

**REMOVAL OF REACTIVE BLUE 19 FROM
AQUEOUS SOLUTION AND INDUSTRIAL
WASTEWATER USING ACTIVATED CARBON
AND IRON MODIFIED ACTIVATED CARBON**

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by

NUR FARAH BINTI WAHEED TAJUDEEN

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LIST OF ABBREVIATIONS

AC	Activated carbon
AOPs	Advance oxidation processes
BET	Brunauer-Emmett-Teller
C.I.	Color Index
CAS	Chemical Abstracts Service
COD	Chemical oxygen demand
DO	Dissolved oxygen
EAC	Extruded activated carbon
EDX	Energy dispersion X-ray
Etc	Et cetera
FeAC	Iron modified activated carbon
Fe/ACM	AC based catalyst iron doped with melamine
FTIR	Fourier transform infrared spectroscopy
GAC	Granular activated carbon
i.e	Id est
JCPDS	Joint committee on powder diffraction standards
MCM	Maghemite cellulose membrane
MWCNT	Multi-walled carbon nanotube
NIA	No information available
•OH	Hydroxyl radical
•OOH	Hydroperoxyl radical
PAC	Powdered activated carbon
pH _{pzc}	pH of point of zero charge
RB 19	Reactive Blue 19
Rpm	Rate per minute

SEM	Scanning electron microscopy
TEM	Transmission electron microscopy
USEPA	United States of Environmental Protection Agency
UV-Vis	Ultraviolet visible spectroscopy
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
Fe/ZSM5	Iron doped zeolite socony mobil-5

LIST OF SYMBOLS

C_o	Initial concentration (mg/L)
C_e	Concentration at equilibrium (mg/L)
C_t	Concentration at any time (mg/L)
D_p	Pore diameter (nm)
h	Hour
m	Mass of the adsorbent (g)
mM	Millimolar
M	Molarity
min	Minutes
pH_i	Initial pH
pH_f	Final pH
pK_a	Acid dissociation constant
q_e	Amount of the dye adsorbed at equilibrium (mg/g)
q_t	Amount of dyes adsorbed at any time (mg/g)
t	Time
V	Volume of solution (L)
w/w	Weight per weight
%	Percentage of dye removal
ΔpH	Difference between initial and final pH
$^{\circ}C$	Degree Celsius
λ_{max}	Maximum wavelength

**PENYINGKIRAN REAKTIF BIRU 19 DARIPADA LARUTAN AKUEUS
DAN AIR SISA BUANGAN INDUSTRI MENGGUNAKAN
KARBON TERAKTIF DAN KARBON TERAKTIF TERUBAH SUAI FERUM**

ABSTRAK

Dalam kajian ini, karbon teraktif terubah suai ferum (FeAC) telah disintesis melalui kaedah pengaktifan kimia untuk meningkatkan potensi penjerapan karbon teraktif (AC) terhadap penyingkiran pewarna Reaktif Biru 19 (RB 19) dalam air buangan industri dan larutan akueus. Bahan penjerap yang dihasilkan dicirikan menggunakan analisis isoterma penjerapan-penyahjerapan N_2 , mikroskop pengimbasan elektron dan tenaga penyerakan sinar-X (SEM/EDX), mikroskop transmisi elektron (TEM), analisis pembelauan sinar-X (XRD), pH titik caj sifar (pH_{pzc}) dan spektroskopi inframerah jelmaan Fourier (FTIR) sementara air buangan industri dan larutan akueus RB 19 dicirikan melalui analisis FTIR, spektroskopi ultraviolet-sinar tampak (UV-Vis) dan keperluan oksigen kimia (COD). Pengubahsuaian permukaan AC dengan prekursor ferum mengurangkan luas permukaan daripada 1043 kepada 612 m^2/g sementara diameter liang meningkat daripada 1.76 kepada 2.42 nm. Pengubahsuaian ferum ke atas AC juga menyebabkan penurunan pH_{pzc} (5.0) berbanding pH_{pzc} bagi AC (7.2). Kajian kesan pelbagai parameter seperti dos penjerap, jumlah isipadu H_2O_2 , masa sentuhan, kepekatan awal pewarna RB 19, pH dan juga penggunaan semula penjerap dijalankan dengan kehadiran dan ketiadaan 30 % w/w H_2O_2 . Sampel FeAC dengan kehadiran H_2O_2 menunjukkan peratusan penyingkiran tertinggi terhadap RB 19 dengan 94.2 dan 99.5 %, masing-masing untuk air buangan industri dan larutan akueus menggunakan 0.2 g dos penjerap, 10 mL 30 % w/w H_2O_2 dan pH ambien dalam masa 480 minit. Dari segi

kebolehgunaan semula, sampel FeAC dengan kehadiran H_2O_2 menunjukkan kecekapan penyingkiran tertinggi ($\approx 90.0\%$) berbanding sampel lain dengan hanya sedikit penurunan kecekapan penyingkiran selepas empat kitaran. Kajian ini menunjukkan bahawa pengubahsuaian AC dengan Fe meningkatkan kapasiti penjerapan FeAC. Kehadiran H_2O_2 pula meningkatkan lagi kecekapan penyingkiran dan kebolehgunaan semula penjerap karbon terubah suai ferum, FeAC melalui proses penjerapan-pengoksidaan Fenton untuk penyingkiran RB 19 dalam air buangan industri dan larutan akueus.

**REMOVAL OF REACTIVE BLUE 19 FROM AQUEOUS SOLUTION AND
INDUSTRIAL WASTEWATER USING ACTIVATED CARBON AND IRON
MODIFIED ACTIVATED CARBON**

