University of Cincinnati

Date: 10/31/2013

I, Osmay C Contreras, hereby submit this original work as part of the requirements for the degree of Master of Science in Environmental Engineering.

It is entitled:
A comparative study of tailored activated carbon from waste tires against commercial activated carbon (F400) for the removal of Methylene Blue

Student's name: Osmay C Contreras

This work and its defense approved by:

Committee chair: George Sorial, Ph.D.
Committee member: Pablo Campo-Moreno, Ph.D.
Committee member: Margaret Kupferle, Ph.D., P.E.
A Comparative Study of Tailored Activated Carbon from Waste Tires against Commercial Activated Carbon (F400) for the Removal of Methylene Blue

A thesis submitted in partial fulfillment of
The requirement for the degree of

MASTER OF SCIENCE

In the Department of Biomedical, Chemical and Environmental Engineering

October, 2013

Prepared by:

Osmary Contreras
B.S. Universidad de Carabobo, 2008

Thesis Committee Chair:

Dr. George Sorial

Thesis Committee Members:

Dr. Margaret Kupferle
Dr. Pablo Campo-Moreno
Abstract

Although color represents a non-mandatory water quality standard, organic compounds such as dyes must be removed from wastewater before discharge. Dyes are considered to be aesthetic and toxic pollutants in water. Various water treatment processes have been studied in order to obtain an optimum removal of dyes. Adsorption by activated carbons (ACs) has demonstrated to be the technique of preference. However, the high cost of the precursor material and process for production could influence for its application. Therefore, it is necessary to find raw materials of low cost that requires limited processing and is easily available. In this study, chemical activation of waste tires for developing activated carbons was evaluated. Tires of 400\(\mu\)m nominal size were impregnated with potassium hydroxide (KOH) in different w/w ratios (0:1, 1:1, 2:1, 3:1, 4:1 and 5:1) and two other parameters were selected in order to obtain the best conditions for the desirable carbon; One is the activation temperature (600, 700 and 800 \(^\circ\)C) and the second is contact time during activation (1, 2 and 3 h). BET specific surface area and pore size distribution (PSD) for each carbon was determined. The activated carbon from waste tires with higher BET specific surface area and mesopore percentage was obtained with a KOH/tires (2/1), temperature 800 \(^\circ\)C and activation time 1 h. Adsorption isotherm, kinetic studies and microcolumn experiments were conducted with the selected activated carbon from waste tires (ACWT) and commercial activated carbon (F400) for the removal of methylene blue (MB). ACWT has demonstrated to be an effective adsorbent in removing MB but with lower adsorption capacity than that of F400, suggesting further studies need to be conducted for enhancing the activation process of waste tires.

Keywords: Activated carbon; adsorption; chemical activation; dyes; methylene blue; waste tires
Acknowledgements

First, I would like to thank to God, the Almighty One, for blessing me and accompanying me in every step of my life.

I would like to thank my academic advisor, Dr. Sorial for his helpful guidance and supervision in every stage of my thesis and in my career. I would also like to thank to Dr. Liang Yan for his valuable help and patience in various parts of this research. Thanks to Dr. Margaret Kupferle and Dr. Pablo Campo-Moreno for their suggestions and interest in this thesis. Thanks to my office mates; Hengye Jing, Bineyam H. Mezgebe and Zhen Li for their friendship and help in my experiments.

I am most thankful to my lovely husband (Paul Wagner) for his company, support, and patience throughout my years at University of Cincinnati. I acknowledge my deepest appreciation to my parents (Morella Madriz and Osvaldo Contreras), parents in law (Bill and Vivian Wagner), Grandparents (Benita Madriz) and sister (Marioxy Contreras) for their powerful prayers and continuous love.

Finally, I would like to thank Ann Hubbard, Graciela and Lou Bilionis, Patricia Leyva, and Dina Henderson for their faithful and unconditional friendship over the past years.
# Table of Contents

1. Introduction .......................................................................................................................... 1  
   1.1 Statement of the Problem ................................................................................................. 1  
   1.2 Research objectives ........................................................................................................ 2  
   1.3 Research structure ......................................................................................................... 3  
   1.4 References .................................................................................................................... 4  

2. A Review of emerging and efficient adsorption techniques for the removal of dyes in the wastewater of the textile industry ................................................................. 5  
   Abstract ............................................................................................................................... 5  
   2.1 Introduction ................................................................................................................... 5  
   2.2 Technologies for dye removal ....................................................................................... 7  
       2.2.1 Advance Oxidation Techniques .............................................................................. 7  
       2.2.2 Separation Techniques .......................................................................................... 16  
       2.2.3 Sorption ............................................................................................................... 20  
       2.2.4 Biological Treatment ............................................................................................ 23  
   2.3 References .................................................................................................................... 31  

3. A comparative study of tailored activated carbon from waste tires against commercial activated carbon (F400) for the removal of methylene blue ....................................................................... 36  
   3.1 Introduction ................................................................................................................... 36  
   3.2 Materials and methods ................................................................................................. 39  
       3.2.1 Preparation of Activated Carbon from Waste Tires (ACWT) ............................. 39  
       3.2.2 Physical analysis of the activated carbons from waste tires ......................... 40  
       3.2.3 Chemical analysis of the ACWT and F400 .......................................................... 41  
       3.2.4 Adsorption Isotherm ............................................................................................ 42  
       3.2.5 Kinetics studies .................................................................................................... 43  
       3.2.6 Column studies .................................................................................................... 43  
   3.3 Results and discussions ................................................................................................. 44  
       3.3.1 Tailoring of Activated Carbons from Waste tires .............................................. 44  
       3.3.2 Adsorption isotherm of MB onto F400 and ACWT ........................................... 48  
       3.3.3 Kinetics of MB adsorption onto F400 and ACWT ............................................. 53  
       3.3.4 Microcolumn experiments ................................................................................. 57  
   3.4 Summary of comparison between ACWT and F400 .................................................... 58  
   3.5 References .................................................................................................................... 96  

4. Conclusions and suggested future work ............................................................................. 99
List of Tables

Table 2.1 Common dyes used in the Textile industry...........................................28
Table 2.2 Treatment technologies for the removal of textile dyes...........................29
Table 3.1 Molecule characteristics of Methylene Blue.........................................88
Table 3.2 Physical and chemical characteristics of activated carbon........................89
Table 3.3 Effects of KOH/tires ratio on the surface characteristics of activated carbons from waste tires.................................................................90
Table 3.4 Effects of activation time and temperature on the surface characteristics of activated carbons from waste tires.........................................................91
Table 3.5 Physical and chemical characteristics of activated carbons.......................92
Table 3.6 Adsorption isotherm constants for MB onto ACs.....................................93
Table 3.7 Kinetics parameters for MB adsorption onto AC.....................................94
Table 3.8 Microcolumn experiments for MB removal by ACs..................................95
List of Figures

Figure 3.1 Methylene blue synthetic route scheme...............................................................59

Figure 3.2 Methylene blue molecule..................................................................................60

Figure 3.3 Adsorption isotherm of MB onto F400 and AC-A..............................................61

Figure 3.4 Pore size distribution of F400 and AC-A...........................................................62

Figure 3.5 N₂ adsorption isotherm of activated carbon from waste tires created at different KOH/tires ratio........................................................................................................63

Figure 3.6 Pore size distribution of activated carbon from waste tires created at different KOH/tires ratio........................................................................................................64

Figure 3.7 N₂ adsorption isotherm of activated carbon from waste tires created at different activation temperature.....................................................................................................65

Figure 3.8 Pore size distribution of activated carbon from waste tires created at different activation temperature.....................................................................................................66

Figure 3.9 N₂ adsorption isotherm of activated carbon from waste tires created at 800 °C with different activation time..........................................................................................67

Figure 3.10 Pore size distribution of Activated carbon from waste tires created at 800 °C with different activation time..........................................................................................68

Figure 3.11 N₂ adsorption isotherm of activated carbon from waste tires created at 700 °C with different activation time..........................................................................................69

Figure 3.12 Pore size distribution of Activated carbon from waste tires created at 700 °C with different activation time..........................................................................................70

Figure 3.13 N₂ adsorption isotherm of activated carbon from waste tires created at 600 °C with different activation time..........................................................................................71

Figure 3.14 Pore size distribution of Activated carbon from waste tires created at 600 °C with different activation time..........................................................................................72

Figure 3.15 N₂ adsorption isotherm of ACWT and F400.......................................................73

Figure 3.16 Pore size distribution of ACWT and F400.......................................................74
Figure 3.17 Adsorption isotherm of MB onto F400, AC-A and ACWT…………………………….75

Figure 3.18 Langmuir adsorption isotherm model for the removal of MB onto F400 and ACW………………………………………………………………………………………………………………76

Figure 3.19 Freundlich adsorption isotherm model for the removal of MB onto F400 and ACWT………………………………………………………………………………………………………………………………………………………..77

Figure 3.20 Redlich-Peterson adsorption isotherm model for the removal of MB onto F400 and ACWT………………………………………………………………………………………………………………………………………………………..78

Figure 3.21 Time variation MB adsorption onto ACs………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………..79

Figure 3.22 First-order kinetic graph of MB adsorption onto AC…………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………..80

Figure 3.23 First-order reversible reaction of MB adsorption onto AC…………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………..81

Figure 3.24 Pseudo-first-order reaction of MB adsorption onto AC…………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………..82

Figure 3.25 Pseudo-second-order reaction of MB adsorption onto AC…………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………..83

Figure 3.26 Intra-particle diffusion model of MB adsorption onto F400…………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………..84

Figure 3.27 Intra-particle diffusion model of MB adsorption onto ACWT…………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………..85

Figure 3.28 Plot of Bt vs. t for determining the actual rate controlling the adsorption of MB onto F400…………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………..86

Figure 3.29 Plot of Microcolumn experiment for MB removal by ACWT and F400…………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………..87
1. Introduction

1.1 Statement of the Problem

Among the existing techniques, such as advanced oxidation technique, separation methods, and biological degradation, adsorption by commercial activated carbon is considered the most effective process for removal of textile dyes from the wastewater. It relies on the attachment of the dye molecule on the surface of the adsorbent by one of the two mechanisms physisorption or chemisorption [1]. Nowadays, the removal of coloring materials by commercial activated carbon is being affected by the high cost of its application such as use of natural precursor materials and low regeneration efficiency [2-4]. Therefore, several studies have been conducted to find low cost materials for the creation of activated carbons (AC), and improvement of their adsorption capacity toward textile dyes [5]. Waste tires have shown to be a promising raw material for the creation of activated carbons for the removal of large molecule sizes such as methylene blue (a cationic common dye for textile applications), offering an adsorbent for the removal of organic contaminants and at the same time provides a solution of waste disposal [2]. However, the study of creating activated carbon from waste tires with chemical activation is very limited. This situation has motivated the authors to perform further research in order to understand the mechanism of adsorption of methylene blue onto activated carbon from waste tires with potassium hydroxide and compare it with commercial activated carbon (F400).
1.2 Research Objectives

The first objective of this research is to review previous publications concerning the most common techniques applied for the removal of dyes from the textile effluents and to explore the different existing dyes in the industry. The adsorption efficiency of textiles dyes is affected by the physical and chemical characteristics of the activated carbon and dye molecule.

The second objective involves:

- To prepare activated carbons from waste tires with potassium hydroxide (ACWT)
- To perform adsorption isotherms, kinetics studies and Microcolumn experiments for the removal of methylene blue (MB) by ACWT and F400
- To compare removal performances of MB by ACWT against F400

The adsorption capacity of ACWT toward MB is lower than that of F400. However, for more accurate results regarding environmental and cost benefits, a Life Cycle Assessment (LCA) and a Life Cycle Costing (LCC) analysis should be carried out.
1.3 Structure of Research

This study presents four chapters. Chapter 1 (present chapter) is an introduction for the thesis. Chapter 2 is a review paper of commercial dyes in the textile industry, available treatment technologies for the removal of colour in textile effluents, and processes involved in those techniques. Chapter 3 is the main research. It explains in more details the conducted experiments in this thesis, the list of materials and methods, process preparation, and discussion of experimental results. Lastly, chapter 4 contains a summary of the present work and suggestions for future research in this area.
1.4 References


2. A review of Emerging and efficient adsorption techniques for the removal of dyes in the wastewater of the textile industry

Abstract

Dyes, are classified as aesthetic, and toxic contaminants used by the textile and other industries to color their products. The molecule of dyes contain organic compounds classified as carcinogens and dangerous for human consumption. Their presence in sources of drinking water produces serious environmental problems and public concerns. Therefore, studies have been conducted on various treatment techniques for the removal of these compounds from industrial effluents. Different existing technologies for decolorization such as advanced oxidation techniques, separation methods, sorption, and biological degradation have been demonstrated to be effective in their removal and economically sound. In addition, the effectiveness of each process depends on the chemical, material and conditions used. In this study, a review of different removal techniques of various dyes is presented. The review also provides an explanation of the fundamental mechanism promoting decolorization, thus providing possible updated information on emerging techniques for the removal of dyes.

2.1.- Introduction

The presence of dyes in the textile industry effluents have always been a concern [1, 2]. Dyes are aromatic organic compounds with a complex molecule structure. They are binding with a compound which give color (chromophore group) and an ionizing group (auxochromes) which provides a bonding affinity toward the fiber [3]. Some of the chromophore groups include azo (-N=N-), carbonyl (=C=O), methine (-CH=), carbon (=C=C=), carbon-nitrogen (>C=NH or –H=N), nitroso (-NO or N-OH), nitro (-NO_2 or =NO-OH), and sulfur (C=S). The auxochrome group includes hydroxyl (-OH), amino (-NR_2), bisulfite (-HSO_3^-), and Carboxyl (-COOH). It is estimated that there are more than 100,000 available dyes with different tonnes of dyestuff, and industries such as textile, cotton, wood, leather, etc, use them to color their products [4]. Dyes can be
classified by their chemical structure (azo, anthroquinone, diazo, basic, and acidic) or by their mode of application to the fiber. Part 1 of the 3rd edition of the Color Index classify them by the mode of application such as acid, basic, direct, disperse, mordant, reactive, sulfur, vat and others. Table 2.1 illustrates this classification [5]. Industrial processes that use dyes consume a great amount of water hence providing a source of color contamination. Wastewater contaminated with dyes is caused by the production of these compounds and also as a consequence of its use by the above mentioned industries. Removal of dyes by conventional aerobic process in the public wastewater facility is inefficient, causing their discharge in natural waters. The presence of dyes in sources of drinking water is easily revealed by their color such as yellow, orange, red, violet, blue, green, brown and black [5]. A low concentration, less than 1 mg/L, can be captured by human eyes causing aesthetic concerns to the public [1]. In addition to the aesthetic problems, these compounds have the ability to absorb sunlight taking up energy that is necessary for organism to develop under water. Furthermore, their chemical structure have carcinogenic properties and toxic effects for the aquatic system such as contribution of chemical oxygen demand (COD), biochemical oxygen demand (BOD), and total organic carbon (TOC) [6].

