UNIVERSIDADE FEDERAL DE MINAS GERAIS
Curso de Pós-Graduação em Engenharia Metalúrgica e de Minas

Dissertação de Mestrado

"Evaluation of the cold-pressed cake from *Raphanus sativus (L. Var.)* seeds activated carbon as an adsorbent for the removal of basic dyes from dilute aqueous solutions"

"Avaliação do carvão ativado da torta prensada de *Raphanus sativus (L. Var.)* como adsorvente para a remoção de corantes básicos presentes em soluções aquosas diluídas"

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Orientador: Prof. Marcelo Borges Mansur

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À Prof. Adriana Silva França

Dedico.

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SUMMARY

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RESUMO

Nesta dissertação de mestrado, avaliou-se o desempenho do carvão ativado da torta prensada a frio de *Raphanus sativus (L. Var.)*, um resíduo sólido oriundo da produção de biodiesel, como material adsorvente para a remoção de corantes básicos visando o seu emprego no tratamento de efluentes gerados na indústria têxtil. O azul de metileno (AME), em soluções aquosas diluídas, foi escolhido como adsorvato. O estudo compreendeu duas etapas principais. Na primeira etapa, o carvão ativado da torta prensada a frio de *Raphanus sativus (L. Var.)* foi produzido, tendo sido realizados testes de adsorção focando a avaliação do equilíbrio e da cinética, incluindo a avaliação dos principais parâmetros operacionais. Ensaios de adsorção em batelada foram conduzidos à temperatura ambiente (25^{o}C) e os efeitos de tamanho de partículas, do tempo de contato, da concentração de adsorvente e pH foram investigados. A cinética de adsorção foi determinada ajustando-se modelos cinéticos de primeira e segunda ordens aos dados experimentais, sendo que o modelo de segunda ordem forneceu a melhor descrição da adsorção do AME no adsorvente preparado. O processo de adsorção pode ser descrito por dois estágios cinéticos: adsorção mais rápida nas primeiras seis horas, seguido de uma taxa de adsorção mais lenta. O equilíbrio foi atingido após 12 horas para uma concentração inicial do corante de 100 mg L^{-1}. Os dados experimentais de adsorção após 72h foram ajustados aos modelos de Langmuir e Freundlich, sendo que o primeiro forneceu o melhor ajuste. A capacidade máxima de adsorção de AME, obtida pelo ajuste de Langmuir foi de 19,8mg.g^{-1}, maior que a capacidade de adsorção obtida por adsorventes de resíduos similares como a torta de girassol ou torta prensada de grãos de café. A segunda parte do estudo compreendeu a caracterização do carvão ativado. O foco da caracterização residiu no estudo morfológico do adsorvente, incluindo o estudo de propriedades físicas e texturais como área superficial, volume total e diâmetro médio dos poros, bem como o estudo da variação estrutural do carvão ativado de *Raphanus sativus (L. Var.)* antes e após a adsorção de AME. Foram utilizados métodos clássicos de caracterização, como o cálculo da área superficial pelo método de Brunauer-Emmet-Teller (BET), obtenção dos parâmetros dos poros pelo modelo de Barrett-Joyner-Halenda (BJH) e caracterização morfológica do adsorvente, através de Microscopoa Eletrônica de Varredura (MEV) e Espectrometria de Energia Dispersiva de raios X (EDS), e também a análise de espectroscopia Raman, que se mostrou um método potencial para a caracterização de parâmetros físicos de carvões ativados, através do estudo de sua estrutura porosa, bem como uma potencial ferramenta para a avaliação do mecanismo de adsorção do carvão ativado, através do estudo da ligação entre o carvão ativado e o adsorvato. Uma estrutura microporosa foi observada qualitativamente (MEV e análise Raman), indicando que a adsorção com azul de metileno ocorreu, predominantemente, na superfície do adsorvente (área superficial=236.3 $m^2.g^{-1}$, volume dos poros = 0.06 $cm^3.g^{-1}$; tamanho médio dos poros = 1.4 nm. A adsorção provavelmente ocorre pela ligação, no adsorvente, do átomo central de nitrogênio da molécula de azul de metileno.

