

**PREPARATION, CHARACTERIZATION AND  
APPLICATIONS OF MULTI-FUNCTIONAL IRON  
OXIDES-IMPREGNATED ACTIVATED CARBON  
MATERIALS**

**IRFAN SHAH**

**UNIVERSITI SAINS MALAYSIA**

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APPLICATIONS OF MULTI-FUNCTIONAL IRON  
OXIDES-IMPREGNATED ACTIVATED CARBON  
MATERIALS**

**by**

**IRFAN SHAH**

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**for the degree of**

**Doctor of Philosophy**

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## DECLARATION

Saya isytiharkan bahawa kandungan yang dibentangkan di dalam tesis ini adalah hasil kerja saya sendiri dan telah dijalankan di Universiti Sains Malaysia kecuali dimaklumkan sebaliknya. Tesis ini juga tidak pernah diserahkan untuk ijazah yang lain sebelum ini.

I declare that the content which is presented in this thesis is my own work which was done at Universiti Sains Malaysia unless informed otherwise. The thesis has not been previously submitted for any other degree.

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Tandatangan calon/ *Signature of student*

---

Tandatangan Penyelia/ *Signature of Supervisor*

Nama calon/ *Name of student:*

Nama Penyelia/ *Name of Supervisor:*

**Irfan Shah**

**Prof. Dr. Rohana Adnan**

Passport No.: **KY5149562**

K/P /Passport No.:

## **DEDICATION**

“This dissertation is dedicated to all those loving people who contributed to my every achievement, directly or indirectly, in any ways in their own capacity”

**Irfan Shah**

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## LIST OF ABBREVIATIONS

AAS	Atomic Absorption Spectrophotometer
AC	Activated Carbon
ACC	Activated Carbon Cloth
BET	Brunauer Emmett Teller
BJH	Barrett Joyner Halenda
BOD	Biochemical Oxygen Demand
CHN	Carbon, Hydrogen and Nitrogen
C.I.	Color Index
CNTs	Carbon Nanotubes
COD	Chemical Oxygen Demand
CTAB	Cetyltrimethylammonium bromide
CTAC	Cetyltrimethylammonium chloride
DFT	Density Functional Theory
DNA	Deoxyribonucleic acid
DO	Dissolved Oxygen
DTA	Differential Thermal Analysis
E	Iron-modified AC with molar ratio 1 M $\text{KMnO}_4$ : 1 M $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
EDX	Energy Dispersion X-ray
FAA	Free Fatty Acids
FAME	Fatty Acid Methyl Ester
FeACs	Iron-Modified Activated Carbon materials
FTIR	Fourier Transform Infrared Spectroscopy
GAC	Granular Activated Carbon
HRTEM	High Resolution Transmission Electron Microscopy
JAC	<i>Jatropha curcus L.</i> based Activated Carbon
JCPDS	Joint Committee on Powder Diffraction Standards
MB	Methylene Blue
MG	Malachite Green
MO	Methyl Orange
MRI	Magnetic Resonance Imaging
NaLS	Sodium lauryl sulfate
NIA	No information available

OMCs	Ordered Mesoporous Carbons
PAC	Powdered Activated Carbon
PEI	Polyethyleneimine
$\text{pH}_{eq}$	pH at Equilibrium
$\text{pH}_{pzc}$	pH of Point of Zero Charge (PZC)
PSD	Pore Size Distribution
R	Universal gas constant
$r^2$	Regression coefficient
SAA	Surface Area Analysis
SAED	Selected Area Electron Diffraction
SD	Standard Deviation
SEM	Scanning Electron Microscopy
TCC	Total Carbon Contents
TDS	Total Dissolved Solids
TEM	Transmission Electron Microscopy
TG/DTA	Thermo Gravimetric / Differential Thermal Analyses
TIC	Total Inorganic Carbon
TOC	Total Organic Contents
TPR	Temperature Programmed Reduction
TPD	Temperature Programmed Desorption
TSS	Total Suspended Solids
UNICEF	United Nations International Children's Emergency Fund
USEPA	United States Environmental Protection Agency
VSM	Vibrating Sample Magnetometer
WCO	Waste Cooking Oil
WHO	World Health Organization
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray Diffraction

## LIST OF SYMBOLS

$A$	Arrhenius factor (g/mg min)
$\text{\AA}$	Angstrom
$C_o$	Initial concentration (mg/L)
$C_e$	Equilibrium concentration (mg/L)
$D_p$	Pore's diameter (nm)
$E_a$	Activation energy (kJ/mol)
$h$	Hour or hours
$K_L$	Binding energy constant (L/mg)
$k_1$	Pseudo-first order rate constant (1/min)
$k_2$	Pseudo-second order rate constant (g/mg min)
$k_i$	Rate constant for intraparticle diffusion model (mg/g min <sup>0.5</sup> )
$m$	Mass/weight of the material taken (g)
$q_e$	Amount adsorbed at equilibrium (mg/g)
$q_{ref}$	Amount adsorbed at $t_{ref}$ (mg/g)
$q_t$	Amount adsorbed at time t (mg/g)
$R_E$	Dimensionless factor for Bangham model
$R_L$	Separation factor
$R_t$	Retention time (min)
$T$	Temperature (K and/or °C)
$t$	Time (min)
$t_{ref}$	Reference time for Bangham model (min)
$V$	Volume of dye taken (mL)
$V_{mac}$	Volume occupied by macropores (cm <sup>3</sup> /g)
$V_{mes}$	Volume occupied by mesopores (cm <sup>3</sup> /g)
$V_{mic}$	Volume occupied by micropores (cm <sup>3</sup> /g)
$X_m$	Maximum amount adsorbed (mg/g)
$\Delta G$	Gibb's free energy change (kJ/mol)
$\Delta H$	Enthalpy change (kJ/mol)
$\Delta S$	Entropy change (J/mol K)

# **PENYEDIAAN, PENCIRIAN DAN APLIKASI KARBON TERAKTIF TERUBAHSUAI FERUM OKSIDA PELBAGAI FUNGSI**

## **ABSTRAK**

Kajian ini telah dijalankan untuk mengkaji penyediaan, pencirian dan aplikasi berbeza karbon teraktif terubahsuai ferum oksida (FeACs). Permukaan karbon teraktif (AC) pada awalnya telah dioksidakan dengan menggunakan kalium permanganat ( $\text{KMnO}_4$ ) diikuti impregnasi ferum dengan ferum sulfat ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ) sebagai prekursor ferum dengan nisbah molar agen pengoksidaan kepada ferum berbeza untuk mengkaji kesan impregnasi ferum terhadap ciri fizikokimia bahan karbon baru yang disediakan. Pelbagai teknik pencirian seperti analisis luas permukaan, SEM, EDX, TEM, HRTEM, SAED, XRD, FTIR, CHN, TCC, TG/DTA, XPS, VSM, TPR / TPD dan  $\text{pH}_{\text{pzc}}$  telah dijalankan. Permukaan impregnasi AC merubah dengan banyak luas permukaan disamping keliangan bahan yang baharu disediakan. Peningkatan luas permukaan sehingga  $1640 \text{ m}^2/\text{g}$  didapati untuk AC yang terubahsuai, dengan nisbah molar  $0.1 \text{ KMnO}_4 : 0.1 \text{ FeSO}_4 \cdot 7\text{H}_2\text{O}$  (B), adalah lebih tinggi daripada AC mentah ( $1094 \text{ m}^2/\text{g}$ ). Walau bagaimanapun, AC yang terubahsuai dengan nisbah molar  $1 \text{ KMnO}_4 : 1 \text{ FeSO}_4 \cdot 7\text{H}_2\text{O}$  (E), menunjukkan luas kawasan permukaan  $543 \text{ m}^2/\text{g}$  dan diameter liang paling besar ( $5.49 \text{ nm}$ ) jika dibandingkan dengan semua bahan lain. Morfologi permukaan bahan karbon terubahsuai ferum adalah tidak seragam dan menunjukkan kehadiran zarah ferum pada permukaan dan liang AC. Corak XRD menunjukkan kehadiran  $\text{Fe}_2\text{O}_3$  dan  $\text{Fe}_3\text{O}_4$ . Selain daripada peningkatan kumpulan berfungsi permukaan, bahan karbon terubahsuai ferum juga menunjukkan sifat kemagnetan melalui analisis VSM. Keputusan TPR/TPD bahan terubahsuai ferum menunjukkan potensi untuk digunakan sebagai mangkin