Due to the above mentioned concerns of dyes in natural sources of drinking water, there is an effort from public and private industries to remove dyes from wastewater. The treatment technologies of dye effluents that have been highly investigated include advanced oxidation techniques, separation techniques, sorption, and biological degradation. Each of these techniques involves other sub-techniques that are differenced by the conditions of the process, mechanism of removal or chemicals used. Therefore, this study reviews recent technologies for the removal of textile dyes from the wastewater, advantages, consequences, and removal efficiency.
2.2.- Technologies for dye removal

Table 2.2 presents a summary of recent studies on the removal of dyes by different technologies. Depending on the type of dye, different technologies could be effective in removing the molecule hence eliminating color from the wastewater. For instance, due to the presence of one or more azo bonds in the structure of azo dyes, anaerobic degradation is effective in degrading azo dyes and forming less harmful compounds, which can be removed or mineralized by further treatment techniques.

2.2.1.- Advanced Oxidation Techniques

Advanced Oxidation Techniques (AOTs) embrace water treatment process where a strong nonselective oxidizing agent is created (mostly hydroxyl radicals). The highly reactive radical is produced at sufficient quantity that decompose the contaminant in water to smaller or less harmful compounds and sometimes complete mineralization [7]. The advanced oxidation Processes widely investigated for the removal of dyes are; Ozonation, Fenton Reagents, Photocatalysis, and Ultrasonic Irradiation.

Ozonation

Ozonation technique uses ozone as the strong oxidant to degrade colour. Ozone is the fourth more powerful oxidant. It has standard oxidation potential (E°) of 2.06 V, and is highly soluble in water. The degradation of a pollutant by ozone can be divided in two ways; direct and indirect oxidation. In direct oxidation, ozone reacts with the unsaturated chromophoric bonds (–C=C– or –N=N-) of the dye molecule and produces secondary compound which has to be removed by another treatment technique. For the indirect oxidation mechanism, hydroxyl radicals are created by the decomposition of ozone at specific pH, which are then responsible in mineralizing the hydrocarbon contaminant to CO₂ and H₂O [8].
Ozonation is a treatment technique that is emerging and has increasing interest due to the ozone capacity for electrophilic attack towards the double bond chromophoric group of the dye. The application of ozone alone has been performed for some dyes and the results indicated that the ozone molecule destroys the compound responsible for color in the dye molecule [9, 10]. However, this degradation originates other smaller compounds that contribute to COD values in the water, such as acetic acid, ketones, epoxides, etc. Therefore, the addition of other chemicals or techniques has been investigated for the improvement of Ozonation [8, 11-13]. Basiri and Hagh [8] performed some modifications to the ozonation technique for the removal of Acid Blue 92. This modification consisted of comparing three methods which are; ozonation, ozonation with hydrogen peroxide, and ozonation with activated carbon. As a result, ozone alone removed the color but increased the values of COD. Optimum removal was obtained with the ozonation and activated carbon process because activated carbon serves as a catalyst for the reaction and as an adsorbent for the secondary pollutants.

Cuiping [11], performed three ozonation processes of UV/ozone, Ultrasound/ozone and ozone in order to know which would be more effective in removing rhodamine B. The maximum removal was obtained with UV/ozone process because UV light enhances the oxidation of ozone to more hydroxyl radicals which degrade the contaminant. The results also indicated that there were removal of COD, where UV/ozone process removed up to 47.43% after 15 minutes, followed by US/ozone and the less efficient was ozone by itself. Some of the smaller organic compounds created from this process were; formic acid, acetic acid and N, N-diethylformamide, which could be removed by biological techniques.

Liu [12] studied the influence of solid catalyst (Fe-Cu-O, Fe$_2$O$_3$, and CuO) in the performance of Ozonation. Several points were observed in this study; first higher concentrations (100 mg/L to 500 mg/L) of acid red B were removed by the ozone/catalyst process. Second, the removal efficiency of color and COD was obtained with the introduction of catalyst in the following order;
O₃ < O₃(CuO) < O₃(Fe₂O₃) < O₃(Fe-Cu-O). Finally, the mechanism of degradation by the Fe-Cu-O catalyst was for direct and indirect oxidation. Direct oxidation was created after ozone and acid red B molecule were adsorbed in the surface of the catalyst, and indirect oxidation took place when hydroxyl radicals are created by the chemical reaction of hydroxyl surface groups on the surface of the catalyst and oxidation of ozone into \( O_2^- \) and \( HO^- \).

In summary, the publications presented on the use of Ozonation for the removal of dyes in wastewater indicated that an efficient elimination of color and organic compounds can be achieved. However, additional processes have to be combined with this method in order to remove the mineralized compounds because ozone alone is not enough for the complete mineralization of the dye. If just ozone is required to be applied, low dye concentrations and high ozone dosage would have to be used for an optimum treatment. In addition, the effect of pH on the process will depend on the type of dye, some researchers obtained maximum ozone decomposition when increasing pH values, but other investigations found contrary results [9].

**Fenton reagents**

The Fenton reagent technique for the removal of organic pollutants was created in 1876 [14]. It is explained that this name means “solution of Fe(II) and \( H_2O_2 \)”. This is a recommended method for the removal of organic contaminants that are resistant to biological treatment [15]. It is reported that this technique is cheaper, easier to treat, feasible for a wide array of organic compounds and does not result in secondary harmful compounds [16]. Advanced oxidation process using Fenton’s reagents, consists of the degradation of the molecule of the contaminant by hydroxyl radicals to biodegradable and less harmful compounds. The hydroxyl radical is a strong oxidant and it is the result of the reaction of ferrous ion (\( Fe^{2+} \)) and hydrogen peroxide (\( H_2O_2 \)). Eq. 1 describes this reaction [17]:

\[
Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^-OH^-
\]  

The degradation of the pollutants is then presented by the following equation [17]:
Several studies have been conducted in order to evaluate the effectiveness of this method in the removal of dyes from water. Reported articles agree that the degradation of dyes by Fenton reagents depend on initial solution pH, initial hydrogen peroxide concentration, initial ferrous concentration, initial dye concentration, temperature, and nature of acid used to adjust pH [14, 16, 18, 19].

Hameed and Lee [16] found that the optimal parameters for the degradation of malachite green by conventional Fenton process are; solution pH 3.4, initial H$_2$O$_2$ concentration 0.50 mM, initial ferrous concentration 0.10 mM, initial Malachite green concentration 20 mg/L and temperature 30 °C. A pH range of 2.7 to 3.5 is recommended for efficient Fenton reactions, this is because depending on the concentration of the Hydrogen ion (H) in solution, it will be the iron ion oxidation condition and concentration. The initial concentration of hydrogen peroxide influenced the rate of dye degradation. At higher H$_2$O$_2$ concentrations, the reaction of degradation will be faster. However, an excess of H$_2$O$_2$ concentrations showed that spoils the process due to the formation of hydroperoxyl radicals (HO$_2$) which does not contribute to the oxidation of the contaminant. Recommended concentrations of H$_2$O$_2$ could be in the range of 1.2 to 2.5 mM. Initial ferrous concentrations also impacted the rate of dye oxidation; at higher concentrations, faster will be the catalytic reaction. The recommended concentrations values are in the range of 0.06 to 0.10 mM of ferrous ion [16, 18], values higher than 0.10 mM could promote the production of another reaction where ferrous ion in excess will react with hydroxyl radicals (Eq. 3).

\[
Fe^{2+} + HO^- \rightarrow Fe^{3+} + HO^-
\]

As other chemical reactions, Fenton reagent process depends on temperature. It has been demonstrated that high temperatures increase the rate of degradation but decrease the yield [18]. This low yield is presented for the disintegration of H$_2$O$_2$ at high temperatures. Recommended values of temperature for wastewater are in the range of 30-40 °C. Regarding
dye initial concentration, lower discoloration efficiency was obtained with higher initial concentrations [20]. This can be explained by the effect that more oxidant is available and less contaminant is presented for degradation.

Besides the reaction parameters mentioned above, Bouasla et al. [18] evaluated the effect of nature of the acid used to adjust the pH, stirring speed and nature of the iron ion oxidation stage. They indicated that sulfuric acid is recommended for adjusting the pH, 240 rpm is an optimum stirring speed for an adequate mass transfer between the involved compounds. The catalyst at oxidation state of +2 (Fe$^{2+}$) was better than at oxidation state of +3 (Fe$^{3+}$).

Finally, Fenton reagents process is being modified and combined with other treatment techniques in order to regenerate Fe$^{2+}$ from Fe$^{3+}$ hence more efficiency for the yield of decomposition of the contaminant. Some of these studies include: the use of Fenton oxidation for improvement of wastewater characteristics for later biodegradability [21], heterogeneous Fenton and Fenton-like catalyst [17], the used of external energy for the degradation of dyes such as Electro, Photo, Sono,- Fenton process, and Sono, Photo- Electro Fenton process [19].

**Photocatalysis**

Photocatalyst is the semiconductor used in Photocatalysis process, which experiences electron-hole generation in the presence of light [7]. Photocatalysis is a chemical reaction which consists of the production of hydroxyl radicals (highly nonselective oxidation agent) by two processes. One is the oxidation of the holes with water molecules or hydroxide ions. These holes are created when the system is exposing to light, which generates the departure of an exited electron from the valence band to the conduction band at the surface of the semiconductor. The second is a reduction reaction of the gained electrons with oxygen in the conduction band. Hydroxyl radicals destroy the dye molecule after it is adsorbed on the surface of the semiconductor. Most of the catalysts used as semiconductor nowadays are cadmium sulfide (CdS), Titanium dioxide (TiO$_2$), Zinc oxide (ZnO), and tungsten trioxide (WO$_3$). Due to its
nontoxicity effects and cheapness, TiO$_2$ is the semiconductor mostly used in this treatment technique and more researches are still emerging on new applications with this compound. Kuo and Ho [22] evaluated the Photocatalysis of methylene blue with solar and artificial (UV lamp) light sources. The optimum pH value was at 4. UV light system alone demonstrated to be less efficient removing methylene blue than when TiO$_2$ was introduced. It is explained that at pH of 4, the methylene blue ion (C$_{16}$H$_{18}$N$_3$SCl) was electrostatic attached on the surface of TiO$_2$ hence hydroxyl radicals react more easily with the contaminant. In addition, similar results were obtained with the UV light system, where higher color removal was obtained with the addition of TiO$_2$ than with UV light alone. Photocatalysis was more efficient with solar light than with UV light. These results correspond to the capacity of methylene blue molecule to experience photosensitization, which produces more free radicals hence more degradation.

Akbal [23] studied the effect of UV and solar light on the Photocatalysis of a cationic dye (Methylene Blue) and an anionic dye (methyl orange). The effect of initial pH was noticed when varying the values from 3.0-8.0, removal efficiency increased at low pH. The high removal efficiency in acidic conditions can be explained for the positively charged surface that TiO$_2$ acquires in this condition, hence the anionic dye, methyl orange, and methylene blue ions are adsorbed on the surface of the catalyst, thus allowing easier degradation. The effect of TiO$_2$ concentration was also evaluated, showing higher removal when the concentration was increased from 0.2 to 0.5 g/L. The addition of H$_2$O$_2$ to the TiO$_2$ system was evaluated, showing improvement in the degradation process. H$_2$O$_2$ is an excellent electron acceptor which present reduction reaction with the electrons in the conduction band and produce more hydroxyl radicals. On the other hand, the initial dye concentration has two main effects in the decoloration rate, one is that at higher concentration more would be the material for degradation, and second more obstacle would be for the penetration of light to the system thus less photons would be able to reach the surface of TiO$_2$. Therefore, lower initial concentrations of dye solution and the use of solar light were more beneficial for an effective process.
The use of metal oxide or metal sulfide such as TiO$_2$ has been limited for industrial application because of several disadvantages such as low specific surface area, complication for regeneration, unable for visible light respond, and expensive in large-scale applications. In order to overcome these limitations, an effort is being done to improve the photo-catalytic properties of some semiconductors [24-26]. Saravanan et al. [26] synthesized nanosized ZnO semiconductor with the methods of sol-gel, precipitation, and thermal decomposition. The higher degradation of methylene blue and methyl orange was evaluated, obtaining higher efficiency with the catalyst prepared by the Sol-gel method (99% for methylene blue and 63% for methyl orange). The Sol-gel method produced materials with smaller crystallite size (16 nm) and higher specific surface area hence more sites where the electron-hole chemical reaction can take place.

Finally, Xia et al. [24] created recyclable catalysts, with visible light adsorption rate and high degradation rate for methylene blue and methyl orange. The novel catalysts were created with the synthesis of Layered double hydroxides with different Ti-types. Three Ti-based Layered double hydroxides materials were synthesized by ion exchange, calcination method, and coprecipitation, obtaining compounds with high photocatalytic respond under visible-light and higher degradation for methylene blue and methyl orange. The compounds could be regenerated efficiently more than three times and the degradation process fitted well pseudo-first-order kinetics.