ABSTRACT

In this research, iron modified activated carbon (FeAC) was prepared through chemical activation method to enhance the adsorption potential of activated carbon (AC) towards the removal of Reactive Blue 19 (RB 19) dye in industrial wastewater and aqueous solution. The adsorbents were characterized by various characterization techniques such as N₂ adsorption-desorption isotherm, scanning electron microscope and energy dispersion X-ray (SEM/EDX), transmission electron microscope (TEM), X-ray diffraction analysis (XRD), pH of point of zero charge (pH_{pzc}) and Fourier transform infrared (FTIR) spectroscopy while the RB 19 industrial wastewater and aqueous solution were characterized via FTIR, Ultraviolet-visible spectroscopy (UV-Vis) and chemical oxygen demand (COD) analysis. Modification of AC surface with iron precursor decreased the surface area from 1043 to 612 m²/g while the average pore diameter increased from 1.76 to 2.42 nm. The modification of iron onto AC also resulted in a decrease in the pH_{pzc} (5.0) compared to pH_{pzc} of AC (7.2). The effects of various parameters such as adsorbent dosage, amount of H₂O₂, contact time, initial RB 19 dye concentration, pH and the reusability of the adsorbent in the presence and absence of 30 % w/w H₂O₂ were investigated. In the presence of H₂O₂, FeAC exhibited the highest removal efficiencies for RB 19 dye with 94.2 and 99.5 % in industrial wastewater and aqueous solution, respectively using 0.2 g adsorbent, 10 mL of 30 % w/w H₂O₂ and at ambient pH within 480 minutes. In terms of reusability, in the presence of H₂O₂, FeAC has the highest removal efficiency (≈ 90.0 %) compared to

the other samples and only a slight decrease in the removal efficiencies was observed after the fourth cycle. This study shows that while the modification of AC with Fe improved the adsorption capacity of FeAC, the removal efficiencies and reusability were further enhanced in the presence of H₂O₂ through the adsorption-Fenton oxidation process for the removal of RB 19 in both industrial wastewater and aqueous solution.

CHAPTER 1

INTRODUCTION

1.1 Research background

The rapid development of industrialization involving paper, plastics, leather, cosmetics and textile has led to the ever-growing discharge of colored dye wastewater. Statistical data show that approximately 1 million tonne of dyes were produced annually (Sugumar & Thangam, 2012) and among the dyes produced, organic dye made up about 75 % of total world dye production (Chakraborty, 2010). Besides, more than 15 % of worldwide dye production is related to the textile industry (Fayazi *et al.*, 2016).

The tremendous amount of dyestuff released has become a major worry because it gives unpleasant color to the water body (Rafatullah *et al.*, 2010) disturbing the ecosystem, increasing chemical oxygen demand (COD) hence, becoming a source of water pollution that cannot be ignored (Dulman & Cucu-Man, 2009). Industrial wastewater containing dyes and dyestuff are often considered as toxic, carcinogenic and even mutagenic to human and environment since the dyes are very stable (Nasuha *et al.*, 2017; Ozcan *et al.*, 2007). In fact, dye effluent contains high COD value (>150 mg/L) that led to decreased aesthetic value in water resources (Buthiyappan *et al.*, 2016; Holkar *et al.*, 2016). The aftermath of this unfavorably affects the aquatic environment due to the lack of light penetration which ultimately affect the ecosystem (Buthiyappan *et al.*, 2016). Thus, wastewater containing dyes have to be treated prior to being discharge into water bodies and the step is crucial for environmental pollution abatement.

Numerous methods have been designed by various researchers to treat the recalcitrant dye effluents. However, every single method has its advantages and

drawbacks. Sometimes single method treatment of the system is not sufficient for the total decomposition of organic pollutants in wastewater. In some cases combination of two or more methods are required to obtain a fruitful result. Wastewater treatment can be classified into three main categories: physical, chemical and biological methods (Crini, 2006). Generally, there are a variety of adsorbents used to treat the dye effluent via those wastewater treatment methods. Literature survey reveals the adsorbents include activated carbons (Aljeboree *et al.*, 2017; El-Naas *et al.*, 2017; Ghaedi *et al.*, 2014; Hu *et al.*, 2015; Kocer & Acemioglu, 2015), zeolites (Wolowiec *et al.*, 2017), clay minerals (Lopez-Galindo *et al.*, 2007), alumina (Ali *et al.*, 2017), silica gel (Zhang *et al.*, 2012) and cellulose-based adsorbents (Annadurai *et al.*, 2002; Suhas *et al.*, 2016).

Nevertheless, activated carbon (AC) is one of the most prominent and well-developed adsorbent widely used in the removal of dyes from wastewater. The versatile properties of AC are responsible for the great potential and application for the removal of organic pollutants including dyes. Even so, researchers continue to make attempts to modify the surface of AC with transition metals (Shah *et al.*, 2014; Tsoncheva *et al.*, 2013) in order to enhance its sorption affinity. Among the transition metals, iron (Fe) is chosen in this study as it is the fourth most abundant element present in the earth crust with unique characteristics (Pouran *et al.*, 2014).

Adsorption by AC or modified AC is a physical method treatment that are widely used and is significant in wastewater treatment due to its high efficiency, low cost, flexibility and simplicity of design (Mahmoodi *et al.*, 2011). It is a superior technique for wastewater treatment in order to reduce harmful organic and inorganic pollutants exist in the sewage (Kant, 2012). However, due to the complex nature of the effluents, the method alone is not adequate as mentioned earlier. Thus, combination of

various techniques are necessary to give a better solution for the wastewater treatment (Santos *et al.*, 2009). Hereby, advanced oxidation processes (AOPs), a chemical treatment method, offer an alternative. All AOPs based methods involved the generation of hydroxyl radicals to oxidize organic pollutants present in the water matrix and to decolorize dye in wastewater (Forgacs *et al.*, 2004; Gogate & Pandit, 2004). Among AOPs, Fenton oxidation process has emerged as one of the most promising method and has been successfully used to treat wastewater (Guo *et al.*, 2017; Khamaruddin *et al.*, 2011). The focus of this study is the potential application for the treatment of wastewater containing RB 19 dye in aqueous solution and industrial wastewater adopting the combine adsorption-oxidation methods. Dye Reactive Blue 19 (RB 19) is chosen in this study because it is the dominant dye in the industrial wastewater sample collected from a Batik Factory here in Penang.

1.2 Research objectives

The objectives of this research are:

1. To synthesize iron modified activated carbon from commercial activated carbon.
2. To characterize commercial activated carbon and iron modified activated carbon.
3. To study the removal of Reactive Blue 19 (RB 19) dye in aqueous solution and industrial wastewater using commercial activated carbon (AC) and iron modified activated carbon (FeAC).
4. To study the effect of different experimental parameters including adsorbent dosage, amount of H₂O₂, contact time, initial dye concentration, pH and reusability study on the efficiencies of the AC and FeAC.

1.3 Thesis layout

This thesis consists of five chapters. The first chapter of this thesis describes the general overview of this study including the problem statement and research objectives. The second chapter provides a literature review of the topic. The third chapter of the thesis discusses the methodology and characterization techniques of the activated carbon, iron modified activated carbon, the aqueous solution and industrial wastewater. In the fourth chapter, the findings of the results including characterization and dye removal in industrial wastewater and aqueous solution are discussed and compared. Finally, the fifth chapter concludes the findings of this work and proposes future study in this field.