heterogen. AC terubahsuai ferum menunjukkan perubahan drastik pada  $pH_{pzc}$  berbanding AC. Bahan yang telah disediakan telah digunakan bagi penjerapan Metilena Biru (MB) sebagai model pewarna. Penyingkiran MB menggunakan AC dan E telah dikaji dengan pelbagai parameter seperti pH, dos penjerap, kelajuan goncangan, suhu, kepekatan awal pewarna, masa sentuhan dan kekuatan ionik. Penyingkiran MB didapati meningkat dengan peningkatan pH dan kecekapan penyingkiran pewarna mencapai kepada 89 dan 95 %, masing-masing untuk AC dan E. Walau bagaimanapun, kecekapan penyingkiran MB oleh E mencapai sehingga 98 % hanya dengan menggunakan 0.2 g, manakala kecekapan yang sama telah ditunjukkan oleh AC menggunakan dos yang lebih tinggi (1 g). Selain itu, kelajuan goncangan tidak menunjukkan kesan drastik terhadap penyingkiran MB melebihi 400 rpm. Sementara itu, kesan suhu menunjukkan bahawa penjerapan MB oleh AC dan E adalah eksotermik dan model isoterma Langmuir adalah yang terbaik untuk menerangkan mekanisme tindak balas. Disamping itu, kajian kinetik menunjukkan bahawa model kinetik tertib pseudo-kedua adalah padanan model terbaik kepada data yang telah dianalisis. Penjanaan semula penjerap yang telah digunakan menunjukkan AC terubahsuai ferum, E, dapat digunakan sehingga 10 kitaran berturut-turut tanpa pengurangan kecekapan yang signifikan ( $\approx 98\%$ ). Satu lagi aplikasi AC terubahsuai ferum yang turut dikaji adalah tindak balas bermangkin penukaran sisa minyak masak (WCO) kepada biodiesel menerusi tindak balas pengesteran dan trans-pengesteran. Sifat pemangkinan E didapati yang terbaik dikalangan semua bahan karbon yang disediakan dengan hasil FAME sebanyak 78 %. Disamping itu, penilaian kebolegunaan semula E juga menunjukkan hasil FAME yang tinggi dan konsisten (sehingga 75–78 %) sehingga kitaran ketiga yang kemudiannya turun kepada 50 % pada kitaran keenam.



# PREPARATION, CHARACTERIZATION AND APPLICATIONS OF MULTI-FUNCTIONAL IRON OXIDES-IMPREGNATED ACTIVATED CARBON MATERIALS

## ABSTRACT

This study was conducted to investigate the preparation, characterization and different applications of iron oxides-impregnated activated carbon materials (FeACs). The surface of activated carbon (AC) was initially oxidized by using potassium permanganate ( $\text{KMnO}_4$ ) followed by the iron impregnation using ferrous sulphate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ) as iron precursor using different molar ratios of the oxidizing agent to the iron precursor to examine the impact of iron impregnation on the physicochemical characteristics of the newly prepared carbon materials. Various characterization techniques such as surface area, SEM, EDX, TEM, HRTEM, SAED, XRD, FTIR, CHN, TCC, TG/DTA, XPS, VSM, TPR/TPD and  $\text{pH}_{\text{pzc}}$  analyses were carried out. The surface impregnation of AC varies the surface area as well as the porosity of the newly prepared materials to a great extent. It depicted an increase in the surface area up to  $1640 \text{ m}^2/\text{g}$  for modified AC having molar ratio  $0.1 \text{ KMnO}_4 : 0.1 \text{ FeSO}_4 \cdot 7\text{H}_2\text{O}$  (B), which was comparatively higher than the raw AC ( $1094 \text{ m}^2/\text{g}$ ). Modified AC having molar ratio  $1 \text{ KMnO}_4 : 1 \text{ FeSO}_4 \cdot 7\text{H}_2\text{O}$  (E), however, shows a decrease in surface area to  $543 \text{ m}^2/\text{g}$  and the highest pore diameter (5.49 nm) as compared to all other materials. Surface morphology of the iron-impregnated materials was non-uniform and depicted the iron particles penetration on the surface and the pores of AC. XRD pattern revealed the presence of iron oxide in the form of  $\text{Fe}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$  in the iron-modified materials. Besides the increased in the surface functional groups, the iron-impregnated materials have shown magnetic character as revealed from

VSM analyses. In addition, TPR/TPD results reveal the potential application of FeAC material as heterogeneous catalyst. The iron impregnation of AC also resulted in a drastic change in the  $\text{pH}_{\text{pzc}}$  of the modified materials compared to the AC. The prepared materials were investigated for the adsorption of Methylene Blue (MB) as a model dye. MB removal capacity of AC and E was examined using various parameters such as pH, adsorbent dosage, shaking speed, temperature, initial concentration of dye, contact time and the ionic strength. The MB removal increased with the increase in pH and the dye removal efficiency reached 89 and 95 % for AC and E, respectively. However, MB removal efficiency of E reached 98 % using only 0.2 g, while the similar efficiency was observed by AC at higher AC dosage (1 g). The shaking speed did not show any drastic changes in the MB removal above 400 rpm. Meanwhile, the temperature effect study revealed that MB adsorption on AC and E was exothermic and Langmuir isotherm model was the best to explain the reaction mechanism. In addition, the kinetics studies demonstrated that pseudo-second order kinetic model was the best model fitted to the data analyzed. The regeneration of the spent adsorbent E was successfully applied up to 10 consecutive cycles without any significant loss in its efficiency ( $\approx 98\%$ ). Another application of the iron-impregnated AC materials is in the catalytic conversion of waste cooking oil (WCO) into biodiesel following the esterification and transesterification. The catalytic potential of E was found the best among all materials with FAME yield of 78 %. In addition, the reusability of E was also evaluated and the Fe modified AC shows consistently high FAME yield, up to 75–78 %, for the first three cycles and reduced to below 50 % in the sixth cycle.

## CHAPTER 1

### INTRODUCTION

#### 1.1 Background of the Study

Activated carbon (AC) is widely known and used as adsorbent material for removing both organic and inorganic pollutants from aqueous system. AC is generally produced from biomass with high carbon contents such as wood, coal, lignin etc. following the pyrolysis of the organic matter and the activation of char residue either at higher temperature i.e. physical treatments (Amin, 2009; Baklanova et al., 2003) or using chemical reagents (Prahas et al., 2008; Qian et al., 2008) or following both physical and chemical treatments (Bansal et al., 1988; Kopac & Toprac, 2007; Suhas et al., 2007). The surface chemistry of AC plays an important role during the adsorption of organic pollutants from water (Moreno-Castilla, 2004). It has been found that, the surface charge density, surface area of the sorbent and correspondingly the charge of the respective adsorbate molecules influence the removal of pollutants from the bulk.