**Ultrasonic Irradiation**

Ultrasonic Irradiation (also called sonochemistry) consists of the application of power to the liquid at frequency waves ranging from 300 to 500 kHz. This introduction of power acts upon the aqueous solution causing the formation, and collapse of vapor cavities (bubbles) that enhance sonochemical reactions for the degradation of contaminants. Highly reactive species such as...
hydrogen and hydroxyl radicals ($H^-$ and $HO^-$) are resulted from the extreme conditions of localized high temperatures and pressures, generated by the ultrasonic waves (Eq. 4) [27].

$$H_2O \rightarrow H^+ + HO^-$$ (4)

Recently, several studies have been conducted in the ultrasonic degradation of dyes [28, 29]. Kobayashi et al. [28] investigated the effect of ultrasonic energy on the degradation rate of Methylene Blue. They demonstrated that at higher frequency and ultrasonic power the dye decomposition was higher. These findings agree with Adewuyi [27] who explained that degradation rate increased until an optimum point, and then the reaction rates started to decrease. In addition, the mechanism of degradation by ultrasonic irradiation is different for all organic contaminants. The three chemical reactions that could be taking place in sonochemistry are; pyrolytic reactions in the cavity interior of the bubble (volatile and hydrophobic molecules), radical and pyrolytic reaction in the bubble-bulk liquid interface, and oxidation of hydroxyl radicals in the bulk phase (hydrophilic and soluble molecules) [30].

Moumeni et al. [29] studied the removal of malachite green by Ultrasonic Irradiation. It was found that malachite green concentration decreased with ultrasonic irradiation time. Concentrations of hydrogen peroxide also increased with time but at lower rate compared with the sample without substrate. It is explained in this study that ultrasonic reactions produced hydroxyl radical which can combine and create hydrogen peroxide. However, the presence of a contaminant such as malachite green competes for $HO^-$ radicals hence decreasing the production of $H_2O_2$. Therefore, Fe(II) was added to the system; obtaining higher degradation of malachite green. This result is explained for the creation of more $HO^-$ radicals by the combination of $Fe^{2+}$ and $H_2O_2$ (Eq. 5 and 6)

$$2HO^- \rightarrow H_2O_2$$ (5)

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^- + OH^-$$ (6)
Moumeni et al. [29] also investigated the effect of malachite green initial concentration, ultrasonic power, and initial pH. It was observed that higher malachite green initial concentrations will react better with the local concentration $HO^-$ radicals enhancing the degradation efficiency. While at lower concentrations, the reaction between the dye molecule and hydroxyl radicals is less probable hence causing more recombination of hydroxyl radicals for the formation of hydrogen peroxide. Similar to the above explanation, the increase of ultrasonic power increased malachite green degradation, which was explained as more violent collapse of bubbles hence more concentration of oxidant radicals in the liquid phase. Finally, due to the hydrophobicity of the malachite green molecule in acidic conditions (pH of 2), degradation efficiency was enhanced for the high concentration of hydroxyl radicals at the bubble-liquid interface.

Merouani et al. [31] studied the effect of additives such as iron, carbon tetrachloride, $H_2O_2$, tert-butyl alcohol, sodium sulfate, sucrose and glucose on the degradation of Rhodamine B by Ultrasonic Irradiation. The systems with the addition of Iron (II) obtained the higher initial degradation rates due to the combination of Fe(II) with $H_2O_2$ and generation of more $OH^-$ radicals (Fenton reagent process). It was demonstrated that the sonochemical degradation rate of Rhodamine B was higher when increasing initial dye concentration. At high concentrations, $OH^-$ radicals are busy reacting with the molecule of the contaminant and lower would be the option for $OH^-$ radicals to recombined and form $H_2O_2$. In addition, the effect of ultrasonic power was evaluated, obtaining more rapidly pulsation and collapse of cavitation bubbles with higher values, hence more $OH^-$ radicals for the degradation of Rhodamine B. Finally, the effect of pH and temperature showed once again to be important parameters in sonolytic reactions, obtaining higher degradation in strong acidic and basicity conditions (pH 1 and pH 13) and high temperature (55 °C).
In Conclusion, These four different processes of advanced oxidation techniques have demonstrated to be effective on the partial or complete degradation of the dye molecule. However, in some cases complete mineralization or removal is not achieved. Therefore, more studies are being performed in order to increase efficiency and reduce cost for their application at the industry level.

### 2.2.2.- Separation Techniques

These processes consist of the separation and complete removal of the contaminant molecule from the liquid phase, and not a partial decomposition or mineralization, which can produce other non-desirable contaminants.

**Coagulation/flocculation**

Coagulation/flocculation consists of a two part process. First, coagulation takes place with a slow mixing of a chemical compound, called coagulant, and the solution that contains the contaminant. This mixing provokes the destabilization and attraction of small particle in suspension. Then, the immediate step, flocculation is called when the smaller particles accumulate to form flocs that can be removed by other process such as gravity sedimentation and filtration [6]. For coagulation, the compounds mostly used include metal salts such as ferric chloride or aluminium sulphate, pre-hydrolyzed metal salts such as polyaluminum chloride, lime and alum. For flocculation the most common flocculants are inorganic, organic and natural compounds such as organic polymers [6].

In the last decades, several studies have been performed in order to find materials that can be used as coagulants or flocculants but without health or environmental impact, economic and efficient [6]. Sanchez-Martin et al. [32] used tannin-based product, called Tanfloc as coagulant in a pilot and batch study. Tanfloc is a coagulant with great flocculant properties, produced by
the physicochemical transformation of its Natural origin (Tannin). It was indicated that this material is not a health problem when used at needed concentrations and produced the intentional aggregation of dye molecule for later removal in a sand filtration process.

Sadri Moghaddam et al. [33, 34] studied the mechanism of coagulation/flocculation process with ferric chloride sludge and polyaluminium chloride sludge for the removal of Acid Red 119. It was observed that very acidic conditions are beneficial for the neutralization of the negative charge (anionic dye), resulting in a maximum dye removal with less coagulant dosage. pH has demonstrated to be an important factor in dye removal because their color intensity and ionization stage depends on the concentration of hydrogen ions in solution, thus process pH must be optimized depending on the type of dye and coagulants [34]. Due to the much higher content of metal (Fe), Ferric Chloride Sludge demonstrated to be a better material as coagulant aid than polyaluminium chloride sludge for the removal of Acid Red 119. These coagulants resulted in comparable removal efficiency than that of commercial products. However, the availability, sustainable reuse, lower sludge production and cost benefits make waterworks sludge an attractive option for coagulation/flocculation methods.

Later, Sadri Moghaddam et al. [35] compared the removal efficiency of Acid Red 119 by an inorganic polymer flocculant called Polyaluminium Chloride (PAC) and a water treatment sludge called Polyaluminium Chloride Sludge (PACS). It was observed that Polyaluminium Chloride showed a better coagulation behavior than that of Polyaluminium Chloride Sludge because it posed higher charge neutralization ability and bridging flocculation. However, the reuse idea of Polyaluminium Chloride Sludge makes it equally desirable for applications. Polyaluminium Chloride and Polyaluminium Chloride Sludge resulted on 95.25% and 94.1% dye removal efficiency at pH of 3.8 and 3.42 respectively, coagulant dosage of 57 mg PAC/L and 4.55 g dried PACS/L, and initial dye concentration of 150 mg/L.
Rodrigues et al. [36] evaluated the coagulation/flocculation process with ferrous sulphate (FeSO$_4$ · 7H$_2$O) as coagulant and Magnafloc 155 or Superfloc C-573 as the flocculants for the removal of effluents from the cotton, acrylic and polyester dyeing process. It was observed once again that removal efficiency depends on the pH of the solution, temperature and coagulant dosage. The optimal conditions for the synthetic effluent were pH of 8.3, 9.4, and 7.2, Fe$^{+2}$ Concentration of 200, 200, and 3000 mg/L for Polyester, Cotton, and Acrylic respectively, and temperature at 22 °C for all the effluents. In addition, the flocculant Magnafloc 155 enhanced the removal of the acrylic effluent, obtaining 93.8% of color removal, and Superfloc C-573 produced a colour removal of up to 91.4% for the cotton effluent.

*Membrane filtration*

Membranes act as barriers that filter the influent that enters to the membrane module, producing a permeate (purified effluent). The most well-known membrane process includes microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO). Membranes contain pore size in the following range, MF (>0.1 μm), UF (0.1-0.01 μm), NF (0.01-0.001 μm), and RO (<0.001 μm) [37]. In the textile industry, membranes technology is highly recommended for the removal of color in the effluents of dye baths [38]. The most common parameters defining the membrane process involve operating pressure, feed flow, pH of solution, initial dye concentration, dissolved salts, and feed temperature [39-41].

Huang et al. [39] studied the effect of operating pressure, feed flow and membrane cleaning on the permeate volume flux and rejections percentage for a self-made 2-hydroxypropyltrimethyl Ammonium Chloride Chitosan/poly (sulfone) Composite positively charged NF membrane. As a result, the optimum conditions of operating pressure and feed flow were 10 bars and 40 L/h respectively, obtaining a 100% removal of color. The produced permeate was acceptable
enough to be reuse through the membrane, and the membrane was also satisfactory cleaned with 1% of NaOH solution.

Abid et al. [40] evaluated the resulting permeate flux and dye rejection percentage for the variation of initial dye concentration, pH of solution, feed temperature, dissolved salts, and operating pressure when a RO and NF membranes were used for the removal of dyes of a Iraq textile wastewater industry. The RO membrane, which has smaller pore sizes, resulted with higher rejection percentage of the three dyes (Acid red, Reactive black and Reactive blue). This means that sieving mechanism was the main mechanism controlling the filtration process. In addition, reactive black and blue are less soluble dyes hence their removal was higher but also produced membrane fouling. Changes in initial dye concentration, salt concentration (NaCl), pH and operating pressure described a positive trend of dye removal at higher values. However, temperature showed different results, and it is explained that the decrease of dye removal by increasing temperature is caused by increases of water permeability and pore sizes in the membrane; thus facilitating the molar mass diffusion of the dye molecules. In conclusion, this study demonstrated that RO and NF membrane (both of composite polyamide material) treatment at operating pressure of 10 bars, pH of 8.3, and T of 39 °C resulted in greatly higher dye removal than that of biological treatment process (ISO9888).

A commercial NF DK 2540F membrane was used to compare the removal efficiency of two dye effluents by coagulation/flocculation, enzyme catalysis and NF process [42]. The two synthetic dye effluent included one with only reactive dyes (Reactive black Novacron R (BNR) and Blue Bezaktiv S-GLD 150 (BB150), and the other effluent with reactive dyes (BNR and BB150) and salts (Sodium hydroxide, sodium carbonate, sodium chlorate, detergent, Beavin BPA). Out of the three processes, NF demonstrated to be the best technology removing dyes (more than 99% removal) with or without the presence of salts in the solution. Enzymatic catalyst process was dependent on the type of dye and compounds in the solution, reaching up to 99% of dye
removal. Finally, coagulation/flocculation process was the less efficient obtaining up to 94% dye removal.

Therefore, due to its high efficiency, membrane process has been largely investigated. Specially NF membranes are the most used in the treatment of dyeing effluents [41]. NF presents desirable molecular weight cut off, pore size distribution and surface charge for rejection of most dyes. Therefore, several studies have been done on the fabrication of NF membranes including phase inversion, dip-coating, graft polymerization, and interfacial polymerization [41]. For instance, Shao et al. [41] explored the creation of a hollow fiber NF membrane with Interfacial polymerization process and a combination of m-phenylenediamine and piperazine (PIP) reacted with 1,3,5-benzenetriacarboxylic acid chloride. The novel membrane removed up to 90% two water-soluble dyes (Safranin O and Aniline blue).

2.2.3.- Sorption

In this treatment technique, the removal of the dye molecule is performed by the attachment of the adsorbate on the surface of the adsorbent material [43]. This attachment takes places by physical or chemical forces between the surface and the molecule or ion. When physical forces such as Van der Waals forces, electrostatic attraction, and solvent ordering and hydrophobic force, are present the process is called Physisorption. Thus, when chemical bonds or electron transfer is present, the sorption phenomenon is called chemisorption [43]. Since sorption is a surface phenomenon, it will highly depend on the specific surface area or available sites for the dye molecule to access the surface of the adsorbent material [2]. Commercial activated carbon is the most popular material to be used as adsorbent in the sorption process, and several studies have been conducted using this material [2, 44-47]. However, the application of commercial activated carbon for the removal of dyes is known to be very expensive hence
studies have been performed to find agricultural, industrial or municipal waste materials for the creation of activated carbon [4, 46, 48-55] or the use of untreated materials as adsorbents [56-59].

**Physisorption**

This is known to be a reversible and not site specific reaction. For instance, El Qada et al. [45] studied the adsorption mechanism of three basic dyes including methylene blue (MB), Basic red 22 (BR22), and Basic Yellow 21 (BY21) onto various activated carbons (PAC1, PAC2, and F400). Methylene blue is a cationic dye which Physisorption force is highly present at high solution pH (alkalinity solutions). At high pH, the surface of the activated carbon acquire a negative charge (pH>pH_{PZC}), which facilitates the electrostatic attraction of electropositive molecules such as MB, BR22, and BY21. On the other hand, specific surface area and pore size distribution are important for adsorption; high specific surface area means more available sites for attachment and depending on the molecule size, better access will have to pores with similar size.

Vijayaraghavan et al. [47] studied the removal efficiency of four Remazol dyes in the textile industry by two commercial activated carbons such as SPS-200 (Sawdust-based) and SPC-100 (coal based). It was observed that even though the regeneration of the carbons after single-solute adsorption was low, the adsorption kinetics of the dye effluent was well correlated with pseudo-first-order kinetics. The authors indicated that more thermodynamic experiments may be necessary to define the mechanism of adsorption. However, the most important finding in this study is that adsorption efficiency was not affected for the auxiliary chemicals, obtaining 100% decolorization of the Remazol effluent by SPS-200, which contains bigger pores (1.6-3.0nm).
Berrios et al. [48] conducted batch experiments to understand the adsorption mechanism of MB onto, an abundant and cheap agriculture waste material in Mediterranean countries, olive stones. Physical adsorption was identified as the main mechanism in the process because the adsorption capacity decreased with increase of temperature and at the same time no significant change in adsorption capacity was noticed for studies run at temperatures in the range of 25-40 °C. In addition, Firs-order kinetics reaction with multilayer of adsorption on the surface implies the Physisorption mechanism. The low adsorption capacity toward MB is due to the high microporosity of the activated carbon from olive stones, when MB molecule is better adsorbed in the mesopore system of the adsorbent.