ABSTRACT

The performance of the cold-pressed cake from *Raphanus sativus (L. Var.)* oilseeds activated carbon, a solid residue from biodiesel production, was evaluated as an adsorbent for basic dyes. The main objective is to use the adsorbent in the treatment of effluents generated by textile industries. Methylene blue (MB) dissolved in dilute aqueous solutions was chosen as the adsorbate. The study comprised two main steps. In the first step, activated carbon from *Raphanus sativus (L. Var.)* cold-pressed cake was produced and adsorption tests focusing on the evaluation of equilibrium, kinetics and the effects of main operational parameters were conducted. Batch adsorption tests were performed at room temperature (25^oC) and the effects of particle size, contact time, adsorbent dosage and pH were investigated. Adsorption kinetics was determined by fitting first and second-order kinetic models to the experimental data, with the second-order model providing the best description for MB adsorption onto the prepared adsorbent. The adsorption process can be described by a two-stage kinetic behavior, with a rapid initial adsorption during the first 6 hours, followed by a much slower rate afterwards. Equilibrium was attained after 12 hours for an initial dye concentration of 100 mg L^{-1} .The experimental adsorption data after 72 hours were fitted to Langmuir and Freundlich adsorption models, with the former model providing the best fit. Langmuir based maximum MB uptake capacity was 19.8 mg.g^{-1}, higher than other adsorbents employing similar types of residues such as sunflower oil cake, coffee seeds press cake and date pits. The second part of the study comprised the characterization of the activated carbon. It was focused on the study of the morphology of the adsorbent, including textural properties such as surface area, total volume and average pore diameter as well as the structural variation of *Raphanus sativus (L. Var.) (L. Var.)* activated carbon before and after MB adsorption. Classical characterization methodologies such as surface area calculation through the Brunauer-Emmet-Teller method (BET), pore parameters calculation through Barret-Joyner-Halenda method (BJH) and morphological adsorbent characterization through Scanning Electron Microscopy (SEM) and X-ray Energy Dispersive Spectrometry as well as Raman spectroscopy that was found to be a potential method to physical characterization of the porous structure of activated carbons and as a tool to study the adsorption mechanism of an activated carbon, through the determination of adsorption bonding

between activated carbon and adsorbate. A microporous structure was verified qualitatively (SEM and Raman analysis) indicating that MB adsorption occurs predominantly at the surface of the adsorbent (surface area = 236.3 $m^2.g^{-1}$, pore volume = 0.06 $cm^3.g^{-1}$; pore size = 1.4 nm). Adsorption probably occurs by MB bonding of monomer species through central nitrogen atom

1. INTRODUCTION

Environmental consequences from the massive use of fossil fuels such as greenhouse gas emissions, global climate change and concerns about petroleum's supplies and price have stimulated the search for renewable biofuels. In order to be viable, a biofuel should provide a net energy gain, have environmental benefits, be economically competitive, and also be producible in large quantities without reducing food supplies (Hill et al., 2006).

In Brazil, some important successful initiatives encouraging the use of renewable sources of energy have been taken over the last decades. The production and use of ethanol from sugarcane (*Saccharum L.*) is a global model for ethanol production, distribution and use. In fact, the Brazilian ethanol industry has attracted interest from scientists, producers, and governments from both developed and developing countries. Similarly to ethanol, biodiesel is also receiving a great interest in Brazil. Figure 1.1 illustrates how much the energy produced from biomass is important for the current Brazilian energetic matrix (Nass et al., 2007). Several oily species have been used and many others have being investigated as potential sources for biodiesel production. Some examples are soybean, coconut, peanut, cotton, palm tree, babassu, sunflower, rapeseed and castor bean (Silva and Freitas, 2008)