The significance of AC is evident from the variety of their applications and in whatever form they have been used. However, a notable thing is the treatment of ACs surface during preparation and afterwards. There are many data available showing that the efficiency of AC can be enhanced further via surface modifications as summarized in a detailed review by Yin et al. (2007). The surface chemistry and characteristics of AC can be tailored according to the applications. In general, chemical, physical and/or biological treatments are adapted to modify the surface of AC. Ultimately, the surface area and surface charge density of AC varies and the newly developed physicochemical character lead to the enhanced sorption affinity of AC towards wide range of adsorbates.

One of the most essential elements of life on earth is the provision of clean water. No doubt, the economical supply and availability of the fresh water is the challenge of this century (Mukherjee et al., 2014). In a report by World Health Organization, WHO (2012), a significant proportion of human population (780 millions) is facing the scarcity of drinking water. Hence, it is indispensable to save water resources to save life. The sources for drinking water are generalized as ground water, seawater, lakes, canals, rain water and reservoirs. Back in the early 20<sup>th</sup> century, particularly in Sub-Saharan Countries, less attention was paid to the environmental aspects of the wastewater produced, sanitation and provision of fresh drinking water (WHO/UNICEF, 2010). In the past, there were no such regulations set as recommendation limits for the wastewater contaminants (Gupta & Suhas, 2009). Only physical treatment through sedimentation to maintain the pH of the discharge water and to remove total suspended solids (TSS) and total dissolved solids (TDS) from the wastewater were used. However, since the last couple decades, the research on treating wastewater for environmental safety has been given more attention. In this respect, governments, users and manufacturers equally contribute to deliver treated water following various water remediation pathways.

Dyes have been preferentially used as chemical compounds for coloration giving more brightness and good finishing to the cloth/fabric. Synthetic dyes are frequently used in textile industries, dyes manufacturing, paper, food processing, printing, cosmetics, rubber, plastics and leather tanning industries. Most of the dyes known are organic molecules having complex origin and are highly resistant to detergents, light and chemicals etc. The molecular structure of the dyes consists of auxochromes and

chromophores. The auxochromes (e.g.  $-\text{COOH}$ ,  $-\text{NH}_2$ ,  $-\text{OH}$  and  $-\text{SO}_3\text{H}$  etc.) are the substituents which donate or withdraw electron and help in intensifying the color of dyes and provide the base to the chromophore and increase its solubility in water as well as enhance its affinity towards fabric. Whereas, the chromophores (e.g.  $-\text{C}=\text{N}-$ ,  $-\text{C}=\text{C}-$ ,  $-\text{C}=\text{O}$ ,  $-\text{NO}_2$  and  $-\text{N}=\text{N}-$  etc.) have delocalized electron system (alternating double bonds) in their structure and gives color to the dyes molecules (Verma et al., 2012). Based on the charged carried by the dissociated species of parent dye molecule, dyes are classified as cationic dyes such as methylene blue (MB) and anionic dyes such as methyl orange (MO).

Adsorption is commonly described as a surface phenomenon, whereby an incoming molecule both from a gas or a liquid (adsorbate) interact with the surface of a solid (adsorbent) and get accumulated forming a mono- or multi-layers (Atkins, 2010; Dabrowski, 2001). According to these authors, adsorption dealt with the gathering or concentration of the adsorbate molecules on the surface of the adsorbent. Whereby, the reverse phenomenon of adsorption i.e. the removal of accumulated adsorbate molecules from the surface of adsorbent back into the bulk is called desorption (Yagub et al., 2014). Sometime, both adsorption and desorption occur simultaneously until an equilibrium state is established. Another closely related term is called absorption, which is defined as the penetration or diffusion of the adsorbate molecules into the solid phase of adsorbent. In some cases, when the adsorption and absorption phenomena are unclear to be identified, a collective term sorption is used instead. Adsorption has been further divided into chemical adsorption (or chemisorption) and physical adsorption (or physisorption) (Salleh et al., 2011). Both types of adsorption processes are based on the

strength of the intermolecular attraction forces between the adsorbent and the adsorbate. In general, if the adsorbent and adsorbate interaction involve chemical bonding, then the incoming molecules will be strongly adsorbed and the process will be chemisorptions. However, if the interactions between adsorbent and adsorbate are weak due to van der Waal forces, then physisorption will occur. The selection of suitable adsorbent material for water remediation is generally based on factors like non hazardous nature of the material, easily available, inexpensive and reusable (Ali et al., 2012).

Adsorption in general and adsorption via AC in particular, has been found the best and oldest wastewater treatment technology due to the low cost, ease of operation, high precision, simple design, suitable for laboratory scale as well as industrial scale applications and effective for the uptake of a wide range of pollutants (Hameed et al., 2007a; Kannan & Sundaram, 2001; Rafatullah et al., 2010; Tan et al., 2008). However, there are some limitations to the adsorption of dyes pollutants or any other pollutant on the adsorbents resulted from the dumping of loaded spent material. These spent adsorbents can be disposed as such, incinerated or regenerated. However, the disposed used materials will become secondary pollutants which ultimately increase the operational cost and badly affect the environment (Sabio et al., 2004). Similarly, the incineration of spent adsorbent may increase the greenhouse gases as well as destroy the surface properties of the materials (Singh & Ward, 2013).

Worldwide debate on energy crises and global warming due to the extensive use of fossil fuels as the ultimate energy source prompted researchers to explore alternative energy sources. An interesting idea has been adapted in the form of biodiesel which has been identified as clean burning fuel having low quantity of sulphur and aromatics

contents, high cetane number and lubricity, and also is helpful in reducing greenhouse gases emission (Ma et al., 1999; Takase et al., 2014). The other advantageous aspects of biodiesel are biodegradability, environmentally friendly, renewability and can be used as such in the conventional ignition engines without requiring any specific setup of the existing engines (Lee et al., 2005; Semwal et al., 2011). In general, the catalytic transesterification of edible or non edible oils in the presence of alcohol (i.e. methanol or ethanol etc) produces fatty acid methyl ester (FAME) referred to as biodiesel along with a bye-product glycerin (Almeida et al., 2012). There are three major classes of catalysts namely biocatalyst, homogeneous and heterogeneous catalysts used for the catalytic conversion of glycerides and alcohols into biodiesel (Helwani et al., 2009; Lam et al., 2010; Math et al., 2010; Meher et al., 2006).

## **1.2 Problem Statements**

A simple and cost effective method to produce a reusable AC material with improved physicochemical characteristics is the centre of our current study. Notably, a comprehensive characterization of the powdered materials to investigate the physicochemical properties of AC substrate before and after the surface modifications is often overlooked to identify the properties as well as its potential applications. The impact of surface modification of AC is to expand the utilization of AC and not limit its usage only as adsorbent.

Despite the significant results associated with AC in the water remediation, there exist some problems associated with the adsorption process itself. The foremost problem is the dumping of the spent adsorbents loaded with toxin. These spent AC will be the secondary pollutants to the environment if not properly treated. The regeneration of

spent adsorbents with consistent performances is still a challenge for many researchers to be resolved as well as to make adsorption process more environmentally friendly and cost effective. If otherwise, a bulk quantity of solid waste will be introduced into the environment creating problems for the mankind.