More recently, Auta and Hameed [60] studied the adsorption mechanism of MB onto acid modified local clay (MHC) and non-modified local clay (RHC). Effective adsorption of the MB molecule was effective at high hydroxide ion concentrations due to electrostatic forces being the mechanism of adsorption. They confirmed, once again, that at higher solution pH, the surface of the adsorbent becomes more negative, attracting the positive charge molecule of MB. In addition, acid treatment of the dried local clay increased the specific surface area, and pore volume, creating a material with higher adsorption capacity toward MB.

**Chemisorption**

This sorption process is known to be irreversible and occurring in one single layer on the surface of the adsorbent. Noroozi et al. [58] studied the adsorption mechanism of Basic Blue 41 by silkworm pupa (SWP), a natural waste from the silk spinning industry. As a result, SWP is a natural adsorbent which contains low porosity and a heterogeneous surface. The main sorption mechanism is identified as chemisorption, where the –NH₃⁺ groups in the dye structure and the negative charges of amino acids groups in the SWP surface, have a chemical affinity. The chemisorption process was also affected by changes in temperature from 20 to 40 °C. Higher
removal of Basic blue 41 was observed at 40 °C, confirming the endothermic nature of the process.

Additionally, Hameed et al. [56] conducted adsorption isotherm and kinetics experiments for the removal of MB by Spent tea leaves. Spent tea leave is an abundantly available waste which is obtained after the extraction for tea beverage. It was observed that this natural waste removed more than 90% of MB when initial concentration was 390 mg/L, proving high adsorption capacity toward the dye. The high R² value (>0.99) confirm good experimental fit with Langmuir model, which assumes monolayer adsorption of MB onto the surface. In addition, the agreement with the pseudo-second-order kinetics confirmed the presence of chemisorption forces in the process.

As a conclusion of the sorption process, dye molecules are suitable to be completely removed by sorption from the wastewater effluents without formation of other toxic compounds or mineralization. Commercial activated carbon is the adsorbent used nowadays by the textile industry to remove dyes, but a big effort is still growing in order to find cheaper and more available materials. Chemical and physical characteristics of the adsorbent such as chemical surface functional groups, pore size distribution, and specific surface area are the main factors affecting the sorption process. Moreover, due to their positively molecule charged, basic dyes such as methylene blue is widely used in sorption studies for its high attraction toward the negatively charged surface of the adsorbent.

2.2.4.- Biological Treatment

Biological treatment involves the action of microorganism for the transformation and mineralization of biodegradable compounds into harmless end products. It has been explained that dyes are toxic and complex organic compounds resistant to biological degradation. However, there are still emerging technologies, including aerobic (presence of oxygen) and
anaerobic (absence of oxygen), proposing favorable conditions for the growth of specific microorganisms able to biodegrade synthetic dyes [61, 62]. The microorganism with higher resistance to treat dye effluent include fungi (white-rot fungi) and bacteria [61, 63]. The biodegradation of dyes depend on various factors, mainly the type of dye, microorganisms, process conditions, and other components in the system. For instance, in aerobic and anaerobic, the reduction or cleavage of azo (-N=N-) linkage is the first reaction taking place by enzymes, redox mediator or the presence of reductants.

**Aerobic**
Recently, Barakat [62] isolated a marine Lysobacter strain (Lysobacter sp T312D9) from the Mediterranean Sea for the biological degradation of two azo dyes (methyl red and Congo red). The Lysobacter sp T312D9 could degrade 90-100% and 95-100% of methyl red and congo red, respectively, in 30 h. It was also demonstrated that the enzymes identified as NADH-DCIP reductase and tyrosinase played a major role in the mineralization of the tested dyes.

Zuraida et al. [63] studied the effect of mixing, pH and temperature on the growth of Lactobaciilllus delbruckii ATCC 12315 and its performance in degrading dyes from the Batik industry effluent. Once again, it was demonstrated that bacteria growth depends on pH, mixing speed and temperature. However, the degradation of color did not depend on bacteria growth. The optimum biodegradation conditions, removing 52% of color, were obtained in acidic medium (pH of 6), temperature of 37 °C and zero (0) mixing speed.

Moreover, Moreira-Neto et al. [64] observed the degradation of an anthraquinonic and azoic dyes by 12 fungal strains (Brazilian basidiomycetes) in a salt-alkaline medium (pH of 8.1 and 9.1). In this study two treatment conditions were evaluated with the 12 strains; one in vivo and other in vitro. The in vivo treatment resulted in higher removal percentage (66-77%) than that of in vitro (52-74%) at a pH of 8.1. Decolorization was highly achieved by Trametes villosa
CCIBT2628, obtaining a mean±standard deviation of 78±5 for in vivo and 65±3 for in vitro treatment. The removal efficiency was then tested in a more alkaline medium with pH of 9.1, where higher decolorization (around 60%) was obtained in vitro treatment with Peniophora cinerea CCIBT2541, Pleurotus ostreatus CCIBT2347, and Trametes villosa CCIBT2513. In addition, Laccase was the enzyme with higher activity and significant induction than that of lignin peroxidases, manganese-dependent peroxidases, VAO for the degradation process. Tan et al. [65] found a novel yeast strain TL-F1, isolated from the sea mud, identified as Candida tropicalis for the degradation of various azo dyes. The strain TL-F1 obtained a maximum removal efficiency of 97.2, 95.4, 94.2, 92.7, 91.1, 90.7, 82.6, and 60.5% for Acid Brilliant Scarlet GR, Reactive Brilliant Red K-2G, Reactive Yellow 3RS, Acid Orange II, Acid Orange G, Acid Red B, Reactive Green KE-4BD, and Reactive Brilliant Red X-3B respectively, at initial dye concentration of 20 mg/L. Due to the colorless appearance of the residue, and end products, it was demonstrated that biodegradation was the main mechanism in decoloration. The process had intermediates for the biodegradation of Acid Brilliant Scarlet GR including 1-aminonaphthylene-2-hydroxyl-3,6-disulfonic acid (I), aniline (II), and 3,7-dihydroxy-octahydro-naphthalene-2,6-dione (IV). The phytotoxicity test revealed that the formed intermediates after complete degradation were compound with high biodegradability and low toxicity.

**Anaerobic**

Anaerobic degradation of dyes have been widely studied [61]. For instance, Khan et al. [66] presents an updated list of anaerobic microorganisms that have degraded azo dyes satisfactorily. However, a big effort is still on its way to overcome the drawback of slow degradation rate in anaerobic systems. Baeta et al. [67] studied the use of yeast extract as carbon source and redox mediator for the anaerobic degradation of an azo dye (Drimaren blue HFRL). The author prepared six different conditions in an Upflow Anaerobic Sludge Blanket (UASB). The two conditions that resulted on high dye and COD removal were as following; the...
operational phase No. 4 which presented 350 mg/L of glucose and 100 mg/L of yeast extract, and the operational phase No. 6 which had 500 mg/L of yeast extract and did not presented glucose. The Operational phase No. 4 presented the higher dye removal of 93% but low COD removal (~35%). Moreover, the phase No. 6 presented similar dye removal (91%) than that of phase No. 4, but higher COD removal (55%), and the highest rate of degradation. Base on the obtained results the author concludes that yeast extract could be used in waste water treatment plant for its role as redox mediator (riboflavin) and carbon source.

Additionally, Toro et al. [68] confirmed that polyacrylonitrile-based activated carbon fiber (ACF) is an excellent redox mediator in anaerobic biodegradation for increasing the rate of decolorization and removal efficiency of an azo dye (methyle red). Moreover, chemical oxidation of ACF with HNO₃ increased the concentration of oxygenated functional groups (carbonyl, carboxyl and lactonic groups), which increased the capacity of active sites, removing more than 98% of methyl red and increasing the biodegradation rate up to 8 time compared with samples without ACF. The role of ACF in this process was to act as a channel for electrons transportation and as supporting medium for biofilm growth.

More recently, Pereira et al. [69] presented two novel carbon materials as redox mediator. The authors conducted experiments on the anaerobic biodegradation of three azo dyes (Mordant yellow 10, Reactive red 120, and Acid orange 10), one real effluent of a textile industry, and a model effluent without salts nor additives with three carbon materials including Carbon Xerogels (CX), Carbon nanotubes (CNT), and microporous thermal treated activated carbon (AC₉₂) as redox mediators. As a general result, the carbon material with higher larger pores (carbon nanotubes) was the most efficient redox mediator increasing the decolorization rate and removal percentage of the three azo dyes and colour effluents. This study demonstrated that pore size distribution of the redox mediator is an important factor for the easy access of the dye molecule to the surface of the material and available sites for biomass growth. Finally, it is once
again confirmed that the type of dye and initial concentration define the rate and percentage of removal. Azo dyes are the most common dyes used for anaerobic process because the azo bond acts as electron acceptor and its reduction induce the formation of aromatic amines such as sulfanilic acid (SA), and 5-aminosalisiloic acid (5-ASA). It is also found that dyes with low molecular weights, and one-azo bond in the molecule structure, present higher reduction rates.
Table 2.1. Common dyes used in the textile industry [5]

<table>
<thead>
<tr>
<th>Dye class</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid</td>
<td>Water-soluble anionic compounds</td>
</tr>
<tr>
<td>Basic</td>
<td>Water-soluble, applied in weakly acidic dyebaths; very bright dyes</td>
</tr>
<tr>
<td>Direct</td>
<td>Water-soluble, anionic compounds; can be applied directly to cellulosics</td>
</tr>
<tr>
<td></td>
<td>without mordants (or metals like chromium and copper)</td>
</tr>
<tr>
<td>Disperse</td>
<td>Not water-soluble</td>
</tr>
<tr>
<td>Reactive</td>
<td>Water-soluble, anionic compounds; largest dye class</td>
</tr>
<tr>
<td>Sulfur</td>
<td>Organic compounds containing sulfur or sodium sulfide</td>
</tr>
<tr>
<td>Vat</td>
<td>Water-insoluble; oldest dyes; more chemically complex</td>
</tr>
</tbody>
</table>
Table 2.2. Treatment technologies for the removal of textile dyes

<table>
<thead>
<tr>
<th>Treatment technology</th>
<th>Published studies</th>
<th>Advantages</th>
<th>Disadvantages</th>
<th>Removal efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fenton reagent</td>
<td>Malachite Green [17] and Methyl violet 6B [18]</td>
<td>Environmentally friendly, cost effective, high removal for a wide types of dyes, faster reaction and degradation time, not need of complicated instruments</td>
<td>Generation of excessive heat, expensive operational cost for contaminants with high initial concentration, high iron sludge</td>
<td>up to 99%</td>
</tr>
<tr>
<td>Ozonation</td>
<td>Rhodamine B [11], Acid red B [12], Acid red 131 [10], Reactive orange 16 [9] and Acid blue 92 [8]</td>
<td>not increase of wastewater volume,</td>
<td>Secondary treatment technique for removal of COD, short half-life, low dye concentration, limited mineralization of the dye</td>
<td>up to 97%</td>
</tr>
<tr>
<td>Photocatalysis</td>
<td>Methylene blue and methyl orange [22, 23, 26]</td>
<td>Mineralization of organic compounds, semiconductors are inexpensive</td>
<td>lower efficiency at high dye initial concentrations</td>
<td>up to 97%</td>
</tr>
<tr>
<td>Ultrasonic Irradiation</td>
<td>Methylene Blue [28], Malachite green [29], and Rhodamine B [31]</td>
<td>minimal sludge, and disposal problems, low cost, safe technique, energy conservation, efficient for high dye initial concentrations</td>
<td>lower efficiency at high dye initial concentrations</td>
<td>up to 97%</td>
</tr>
<tr>
<td>Coagulation/flocculation</td>
<td>Acid black 210 [70] and Acid red 119 [33-35]</td>
<td>Removal of complete dye molecule, simple operation</td>
<td>Large amount of sludge production</td>
<td>up to 97%</td>
</tr>
<tr>
<td>Membranes</td>
<td>Acid red, Reactive black, and Reactive blue [40], Safranin O, and Aniline blue [41], Novacron R, and Bezaktiv S-GLD [42]</td>
<td>Maximum removal for high dye initial concentrations</td>
<td>Membrane fouling and concentration polarization</td>
<td>up to 100%</td>
</tr>
<tr>
<td>-----------</td>
<td>---------------------------------------------------------------------------------------------------------------------------------</td>
<td>-------------------------------------------------</td>
<td>-----------------------------------------------</td>
<td>-------------</td>
</tr>
<tr>
<td>Physisorption</td>
<td>Methylene blue [2, 45, 48], Basic red 22, and basic yellow [45]</td>
<td>Efficient removal for high initial dye concentration, complete removal of dye molecule, efficient regeneration</td>
<td>expensive</td>
<td>up to 99.8%</td>
</tr>
<tr>
<td>Chemisorption</td>
<td>Methylene blue [56], and Basic blue 41 [58]</td>
<td>Efficient removal for high initial dye concentration</td>
<td>Difficult to regenerate, expensive</td>
<td>up to 91%</td>
</tr>
<tr>
<td>Aerobic biodegradation</td>
<td>Methyl red, and Congo red [62], Acid Brilliant Scarlet GR, Acid red B, Acid Orange II, Acid Orange G, Reactive Brilliant Red X-3B, Reactive Brilliant Red K-2G, Reactive Yellow 3RS and Reactive Green KE-4BD [65].</td>
<td>Environmentally friendly and cost effective</td>
<td>low initial dye concentration</td>
<td>up to 100%</td>
</tr>
<tr>
<td>Anaerobic biodegradation</td>
<td>Methyl red [68], Drimaren blue HFRL [67], Mordant yellow 10, and Reactive red 120 [69].</td>
<td>Environmental friendly, cost effective</td>
<td>slow process, formation of toxic end components</td>
<td>up to 98%</td>
</tr>
</tbody>
</table>
2.3.- References


25. Gamage McEvoy, J.; Cui, W.; Zhang, Z., Synthesis and characterization of Ag/AgCl–activated carbon composites for enhanced visible light photocatalysis. *Applied Catalysis B: Environmental* 2014, 144, (0), 702-712.