1.4 Scope of study

This study corroborates the applications of the most extensively used adsorbent, commercial AC and FeAC for RB 19 aqueous solution and industrial wastewater treatment via adsorption and Fenton oxidation process. The study includes detailed characterizations of the adsorbents such as N₂ adsorption-desorption isotherm, SEM/EDX, TEM, XRD, FTIR and pH_{pzc} to explain the physicochemical characteristics of the adsorbent. The applications of AC and FeAC were investigated at different parameters including dosage, amount of H₂O₂, contact time, pH and initial RB 19 concentration. Finally, the reusability of the spent adsorbents in the presence and absence of H₂O₂ were also studied using eluents i.e distilled water, NaOH and H₂SO₄.

CHAPTER 2

LITERATURE REVIEW

2.1 Classification of dyes

Dyes are coloring agent widely used in many fields and industries. According to Witt theory of color, a dye molecule must have a chromophore group and auxochrome group (Bafana *et al.*, 2011). Chromophores are delocalized electron systems with conjugated double bonds such as azo ($-N=N-$), thio ($>C=S$), nitroso ($-N=O$), nitro ($-NO_2$), carbonyl ($-C=O-$) and methano ($R_1-CH=R_2$) groups. Meanwhile, auxochromes are electron-withdrawing or electron-donating substituents that intensify the color of the chromophore and this includes the hydroxyl ($-OH$), alkoxy ($-OR$), amino ($-NH_2$) and alkylated amino ($-N-R$) groups. An organic compound should possess at least one chromophore group on an aryl ring forming an alternating single and double bonds to produce color (Renfrew, 1999).

Color Index (CI) has been the most popular classification system of dyes and pigments since its first publication in 1924 (Clarke & Anliker, 1980). Dyes are also classified based on the structure and particle charge upon dissolution in aqueous medium (Purkait *et al.*, 2005). For example, dyes are classified as cationic (basic dyes), anionic (direct, acid, reactive dyes) and non-ionic (disperse dyes) (Ratnamala *et al.*, 2012; Mall *et al.*, 2006). Table 2.1 shows the classification of dyes according to methods of application and chemical constitution.

Anthraquinone dyes are the second most important class of dyes after azo dyes. It is an aromatic organic compound wherein the keto group are located on the central ring. Reactive Blue 19 (RB 19), Figure 2.1, is an anthraquinone derivative of vinyl sulfone reactive group and is an anionic dye (Lazim *et al.*, 2015). The dye is very

Table 2.1 Classification of dyes according to methods of application and chemical constitution (Hunger, 2007)

Classification according to method of application (Generic name groups)	Classification according to chemical constitution (Chemical classes)
Acid dyes	Azo
Direct dyes	Anthraquinone
Reactive dyes	Triarylmethane
Basic dyes	Phthalocyanine
Disperse dyes	
Solvent dyes	
Pigments	
Vat dyes	

resistant to chemical oxidation as its aromatic structure is stabilized by resonance (Isah *et al.*, 2015). The dye has little fixation ability (75-80 %), a state which is concerned with achieving an acceptable degree of adherence of coloring matter to fiber substrate (Buthiyappan *et al.*, 2016). Normally, the poorest fixation belongs to reactive dyes. This is ascribed to the opposition between the formation of vinyl sulphone and the hydrolysis reactions (Memon & Memon, 2012). The physiochemical properties of RB 19 dye are summarized in Table 2.2.

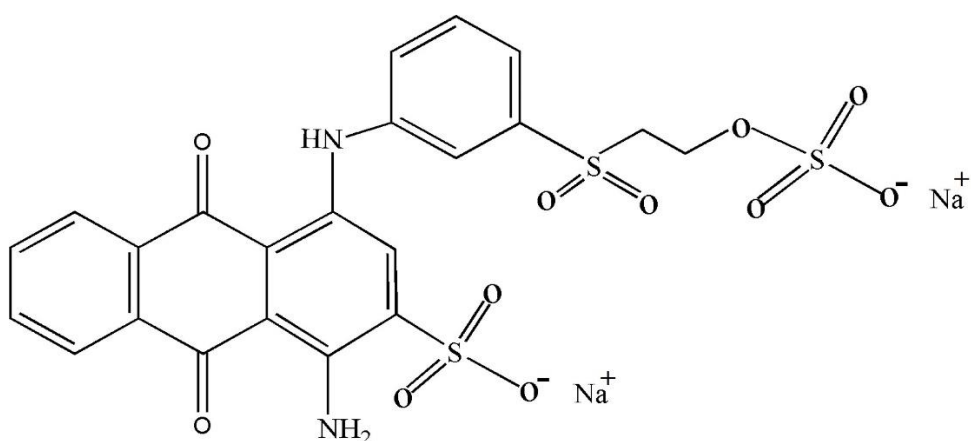


Figure 2.1 Chemical structure of Reactive Blue 19 (RB 19)

Table 2.2 Physicochemical properties of RB 19 (PubChem Compound Database)

Item	Basic information
Chemical name	Reactive Blue 19
Commercial name	Remazol Brilliant Blue R
Type	Anthraquinone Reactive Dye
Abbreviation	RB 19
Chromophore	Vinyl sulfone
C.I. number	61200
CAS number	2580-78-1
Molecular formula	C ₂₂ H ₁₆ N ₂ Na ₂ O ₁₁ S ₃
Molecular weight (g/mol)	626.54
Solubility in H ₂ O at 25 °C (g/L)	50
pH (solution form)	7.33
λ_{\max} (nm)	592
pKa	-3.29

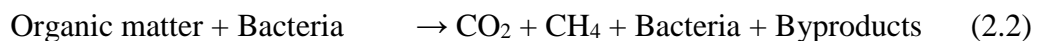
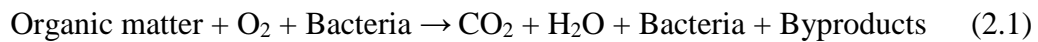
2.2 Different types of wastewater treatment for color effluents

Nowadays, a lot of efforts have been done by researchers around the world to explore various wastewater treatments. A variety of treatment methods have been developed by researchers in order to find a solution to abate water pollution. The three main classifications of wastewater treatment techniques are biological, physical and chemical methods (Crini, 2006). Regardless of what technology is employed, it is important to choose wisely a suitable method of operation that lead to a greener and sustainable environment. The main techniques mentioned above are further discussed in the following sections.