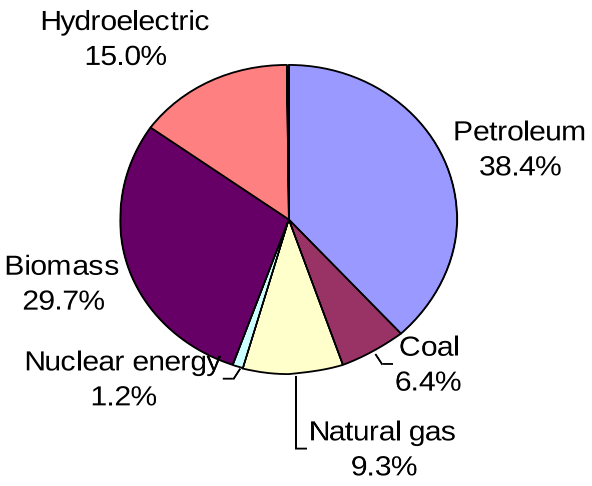

Figure 1.1 - Brazilian energetic matrix (Adapted from Nass et al., 2007).

Raphanus sativus (L. Var.) is a plant from the *Brassicaceae* (or *Cruciferae*) family that has been historically used for oil production, mostly in Eastern Asia. It has great ability to recycle soil nutrients, mainly nitrogen and phosphorus, becoming a suitable forage to be used between harvests and natural green fertilizer. This plant can grow in continental, tropical and temperate climates, being resistant to late frosts. It yields to an elevated green mass production during the coldest seasons, which makes *Raphanus sativus (L. Var.)* an important source of cattle feed (Teixeira and Zampierom, 2007). Also, *Raphanus sativus (L. Var.)* seeds contain from 40% to 54%% of their weight of oil, which can be easily extracted by simple mechanical pressing (Crusciol et al., 2005). Due to such aspect, Domingos et al. (2005) have recently investigated and optimized the production of biodiesel from *Raphanus sativus (L. Var.)* oil seeds using ethanol as the alcoholysis agent.

The production of biodiesel from *Raphanus sativus (L. Var.)* results in a cake with oil content approximately 7% to 8% of its weight. This residue can be used as a supplement for grazing beef cattle and it was found to be a good quality ingredient as a protein source (Mello et al., 2008). However, due to the increasing demand for biodiesel production, a relative large quantity of solid residue is expected to be produced. So, in a long term, only part of the *Raphanus sativus (L. Var.)* residue used as cattle feed would be effectively consumed. Hence, their use in the preparation of adsorbent materials could give a sustainable destination to this residue thus avoiding or reducing environmental issues. After utilization, the preferred disposal method for the adsorbed activated carbon is dewatering, drying and burning. Gupta and Suhas (2009) suggested that the heat of combustion of the adsorbents after utilization can be recovered as waste heat and used for the proper adsorbent drying and steam generation.

Recently, many authors have investigated the feasibility of using alternative materials as precursors for the production of absorbents (Crini, 2006; Ioannidou and Zabaniotou, 2007; Hernandez-Ramirez and Holmes, 2008). Oliveira and Franca (2008) recently published a review on the preparation and application of adsorbents from agri-food wastes. According to these authors, sorbents prepared from agricultural and food wastes may be the most promising type of biomaterials that will lead to a globalized bio-based economy due to its low-cost and effectiveness. These materials, including seed press cakes from biodiesel production, usually contain high levels of cellulose, hemicellulose, lignin and proteins, and might constitute renewable natural resources for a diversity of inexpensive eco-friendly and sustainable materials, including inexpensive adsorbents.

One important application for such novel adsorbents is the removal of dyes from textile industrial effluents. The textile industry is among the major producers of hazardous wastewaters that may cause severe negative environmental impact when discharged without adequate treatment. The discharge of colored wastewaters into natural streams may cause many significant problems such as the increase of toxicity and chemical oxygen demand (COD), and also the reduction of the light penetration which has a derogatory effect on photosynthetic phenomena (Bulut and Aydin, 2006).