52. Hameed, B. H., Adsorption of basic dye (methylene blue) onto activated carbon prepared from rattan sawdust. *Dyes and pigments* 2007, 75, (1), 143-149.


3. A comparative study of tailored activated carbon from waste tires against commercial activated carbon (F400) for the removal of methylene blue

Abstract

Adsorption of dyes by Commercial Activated Carbon has shown to be an effective, but very expensive technique. Therefore, in this study, the use of waste tires as a raw material for developing activated carbon was evaluated. Tires of 400 μm nominal size were impregnated with potassium hydroxide in different w/w ratios (0:1, 1:1, 2:1, 3:1, 4:1 and 5:1) and two different conditions were selected in order to obtain the best conditions for the desirable carbon; One is the activation temperature (600, 700 and 800 °C) and the second is contact time (1, 2 and 3 h). The BET specific surface area and pore size distribution for each carbon was determined. The condition that provided the highest surface area and desirable pore size distribution was then used to evaluate batch adsorption and fixed-bed column mechanisms for the removal of methylene blue (Textile dye). Finally, the performance of the obtained activated carbon (ACWT) was compared with commercial activated carbon (F400). ACWT resulted to be an effective adsorbent removing methylene blue (MB) but with lower adsorption capacity than that of F400, suggesting that more ACWT is required to remove an initial concentration of 300mg/L of MB.

3.1 Introduction

The presence of dyes in the textile industry effluents have always been a concern [1, 2]. Dyes are aromatic organic compounds with a complex molecule structure. They are binding with a compound which give colour (chromophore group) and an ionizing group (auxochromes) which provides a bonding affinity toward the fiber [3]. It is estimated that there are more than 100,000 available dyes with different tonnes of dyestuff, and industries such as textile, cotton, wood, leather, etc, use them to give colour to their products [4]. Dyes are classified in the Part 1 of the 3rd edition of the Colour Index as acid, basic, direct, disperse, reactive, sulfur and vat. Among the different types of dyes existing nowadays, MB is the most used in the textile industry [1].
is a cationic (positively charged) dye with Thiazine chemical structure. It is a heterocyclic hydrophobic molecule of weak hydrogen bond acceptor. In water, this ionic aromatic organic compound dissociates like electrolytes into methylene blue cation and chloride ions [2]. It is also called Basic Blue 9, Swiss blue, solvent Blue 8 and Methylthioninium chloride. Chemical characteristics of Methylene Blue can be seen in Table 3.1. Methylene blue is classified as a toxic chemical in the Material Safety Data Sheet. A scheme of the synthetic route of methylene blue molecule is presented in Fig. 3.1. The creation of this dye is by the treatment of \( N,N \)-dimenthylbenzene-1,4-diamine with sodium thiosulfate, then the resulted compound is oxidized with \( N,N \)-dimethylaniline, which later will spontaneously cyclizes to methylene blue [5]. As a drug, MB is used in the medicine industry to treat Alzheimer disease [6] and as an antidote for cyanide poisoning. However, the presence of MB in the effluents of these industries causes aesthetic, toxicological and environmental effects. Some of the toxicological consequences are; eye burn and permanent injury to the eyes of humans and animals. It can cause rise to short periods of rapid or difficult breathing and if it is consumed, it produces nausea, vomiting, burning sensations, mental confusion and methemoglobinemia [1, 4]. At very low concentrations, MB catches the attention of the public causing aesthetics concerns of water quality. As an environmental problem in water resources, Dyes such as MB adsorb and reflect sunlight which spoil the growth of bacteria that biologically eliminate contaminants in the water [3]. Furthermore, MB may experiment chemical and biological changes in wastewater, consuming dissolved oxygen and extinguish aquatic life.

Even though color is not being considered as a pollutant that must be eliminated before discharge, it is classified as a National Secondary Drinking Water Contaminant by the Environmental Protection Agency (EPA). A big effort is being made to limit the organic material in the effluents of textile industries [7]. Furthermore, drinking water treatment plants must remove color from water before releasing it to the distribution system. Removal of some organic
pollutants such as dyes by commercial activated carbons has shown to be the technique of preference. However, due to the high cost of activated carbon precursors, production process and regeneration efficiency, commercial activated carbon treatment is very expensive [8]. Therefore, various studies have been done in order to present other raw materials and methods for the creation of activated carbons (ACs) with high adsorption capacity and high regeneration efficiency.

Waste materials (from municipal, agriculture and industrial activity) are attractive precursors for the creation of ACs from the point of view of helping solid waste management issues. ACs for the removal of methylene blue has been created from bamboo dust, coconut shell, groundnut shell, rice husk and straw, waste tires, polyvinylchloride (PVC), polyethyleneterephthalate (PET), and others [4].

In November of 2003, [9] EPA reported an estimation of 57 million scrap tires stockpiles in the United States. The same durable characteristics that make tires desirable for marketing in the automobile industry make them undesirable for disposal. Its, immunization to biological degradation, fire hazards, and carrying pets, cause problems when tires are stockpiled or landfilled. Therefore, recycling and beneficial use have been growing since 2000 for this material. Some of the actual markets are tire derived fuel, civil engineering applications and ground rubber applications/rubberized asphalt. However sometimes the benefits obtained from managing waste tires is upset for expensive technology on meeting pollution legislation. In addition, there are still a high percentage of these wastes that don’t have an end market. Therefore, other technologies have been investigated as a solution for waste tires usage, such as activated carbon. The use of waste tires as activated carbons offers double environmental solutions; another end market and an adsorbent to remove pollutants such as methylene blue from wastewater. Mui et al. [10] reviewed various studies that created activated carbon from
waste tires with chemical activation [11] and physical activation [12]. As a result of these studies, the potential of these products as possible adsorbents for various pollutants has been assessed and found to be very successful, thus stimulating a serious research interest. Some of the contaminants removed by activated carbon from waste tires are basic dyes [13], metals [14], phenols and storage of natural gas [15].

Besides the above mentioned characteristics of MB, other researches have demonstrated that MB molecule (Fig. 3.2) is better adsorbed in the mesopore system of ACs [16, 17]. The International Union of Pure and Applied Chemistry (IUPAC) have recommended a pore size classification in porous materials, which include micropores (< 2nm), mesopores (2-50nm), and macropores (>50nm) [18]. Chemical activation of waste tires has produced materials with higher mesopore percentage than micropores [11]. Therefore, an activated carbon from waste tires with pore volumes mostly distributed in the mesopore system for the removal of MB is presented. This study also compares the batch adsorption capacity, kinetics parameters and column studies of the adsorbent created to a commercial activated carbon (F400).

3.2 Materials and Methods

3.2.1 Preparation of Activated Carbon from Waste Tires (ACWT)

Shredded waste tires (obtained from Break Rubber Technologies, LLC) of nominal size 400 µm and without steel wires were washed with de-ionized water (DI), dried over night at 110 °C and then stored in a desiccator until use. The tires were impregnated at 85 °C with a solution, containing 25 mL of water and KOH concentration to adjust KOH/tires ratios of 0:1, 1:1, 2:1, 3:1, 4:1 and 5:1, for 3 h. After impregnation, tires were filtered and dried overnight at 110 °C in the absence of oxygen under N₂ continue flow rate in a horizontal quartz reactor (Thermolyne tube
furnace model 79400). After 24 h the sample was pyrolyzed at different temperatures (600, 700 and 800 °C) and time (1, 2 and 3 h.) in a continuous nitrogen flow rate (150 mL/min). After activation, each carbon is cleaned with hydrochloric acid (5 M) to remove the excess KOH and then with DI water to remove the acid, until the effluent pH is the same of DI water. Finally, each activated carbon from waste tires (ACWT) was dried in the oven for 24 h, grounded and sieved so all the carbons have the same nominal size of 212 µm. The nomenclature of each carbon was assigned as activated carbon from waste tires (ACWT), heating temperature in centigrade (°C) and time in hours (h) [19]. For example, an activated carbon from waste tires prepared with a KOH/tires ratio of 2, at 800 °C for 1 h would be written as ACWT-2-800-1. After physical analysis of each activated carbon from waste tires, the sample with desirable surface characteristics will be selected as the adsorbent for further experiments and named experimental activated carbon from waste tires (ACWT).

A Commercial Activated Carbon, Filtrasorb 400 (F400) from Calgon, Pittsburgh, PA, and a developed carbon created in a previous study (AC-A) were used to compare adsorption capacity with the experimental carbon. The AC-A was prepared by Yan and Sorial [19] with chemical activation of bituminous coal. Chemical activation of AC-A was performed with a KOH/coal ratio of 2/1, temperature of 650 °C for 2 h under 200 mL/min of continue N₂ flow. F400 and AC-A were cleaned with DI water to remove impurities, dried in oven for 24 h and sieved it to the same nominal size than the activated carbon from waste tires. The surface characteristics of F400 and AC-A can be seen in Table 3.2.

3.2.2 Physical analysis of the activated carbons from waste tires

Physical characteristics (surface area and pore size distribution) of the carbons were obtained by gas adsorption of nitrogen with a micromeritics apparatus (TRI3000) at 77 K [19]. Before
analysis, the carbons were degassed at 423 K for 2 h. The BET equation was used to calculate the surface area of the samples and other two well-known methods were used to calculate the pore size distribution; the t-plot method for micropores (<20 Å) and the BJH method for meso-macro pore size distribution. The total pore volume was calculated from the total amount of N\textsubscript{2} adsorbed at pressures near unity (p/p\textsubscript{0}=0.99). The micromeritics instrument calculates the micropore volume and the meso-macro pore volume was calculated by subtracting the micropore volume from the total volume.

3.2.3 Chemical analysis of the ACWT and F400

3.2.3.1 pH of point of zero charge (pH\textsubscript{PZC})

pH\textsubscript{PZC} of ACWT and F400 was determined with the batch equilibrium method [19]. 100 mg of carbon was introduced in several 25 mL vials with solutions of different initial pH (2, 4, 6, 8, 9, 11 and 12). The initial pH was adjusted with solutions of 0.5 N HCl or NaOH. Two blanks were also created for control. Then the vials were sealed with parafilm and placed in a rotary tumbler for 48 hours at room temperature. After 2 days, the samples were filtered and final pH was measure. The pH\textsubscript{PZC} was calculated as the pH of the solution that did not change after contact with the activate carbons.

3.2.3.2 Total acidity and basicity

NaOH and HCl uptakes methods were performed in order to calculate the concentration of total acidic and basicity groups on the surface of the activated carbons (ACWT and F400). 500 mg of each carbon was contacted with 100 mL of 0.05 N NaOH or 0.05 N HCl solutions in various 125 mL bottles. The sealed bottles were placed in a tumbler at room temperature for 48 h. Two bottles without carbon were also used as blanks. At the end of the two hours, forty milliliter of
the solution was titrated with 0.05 N NaOH or 0.05 N HCl solutions. The total acidity and basicity was calculated as the amount of acid or base required to titrate the blank and samples to the same pH.

3.2.4 Adsorption Isotherms

Adsorption is the attachment of the molecule contaminant (adsorbate) on the surface of a solid (adsorbent). Usually this process depends on the temperature (T), pressure (P), and potential (E). However, when the experiment is conducted at constant temperature is called adsorption isotherm. Therefore, adsorption isotherms were performed to determine the adsorption capacity of the activated carbons toward MB. MB was selected for its wide usage in the textile industry and its molecule preference to be adsorbed on the mesopore system of the ACs. A bottle point method was used for the experiments. Initial masses of the carbons were calculated with the mass balance equation (1) and Langmuir parameters presented in other studies for Activated carbon from waste tires [20] and F400 [21]. Masses (±0.1 mg) of ACWT and F400 were contacted with three different solution concentrations of MB (150, 300 and 600 mg/L) in 250 mL glass-amber bottles. Two blanks per concentration were also prepared as controls. The bottles were sealed with parafilm and placed in a rotary tumbler for 14 days at 23 ± 1 °C [19]. After reached equilibrium, the solutions were filtered using 0.45 µm nylon filters (Micron Separation, Inc.) Filtered samples were diluted and analyzed in a UV-vis spectrophotometer (UV Mini 1240, Shimadzu, Japan) at a wavelength of 663 nm.

\[
q_e = \frac{\text{mass adsorbate (mg)}}{\text{mass adsorbent (g)}} = \frac{(C_0-C_e)V}{m} 
\]  

(1)

Where:

\( q_e \) is mass of adsorbate (mg) per mass of adsorbent (g) at specific time

\( C_0 \) is initial methylene blue concentration (mg/L)
C₀ is final concentration at any time usually within 10% and 90% increments (mg/L)

V is volume of solution (Liters)

m is mass of dried activated carbon (g)

### 3.2.5 Kinetic studies

Adsorption kinetics considers the solute sorption rate of the reaction, which control the residence time of methylene blue uptake by the adsorbent. This experiment was conducted in a similar way as the adsorption isotherm experiments but same carbon mass (the carbon masses will depend on adsorption isotherm results) was contacted with 300 mg/L initial concentration of MB solution, 6 bottles without adsorbent were also used as a blanks. The bottles were placed in a tumbler for 14 days. A set of 2 replicates bottles were drawn during planned time, filtered with a 0.45 µm Nylon membrane and their concentrations were analyzed with a UV-vis spectrometer [22]. The results of the dynamic adsorption will be described by Pseudo-first-order and Pseudo-second-order reaction models, and intra-particle diffusion studies.