Besides the adsorption characteristics of activated carbon based materials, detailed knowledge of its potential to be used as carbon catalysts are still limited. In addition to that, data on reusable character of the previously investigated catalysts is insufficient. Moreover, the high production cost of biodiesel due to expensive feedstock such as fresh oil, is an obstacle to overcome (Lim & Teong, 2010). This study describes an environmentally friendly pathway of converting waste cooking oil into biodiesel using a reusable AC based heterogeneous catalyst, which advances the carbon material's applications in energy and environmental sectors.

### **1.3 Objectives of the Proposed Study**

This thesis reports on the preparation of reusable, cost effective and multi-function adsorbent, following the surface modification of AC by iron impregnation. The specific objectives of the proposed study are;

1. To prepare iron-modified activated carbon materials (FeACs) with improved physicochemical characteristics via simple surface oxidization and foreign materials impregnation.
2. To characterize the parent AC and its iron-modified derivatives thoroughly using various characterization techniques and identify its potential applications.



3. To compare the efficiencies of AC and the selected iron-modified activated carbon material towards the adsorption of methylene blue (MB) besides examining the regeneration capacity of the spent adsorbents.
4. To investigate the catalytic potential of the iron-modified AC substrate in the conversion of waste cooking oil (WCO) to biodiesel.

#### **1.4. Scope of the Proposed Study**

This study corroborates the improved characteristics and applications of classical material AC, mainly used as adsorbent material for water purification. The surface modification of AC is beneficial in the enhancement of the overall performance of otherwise inert AC. Detailed characterization of unmodified and modified AC materials shed light on the various possible applications of the modified AC materials. Particularly, the substantial dye's removal efficiency and regeneration of the spent iron-modified AC material are the advantageous factors of the proposed study. Moreover, the successful conversion of waste cooking oil into biodiesel will be beneficial from environmental aspects as well as will be crucial in the energy sector using waste feedstock and low cost heterogeneous catalyst i.e. iron-modified AC material. Furthermore, the reusable character of the proposed heterogeneous catalyst is crucial for an eco-friendly pathway of producing biodiesel.

## CHAPTER 2

### LITERATURE REVIEW

#### 2.1. Activated Carbon

The use of activated carbon as adsorbent material is very classical and many data is available reporting the water decontamination using AC material. As briefly described in Chapter 1, the widespread use of AC as adsorbent, is due to its unique surface characteristics and high affinity towards a wide range of pollutants. Out of many data reported, research on natural and commercial production of AC is summarized below.

Naturally, peat residue which is consists of the plants debris (i.e. roots, barks) and decayed products undergo various changes with time under the influence of heat and bacterial action, and is transformed into coal (Figure 2.1). The degradation and transformation of the widespread resources of organic and inorganic matter in early ages resulted in dumped deposits of carbonaceous materials, the raw material for AC (Jansen et al., 2013). Besides that, biomass residues from the widespread deforestation or burning of plant materials have also been used as the raw materials for AC production (Wang et al., 2010a). ACs have high surface areas and unique porous texture. ACs are chemically and thermally stable materials with a variety of surface functional groups (Boumaza et al., 2012; Shi et al., 2010; Tongpoothorn et al., 2011; Yalcin & Sevinc, 2000; Yang & Qiu, 2010). The surface areas of AC have been reported to be between 500 to 2000 m<sup>2</sup>/g with a wide pore range of micropores (< 2 nm), mesopores (2–50 nm) and macropores (> 50 nm) (Ahmad et al., 2007; Aljundi & Jarrah, 2008; Aworn et al., 2008; Bhatnagar & Silanpaa, 2010; Girgis et al., 2007).

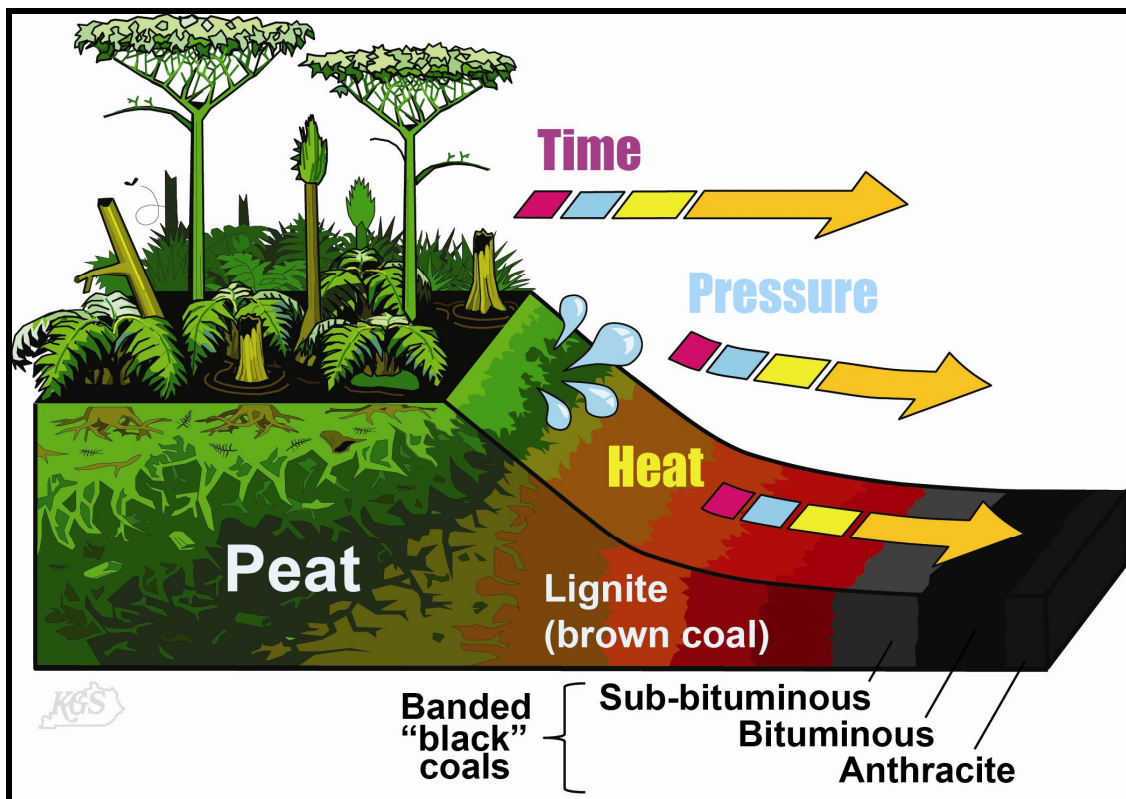


Figure 2.1. Coalification process of plants and plants residues (Adapted from Kentucky Geological Survey, 2012).

The activation of carbonaceous materials to produce AC is usually carried out in the absence of air or any other gas (pyrolysis) to ensure that the raw materials are transformed into char without undergoing gasification. However, to improve the porous texture and enhance surface area, activation of the native material has been conducted via oxidization in the presence of steam (El-Qada et al., 2006), gas such as carbon dioxide (Toles et al., 2000a) or both simultaneously (Li et al., 2002). On the other hand, chemical activation of carbonaceous materials is carried out using activating agents like acids (Boumaza et al., 2012; Khadiran et al., 2015; Toles et al., 2000b), alkaline solution (Lozano-Castello et al., 2001; Nowicki et al., 2010) or oxidizing agents such as  $H_2O_2$ ,

HNO<sub>3</sub>, (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (Moreno-Castilla et al., 2000). These treatments alter the surface area, morphology, porosity and functionalities on the surface of AC.