In recent studies, it has been shown that adsorbents prepared from seed press cakes, specially activated carbons can be employed for adsorption of dyes yielding to satisfactory results. Examples include methylene blue adsorption by oil palm fibre (Tan et al., 2007), sunflower oil cake (Karagöz et al., 2008) and defective coffee beans press cake (Nunes et al., 2008).

In view of the aforementioned, the objective of this work is to evaluate the feasibility of using cold-pressed cake from *Raphanus sativus (L. Var.)* seeds, a solid residue from the biodiesel production industry, as precursor for the preparation of a activated carbon for the removal of basic dyes like methylene blue from dilute aqueous solutions as an attempt to treat effluents from the textile industry.

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2. OBJECTIVES

2.1 General purpose:

Evaluation of the performance of the activated carbon prepared from *Raphanus sativus (L. Var.)* oilseeds cold-pressed cake, a solid residue from biodiesel production, as an adsorbent for basic dyes, considering the technical aspects and the viability of preparing such activated carbon. For the study, methylene blue dissolved in dilute aqueous solutions was chosen as dye adsorbate species in order to simulate effluent conditions after textile industry wet finishing processes.

2.2 Specific purposes:

(1) Investigation of the technical viability of producing activated carbon from *Raphanus sativus (L. Var.)* cold-pressed cake and adsorption studies with this activated carbon. The adsorption studies comprise the investigation of equilibrium and kinetics, as well as the effect of main operational parameters related to the adsorption process.

(2) Characterization studies of the activated carbon from *Raphanus sativus (L. Var.)* oilseeds cold-pressed cake through the study of the morphology of the adsorbent, employing textural properties such as surface area, total volume and average pore diameter as well as the structural variation of *Raphanus sativus (L. Var.)* activated carbon before and after MB adsorption, utilizing classical characterization methodologies such as BET, BJH and SEM analyses as well as Raman spectroscopy.

3. REVIEW OF THE LITERATURE

3.1. Textile industry effluents

The main stages of textile processing are spinning, weaving and dyeing. The finishing wet processes which comprise dyeing consume large quantities of water and chemical products, and therefore yield to a significant discharge volume of effluents. The amount of water consumed varies widely in the textile industry, depending on the specific process stage, and the largest effluent release is related to the washing water from preparation and continuous dyeing steps (EPA, 1997).

The most important wet finishing processes are desizing, scouring, bleaching, mercerizing and dyeing process. These operations utilize a significant number of reagents, varying from organic to inorganic compounds like size agents, alkalis, salts, bleaching products, and a variety of dyes, thus generating wastewaters composed of a wide range of pollutants and color-causing products. Table III.1 shows the main pollutants involved in each of these wet processing operations.

Table III.1 – Operations steps involved in textile cotton industry and main pollutants generated in each step (EPA, 1997).

Operation	Main pollutants
Desizing	Size agents, enzymes, starch, lubricants, biocides and static compounds
Scouring / Washing	Disinfectants, insecticides residues, NaOH, detergents, oils, waxes, pectin, oils, knitting lubricants, spin finishes and solvents
Bleaching	Hydrogen peroxide, organic stabilizer and sodium silicate
Mercerizing	Sodium hydroxide and salts
Dyeing	Metals, salts, surfactants, organic processing assistants, cationic materials, sulfide and dyes

According to Santos et al. (2007), textile wastewaters can be characterized by large variations in many parameters such as chemical oxygen demand (COD), biochemical oxygen demand (BOD), pH and dissolved solids. Table III.2 shows a typical characterization of cotton wet processing wastewaters and water usage in liters per kilogram for each step.

Table III.2 – Characterization of cotton wet processing wastewaters (Santos et al., 2007).