2.2.1 Biological treatment method

Biological method is a biodegradation process that uses microorganisms such as bacteria, fungi, algae or yeast (Crini, 2006; Ahmed *et al.*, 2017) to degrade various pollutants into water, carbon dioxide and ammonia (Gupta *et al.*, 2012). Sometimes, the microbes convert the organic matter into other products such as alcohol, glucose, nitrate, etc. and detoxify toxic inorganic matter (Gupta *et al.*, 2012). The method can

be aerobic, anaerobic and/or combination of both aerobic and anaerobic. For aerobic treatment, oxygen is required for the biodegradation of organic matter in the wastewater. Whereas, anaerobic treatment took place in the absence of oxygen. The following equation shows the simplified forms of aerobic or anaerobic decomposition (Equation 2.1-2.2), respectively (Gupta *et al.*, 2012):



Biodegradation method using pure and/or mixed cultures of microorganisms are also used for the removal of pollutants such as cresol, phenol and 4-chlorophenol (Leong *et al.*, 2017) and for industrial effluents treatment (Ahmed *et al.*, 2017). However, the application is restricted due to certain constraints faced in the experimental conditions such as it takes longer time and is not applicable for all dyes or organic pollutants. Other biological method includes the used of microbial cultures to decolorize dyes but the drawback is that azo dyes are not easily metabolized under aerobic conditions (Yagub *et al.*, 2014).

2.2.2 Chemical treatment method

Chemical treatment methods are technologies that use chemicals or chemical processes to treat dyes. Various chemicals including oxidizing agents, such as hydrogen peroxide, potassium permanganate, ozone etc. are used in the treatment. Coagulation, flocculation, electrochemical and oxidation (Crini, 2006) are examples of chemical treatment technologies. Addition of coagulants/flocculants, such as calcium or aluminum into the effluent induced the coagulation and flocculation process. In this case, the sedimentation rate is increased with the formation of suspended solid particles (Luo *et al.*, 2014). The coagulation or flocculation methods

are also used for wastewater detoxification (Selcuk, 2005). In chemical oxidation, organic compounds are oxidized into water, carbon dioxide or some other products which are readily degradable. Advance oxidation processes (AOPs) is an emerging powerful techniques used. The subordinate of the AOPs treatment methods are discussed in the later part, Section 2.5.

2.2.3 Physical treatment method

Physical treatment method refers to the removal of substances by using naturally occurring forces which includes gravity, electrical attraction, van der Waals forces or use of physical barriers such as filters or microscreens (Woodard & Curran, 2006). This method which is composed of membrane filtration, reverse osmosis, ion exchange and adsorption offers some benefit over the biological treatment. Membrane filtration usually use filters made of cotton, wool, cellulose, fiberglass, nylon, etc. and they are organized in various forms, for example tubular, disc, plates, spiral or hollow fibers (Gupta *et al.*, 2012). Reverse osmosis is also a type of method that relies on membrane such as cellulose, polyester or polyamide. The reverse osmosis membrane has a similar arrangement as the membrane filtration. Ion exchanger on the other hand is a solid material in which non-toxic ions are exchanged with toxic ions in wastewater. The ion exchangers can be cations or anions such as sodium silicates, zeolites, polystyrene sulfonic acid, etc. (Gupta *et al.*, 2012). However, adsorption which will be discussed in Section 2.4 has been reported to be one of the most effective physical treatment method (Dabrowski, 2001). Physical methods possess many advantages including removal of wide variety of dyes and are economically feasible (Yagub *et al.*, 2014).

2.3 Activated carbon (AC)

AC is a carbonaceous complex structure composed of primarily carbon atoms. The networks of pores in AC are channels created within a rigid skeleton of disordered layers of carbon atoms and stacked unevenly between the carbon layers (Alvarez *et al.*, 2009). As mentioned earlier in Chapter 1, AC is the most extensively used adsorbents among all the adsorbents for the removal of pollutants from wastewater (Depci, 2012; Alvarez *et al.*, 2009). Moreover, the United States of Environmental Protection Agency (USEPA) has cited AC as one of the best viable technologies for environmental control (Derbyshire *et al.*, 2001).

2.3.1 Properties of AC

AC is mainly available in three forms or shapes: powder, granular and extruded. Powdered activated carbon (PAC) have a coarser and finer grades with an average diameter between 0.15 and 0.25 mm. Whereas, granular activated carbon (GAC) is an irregular shapes with larger particles size (0.2 to 5.0 mm) compared to PAC formed by milling and sieving. Extruded activated carbon (EAC) is a cylindrical shaped pellet with diameters from 0.8 to 5.0 mm (Rashidi & Yusup, 2017). AC has an amphoteric quality with highly porous texture (Buthiyappan *et al.*, 2016). The pore size distributions include macropores ($D_p > 50$ nm), mesopores ($2 \text{ nm} < D_p < 50 \text{ nm}$), micropores ($0.7 \text{ nm} < D_p < 2 \text{ nm}$) and ultramicropores ($D_p < 0.7 \text{ nm}$) (Marsh & Reinoso, 2006). It also possesses unique molecular structure with high surface area (between 500-1500 m^2/g), high adsorption capacity, high stability and variety of surface functional groups (Buthiyappan *et al.*, 2016; Monser & Adhoum, 2002). The functional groups AC

includes carboxyls, phenols, lactone and carbonyls as well as quinone and carboxylic anhydride (Figueiredo *et al.*, 1999; Toles *et al.*, 1999).

Commercial activated carbon available worldwide is an alternative to other costly adsorbents for the removal of organic pollutants from wastewater. It is also designed for diverse applications which includes heavy metals removal, water purification and also as catalyst supports (Crini, 2006; Gong *et al.*, 2013). Generally, the commercial ACs are prepared from different raw materials which include solid waste and/or agricultural waste such as coir pith (Santhy & Selvapathy, 2006), coal (Kim *et al.*, 2013), coconut shell (Cazetta *et al.*, 2016), lignin hydrochar (Hao *et al.*, 2017), olive seeds (Salman & Kadhum, 2017), date seeds (Rahman *et al.*, 2017) and sawdust (Malik, 2004). Table 2.3 lists the various raw materials used for the preparation of AC.