### **2.1.1 Production of AC from Raw Materials and Their Activation Processes**

The naturally occurring resources which are used as feedstock to produce activated carbon consist of coal, wood, lignite and peat. These AC sources usually contain 40–90 % carbon contents and having a density ranging from 0.4 to 1.45 g/mL (Maurice Deul, 1959). Numerous studies including a number of detailed reviews (Dias et al., 2007; Gupta & Ali, 2002; Ioannidou & Zaibaniotou, 2007; Mohan & Pittman, 2006; Rafatullah et al., 2010) have been reported in the literature, highlighting the use of waste materials to produce AC.

Several other researchers have reported the use of raw materials such as industrial wastes (Bhattnagar & Jain, 2005), plants remains (Bulut & Aydin, 2006; Hameed, 2009; Thinakaran et al., 2008; Wang et al., 2010a), agriculture waste such as bamboo (Hameed et al., 2007b; Ip et al., 2009; Wang, 2012), coconut husk (Al-Aoh et al., 2014; Tan et al., 2008), oil palm frond (Salman et al., 2011), hermal seed residue (Tofighi & Mohammadi, 2014), oil palm fiber (Tan et al., 2007), and vegetal fiber (Cherifi et al., 2013) for manufacturing AC. In addition, organic precursors with high carbon contents such as animal bone char (Ip et al., 2010), commercial wood based carbon (Seredych & Badosz, 2011), and coal based carbons (Li et al., 2014) have also been used to prepare high quality activated carbons. Moreover, biomass such as *Pisum sativum* (Gecgel et al., 2013), *Eucalyptus camaldulensis* barks (Balci et al., 2011), *Punica granatum* pulp (Guzel et al., 2012), *Salix psammophila* (Bao & Zhang, 2012),

*Prosopis cineraria* (Garg et al., 2004a), and *Pinus radiata* (Sen et al., 2011) have also been attempted to produce AC for the treatment of polluted water. Generally, the raw materials are subjected to certain treatments to produce good quality AC, following any of the routes depicted in Figure 2.2.

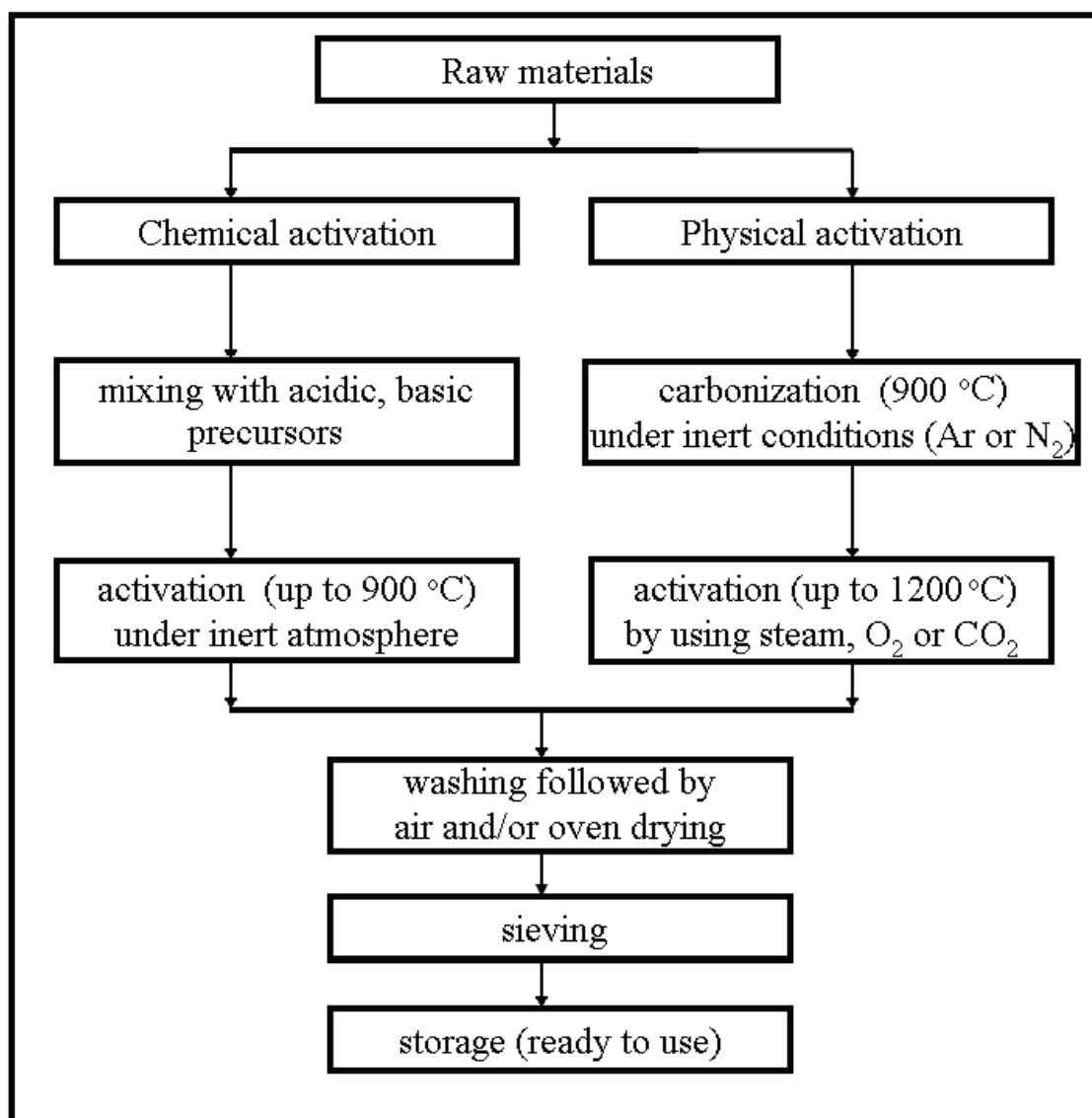


Figure 2.2. Commonly used strategies to produce AC via activation of raw materials (Mohan & Pittman Jr., 2006).

Besides the aforementioned works, a few more studies reported in the literature depicting the use of raw materials to produce AC, surface treatments, impacts on its physicochemical characteristics and the adsorption affinity towards different pollutants have been summarized in Table 2.1.

Table 2.1

*Summary of Applications of ACs Prepared from Various Precursors, Surface Treatments, and Their Physical Characteristics*

Precursor	Treatment	Surface area (m <sup>2</sup> /g)	Pore diameter (nm)	Pollutant	Reference
<i>Raw materials</i>					
Coal blends	Oxidation under CO <sub>2</sub>	1215	3.50	Arsenic	Li et al. (2014)
Peat	Air dried and soaked in HCl	NIA	NIA	Methylene Blue	Fernandes et al. (2007)
Commercial bituminous coal	No treatment applied	1100	NIA	Remazol Yellow and Remazol Black	Al-Degs et al. (2009)
Sucrose	Sol-gel technique was applied by mixing sucrose with H <sub>2</sub> SO <sub>4</sub> and followed by carbonization	650	1.35	Reactive Black, Naphthol Blue Black and Remazol Brilliant Blue R	Galan et al. (2013)
<i>Agricultural waste</i>					
Rattan sawdust	Activation with H <sub>3</sub> PO <sub>4</sub>	1037	2.56	Disperse dye	Ahmad et al. (2009)
Bamboo waste	Chemical activation using H <sub>3</sub> PO <sub>4</sub>	988	2.82	Chemical oxygen demand (COD) and color	Ahmad and Hameed (2010)

				removal	
Waste rubber tire	Carbonization, oxidization and chemical treatment	562	NIA	Acid Blue 113	Gupta et al. (2011)
Pomegranate peel	Physicochemical activation	NIA	NIA	Direct Blue-106	Amin, (2009)
<b><i>Biomass</i></b>					
<i>Polygonum orientale</i> Linn (Oriental pepper)	Activation with phosphoric acid followed by the carbonization	1398	1.54	Malachite Green and Rhodamine B	Wang et al. (2010b)
<i>Artocarpus heterophyllus</i> (Jack fruit)	Drying, grinding and heating at 105 °C	NIA	NIA	Methylene Blue	Uddin et al. (2009)
<i>Camellia sinensis</i> (Tea)	Chemical activation with ZnCl <sub>2</sub>	1530	0.78	Methylene Blue	Gao et al. (2013a)