Process	**COD ($g.L^{-1}$)**	**BOD ($g.L^{-1}$)**	**TS ($g.L^{-1}$)**	**TDS ($g.L^{-1}$)**	**pH**	**Colour***	**Water Usage ($L.kg^{-1}$)**
Desizing	4.6-5.9	1.7-5.2	16.0-32.0	-	-	-	3-9
Scouring	8.0	0.1-2.9	7.6-17.4	-	10-13	694	26-43
Bleaching	6.7-13.5	0.1-1.7	2.3-14.4	4.8-19.5	8.5-9.6	153	3-124
Mercerizing	1.6	0.05-0.1	0.6-1.9	4.3-4.6	5.5-9.5	-	232-308
Dyeing	1.1-4.6	0.01-1.8	0.5-14.1	0.05[a]	5-10	1450-4750	8-300

COD, chemical oxygen demand; BOD, biochemical oxygen demand; TS, total solids; TDS, total dissolved solids.

Obs: * American Dye Manufacturer

[a] In case of some reactive dyes, the salt concentration in the dyebath can reach concentrations up to 60-100 $g.L^{-1}$. Therefore, the values listed in the table can vary enormously depending on the type of the fiber and dye class.

The main recalcitrant compounds present in textile effluents are the synthetic dyes which are used during fiber dying processes (Asad et al., 2007). According to Banat et al. (1996), there are more than 8000 chemical products associated with the dyeing process listed in the Colour Index (Society of Dyers and Colourists, 1976). In the 80's, there were more than 100,000 commercially available dyes and over 7×10^5 metric tons of dyestuff were produced annually (Zollinger, 1987). These dyes are classified according to their chemical structure such as azo, diazo, anthraquinone-based and metal-complex dyes, and according to the way they fix on the textile fiber as acidic, basic, direct, disperse, reactive, sulfur and vat. The main characteristics of dyes distributed in the seven most common classes are shown in Table III.3.

Table III.3 – Typical characteristics of dyes used in textile dyeing operations (adapted from EPA, 1997).

Dye Class	Description	Method	Fibers Typically Applied	Typical Fixation (%)	Typical Pollutants Associated
Acid	Water-soluble anionic compounds	Exhaust/ Beck/ Continuous (carpet)	Wool, nylon	80-93	Color, organic acids, unfixed dyes
Basic	Water-soluble, applied in weakly acidic dyebaths; very bright dyes	Exhaust/ Beck	Acrylic, some polyesters	97-98	Color
Direct	Water-soluble, anionic compounds; can be applied directly to cellulosics without mordants (or metal like chromium and copper)	Exhaust/ Beck/ Continuous	Cotton, rayon, other cellulosics	70-95	Color, salt, unfixed dye, cationic fixing agents, surfactant, defoamer, leveling an retarding agents, finish, diluents
Disperse	Not water-soluble	High temperature exhaust Continuous	Polyester, acetate, other synthetics	80-92	Color, organic acids, carriers, leveling agents, phosphates; defoamer, diluents, finish
Reactive	Water-soluble, anionic compounds; largest dye class	Exhaust/ Beck/ Cold pad batch/ Continuous	Cotton, other cellulosics, wool	60-90	Color, salt, alkali, unfixed dye, surfactant, defoamer, diluents; finish
Sulfur	Organic compounds containing sulfur or sodium sulfide	Continuous	Cotton, other cellulosics	60-70	Color, alkali, oxidizing agent, reducing agent, unfixed dye
Vat	Oldest dyes; more chemically complex; water-insoluble	Exhaust/ Package/ Continuous	Cotton, other cellulosics	80-95	Color alkali, oxidizing agents, reducing agents

Aside from aesthetic aspects, the majority of such compounds are of significant health concern even at low concentrations in water. In fact, the presence of very small amounts of dyes in water (less than 1 ppm for some dyes) is highly visible and affects water transparency and gas solubility in lakes, rivers and others waterbodies (Banat et al., 1996), consequently diminishing the photosynthesis. In this aspect, environmental regulations in most countries have made it mandatory to decolorize wastewaters prior to discharge in natural water streams. State and federal agencies in USA require low effluent color limits (< 300 units of American Dye Manufacturers Institute) as stated by the U.S. Pollutant Discharge System (Dafnopatidou et al., 2007).