### 3.2.6 Column studies

Micro-column experiments were performed in order to obtain the activated carbon usage rate (ACUR) removing MB from water under continuous flow conditions. The study was conducted following the approach by Yan el al. [23] to determine the volume of MB solution that can be treated by ACWT and F400 before the effluent out of the column reach 5% of the initial concentration (breakthrough point) of MB. The experiment of the mini-column consists of a SUPELCO HPLC 5 cm Guard Column. The ACWT or F400 masses was packed in a stainless steel tubing of 5 cm*4.6 mm ID and sealed by two end fittings and frits. A MB solution of 300 mg/L initial concentration was pumped at a continuous flow rate of 0.12 mL/min through the mini-column until the effluent concentration reached the influent concentration. The mini-column
approach was selected because it required less activated carbon and MB solution than the pilot-scale GAC column. The effluent concentration of MB was periodically analyzed by a UV-vis spectrophotometer (UV Mini 1240, Shimadzu, Japan) at a wavelength of 663 nm.

3.3 Results and discussion

3.3.1 Tailoring of Activated Carbon from Waste tires

The creation of carbons from waste tires, as the raw material, can be obtained by two main processes; physical and chemical activation. Physical activation involves two steps process; carbonization of the tires (600-900 °C) followed by activation at high temperatures (600-1200 °C) under oxidizing agents such as carbon dioxide or steam [24]. Chemical activation consists of one step process at lower temperatures (450-900 °C), where carbonization and activation of the tires are performed in a single process with a chemical compound as the oxidizing agent [24]. For the creation of activated carbon from waste tires, chemical activation was chosen due to successful results in previous studies obtaining highly mesoporous adsorbents with similar process [11].

As a preliminary experiment, and in order to confirm the desirable activated carbon for the removal of MB molecule, adsorption isotherm was performed with F400 and AC-A (Fig 3.3). It is clearly that F400 has higher adsorption capacity than AC-A. It is worth noting that BET specific surface area of AC-A is higher than that of F400 and the mesopore percentage of F400 is higher than that of AC-A (See Table 3.2 and Fig. 3.4). Therefore, the results coincide with previous studies [13, 17, 25, 26] where the higher adsorption capacity obtained by F400 is mainly due to its superior mesoporosity.

3.3.1.1 Effect of KOH/tire ratio
Previous publications have demonstrated that the activating agent in developing activated carbons is an important factor [11, 19, 27]. For chemical activation, KOH has shown better performance than other compounds (ZnCl₂ and H₃PO₄) for developing a porous structure in activated carbons obtained from waste tires [11]. In our study, various activated carbons from waste tires were created with KOH/tire ratios ranging from 0/1 to 5/1 and keeping other parameters constants such as temperature (700 °C), time (1 h) and N₂ flow rate (150 mL/min) during the activation process.

The International Union of Pure and Applied Chemistry (IUPAC) have proposed six different types of sorption isotherms [28]. This classification has helped the author to identify the type of adsorbent obtained for the chemical activation of waste tires. The N₂ adsorption isotherm of the samples impregnated at different KOH/ratios exhibit type II isotherms (see Fig. 3.5). This behavior is typical of nonporous or highly meso-macro pores materials, where nitrogen gas is continuously adsorbed while increasing the relative pressure [28]. Fig. 3.5 indicates that until the first inflection point, monolayer coverage is finished and multilayer adsorption starts to take place. Similar figures have been obtained from other studies [11, 29], which confirms the creation of activated carbons with large pore sizes. Fig. 3.5 also confirms that the adsorption capacity at relatives pressures near unity increases with the amount of chemical (KOH) used, until a ratio of 2:1 and then decreases with higher ratios.

Furthermore, it is known that Pore size distribution (PSD) is an important value for the removal of MB [16]. This characteristic was calculated from the nitrogen adsorption isotherm. Table 3.3 and Fig. 3.6 indicate the surface characteristics and PSD of the samples. The BET specific surface area increased more than 100% after impregnation of waste tires with KOH, which indicates the influence of chemical treatment on the waste tires before activation [29]. In addition, Table 3.3 presents that with KOH/ratios higher than 2:1, the development of activated
carbons with high mesopore percentage is similar. It is also remarkable that an impregnation ratio of 2:1 is lower cost than higher amount of chemical for the preparation process. Therefore a KOH/tires ratio of 2:1 was chosen for future activations.

### 3.3.1.2 Effect of activation temperature

It has been demonstrated that activation temperature plays an important role in the activation process [11, 19, 27]. High temperature generates the thermal decomposition of the heterogeneous components of waste tires (natural rubber, styrene-butadiene rubber copolymer, sulphur, zinc oxide and carbon black) into simpler compounds and valuable products such as activated carbon. Therefore, the waste tires were pyrolyzed at different heat treatment temperature, varied from 600 to 800 °C, while keeping other parameter constant such as KOH/tires ratio (2/1), N₂ flow rate (150 mL/min) and time (1 h).

Fig. 3.7 provides the liquid nitrogen adsorption isotherm of the samples activated at different temperatures. It can be seen that the plots represent type II of the adsorption isotherms proposed by the IUPAC. The second point of inflection and high capacity of adsorption at higher relative pressure indicate the development of mesopores in the material. All the samples behave similar but ACWT-2-800-1 shows higher nitrogen adsorption capacity than the samples activated at lower temperatures. Linares-Solano et al. [27] demonstrated that the activating temperature is a parameter that enhance the adsorption capacity with a widening of the micropores. At higher temperatures, there is an increased carbon burn off and gasification, which creates new micropores while enlarging existing pores [11].

Table 3.4 shows the texture characteristics of the samples. Both the BET specific surface area and pore volume increase at higher activation temperature to reach a maximum of 373 m²/g and
0.594 cm³/g respectively, at 800 °C temperature for 1 h. It was found that the activated carbons from waste tires have lower BET specific surface area than F400, but higher mesopore volume and percentage. Fig. 3.8 exhibits the pore size distribution of the samples, which confirm the creation of a material highly meso-macroporous. In the current study, an activation temperature of 800 °C will be chosen for future experiments.

3.3.1.3 Effect of activation time

The activation time is important allowing the reaction to take place between all the parameters. The heat of activation time was varied from 1 to 3 hours while keeping the other parameters constant such as KOH/tires ratio (2/1), N₂ flow rate (150 mL/min) and temperature (800 °C). Nitrogen adsorption isotherm (Table 3.4 and Fig. 3.9) and pore size distribution (Fig. 3.10) were obtained for each sample.

It can be seen in Fig. 3.9 and Table 3.4 that the N₂ adsorption capacity and BET specific surface area decreased with increase of activation time (from 1 to 3 h). Table 3.4 shows that after 1 h of chemical activation, there is an excess of thermal treatment causing the decrease of specific surface area and pore volume, hence lower adsorption capacity of the carbons. The impact of activating time was also evaluated by keeping constant different temperature (600 and 700 °C). Fig. 3.11 and 3.12 show N₂ adsorption isotherm and pore size distribution, respectively, of samples activated at 700 °C by varying the activation time. Fig. 3.13 and 3.14 show the characteristics of samples activated at 600 °C with varying time. It is observed that the adsorption capacity of the samples decrease at longer times of heat activation. This behavior may be occurring because at longer time of activation, longer will be the time of reaction between other factors affecting the process which could cause widening of the micropores to
meso-macro pores and breakdown of cross-links in carbon matrix of the material, providing lower BET specific surface area [11].

Therefore, analyzing the above results, plots and tables, it can be concluded that the samples ACWT-2-800-1 which was prepared with a KOH/tires ratio of 2/1, at temperature of 800 °C and activation time of 1 h is the desirable adsorbent to be compared to F400 for the removal of MB from aqueous solution. Other samples resulted in lower BET specific surface area and lower mesopore percentage. The chosen sample (ACWT-2-800-1) will be referred as ACWT for the following experiments and analysis.

3.3.2 Adsorption isotherm of MB onto F400 and ACWT

Fig. 3.15 and 3.16 present the comparison of the N₂ adsorption capacity and pore size distribution of ACWT and F400, respectively. Table 3.5 also shows the physical and chemical characteristics of these activated carbons.

The adsorption isotherm of methylene blue onto ACWT was performed under the same conditions as F400 and AC-A. The data shown in Fig. 3.17 demonstrates that the adsorption capacity of F400 for methylene blue is higher as compared to ACWT and AC-A. In order to explain the obtained results, physical and chemical characteristics of the ACs were considered. The initial pH of the MB solution was always kept at 7.1±0.2. Table 3.2 and 3.5 present the pH of point of zero charge (pHₚ₂₅) for AC-A (pHₚ₂₅>pH), F400 (pHₚ₂₅≈pH) and ACWT (pHₚ₂₅<pH), these values indicate that if electrostatic forces were the dominant mechanism attracting MB (positively charged molecule) onto the activated carbons, AC-A and ACWT would provide higher adsorption capacity than F400 (pHₚ₂₅≈pH). A study by Wang et al. [17] demonstrated that higher adsorption capacity for MB by an activated carbon with lower specific surface area.
and total pore volume and pH$_{PZC}$ lower than pH of solution was obtained as compared to other activated carbons with higher surface area and pH$_{PZC}$ higher than pH of solution. It is explained that when the pH of the solution is lower than the pH$_{PZC}$ of the carbon, the surface is positively charged hence electrostatic interaction is not the mechanism causing adsorption. Therefore, the higher adsorption capacity of F400 is not attributed to attraction of the positively charge molecule to its surface. The influence of the pore size distribution has demonstrated to be more important in the adsorption of methylene blue than the surface functional group.

On the other hand, oxygen complexes (total acidity or total basicity) are known for influencing the adsorption capacity of the carbon. Wang et al. [17] treated an activated carbon with acid in order to evaluate the influence of surface functional groups for the removal of MB. The acid treatment did not influence the physical characteristics of the carbon surface but changed the chemical characteristics. pH$_{PZC}$ of the adsorbents decreased while increasing the acidic surface functional groups. The acid treatment also decreased the adsorption of methylene blue onto the carbon, demonstrating that the presence of acidic surface functional group is disadvantageous to methylene blue adsorption. In this study F400 presents lower acidic surface functional groups than the other two activated carbons (Table 3.2 and 3.5) and, therefore, is favorable for a higher adsorption capacity.

Analyzing the physical characteristics of the activated carbons, it can be observed that although the surface area of AC-A is higher than F400, AC-A has lower mesopore percentage which will provide lower adsorption capacity, since MB is adsorbed on the mesopores system of the activated carbon [17]. ACWT, which contains higher mesopore percentage but lower BET specific surface area, also demonstrated lower adsorption capacity toward MB than that of F400; indicating that ACWT has fewer active sites for the adsorption of MB molecule [30]. Previous studies also have demonstrated that pore size and surface coverage determine the
amount adsorbed by activated carbons [12, 30, 31]. Lian et al. [30] studied the mechanism of adsorption of MB onto four activated carbons with comparable surface characteristics. The higher removal of MB was obtained for the activated carbon with pore diameter in the range of the longer size of MB molecule (1.7 nm). It is explained that pore-filling mechanism is taking place between the adsorbate and adsorbent, making adsorption favorable and strong. Furthermore, Mui et al [12] suggested that the average pore sizes of activated carbons should be 1.7 times the adsorbate molecule width. Therefore, it is observed in our results (Table 3.2 and 3.5) that among the three carbons; AC-A (2.4 nm<1.7MB), F400 (2.9 nm≈1.7MB) and ACWT (6.3 nm>1.7MB), F400 has pore openings that enhances adsorption of MB. Moreover, it can be considered that the porosity developed by ACWT is classified as macropores due to an average pore size greater than 50nm [28].

The equilibrium adsorption isotherm is the base for design of scaling-up process. In order to understand the adsorption mechanism of MB onto F400 and ACWT, three well known isotherm model were used: Langmuir [31], Freundlich [32] and Redlich-Peterson [2]. The Langmuir assumes physisorption of gases or liquid solutes on solids when only a monolayer of adsorbate is formed. The adsorbate behaves as an ideal solute. Adsorbate molecules remain at specific adsorption sites and the adsorption sites are uniformly distributed on the adsorbent surface. The energy of interaction of each adsorption site is similar and there are no interactions between adsorbed molecules [33].

The Langmuir model is expressed by the following equation [32]:

\[ q_e = Q^0 \frac{bce}{1 + bce} \]  

(2)

Where:

- \( q_e \) is the number of mass of adsorbate adsorbed per unit mass of adsorbent (mg/g)
- $Q^o$ is the number of mass of adsorbate adsorbed per unit mass of adsorbent at complete monolayer (mg/g)
- $b$ is the Langmuir constant heat of adsorption (L/mg)
- $C_e$ is adsorbate concentration at equilibrium (mg/L)

The linearized form of Langmuir equation is:

$$\frac{C_e}{q_e} = \frac{1}{b \cdot Q^o} + \frac{1}{Q^o} C_e$$  \hspace{1cm} (3)

Where:
- $\frac{C_e}{q_e}$ is $y$-axis
- $C_e$ is $x$-axis
- $\frac{1}{Q^o}$ is the slope
- $\frac{1}{b \cdot Q^o}$ is the intercept

Adsorption isotherms well described by Langmuir model can be classified as “favorable” or “unfavorable” by a factor “$R_L$”:

$$R_L = \frac{1}{1 + b \cdot C_o}$$  \hspace{1cm} (4)

Where:
- $C_o$ is the highest initial concentration (mg/L)
- $R_L$ is a dimensionless separation factor, depending of the value for $R_L$ the adsorption is favorable ($0 < R_L < 1$), unfavorable ($R_L > 1$), linear ($R_L = 1$) or irreversible ($R_L = 0$).

The Langmuir model plot and model parameters are presented in Fig. 3.18 and Table 3.6, respectively. The high $R^2$ (>0.98) values demonstrate that Langmuir model fits reasonable well the data. Langmuir equation demonstrates the adsorption on the monolayer of the ACs [22]. In the current study, monolayer adsorption capacity of ACWT toward MB was higher than other reported studies [16, 20, 26, 30, 34]. For instance, Lian et al. [30] obtained about 140.36 mg/g
monolayer adsorption capacity of MB for an activated carbon prepared from the carbonization of waste tires and activated with KOH at 850 °C, and Lin et al. [26] obtained a value of 147 mg/g for activated carbons from waste tires with steam activation.