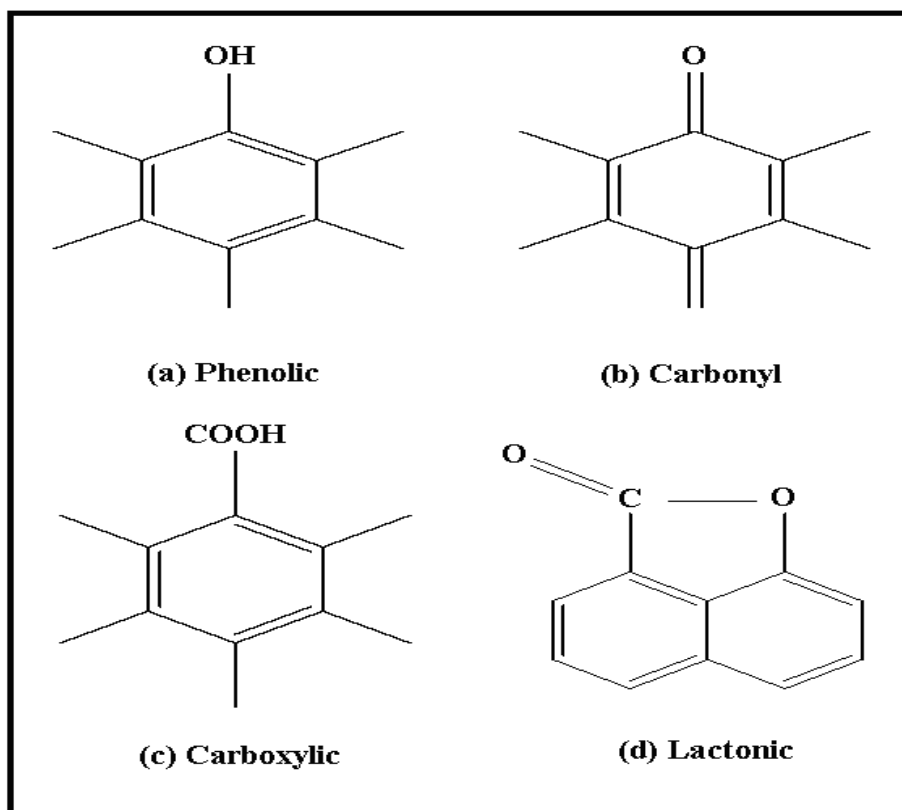
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NIA = No Information Available

### 2.1.2 Surface Functionalities on Activated Carbon

It is well known that physicochemical characteristics of AC including surface area, porosity, functional groups and particle size influence the performance of AC. During the manufacturing of porous AC, the layer by layer arrangement may not be well packed and homogenized thus producing porous texture among the layers (Boehm, 2002). Adsorption studies are usually correlated as the surface phenomenon, hence by changing the surface characteristics, the overall efficiency is affected. Nevertheless, the aforementioned characteristics of AC have great influence on its performance. It is understood that, the adsorption efficiency increases with the increase in surface area as more adsorbate molecules will be exposed to the available sites, while the converse is true for lower surface area. In addition to that, the surface morphology and surface

functionalities greatly affect the performance of adsorbent. The oxygen molecules interacting with the surface of AC generates a number of surface functional groups such as hydroxyl, carbonyl, carboxylic etc. as shown in Figure 2.3.



*Figure 2.3.* Surface functional groups commonly found on the surface of AC (Boehm, 1994).

More often, these oxygen species find their way to the porous AC and bound to it in the form of oxides which are responsible for the surface reactivity of AC. The surface of AC becomes more acidic when the concentration of oxygen contents is high and when the surface oxygen contents are low, AC gains its basic character and is considered good for cationic and/or anionic exchange behavior, respectively (Boehm, 1994). This identification is also crucial for the selective sorption of pollutants from the bulk.



## **2.2 Water Scarcity, Pollution and Remediation**

The development in technology, population growth and increased consumption of available water resources are responsible for the drastic shortage of available water, which will seriously affect the life in the near future, if not properly preserved.

As summarized in a study conducted by Gupta and Suhas (2009), the demand of fresh water supply is the necessity of the day as reported in United Nations World Water Development Report by United Nations Educational Scientific and Cultural Organization (UNESCO). To the best of known statistics, the consumption of water for domestic, industrial and agricultural applications is 8, 22 and 70 %, respectively (UNESCO, 2003). The extensive use of water in industrial processes is finally reverted as discharge released in the form of wastewaters containing toxic pollutants (Helmer & Hespanhol, 1997). These toxins mainly contain the unused dye residues, pesticides, fertilizers etc. and/or the by-products produced during the process.

The robust development worldwide is the outcome of the recently triggered industrialization. While the good impacts of such advancement on life style matter, their environmental apprehension must not be forgotten. In a simple way to elaborate, besides the good quality products introduced into the market, there are always some unwanted and toxic by-products disposed into the environment through industrial effluents. If this sludge is not properly treated prior to their accumulation into the sewerage system, they will adversely affect the quality of life. In this context, the major pollutants which frequently enter the water system are from the textile industries wastes containing the dyes residues.

## **2.3 Dyes as Major Pollutants in the Wastewater**

Although the exact figures are not known, it has been anticipated that approximately 100,000 dyes are commercially available with the annual total production of  $7 \times 10^5$  ton of dyestuff in the market (Crini, 2006). A total of 2 % of the dyes produced were reported to have been directly released into the industrial effluents which eventually enter the ground water. In a separate study by Pereira et al. (2003), the authors revealed that up to 9 % of the total unused dye products was discharged as textile effluents whereas, this amount was even higher (10–15 %) in other reported work by Demirbas (2009). In whatever form, dyes residual sludge along with its by-products are one of the major causes of water pollution.

The first reported dye was believed to be the Blue Indigo dye which was used as organic colorant in the Egyptian tombs for packaging mummies, 4000 years ago. It was claimed that up to the 19<sup>th</sup> century, most of the dyes used were natural dyes and obtained mainly from plants, mollusks and/or insects. The first synthetic dye, mauveine, has been discovered by Perkin in 1856 (Weissenbacher, 2009). This opened a new era for large scale production of synthetic dyes for various industries.

### **2.3.1 Classification of Dyes**

Dyes can be classified on the basis of their structure, which helps in identifying the particular group of dyes with its characteristics such as azo and anthraquinone dyes. However, due to complex dye structures, sometime it is difficult to follow such classification. Dyes can be classified on the basis of their applications following the Color Index (C. I.) system, which have been adopted worldwide. In this system, the

dye's group, its color and a five digit number has been assigned to every dye. For example, C. I. 52015 represents Methylene Blue (MB).