Still according to Banat et al. (1996), the removal of color from wastewaters is often more important than the removal of the soluble colorless organic substances, which usually contribute with the major fraction of the biochemical oxygen demand (BOD). Methods for the removal of BOD from most effluents are fairly well established. Dyes, however, are more difficult to treat because of the their synthetic origin and mainly complex aromatic molecular structures.

3.2. Textile effluent treatment technologies

In former days, municipal treatment systems were the most important manner used for the purification of textile wastewaters. Most of these systems proved to be inefficient mainly for the removal of the more resistant synthetic dyes, because of their biological activity dependency (Moran et al., 1997). Dyes can be damaging to the microbial population present in microbial-based wastewaters treatment process. For this reason, more effective methods were (and still are) developed and tested for dye removal. In practical applications, there is no specific process able to handle decolorization and treatment of all textile wastewaters and, generally, a customized process probably involving a combination of methods could be more applicable (Pereira et al., 2003; Marco et al., 1997). Primarily, they depend on using physical- or chemical-treatment processes, occasionally in conjunction with biological treatment (Groff, 1993; Wilking and Frahne, 1993; Mishra and Tripathy, 1993). Research has been conducted in the fields of combined adsorption-biological treatments in order to improve the biodegradation of dyestuffs and minimize the sludge production (Crini, 2006).

In the literature, several methods are proposed to remove dyes from textile effluents and many reviews discuss these methods, thus comparing their limitations, advantages and disadvantages (Banat et al., 1996; Slokar and Le Marechal, 1998; Robinson et al., 2001; Crini, 2006; Santos et al., 2007). Table III.4 summarizes advantages and drawbacks of some dye removal methods.

Table III.4 - Advantages and drawbacks of some processes for dyes removal (Crini, 2006)

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

3.2.1 Physical-Chemical methods

The physical-chemical methods normally make use of coagulant agents to flocculate dyes, which are, then, separated by filtration or sedimentation. The coagulant agents that are most commonly applied are ferric salts or aluminium polychloride (Santos, 2007). The physical-chemical methods like coagulation–flocculation can be used either as a pre-treatment, post-treatment, or even as a main treatment system (Gahr et al., 1994; Marmagne and Coste, 1996). These methods were successfully applied for color removal of sulphurand, disperse dyes (Marmagne and Coste, 1996). The main drawback about physical-chemical methods is that they normally demand large inputs of chemicals and produce high volumes of polluted sludge that must be treated afterwards (Robinson et al., 2001; Anjaneyulu et al., 2005).

3.2.2 Chemical methods

Chemical methods can be mostly represented by the oxidative process. They utilize an oxidizing agent like ozone, hydrogen peroxide (H_2O_2), sodium hypochloride (NaOCl) or Cucurbituril (Robinson et al., 2001). These methods remove dyes from the dye-containing effluent by oxidation resulting in aromatic ring cleavage of the dye molecules (Raghavacharya, 1997). Ozone is the most widely used reagent because of its high reactivity with many dyes, usually providing good color removal efficiencies (Alaton et al., 2002). In a process called selective oxidation, ozone can be designed in such a way that only –N≡N– bond scission occurs and biodegradable compounds remain non-oxidised (Boncz, 2002). However, ozone’s cost is very high. The main drawbacks about chemical oxidation techniques are the usual low efficiency of both color and COD removals (Santos, 2007).