Preparation of AC involves two main activation processes, i.e physical activation and chemical activation methods. Physical activation refers to a dual stage mechanism that incorporates carbonization process (pyrolysis) under an inert atmosphere, followed by an activation under the oxidizing gas atmosphere using steam, carbon dioxide (CO₂), binary mixture of CO₂ and nitrogen (N₂), or air at a raised temperature, between 800 and 110 °C (Arami-Niya *et al.*, 2011). Meanwhile, chemical activation is a single-stage process that incorporates an impregnation step prior to heat treatment in an inert atmosphere at temperature between 400 to 600 °C (Loredo-Cancino *et al.*, 2013). The later activation method has found immense applications because of its high efficiency, lower activation temperature, shorter processing time and good yield (Hui & Zaini, 2015; Yang *et al.*, 2010). Prior to the activation process, the raw materials must undergo a pre-treatment processes which include washing, sun/oven-drying,

crushing, grinding and sieving to obtain the preferred size and form (Rashidi & Yusup, 2017).

Table 2.3 Survey of recent publications on the various raw materials used for the preparation of AC and its properties

Raw material	Surface area (m²/g)	Pore diameter (nm)	Adsorption capacity (mg/g)	Application	References
Rattan hydrochar	1135	3.55	359	Removal of Methylene Blue	Islam <i>et al.</i> (2017a)
Oil palm biomass	720	1.90	NIA	CO ₂ capture	Rashidi & Yusup (2017)
Denim fabric waste	1582	3.60	292	Removal of Remazol Brilliant Blue R	Silva <i>et al.</i> (2018)
Pineapple leaves	1031	5.87	155.5	Removal of caffeine	Beltrame <i>et al.</i> (2018)
<i>Karanj</i> fruit hulls	828	1.99	154.8	Removal of Methylene Blue	Islam <i>et al.</i> (2017b)
Lignin hydrochar	2875	2.0-4.0	NIA	CO ₂ uptake	Hao <i>et al.</i> (2017)
Date seeds	NIA	NIA	256	Textile wastewater	Rahman <i>et al.</i> (2017)
Pecan nut shell	NIA	NIA	46.4	Removal of tartrazine in water	Torrez-Perez <i>et al.</i> (2018)
Coconut shell	NIA	NIA	62.1	Removal of Maxilon Blue	Aljeboree <i>et al.</i> (2017)
Coconut shell	NIA	NIA	13.8	Removal of Direct Yellow 12	Aljeboree <i>et al.</i> (2017)

*NIA-No Information Available

2.3.2 Surface modifications of AC

Even though AC has a great potential for the removal of pollutants, efforts have been made by researchers to modify the surface of AC to further enhance the adsorption capacity. Modifications of AC can be classified into physical, biological and chemical modifications (Yin *et al.*, 2007). Figure 2.2 shows the categories of AC modification techniques.

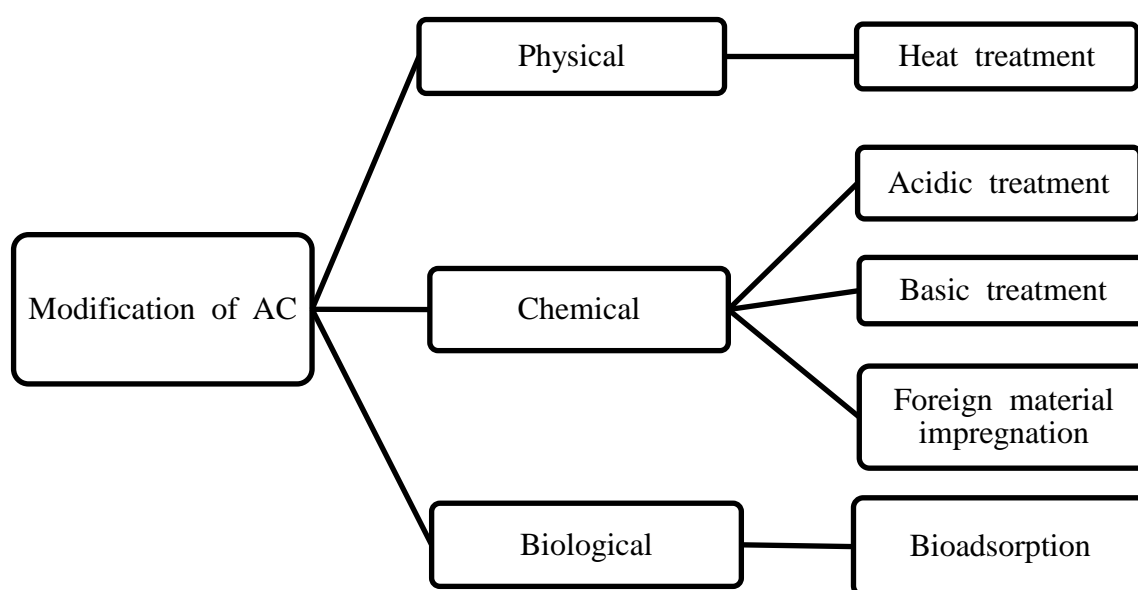


Figure 2.2 Categories of AC modification techniques (Yin *et al.*, 2007)

The physical treatment method of AC involves calcinations at high temperatures above 350 °C (Yoo *et al.*, 2005) and even up to 1000 °C (Rangal-Mendez & Cannon, 2005). However, the problem with this method is that the oxygen functional groups on the AC surface are unstable and are eventually destroyed at high temperature (Attia *et al.*, 2006).

On the contrary, AC surface modification via bioadsorption technique uses various types of microorganisms to adsorb and degrade chemical species such as phenol (Annadurai *et al.*, 2000), nitrite (Morena-Castilla *et al.*, 2003) or heavy metals

(Scott *et al.*, 1995). Yet this method also encounter some drawbacks such as the formation of biofilm which cover the active sites on the AC surface (Yin *et al.*, 2007).

Usually, chemical treatment is used to modify the surface functional groups of AC. It is pertinent to mention that the presence of different functional groups on the AC surface will change the surface to acidic, basic and/or neutral. Mainly oxygen complexes such as carbonyl groups are presence on AC surface and it can be generated by dry or wet oxidation methods. Dry oxidation method involves reactions using gas phase (steam, CO₂) at high temperature, greater than 700 °C (Yin *et al.*, 2007). Whereas, wet oxidation method involves reaction between AC surfaces and oxidizing agent solutions such as H₂O₂, KMnO₄ or HNO₃ under mild temperature between 20-100 °C (Boehm, 2002). The oxidizing solutions used for the surface modification are used to increase the acidic functional groups such as carboxyl, hydroxyl or carbonyl and hereby it is an acidic treatment. Under basic environment, modification of AC is done by using NaOH, NH₃ or phenolic compound to enhance the adsorption capacity (Yin *et al.*, 2007).