In common practices, the dyes classifications can be associated with the charge on the dissociated ions of the dyes in aqueous media such as cationic dye or anionic dye. The relevance of charges on the dissociated dyes molecules and the surface charge density of the solids, are two important factors for the remediation of dyes wastewater. The major groups of dyes have been summarized in Table 2.2.

Table 2.2

*Classification of Dyes* (Demirbas, 2009; Gupta & Suhas, 2009)

<b>Class</b>	<b>Solubility</b>	<b>Name</b>
Acid dyes	Anionic, soluble in water	Azo, anthraquinone, azine, nitro, triphenylmethane, nitroso and xanthene etc.
Basic dyes	Soluble in water, have bright color	Cyanine, diazhemicyanine, hemicyanine, triarylmethane, thiazine, acridine and oxazine
Disperse dyes	Non-ionic, insoluble in water, show higher fixation rate	Azo, nitro, styryl, benxodifuranone and anthraquinone
Direct dyes	Anionic compounds, soluble in water	Polyazo, oxazines, phthalocyanines and stilbenes
Reactive dyes	Anionic compounds, soluble in water	Azo, oxazine, triarylmethane, formazan, phthalocyanine, anthraquinone and triarylmethane
Solvent dyes	Soluble in organic solvents	Azo, triarylmethane, anthraquinone and phthalocyanine
Vat dyes	Insoluble in water	Indigoides and anthraquinone

### **2.3.2 Release of Dyes in Wastewater and Their Adverse Effects**

With the increasing trend in industrialization, particularly in the textile and related industries, the widespread use of water for wet processing is required which ultimately release a large amount of wastewater. The wastewater released from industries contains a large number of toxins that can cause severe problems to human especially. A rough estimate of the amount of water required to produce 1 kg of cloth is 40 to 65 L (Manu & Chaudhari, 2002). Besides water, such industries have been observed to use a wide range of chemicals (inorganic, organic and polymeric compounds) for various operations (Robinson et al., 2001). However, the problems start when the untreated wastewater is released into the hydrosphere. As reported in a comprehensive review by Verma et al. (2012), the dyeing processes result in the release of a large quantity of wastewater generated from disperse dyeing (91–129 L) and direct and reactive dyeing (113–151 L) per ton of the dyestuff produced. Overall, approximately 200 to 350 L wastewaters per ton products are generated during the dyeing and finishing processes. Moreover, the increased chemical oxygen demand (COD) estimated up to 100 kg per ton products was also reported.

Moreover, the extensive release of dyes in ground waters will be responsible for the aesthetic problems and health related risks. In general, the color, COD, biochemical oxygen demand (BOD), toxicity and turbidity of these effluents increased due to the unused fractions of the synthetic dyes. Demirbas (2009) stated that, the wastewater released from dye related textile industries have pH range of 2 to 14, total dissolved solids between 50 to 6,000 mg/L, and COD of 50 to 18,000 mg/L. Dyes are considered the color poison, prevailing color to water and also because the degraded products of

many dyes are toxic (mutagenic character), thus posing adverse effects on living organisms (dos Santos et al., 2007; Salleh et al., 2011).

As reported in a review by Martinez-Huitle and Brillas (2009), even a small quantity (1 mg/L) of dyes in the effluents imparts an undesired but visible color to the discharge water which will limit the penetration of sunlight. Ultimately, the aquatic photosynthesis and their biological activities will be disturbed. This colored water directly or indirectly affects the aquatic flora and fauna which results in the death rise of aquatic lives (plants, fish and mammals etc). Furthermore, the leaching of polluted water into ground water; also affect the quality of the later. In general, the industrial globalization, robust increase in the installation of industrial plants releasing a large amount of effluents and climate change due to the rise in temperature and reduced rainfall are the key factors deteriorating the quality and availability of fresh water.

Upon biological or chemical integration, these colored compounds may result in eutrophication, increase in demand of dissolved oxygen (DO), hindrance in re-oxygenation, and can cause microtoxicity and genotoxicity (Zaharia et al., 2009). Eutrophication, in particular, comes out due to the excessive supply of nutrients upon wastewater released into water bed which serves as feedstock for the growth of plants and other microorganisms. These organisms will consume more oxygen upon their death to be biodegraded; hence, the overall oxygen demand will be increased. The hazardous effects of these toxins upon chronic exposure are respiratory problems, allergy, central nervous system disorder, diarrhea, cyanosis, salivation, jaundice, tissue necrosis, skin or eyes infections, immune diseases, leukemia, lung problems, irritation and vomiting etc (Anliker, 1986; Foo & Hameed, 2010; Mukherjee et al., 2014). The severity of the dyes

adverse health effects have been investigated by various authorities such as World Health Organization (WHO), United States Environmental Protection Agency (USEPA) and United Nations International Children's Emergency Fund (UNICEF). From the facts revealed, Verma et al. (2012) quoted the improper wastewater treatments may be one of the reasons for short life span (average 64 years) in developing countries such as India whereas the life span in developed countries such as Japan is 83 year.

#### **2.4 Different Types of Dyes Wastewater Remediation**

Environmental protection agencies and researchers all over the world have made many attempts to develop proper treatment technologies for the wastewater prior to the disposal into the ground water to protect the environment. As reported in a study by Qu et al. (2013), more focus should be given to the basic treatment technologies such as sedimentation, disinfection via ozonation and/ or chlorination etc for the existing water. The ultimate purpose to focuss on these treatments is to set up disinfection technologies that do not produce harmful disinfection by-products. The currently existing water treatment techniques have some limitations to be used to produce good water quality required for the daily use. Hence, in some cases, two or more techniques are carried out simultaneously to treat contaminated water (Chang et al., 2004).

Generally, the industrial wastewater released as effluents from any industrial operations, undergoes three major steps before being disposed into the sewerage system (Perry et al., 1997) which are; (1) primary treatment in which the industrial effluents undergo mineralization (the oxidative decomposition of chemical substances into organic matter which can be used by plants) followed by physical or chemical treatments

to remove the total suspended solids (TSS) and total dissolved solids (TDS), (2) secondary treatment in which the effluents are then treated with microorganism such as bacteria, which stabilizes the waste constituents and finally (3) tertiary treatment which involve various physicochemical treatments such as adsorption, chemical oxidation, ion exchange, and membrane separation to treat the industrial discharge to be delivered to the sewerage system considered to be non toxic for aquatic organisms, irrigation and agricultural reuse (Qu et al., 2013). These techniques can be applied in combination with other treatments or individually.

The treatment technologies were thoroughly investigated and further advanced to the use of filter beds and activated sludge for the biodegradation of wastewater pollutants. Moreover, the research is currently going on to develop techniques which can work alone or in combination to accelerate dyes removal from the wastewater.

The criteria for selecting the suitable method depend upon the ease of operation, cost effectiveness, treatment duration, and efficiency. In a more precise manner, the method should be safer, cleaner and greener. Usually, the wastewater treatment technologies are divided into three broad categories such as; biological, chemical and physical processes as described in detailed reviews reported elsewhere (Aksu, 2005; Pereira et al., 2003; Slokar & Le Marechal, 1998; Yagub et al., 2014). These methods have been in use since depending upon the working condition and the available resources. A few of these methods are briefly discussed here; and more focus will be given to the adsorption process which is a widely used and well known dye removal technique due to its viability, accuracy, safe (no harmful end product) and simple operation and comparatively less expensive (Tan et al., 2008; Xia et al., 2015; Zelmanov

& Semiat, 2014). Numerous physicochemical treatment technologies have been employed for the water and wastewater remediation as described in Figure 2.4.