In order to improve the efficiency of the conventional oxidation processes, new technologies were developed. These new oxidation technologies are classified as advanced oxidation processes (AOP) which are defined as the processes that generate hydroxyl radicals in sufficient quantities to be able to oxidize the majority of the complex chemicals such as toxic chemicals, bio-refractory compounds, pesticides, etc, even in ambient conditions (hydroxyl radicals oxidation potential is about 2.33V, according to Gogate et al., 2002). They include cavitation (generated either by means of ultrasonic irradiation or using constrictions such as valves), photocatalytic oxidation (using ultraviolet radiation, near UV light or sun light in the presence of semiconductor catalyst) and Fenton chemistry (using reaction between Fe ions and hydrogen peroxide, i.e. Fenton’s reagent) (Gogate and Pandit, 2004a). Such advanced techniques can be applied individually or in combination with another advanced technique (hybrid technologies) (Gogate and Pandit, 2004b). Although these processes have the potential to degrade most organic and many inorganic solutes with high rate constants, the majority of these oxidation technologies, however, fail to degrade the complex compounds completely, mainly in the case of real wastewaters and can not be used for processing the large volumes of waste generated. Hence, it may happen that such technologies have to be used only as a pretreatment stage followed by the conventional biological oxidation techniques (Gogate and Pandit, 2004a).

3.2.3 Biological treatments

Many biological treatments for dye decolorization have been reported such as decolorization by fungi, microbial cultures, adsorption by living/dead microbial biomass, anaerobic bioremediation systems (Robinson et al., 2001), biological and chemical reductive decolorization and reductive decolorization of azo dyes in the presence of redox mediators (Santos et al., 2007). The most important advantage of these techniques is the low cost when compared with physical and chemical methods. Also, anaerobic color removal by granular sludge as a pre-treatment for colored wastewaters from dyebath and rinsing steps seems to be a very promising technology (Santos et al., 2007). However, like the other methods described so far, biological treatments also have drawbacks. Biological treatment requires a large land area and it is constrained by sensitivity toward variation during the day as well as toxicity of some chemicals (Bhattacharyya and Sarma, 2003).

3.2.4 Physical methods

There are several known physical methods extensively used as membrane filtration, ion-exchange and adsorption. Membrane filtration such as ultrafiltration, nanofiltration and reverse osmosis can be used for filtering and recycling dyeing effluents, and also to treat mercerizing and bleaching wastewaters. The main advantages of such methods are that they can be operated in a wider range of temperature, in an adverse chemical environment, and they can resist to microbial attack. The disadvantages of membrane filtration are the high initial costs, the need to replacement after membrane fouling and the concentrated residue left after separation which needs to be treated (Robinson et al., 2001).

The ion exchange method can be used to purify textile effluents by passing the wastewater over a cationic or an anionic ion exchange resin that can remove an anion or a cation dye from the effluent. According to Slokar and Le Marechal (1998), ion exchange has not been widely used for the treatment of dye-containing effluents, mainly due to the opinion that ion exchangers cannot accommodate a wide range of dyes. Nevertheless, Rock and Stevens (1975) showed that a packed-bed anion exchange column in series with a nonpolar resin containing column is suitable to eliminate acid, direct and sulphur dyes. Overall, ion exchange methods are not very effective for disperse dyes, and lead to high costs due to the use of organic solvents (Mishra and Tripathy, 1993).

Adsorption has become one the most popular techniques for wastewater treatment and for dye removal from textile effluents due to its efficiency in the removal of pollutants which are too stable to be separated by conventional methods (Choy et al., 1999; Robinson et al., 2001; Crini, 2006). This technique produces a high quality product, and is an economically feasible process which provides an attractive alternative for the treatment of contaminated waters, mainly if the sorbent is inexpensive and does not require an additional pre-treatment step before its application.

Decolorization of textile wastewater containing dye is a result of two mechanisms: adsorption and ion exchange, which is why the binding capacity depends on the dye molecule size and charge, pH and salt concentration (Slokar and Le Marechal, 1998).