Therein, utilization of various transition metals such as silver, copper, nickel, cobalt and iron as foreign materials impregnation for AC surface modification is gaining the attention of various researchers to tailor their physicochemical features and improve its affinity in wastewater (Shah *et al.*, 2014; Tsoncheva *et al.*, 2013). Previously, Karimi and co-workers (2012) reported that silver nanoparticles loaded AC was used for Methyl Orange removal with adsorption capacity of 55.5 mg/g. Meanwhile, Tsoncheva *et al.* (2013) compared modification with three different metals i.e iron, cobalt and copper for methanol decomposition. The study revealed that modification with cobalt showed the best catalytic activity. On the other hand, according to Adhoum and Monser (2002) the efficiency of silver AC for cyanide

removal from aqueous solution was higher, with adsorption capacity of 45.7 mg/g, as compared to nickel (4.3 mg/g).

Besides, studies also revealed that AC performance was more pronounced following treatment with various iron compounds (Muniz *et al.*, 2009). For example, Wang and co-workers (2014) reported that oxidized carbon modified iron (AC/O-Fe) used for phosphate adsorption has an adsorption capacity of 13.12 mg/g, which was much higher as compared to non-oxidized carbon modified iron, AC-Fe (7.46 mg/g). The adsorption capacity also increased with the increase in reaction temperature. In a separate study reported by Depci (2012), iron impregnated activated carbon (FeAC) from Golbasi lignite was used to remove cyanide from wastewater. The maximum monolayer adsorption capacities of FeAC was higher, 67.82 mg/g at pH 7-7.5 and 68.02 mg/g at pH 10-10.5, as compared to AC. Moreover, according to Shah and co-workers (2014; 2015) iron doped carbon material (FeAC) was an effective adsorbent for the removal of Methylene Blue dye. The adsorption capacities of FeAC was higher (30.61 mg/g) as compared to commercial AC (21.84 mg/g) and the catalyst prepared was reusable without significant loss in its efficiency even up to 10 cycles.

2.4 Adsorption studies

As mentioned earlier in Chapter 1, adsorption is one of the most widely used techniques for the treatment of textile effluents. Adsorption can be defined as the accumulation of a substance(s) at the interface of two phases i.e liquid-solid interface and gas-solid interface. Adsorbate is the substance that accumulates on the adsorbent which is the solid on which the adsorption took place (Dabrowski, 2001). Adsorption can be classified into chemisorption and physisorption. Chemisorption is an irreversible process due to the formation of strong chemical associations between molecules or ions of adsorbate to the adsorbent surface due to the exchange of

electrons. Physisorption is a reversible process in most cases, and is characterized by weak van der Waals intraparticle bonds between the adsorbate and the adsorbent (Allen & Koumanova, 2005).

2.4.1 Adsorption via AC

Activated carbon (AC) is broadly and widely used as an adsorbent in the adsorption process owing to its great abilities. Among the various applications of AC include the removal of cyanide (Depci, 2012), caffeine (Beltrame *et al.*, 2018), herbicides (Salman & Kadhum, 2017) and color from landfill leachate (Ghani *et al.*, 2017). Besides, AC is also used as a catalyst support for biodiesel production (Wang *et al.*, 2017), CO₂ capture (Rashidi & Yusup, 2017) and etc. According to Wang *et al.* (2017), soybean oil with calcium loaded on rice husk AC produce a high percentage of biodiesel which is 93.0 % whereas, 91.5 % of herbicide 2,4-dichlorophenoxyacetic acid was removed using AC from olive seeds (Salman & Kadhum, 2017). In addition, Ghani and co-workers (2017) reported that AC from banana pseudo stem removed 91.2 % of color from landfill leachate treatment. Meanwhile, the adsorption capacity of AC from pineapple leaves was 155.5 mg/g towards caffeine removal in aqueous solution (Beltrame *et al.*, 2018). The author describes the adsorption process was exothermic, spontaneous and occurs via physisorption.

Likewise, AC is also used for the removal of various kinds of dyes. In a recent work (Altintig *et al.*, 2017), AC from acorn shell and *Ziziphus mauritiana* nuts were reported to have the adsorption capacities 312.5 mg/g and 152.9 mg/g, respectively towards Methylene Blue. AC from finger citron, a kind of fruit also shows an excellent performance in the adsorption process. The finger citron residues were used for the removal of Methyl Orange and Methylene Blue dyes with a very high adsorption capacities of 935.6 and 581.4 mg/g, respectively (Gong *et al.*, 2013). Other dyes such

as tartrazine was removed from aqueous solution by using AC from babassu coconut which adsorbed 31.1 mg/g as compared to activated bone carbon which only adsorbed 17.2 mg/g (Reck *et al.*, 2018).

2.4.2 Adsorption of Reactive Blue 19 dye

Besides the pollutants mentioned above, Reactive Blue 19 (RB 19) is also an example of the dye widely used. In a previous work, Ahmad and co-workers (2014) reported adsorption capacity as high as 232.59 mg/g for pinang frond based AC over a period of 24 h. According to the authors, the reaction was endothermic and non-spontaneous. Besides, the RB 19 removal study using coconut shell based AC was reported by Isah *et al.* (2015). The study revealed the adsorption process was spontaneous with low adsorption capacity, 2.22 mg/g. On the other hand, AC fiber from denim fabric waste reported a high adsorption capacity of 292 mg/g (Silva *et al.*, 2018). The study indicated that the adsorption process was exothermic and spontaneous.

Besides using AC, adsorption studies for the RB 19 dye removal also have been reported using other types of adsorbents. Recently, Nga and co-workers (2017) reported chitosan films which exhibited adsorption capacities of as much as 799 mg/g at 20 °C. In another study, El-Bindary *et al.* (2016) used rice straw fly ash but the adsorption capacity was only 38.24 mg/g at room temperature in 60 minutes. The adsorption was established as physisorption, spontaneous and exothermic in nature. Likewise, adsorption onto alfa fibers powder towards reactive dyes was carried out by Fettouche and co-workers (2015). The authors reported that the adsorbent only adsorbed 11.33 mg/g of RB 19 dye at 22 °C. These various studies proved that different adsorbents possess different adsorption capacities even towards similar type of dye

removal. Table 2.4 summarizes some of the adsorption studies involving RB 19 dye using various types of adsorbents.