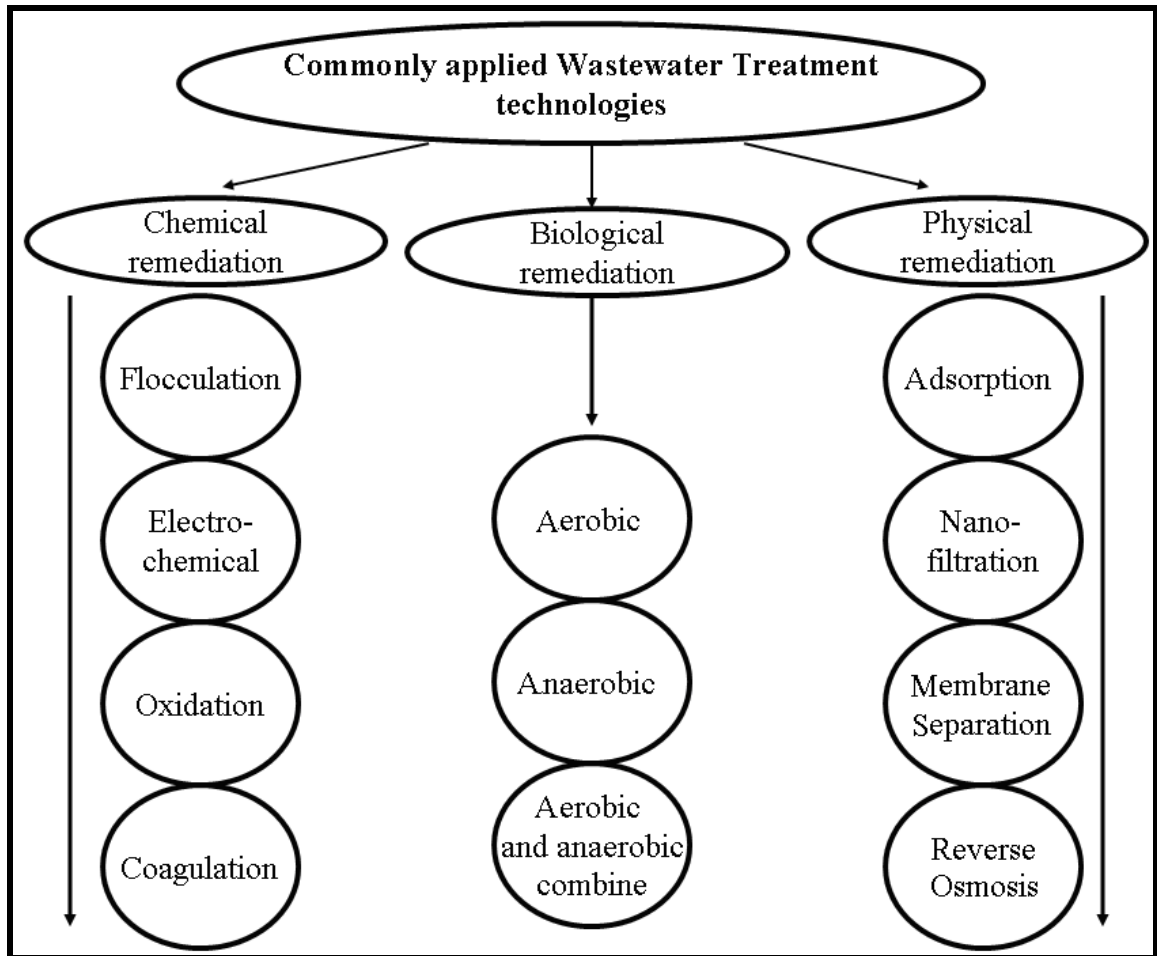


Figure 2.4. Flowchart describing the various wastewater treatment technologies (Crini, 2006).

### 2.4.1 Biological Remediation

Biological remediation processes are based on the use of microorganism such as bacteria, fungi for the biodegradation of organic molecules following biosorption (Aksu,



2005; McMullan et al., 2001). The beneficial aspects of these treatments are the complete mineralization of the dyestuff, no secondary pollution and of course the cost effectiveness (dos Santos et al., 2007). Generally, these processes are classified as aerobic, anaerobic and/or aerobic-anaerobic simultaneously.

Usually, the aerobic treatments are conducted by using various types of fungal or bacterial strains and/or other microorganisms in the presence of oxygen whereby these microorganisms secrete enzymes which are responsible for the breakdown of the dyes molecules to the non toxic end products (Brown & Laboureur, 1983a; Husain, 2006; Pazarlioglu et al., 2005). On the other hand, the anaerobic treatments of dyes wastewaters are conducted in the absence of oxygen. These studies were found effective in the degradation of persistent azo dyes during the aerobic treatments (Brown & Laboureur, 1983b; Delee et al., 1998; Rai et al., 2005; van der Zee et al., 2001). However, more effective remediation of wastewater can be achieved by applying both the aerobic and anaerobic processes simultaneously (Stolz, 2001). The synergistic effects of adsorption and biodegradation using microorganism results in increased mineralization of the organic pollutants (e.g. aromatic amines etc.) besides the bond cleavage of the azo dyes residues, which are usually considered not easy to degrade under ordinary treatment technologies (Aksu, 2005).

Although, biological treatments of water remediation are suitable as they are environmentally friendly and inexpensive, these treatment methods have some limitations if applied in large scale such as longer time duration and poor biodegradation of recalcitrant organic molecules etc (Crini, 2006). These treatments require longer duration for the complete removal and/or mineralization of the dyes (Bhattacharyya &

Sarma, 2003; Robinson et al., 2001). The biodegradation of organics in aquatic system normally requires 28 days (Slokar & Le Marechal, 1998). However, in some cases, the persistent organic molecules may not biodegrade in this limited time. There are various dyes that are either recalcitrant or cannot be transformed to the non toxic by-products under the aerobic conditions. The poor degradation of such pollutants in water may be due to the recalcitrant nature or complex molecular structure of dyes or unfavorable environmental conditions (Claus et al., 2002; Mukherjee et al., 2014). For such pollutants, oxygen catalyzed enzymes are used to degrade them (Stolz, 2001; Yoo et al., 2001). Also, a significant quantity of nutrients is required for the microorganism bioaccumulation. Moreover, the operations of such treatments are temperature dependent i.e. the process can only be operated at certain temperature favorable for the microorganism growth and cannot be carried out at all temperatures. The insufficient BOD removal, refractory organics and other nutrients are also the non-beneficial aspects of these processes (Demirbas, 2009). Lastly, the operational design of the whole system for the application at large scale is difficult to be established requiring a large area for plant installation (Bhattacharyya & Sarma, 2003). Hence, these treatments can only be applied under certain experimental conditions.

#### **2.4.2 Chemical Remediation**

The chemical treatments of dyes involve the use of some chemical agents and are comprised of different processes namely the oxidation (or advanced oxidation processes, AOPs) (Bandala et al., 2008), coagulation (Hao et al., 2000), photocatalysis (Ghorai et al., 2007), electrochemical (Faouzi et al., 2007), ultrasonic waves (Yaqub & Ajab, 2012) and flocculation (Yue et al., 2008) etc. In oxidation process, the oxidizing agents such as