Another commonly used isotherm model is the Freundlich equation. This model describes the adsorption on a heterogeneous surface with sites of different energy and not equally available for adsorption. The Freundlich equation can be written [32]:

\[ q_e = K_F C_e^{1/n} \]  \hspace{1cm} (5)

And the Linearized equation is:

\[ \ln(q_e) = \frac{1}{n} \ln(C_e) + \ln(K_F) \]  \hspace{1cm} (6)

Where:

- \( q_e \) is the number of mass of adsorbate adsorbed per unit mass of adsorbent (mg/g)
- \( K_F \) is the Freundlich constant and adsorption capacity (mg/g)(dm³/mg)\(^n\)
- \( n \) is the Freundlich constant
- \( C_e \) is the adsorbate concentration at equilibrium (mg/L)

The Freundlich model plot and constants are presented in Fig. 3.19 and Table 3.6 respectively. The slope \( \left( \frac{1}{n} \right) \) indicates the adsorption intensity or surface heterogeneity; a value closer to zero represents sites more heterogeneous (For ACWT; \( \frac{1}{n} = 0.059 \) and for F400; \( \frac{1}{n} = 0.023 \)). The value of \( n \), greater than unity, agrees with the values of the Langmuir dimensionless separation factor (0 < \( R_L < 1 \)), which indicates that the adsorption of MB onto ACWT and F400 is favorable. However, the low correlation coefficient for ACWT (R\(^2\)=0.6058) and F400 (R\(^2\)=0.493) demonstrate poor agreement of the Freundlich model. These results confirm that the adsorption of MB onto the ACs (ACWT and F400) is better fitted by Langmuir isotherm model.
The Redlich-Peterson isotherm model considers features of the Langmuir and Freundlich models, and describe the adsorption process for various concentrations [2, 29]. The three constants; \( K_r, a_r \) and \( \beta \) can be estimated from the following linearized equation:

\[
\log\left(\frac{K_r c_e}{q_e} - 1\right) = \beta \log c_e + \log a_r
\]  

(7)

Where:

- \( K_r = K_L \) is the modified Langmuir constant (L/g)
- \( c_e \) is the adsorbate concentration at equilibrium (mg/L)
- \( q_e \) is the number of mass of adsorbate adsorbed per unit mass of adsorbent (mg/g)
- \( \beta \) and \( a_r \) are the Redlich-Peterson constants

The Redlich-Peterson model plot and constants are presented in Fig. 3.20 and Table 3.6, respectively. The near values of \( \beta \) to 1 for ACWT (\( \beta = 1.097 \)) and F400 (\( \beta = 1.061 \)), indicates that the equation represents the ideal Langmuir conditions [29], which once again confirm the application of Langmuir model. The high values of the correlation coefficient for ACWT (\( R^2 = 0.988 \)) and F400 (\( R^2 = 0.994 \)) suggest good fit of the experimental data to this isotherm model.

### 3.3.3 Kinetics of MB adsorption onto F400 and ACWT

Fig. 3.21 and 3.22 exhibit the adsorption kinetic data of the MB onto ACWT and F400. It can be observed that ACWT reached equilibrium very fast, while F400 didn’t. This behavior indicates that the bigger pores of ACWT made easier the transport of the MB molecule to the adsorption sites. F400 presents a wider pore size distribution, where micropores will slow down the process and increase the internal mass transport resistance.
3.3.3.1 Pseudo-first-order reaction model

The process of MB uptake onto the activated carbons may be observed as First-order reversible or Pseudo-first-order models [22, 33, 35, 36]. First-order kinetic reactions would occur if the adsorption of MB to the surface of the ACs is proportional to the concentration of MB in the liquid phase, and the following equation (described elsewhere [36] was used to correlate the reactions):

\[ \ln(1 - U(t)) = -k_1 t \]  

\[ U(t) = \frac{C_{A_0} - C_A}{C_{A_0} - C_{A_e}} \]  

Where:

- \( U(t) \) is the fractional attainment of equilibrium
- \( C_{A_0} \) is the initial concentration of MB in solution
- \( C_A \) is the concentration of MB in solution at any time
- \( C_{A_e} \) is the equilibrium concentration for MB in the solution
- \( k_1 \) is the overall first-order constant

Fig. 3.23 shows the First-order reversible reaction model for the removal of MB by ACWT and F400. It can be observed that this model doesn’t describe a straight line hence it is not a strong evidence to support first-order reactions [33]. Furthermore, the low values of the correlation coefficients for ACWT (\( R^2=0.83 \)) and F400 (\( R^2=0.8174 \)), confirms the hypothesis. Hamadi et al. [36] obtained similar results for the removal of chromium (VI) by activated carbon from used tires.

The reaction can also be represented by a pseudo-first-order with the following equation [36]:

\[ \frac{dq}{dt} = k'_1 (q_e - q) \]
The integration of the pseudo-first-order equation with the boundary conditions of time \((t_0=0\) and \(t=t_e)\) and adsorption capacity \((q_0=0\) and \(q=q_e)\) was developed by Lagergren [36]:

\[
\log(q_e - q_t) = \log q_e - (k'_1/2.303)t
\]  
(11)

Where:

- \(q_t\) is the capacity of adsorption at certain time
- \(t\) is time
- \(q_e\) is the equilibrium adsorption capacity
- \(K'_1\) is the Pseudo-first-order adsorption constant \((\text{min}^{-1})\)

Fig. 3.24 shows the Mathematical expression proposed by Lagergren for the removal of MB by ACWT and F400. In agreement with that of First-order reversible reactions, Lagergren model is not a good description of the kinetics. The kinetic constant and correlation coefficients can be observed in Table 3.7 for both ACs.

### 3.3.3.2 Pseudo–Second-order reaction model

Due to the failure of first-order reactions, MB adsorption onto ACWT and F400 was further treated using a pseudo-second-order model [32]:

\[
\frac{dq_t}{dt} = k'_2(q_e - q_t)^2
\]  
(12)

Hamadi et al. [36] also explains the derivation of the linearized equation that describes this type of reactions [36]:

\[
\frac{t}{q_t} = \frac{1}{k'_2q_e^2} + \frac{t}{q_e}
\]  
(13)

\[
h = k'_2q_e^2
\]  
(14)

Where:

- \(k'_2\) is the rate constant of pseudo-second-order reaction model \((\text{g/min mg})\)
- \(h\) is the initial adsorption rate \((\text{mg/g min})\)
By plotting $\frac{t}{q_t}$ against $t$ (Fig. 3.25), the figure behaves as a straight line for both ACs. In addition, Eq. 13 was used to calculate the Pseudo-second-order constant and correlation coefficients. It can be seen in Table 3.7 that this model fits very well the experimental data ($R^2>0.99$). It has been suggested for other studies [37] that a well correlation of Pseudo-second-order model means chemisorption as the controlling mechanism in the adsorption process. Similar results have been also published for the adsorption of methylene blue by non-conventional low-cost adsorbents [37, 38] and activated carbons prepared from other precursors materials [32].

### 3.2.3.3 Intra-particle diffusion

The Pseudo kinetic models do not explain the diffusion mechanism. Therefore, the intra-particle diffusion model was used to understand the transport of the MB molecule through the pores of the ACs. This process may occur in three-step involving the transport of the adsorbate from the liquid phase to the outer surface of the AC by a process called external or film diffusion. Then, the molecule of the contaminant transports from the adsorbent surface to the interior pores by internal diffusion. Finally, the last step in this process involves the adsorption of the adsorbate on the active sites on the interior pores [22]. From these three transport steps, if the last one is very fast then it doesn’t affect the overall kinetics. The dynamic adsorption may be influenced by the slowest process, which could be film or internal diffusion, the rate controlling.

The rate for intra-particle diffusion ($q_t$) is presented by the following equation [35]:

$$q_t = k_p t^{0.5} + C$$

(15)

Where:

$q_t$ is the intra-particle diffusion rate

$C$ is the intercept and correspond to the thickness of the boundary layer
$k_p$ is the intra-particle diffusion rate constant (mg min$^{0.5}$/g)

The amount of MB adsorbed at different time may be described by multi-linearity correlations, it is illustrated in Fig. 3.26 where the plot presents more than one step occurring during the adsorption process. The first correlation represents the transport of the molecule of MB to the outer surface of F400 by film diffusion. This phenomenon occurs very fast, in the first two hours of the process, at a rate parameter of 12.94 mg/g min$^{0.5}$. The second correlation describes the transport to the internal sites by intra-particle diffusion until equilibrium is reached. This process is performed at a lower rate of 2.429 mg/g min$^{0.5}$ hence it is the slowest step and rate controlling.

In contrast, the adsorption process for MB onto ACWT shows a one-step correlation (Fig. 3.27) but the intercept does not pass through the origin. Therefore, the adsorption of MB onto ACWT is mainly by intra-particle diffusion where the value of the intercept, $C$, in Table 3.7 is the boundary layer thickness. The values of the correlation coefficients are near unity indicating the acceptance of this model. Kannan et al. [35] obtained similar results for the removal of MB onto several activated carbons.

### 3.3.4 Microcolumn experiment

The results obtained in batch experiments demonstrated that ACWT has affinity towards the removal of MB. Therefore, column test was performed in order to predict the activated carbon usage rate (ACUR) in a scaling-down column bed when the effluent concentration reaches the treatment goal (breakthrough point). The microcolumn was packed with masses of 417.9 and 542.4 mg for ACWT and F400 respectively. A breakthrough curve (Fig. 3.29) was created by normalizing the effluent concentration ($C$) by the initial concentration ($C_0$) at increasing time intervals until the effluent concentration reached the influent concentration. It can be observed in
Fig. 3.29 that the curve describes a shape similar to other reported studies [39]. The breakthrough point was assigned to be $5%C_0$ (15 mg/L) and the exhaustion of the bed was set at $95%C_0$ (285 mg/L) [40]. Fig. 3.9 shows that ACWT produced a faster breakthrough than F400. This behavior agrees with the fact that ACWT has lower adsorption capacity for MB and hence its ACUR (activated carbon usage rate, mg carbon/mL of solution) is higher than that of F400. ACUR was 2.524 mg/mL for ACWT and 0.919 mg/mL for F400 (see Table 3.8). In addition, these results confirm the adsorption capacity obtained in batch experiment. The breakthrough adsorption capacity obtained in the column test was 112.94 mg/g for ACWT and 310.22 mg/g for F400 (Table 3.8).

### 3.4 Summary of comparison between ACWT and F400

Chemical activation of waste tires produced an activated carbon with lower surface area and higher meso-macropores percentage than the commercial one. ACWT resulted to be very effective removing MB from water, but with lower adsorption capacity than that of F400 for the batch and column experiments. These results confirm that a mesoporous adsorbent is not the only characteristic defining adsorption of MB onto ACs, specific surface area, pore size distribution, and surface functional groups also play an important role in the process. Finally, due to the lower capacity of ACWT more amounts of carbon are needed than F400 in order to treat until a specific breakthrough point such as $5%C_0$ of MB.
Fig. 3.1 Methylene blue synthetic route scheme [5]
Fig. 3.2. Methylene blue Molecule
(Advanced Chemistry Development – ACD/ChemSketch 12.0 software)
Fig. 3.3. Adsorption isotherm of methylene blue onto commercial activated carbon (F400) and AC-A
Fig. 3.4. Pore size distribution of commercial activated carbon (F400) and AC-A
Fig. 3.5. Nitrogen adsorption isotherm of activated carbon from waste tires created at different KOH/tires ratio (heat activation temperature: 700 °C, heat activation time: 1 h and nitrogen flow rate: 150 mL/min)
Fig. 3.6. Pore size distribution of Activated carbon from waste tires created at different KOH/tires ratio (heat activation temperature: 700 °C and heat activation time: 1 h)
Fig. 3.7. Nitrogen adsorption isotherm of activated carbon from waste tires created at different heat activation temperature (KOH/tires ratio: 2 and heat activation time: 1 h)
Fig. 3.8. Pore size distribution of Activated carbon from waste tires created at different heat activation temperature (KOH/tires ratio: 2 and heat activation time: 1 h)
Fig. 3.9. Nitrogen adsorption isotherm of activated carbon from waste tires created at different heat activation time (KOH/tires ratio: 2 and heat activation temperature: 800 °C)
Fig. 3.10. Pore size distribution of Activated carbon from waste tires created at different heat activation time (KOH/tires ratio: 2 and heat activation temperature: 800 °C)
Fig. 3.11. Nitrogen adsorption isotherm of activated carbon from waste tires created at different heat activation time (KOH/tires ratio: 2 and heat activation temperature: 700 °C)
Fig. 3.12. Pore size distribution of Activated carbon from waste tires created at different heat activation time (KOH/tires ratio: 2 and heat activation temperature: 700 °C)
Fig. 3.13. Nitrogen adsorption isotherm of activated carbon from waste tires created at different heat activation time (KOH/tires ratio: 2 and heat activation temperature: 600 °C)
Fig. 3.14. Pore size distribution of Activated carbon from waste tires created at different heat activation time (KOH/tires ratio: 2 and heat activation temperature: 600 °C)
Fig. 3.15. Nitrogen adsorption isotherm of selected activated carbon from waste tires (ACWT) and commercial activated carbon from waste tires (F400)
Fig. 3.16. Pore size distribution of selected activated carbon from waste tires (ACWT) and commercial activated carbon from waste tires (F400)
Fig. 3.17. Adsorption isotherm of methylene blue onto commercial activated carbon (F400), previous created activated carbon (AC-A) and selected activated carbon from waste tires (ACWT)
Fig. 3.18. Langmuir adsorption isotherm model for the removal of methylene blue onto commercial activated carbon (F400) and selected activated carbon from waste tires (ACWT)
Fig. 3.19. Freundlich adsorption isotherm model for the removal of methylene blue onto commercial activated carbon (F400) and selected activated carbon from waste tires (ACWT)
Fig. 3.20. Redlich-Peterson adsorption isotherm model for the removal of methylene blue onto commercial activated carbon (F400) and selected activated carbon from waste tires (ACWT)
Fig. 3.21. Time variation of methylene blue adsorption onto commercial activated carbon (F400) and selected activated carbon from waste tires (ACWT)
Fig. 3.22. kinetic graph of methylene blue adsorption onto commercial activated carbon (F400) and selected activated carbon from waste tires (ACWT)
Fig. 3.23. First-order reversible reaction of methylene blue adsorption onto commercial activated carbon (F400) and selected activated carbon from waste tires (ACWT)
Fig. 3.24. Pseudo-first-order reaction of methylene blue adsorption onto commercial activated carbon (F400) and selected activated carbon from waste tires (ACWT)
Fig. 3.25. Pseudo-second-order reaction of methylene blue adsorption onto commercial activated carbon (F400) and selected activated carbon from waste tires (ACWT)
Fig. 3.26. Intra-particle diffusion model of methylene blue adsorption onto commercial activated carbon (F400)
Fig. 3.27. Intra-particle diffusion model of methylene blue adsorption onto selected activated carbon from waste tires (ACWT)
Fig. 3.28. Plot of $Bt$ vs. $t$ for determining the actual rate controlling of the adsorption of methylene blue adsorption onto commercial activated carbon (F400)
Fig. 3.29. Plot of Microcolumn experiment for methylene blue removal by commercial activated carbon (F400) and selected activated carbon from waste tires (ACWT).
Table 3.1. Molecule characteristic of Methylene Blue