Table 2.4 List of various adsorbents used in adsorption studies of Reactive Blue 19 (RB 19) dye

Adsorbent	Sorption capacity (mg/g)	Initial dye concentration (mg/L)	pH	Reference
Coconut shell based activated carbon	2.22	50	unadjusted	Isah <i>et al.</i> (2015)
Pomegranate seed powder	3.61	50	NIA	Dehviri <i>et al.</i> (2015)
Orange peel, Spent tea leaves	8.51 8.86	1000	NIA	Lazim <i>et al.</i> (2015)
Alfa fibers powder	11.33	25	2.0	Fettouche <i>et al.</i> (2015)
Bone char prepared by CO ₂	20.6	100	unadjusted	Bedin <i>et al.</i> (2017)
Red mud	26.17	70	NIA	Ratnamala <i>et al.</i> (2012)
Rice straw fly ash	38.24	100	1.0	El-Bindary <i>et al.</i> (2016)
Pinang frond-activated carbon	232.59	500	unadjusted	Ahmad <i>et al.</i> (2014)
Activated carbon fiber	292.0	500	2.0	Silva <i>et al.</i> (2018)

* NIA- No Information Available

2.5 Advanced Oxidation Processes

Advanced oxidation processes (AOPs) employ either oxidant (such as ozone or hydrogen peroxide), UV light, ultrasound and/or combination of oxidants with catalysts (Sillanpaa *et al.*, 2018). The basis for the development of this chemical

remediation method is the generation of hydroxyl radicals ($\bullet\text{OH}$). $\bullet\text{OH}$ is a robust oxidant and the second strongest oxidative species after fluorine with oxidation potential of 2.80 V (Legrini *et al.*, 1993; Scott *et al.*, 2000). Figure 2.3 summarizes the features of $\bullet\text{OH}$.

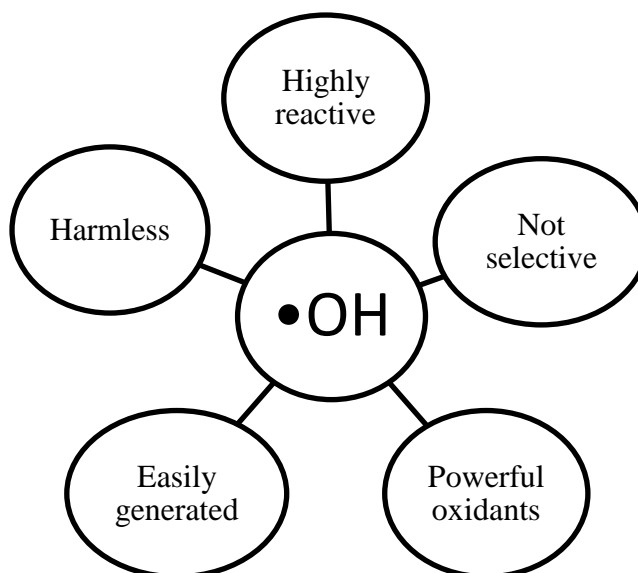


Figure 2.3 Characteristics of hydroxyl radical ($\bullet\text{OH}$) (Buthiyappan *et al.*, 2016)

2.5.1 Classification of AOPs

In general, AOPs are classified as homogeneous or heterogeneous processes. The homogeneous processes are further subdivided into (i) the use of energy (UV radiation, ultrasound or electrical energy) and (ii) without the use of energy but using oxidant (O_3 , H_2O_2 , etc). Whereas, heterogeneous processes involve catalytic oxidation (Poyatos *et al.*, 2009). Specifically, AOPs can be mainly classified into chemical (Fenton and/or ozonation), photochemical and photocatalytic (UV/oxidant or UV/photocatalyst) (Aleksic *et al.*, 2010; Koprivanac & Kusic, 2007), sonochemical and electrochemical processes (Munoz *et al.*, 2015).

Ozonation is an oxidation method that uses ozone (O_3), a powerful oxidant, to degrade organic pollutants in wastewater. However, O_3 generates slightly less hydroxyl radicals (Sillanpaa *et al.*, 2018). Previously, Neppolian and co-workers (2010) reported that As (III) was easily oxidized to As (IV) in the presence of peroxydisulfate ion by using ultrasound. Likewise, this technique have been used to improve carbon nanotubes to nanocomposite performance in the degradation of dyes (Price *et al.*, 2018). Meanwhile, electrochemical oxidation uses electrical energy and it is produced by direct and/or indirect anodic reactions. This means that oxygen is transferred from the solvent to the product to be oxidized (Poyatos *et al.*, 2009). The method is used in the removal of a wide variety of pollutants such as dyes, solvents and surfactants (Canizares *et al.*, 2007; Clematis *et al.*, 2017; Dominguez *et al.*, 2018). With high current usage, a complete COD removal was achieved. However, a high color removal but low COD removal was sometimes observed such as those reported by Fan *et al.* (2008) in which the authors had used AC fiber electrode.

Other than sonochemical and electrochemical methods, photochemical is a light-based process. The source of light can be either artificial light, mercury vapor lamp or sunlight (Sillanpaa *et al.*, 2018). In this method the organic matter were degraded by means of photolysis or photodecomposition and relies upon the ability of targeted compound(s) to absorb the emitted light (Goslan *et al.*, 2006; Sillanpaa *et al.*, 2018). The combination of either UV and oxidants have also been reported. For instance, Esplugas and co-workers (2007) reported the removal efficiencies of contaminants such as pesticides and pharmaceuticals were up to 97-100 % using O_3/H_2O_2 . Whereas, the combination of UV/ H_2O_2 was also recognized for its effectiveness in the removal of organic pollutants in aqueous solution. Usually, UV/ H_2O_2 is used for the treatment of effluent for disinfection purposes (Thompson *et*

al., 2003). AOPs using H₂O₂ with UV/O₃ is the most expensive AOP method compared to the rest since it uses two or more reagents at one time. However, the approach was reported to boost the reaction and promoted the formation of •OH radicals (Poyatos *et al.*, 2009).

Compared to O₃, H₂O₂ is one of the cleanest and green oxidant available, thus the usage is more extensive. These led to the use of H₂O₂ in detergents, wastewater and textile industry treatment, and chemical oxidation process (Campos-Martin *et al.*, 2006). H₂O₂ is commonly used in industrial area since it is miscible in water and one of the most environmentally friendly oxidant that produces water and oxygen as the end products (Campos-Martin *et al.*, 2006). In oxidation processes, H₂O₂ is used as the source of •OH (Raj & Quen, 2005).

