water, Fe(III) undergoes several hydrolysis reactions. At pH 3, almost all Fe(III) is in the form of $Fe(OH)^{2+}$. This iron complex can absorb light in a broad irradiance spectrum, leading to the photo-reduction of Fe(III).

$$Fe(III) + H_2O \rightarrow Fe(III)(OH)^{2+} + H^+ \tag{2.4}$$

$$Fe(III)(OH)^{2+} + hv \rightarrow Fe(II) + OH\cdot \tag{2.5}$$
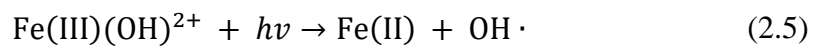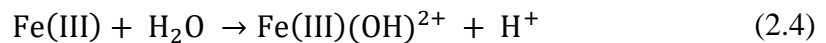
This reaction accelerates the regeneration of Fe(II) from Fe(III), increasing the efficiency of hydroxyl radical production and the reaction velocity. The complex between Fe(III) and H_2O_2 also absorbs polychromatic light leading to the formation of an excited state that accelerates the reduction of Fe(III).

$$Fe(III) - OOH^{2+} + hv \rightarrow Fe(III) - OOH^{2+} * \rightarrow Fe(II) + HO_2\cdot \tag{2.6}$$
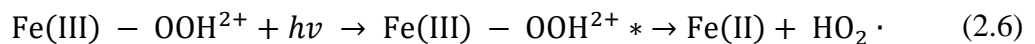
This Fenton reaction with light assistance is known as photo-Fenton reaction (Guz et al., 2014).

In homogeneous Fenton system, iron salt is employed in the form of ferric solution. However, the homogeneous Fenton process has several significant disadvantages. Firstly, the iron ions have to be separated from the system at the end of the treatment by precipitation which are waste of reagents and time consuming. Secondly, it has narrow working pH range (pH 2–3), thus limiting the applicability in

process at circum-neutral pH. Thirdly, iron ions may be deactivated due to complexion with some iron complexing reagents such as phosphate anions and intermediate oxidation products is undesirable. Consequently, it leads to a high iron concentration in the final effluent (Hassan and Hameed, 2011).

To overcome the disadvantages of Fenton type processes, heterogeneous Fenton and Fenton like catalyst have recently received much attention. In heterogeneous Fenton process, iron salts are adsorbed onto the surface of supported catalysts. From the studies, many researchers work in finding the efficient heterogeneous iron catalysts, including mixed oxides of iron and silica, iron exchanged zeolite, and iron-pillared clays. Among the methods, iron-pillared montmorillonite clay as catalyst has received considerable recognition because it is inexpensive and abundant (Chen et al., 2009).

Moreover, Fenton technology can solve the inherent problem in adsorption processes which is regeneration of the spent adsorbents. Regeneration of the adsorbent using Fenton process is considered to offer a promising alternative to hydrothermal processes, since they can be employed on-site at near-ambient conditions. In addition, stability of bentonite towards the oxidative degradation involving hydroxyl radicals makes this alternative possible. Fenton-like oxidation would be a feasible and promising strategy with its ability to transform the adsorbed dyes into less toxic by-products and re-establish the adsorption capacity of the adsorbent for the target pollutant. Through this method, it would render bentonite a suitable candidate for long-lived reusable adsorbent or catalyst support (Gao et al., 2016).

For examples, Gao et al. (2015) found that Fe-supported bentonite showed a strong adsorption performance and an excellent photocatalytic ability for the removal of Rhodamine B (RhB) in aqueous solution. (Chen and Zhu, 2007) have examined the heterogeneous UV/Fenton catalytic degradation of dyestuff by using hydroxyl-Fe