<table>
<thead>
<tr>
<th>Name and symbol</th>
<th>Basic Blue (BB9)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular formula</td>
<td>C_{16}H_{18}N_{3}S(Cl)</td>
</tr>
<tr>
<td>Molecule weight</td>
<td>319.85 g/mol</td>
</tr>
<tr>
<td>Molecule dimension</td>
<td>3.25<em>7.6</em>17.0 Å</td>
</tr>
<tr>
<td>pK_a</td>
<td>3.8</td>
</tr>
<tr>
<td>Wavelength</td>
<td>663 nm</td>
</tr>
</tbody>
</table>
Table 3.2. Physical and chemical characteristics of Activated carbons

<table>
<thead>
<tr>
<th>Sample</th>
<th>( S_{\text{BET}} )</th>
<th>( V_{\text{Total}} ) (cm(^3)/g)</th>
<th>( V_{\text{micro}} ) (cm(^3)/g)</th>
<th>( V_{\text{meso+macro}} ) (cm(^3)/g)</th>
<th>( \text{Meso+Macro} ) (%)</th>
<th>( \text{Average pore} ) (nm)</th>
<th>( \text{pH}_{\text{PZC}} )</th>
<th>Total acidity (meq/g)</th>
<th>Total basicity (meq/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F400</td>
<td>835</td>
<td>0.623</td>
<td>0.316</td>
<td>0.307</td>
<td>49.3</td>
<td>2.9</td>
<td>6.8</td>
<td>0.146</td>
<td>0.260</td>
</tr>
<tr>
<td>AC-A</td>
<td>1021</td>
<td>0.607</td>
<td>0.446</td>
<td>0.161</td>
<td>26.42</td>
<td>2.4</td>
<td>4.3</td>
<td>0.540</td>
<td>0.150</td>
</tr>
</tbody>
</table>
Table 3.3. Effects of KOH/tires ratio on the surface characteristics of Activated carbons from waste tires

<table>
<thead>
<tr>
<th>Sample</th>
<th>KOH/tires</th>
<th>Temp. (°C)</th>
<th>time (h)</th>
<th>N₂ (ml/min)</th>
<th>S_{BET} (m²/g)</th>
<th>V_{Total} (cm³/g)</th>
<th>V_{micro} (cm³/g)</th>
<th>V_{meso+macro} (cm³/g)</th>
<th>M_{eso+macro} (%)</th>
<th>Average pore (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACWT-0-700-1</td>
<td>0</td>
<td>700</td>
<td>1</td>
<td>150</td>
<td>82</td>
<td>0.557</td>
<td>0.003</td>
<td>0.554</td>
<td>99.4</td>
<td>27</td>
</tr>
<tr>
<td>ACWT-1-700-1</td>
<td>1</td>
<td>700</td>
<td>1</td>
<td>150</td>
<td>228</td>
<td>0.483</td>
<td>0.070</td>
<td>0.412</td>
<td>85.407</td>
<td>8.5</td>
</tr>
<tr>
<td>ACWT-2-700-1</td>
<td>2</td>
<td>700</td>
<td>1</td>
<td>150</td>
<td>344</td>
<td>0.452</td>
<td>0.051</td>
<td>0.400</td>
<td>88.546</td>
<td>5.3</td>
</tr>
<tr>
<td>ACWT-3-700-1</td>
<td>3</td>
<td>700</td>
<td>1</td>
<td>150</td>
<td>331</td>
<td>0.513</td>
<td>0.059</td>
<td>0.453</td>
<td>88.305</td>
<td>6.2</td>
</tr>
<tr>
<td>ACWT-4-700-1</td>
<td>4</td>
<td>700</td>
<td>1</td>
<td>150</td>
<td>330</td>
<td>0.536</td>
<td>0.059</td>
<td>0.477</td>
<td>88.966</td>
<td>6.4</td>
</tr>
<tr>
<td>ACWT-5-700-1</td>
<td>5</td>
<td>700</td>
<td>1</td>
<td>150</td>
<td>303</td>
<td>0.471</td>
<td>0.062</td>
<td>0.409</td>
<td>86.735</td>
<td>6.2</td>
</tr>
</tbody>
</table>
Table 3.4. Effects of activation time and temperature on the surface characteristics of Activated carbons from waste tires

<table>
<thead>
<tr>
<th>Sample</th>
<th>KOH/tires</th>
<th>Temp. (°C)</th>
<th>time (h)</th>
<th>N₂ (ml/min)</th>
<th>S_BET (m²/g)</th>
<th>V_Total (cm³/g)</th>
<th>V_micro (cm³/g)</th>
<th>V_meso+macro (cm³/g)</th>
<th>Meso+Macro (%)</th>
<th>Average pore (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACWT-2-800-1</td>
<td>2</td>
<td>800</td>
<td>1</td>
<td>150</td>
<td>373</td>
<td>0.594</td>
<td>0.051</td>
<td>0.543</td>
<td>91.5</td>
<td>6.3</td>
</tr>
<tr>
<td>ACWT-2-800-2</td>
<td>2</td>
<td>800</td>
<td>2</td>
<td>150</td>
<td>349</td>
<td>0.539</td>
<td>0.053</td>
<td>0.486</td>
<td>90.2</td>
<td>6.2</td>
</tr>
<tr>
<td>ACWT-2-800-3</td>
<td>2</td>
<td>800</td>
<td>3</td>
<td>150</td>
<td>292</td>
<td>0.475</td>
<td>0.054</td>
<td>0.421</td>
<td>88.6</td>
<td>6.5</td>
</tr>
<tr>
<td>ACWT-2-700-1</td>
<td>2</td>
<td>700</td>
<td>1</td>
<td>150</td>
<td>344</td>
<td>0.452</td>
<td>0.051</td>
<td>0.400</td>
<td>88.5</td>
<td>5.3</td>
</tr>
<tr>
<td>ACWT-2-700-2</td>
<td>2</td>
<td>700</td>
<td>2</td>
<td>150</td>
<td>325</td>
<td>0.474</td>
<td>0.064</td>
<td>0.410</td>
<td>86.6</td>
<td>5.8</td>
</tr>
<tr>
<td>ACWT-2-700-3</td>
<td>2</td>
<td>700</td>
<td>3</td>
<td>150</td>
<td>297</td>
<td>0.478</td>
<td>0.050</td>
<td>0.428</td>
<td>89.6</td>
<td>6.4</td>
</tr>
<tr>
<td>ACWT-2-600-1</td>
<td>2</td>
<td>600</td>
<td>1</td>
<td>150</td>
<td>282</td>
<td>0.446</td>
<td>0.067</td>
<td>0.379</td>
<td>84.9</td>
<td>6.3</td>
</tr>
<tr>
<td>ACWT-2-600-2</td>
<td>2</td>
<td>600</td>
<td>2</td>
<td>150</td>
<td>242</td>
<td>0.415</td>
<td>0.067</td>
<td>0.349</td>
<td>83.9</td>
<td>6.8</td>
</tr>
<tr>
<td>ACWT-2-600-3</td>
<td>2</td>
<td>600</td>
<td>3</td>
<td>150</td>
<td>212</td>
<td>0.436</td>
<td>0.052</td>
<td>0.384</td>
<td>88.1</td>
<td>8.2</td>
</tr>
</tbody>
</table>
Table 3.5. Physical and chemical characteristics of commercial activated carbon (F400) and selected activated carbon from waste tires (ACWT)

<table>
<thead>
<tr>
<th>Sample</th>
<th>$S_{BET}$</th>
<th>$V_{Total}$ (cm$^3$/g)</th>
<th>$V_{micro}$ (cm$^3$/g)</th>
<th>$V_{meso+macro}$ (cm$^3$/g)</th>
<th>Meso+Macro (%)</th>
<th>Average pore (nm)</th>
<th>$pH_{PZC}$</th>
<th>Total acidity (meq/g)</th>
<th>Total basicity (meq/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F400</td>
<td>835</td>
<td>0.623</td>
<td>0.316</td>
<td>0.307</td>
<td>49.3</td>
<td>2.9</td>
<td>6.8</td>
<td>0.146</td>
<td>0.260</td>
</tr>
<tr>
<td>ACWT</td>
<td>373</td>
<td>0.594</td>
<td>0.051</td>
<td>0.543</td>
<td>91.4</td>
<td>6.3</td>
<td>5.3</td>
<td>0.273</td>
<td>0</td>
</tr>
</tbody>
</table>
Table 3.6. Adsorption isotherm constants for methylene blue adsorption onto commercial activated carbon (F400) and selected activated carbon from waste tires (ACWT)

<table>
<thead>
<tr>
<th>ACs</th>
<th>Langmuir model</th>
<th>Freundlich model</th>
<th>Redlich-Peterson model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Q₀ (mg/g)</td>
<td>b (L/mg)</td>
<td>Kₗ (L/g) R²</td>
</tr>
<tr>
<td>ACWT</td>
<td>217.39</td>
<td>0.05</td>
<td>10.99 0.988 0.032</td>
</tr>
<tr>
<td>F400</td>
<td>476.19</td>
<td>1.91</td>
<td>909.09 0.998 8.71E-4</td>
</tr>
</tbody>
</table>
Table 3.7. Kinetics parameters for MB adsorption onto commercial activated carbon (F400) and selected activated carbon from waste tires (ACWT)

<table>
<thead>
<tr>
<th>AC</th>
<th>First-order reversible</th>
<th>Pseudo-first-order</th>
<th>Pseudo-second-order</th>
<th>Intra-particle diffusion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$k_1$ (min$^{-1}$)</td>
<td>$R^2$</td>
<td>$k_1$ (min$^{-1}$)</td>
<td>$R^2$</td>
</tr>
<tr>
<td>F400</td>
<td>0.0002</td>
<td>0.83</td>
<td>0.000207</td>
<td>0.83</td>
</tr>
<tr>
<td>ACWT</td>
<td>0.0002</td>
<td>0.8174</td>
<td>0.000138</td>
<td>0.8861</td>
</tr>
</tbody>
</table>
Table 3.8 Microcolumn experiment for MB removal by ACs

<table>
<thead>
<tr>
<th>Activated carbons (ACs)</th>
<th>ACWT</th>
<th>F400</th>
</tr>
</thead>
<tbody>
<tr>
<td>Microcolumn length (cm)</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Carbon mass (mg)</td>
<td>417.9</td>
<td>542.4</td>
</tr>
<tr>
<td>Flow rate (mL/min)</td>
<td>0.12</td>
<td>0.12</td>
</tr>
<tr>
<td>MB Initial concentration (mg/L)</td>
<td>300</td>
<td>300</td>
</tr>
<tr>
<td>Breakthrough concentration (mg/L)</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>Breakthrough time (mg/L)</td>
<td>23</td>
<td>82</td>
</tr>
<tr>
<td>Volume treated (mL)</td>
<td>165.6</td>
<td>590.4</td>
</tr>
<tr>
<td>Volume/mass (VTM)</td>
<td>0.396</td>
<td>1.088</td>
</tr>
<tr>
<td>Activated Carbon Usage Rate (mg/mL)</td>
<td>2.524</td>
<td>0.919</td>
</tr>
<tr>
<td>Breakthrough adsorption capacity (mg/g)</td>
<td>112.94</td>
<td>310.22</td>
</tr>
</tbody>
</table>
3.5 References


4. Conclusions and suggested future work

Removal of dyes by adsorption demonstrated to have more advantages over other treatment techniques such as advanced oxidation process, biological degradation and separation. Some of these advantages included complete removal of the dye molecule without producing other harmful organic compounds, efficient removal for a broad range of initial dye concentration, flexibility, regeneration, and simplicity. The drawback of high cost for the raw material can be overcome with the production of activated carbons from natural or waste materials. In our study, chemical activation of a waste tires with potassium hydroxide was conducted. As a result ACWT is a material with low BET specific surface area and high mesopore percentage. ACWT has an affinity towards MB but has low adsorption capacity. Thus, the carbon usage rate for ACWT was 2.5 mg/mL while it was 0.92 mg/mL for the commercial carbon F400. The lower adsorption capacity of ACWT toward MB may be attributed to the lower surface area hence fewer sites available for adsorption. Furthermore, ACWT presented more acidic functional groups than F400, reducing the adsorption process on the surface of the ACWT.

Therefore, for future work the following topics are recommended:

1.- Improving the impregnation method of potassium hydroxide with waste tires by studying in depth the different operational parameters. This study will enhance the activation process, improving the BET specific surface area in the activated carbon.

2.- Performing a complete study of Life Cycle Assessment (LCA) and Life Cycle Costing (LCC) for ACWT and F400. This study will define the environmental and cost benefits of using waste tires as precursor material rather than other natural materials such as bituminous coal.