In comparison to homogeneous AOPs, heterogeneous AOPs are more promising in most of the cases. Recently, Sillanpaa *et al.* (2018) and Ahmed *et al.* (2017) reported that various photocatalysts such as ZnO, Fe₂O₃, Cu₂O and TiO₂ has been used in photocatalytic reaction. Semiconductor metal oxides with narrow band gap are usually used in photocatalysis to solve the drawback of photolysis. Yet photocatalytic degradation of organic pollutants also encounters some technical drawbacks such as ineffective utilization of visible light and post-recovery problem of photocatalysts particles after the treatment (Dong *et al.*, 2015). So, chemical oxidation by means of supported catalysts such as AC and FeAC provide an alternative for the decolorization of dye (Santos *et al.*, 2009). AC can act as an electron-transfer catalyst just like in Fenton process to degrade dye such as Sunset Yellow (Khorramfar *et al.*, 2011; Dominguez *et al.*, 2013). According to Khorramfar *et al.* (2011), in the presence of H₂O₂, AC is oxidized to AC⁺ and •OH. The oxidized AC⁺ is then reduced back to

its original AC that leads to the formation of hydroperoxyl radicals ($\bullet\text{OOH}$), as described as the Equations (2.3-2.4) below:



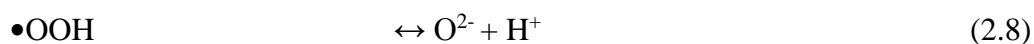
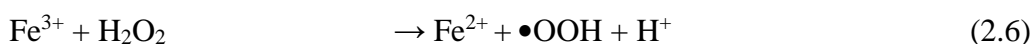
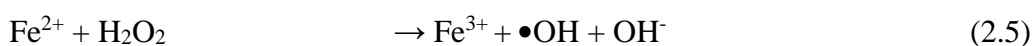
2.5.2 Fenton process

Fenton reaction is another type of chemical oxidation process which has gained attention in recent years due to its effectiveness (Queiros *et al.*, 2015). Fenton oxidation process was discovered by Henry J. Fenton. He reported in his study that H_2O_2 could be activated by iron salts to oxidize tartaric acid (Fenton, 1894). Fenton's reagent basically consists of ferrous salts combined with hydrogen peroxide (H_2O_2) which react to form hydroxyl radicals, $\bullet\text{OH}$ (Haber & Weiss, 1934). The heterogeneous Fenton process has found immense applications compared to the homogeneous Fenton as it can work at near neutral pH and the reuse of the iron promoter is feasible (Buthiyappan *et al.*, 2016; Costa *et al.*, 2008).

Despite the fact that the iron ion reacts readily in the reaction medium, some of the reported disadvantages and drawbacks of homogeneous Fenton reported are (Pouran *et al.*, 2014): (i) pH-dependence of the system as the reaction works in acidic condition, (ii) formation of ferric hydroxide sludge and difficulty in its removal, (iii) generation of sludge may prevent the penetration of radiation in photo-Fenton process and (iv) recovery of the catalyst. This typical reactive system has gained researchers attention since 1990 and continues till nowadays with innovation of the system (Munoz *et al.*, 2015). Heterogeneous Fenton reaction can solve the shortcomings of the homogeneous process. Iron is balanced within the catalyst interlayer space and oxidation of H_2O_2 produce $\bullet\text{OH}$ effectively such that reactions may take place under

uncontrolled pH and no iron hydroxide precipitation was observed (Garrido-Ramirez *et al.*, 2010).

The main reactions involved in Fenton chemistry are shown in Equations 2.5 to 2.7 (Queiros *et al.*, 2015). The generation of •OH radicals from the decomposition of H₂O₂ in the presence of ferrous ion (Fe²⁺) yield ferric ion (Fe³⁺) (Equation 2.5). The Fe³⁺ will react with H₂O₂ producing •OOH and regenerate the Fe²⁺ (Equation 2.6). The highly reactive •OH radicals will react with the organic pollutant producing oxidation products such as CO₂, H₂O and inorganic salts (Equation 2.7). Whereas, the •OOH is converted to its conjugate base, superoxide anion (O²⁻) were both •OOH and O²⁻ exist in equilibrium in aqueous solution (Equation 2.8) (He *et al.*, 2016).



The summary of previous works on heterogeneous Fenton process are listed in Table 2.5. Normally, iron-based materials dispersed well on a support were used in wastewater treatment (He *et al.*, 2016; Pouran *et al.*, 2014). Iron oxides are richly present in the earth crust and among them are magnetite (Fe₃O₄), maghemite (γ-Fe₂O₃), hematite (α-Fe₂O₃), goethite (α-FeOOH) and iron hydroxides which are extensively used in heterogeneous catalysis process for wastewater treatment (Cornell & Schwertmann, 2003). Various features of these oxides including surface area, pore size and the crystalline structure have been said (Xue *et al.*, 2009) to play important roles in the oxidative reactions.

Table 2.5 Summary of heterogeneous catalysts used in Fenton oxidation process

Catalyst	Pollutant	Percentage/ Dosage of H₂O₂	pH	Reference
Iron doped zeolite socony mobil-5 (Fe/ZSM5)	Reactive Blue 137	30/ 10.0 mM	3.0	Aleksic <i>et al.</i> (2010)
Fe/AC	Acid Orange 7	30/ 6.0 mM	3.0	Duarte <i>et al.</i> (2013)
Fe/ordered mesoporous carbon	4-Chlorophenol	NIA/ 6.6 mM	3.0	Duan <i>et al.</i> (2014)
Fe/AC	Chicago Sky Blue	NIA/ 2.25 mM	3.0	Mesquita <i>et al.</i> (2012)
Fe-GAC	Methylene Blue	30/ 1.32 mM	3.0-3.5	Kim <i>et al.</i> (2013)
Iron oxide dispersed over AC	Methylene Blue	50/ 0.1 mL	Unadjusted	Castro <i>et al.</i> (2009)
Multi-walled carbon nanotube (MWCNT) supported Fe ₂ O ₃	Phenol	30/ 9.5 mM	3.0-4.0	Liao <i>et al.</i> (2009)
Iron oxide/SiO ₂	Aniline	NIA/ 50 mM	6.0	Huang <i>et al.</i> (2013)
Pyrite	Textile wastewater	NIA/ 9.7 mM	9.0	Feng <i>et al.</i> (2012)
Maghemite cellulose membrane (MCM-14)	Phenol	NIA/ 0.98 mM	4.0	Xia <i>et al.</i> (2011)

*NIA-No Information Available