Adsorption has been found to be superior to other techniques for water reuse in terms of initial cost, flexibility and simplicity of design, ease of operation and insensitivity to toxic pollutants. Adsorption also does not result in the formation of harmful substances (Crini, 2006). Activated carbon, particularly the commercial activated carbon, is the most common adsorbent and it can be very effective for many dyes (Robinson et al., 2001; Santos et al., 2007). However, it presents some disadvantages. It is quite expensive (the higher the quality of water produced, the greater is the cost), non-selective and ineffective against disperse and vat dyes. The regeneration of saturated carbon is also expensive, not straightforward, and results in loss of the adsorbent (Crini, 2006). These disadvantages previously mentioned led to research into the production of alternative adsorbents to replace the costly activated carbon. Hence, the use of non-conventional low-cost adsorbents based on waste materials has been intensively investigated in recent years and it has become an economically attractive and ecologically based promising technology. (Oliveira and Franca, 2008).

3.3. Adsorption theory

Adsorption has become an even more utilized operation in industry and it is considered a process with high ability for the removal of solutes and purification of solutions even when the solution’s constituents are volatile and degradable at high temperatures.

Adsorption can be described as a mass transfer interfacial phenomena in which solutes (adsorbate) from a fluid phase tend to adhere onto a solid surface (absorbent), yielding to the separation of one or more constituents from the fluid phase solution. The mass transfer can be strongly influenced by the porous structure of the solid phase and by the nature of the fluid phase molecules (Treybal, 1968).

Adsorption can be classified as physical or chemical process, depending on the kind of interaction or strength existing between the adsorbent and the adsorbate (Treybal, 1968; Suzuki, 1990). Physical adsorption occurs when weak interparticle bonds exist between the adsorbate and the adsorbent. Examples of such bonds are van der Waals, Hydrogen and dipole-dipole. In the majority of cases, physical adsorption is easily reversible, what may lead to the absorbent reutilization. Chemical adsorption occurs when strong interparticle bonds are present between the adsorbate and the adsorbent, due to an exchange of electrons. Examples of such bonds are covalent and ionic bonds. Chemisorption is deemed to be irreversible in the majority of cases (Allen and Koumanova, 2005). Table III.5 presents the main differences between the two kinds of adsorption processes (Teixeira et al., 2001).

Table III.5 - Comparison between physical and chemical adsorption (Pomonis and Ladavos, 2006).

Physical adsorption	Chemical adsorption
Due to intermolecular strength	Due to electrostatic strength and covalent bonds
Adsorption heat:10-50 kj/mol	Adsorption heat: 50-200 kj/mol
General phenomena for all species	Specific and selective phenomena
Multilayer formation below the critical temperature	Monolayer formation only
Absorbent is almost unaffected	Absorbent surface is strongly modified

The adsorption ability is related to the surface area available, the pores size distribution and the process kinetics. A large surface area is desirable in order to provide a high adsorption capacity. The pore size distribution is also an important property because it affects the adsorbate molecules access on the adsorbent. The process kinetics is related, in most of the cases, to the intraparticle diffusion of the adsorbate molecules into the interior of the solid adsorbent particles, hence intraparticle diffusion is often the rate-limiting step in many adsorption processes (Suzuki, 1990). Although, in many processes like biosorption processes, adsorption occurs mainly in the surface of the adsorbent and the chemical composition of the surface (functional groups) also plays an important role in the adsorption behavior (Rodríguez-Reinoso and Molina-Sabio, 1998) and consequently to the process kinetics.

Other important parameters that influence the adsorption efficiency are temperature and pH. Usually, adsorption decreases with the increase of temperature because the heat of adsorption is positive, i.e., adsorption is an exothermic process (Do, 1998). Some exceptions in this behavior were observed by Youssef (1993) in the adsorption of acid dyes onto cellulose (and some of its derivatives), and by Bulut and Aydin (2006) in the adsorption of methylene blue onto wheat shells.

The aqueous solution initial pH is one of the most important propriety on adsorption process, especially on dye absorption (Bulut and Aydin, 2006). The pH has been reported to present a significant influence on the adsorptive uptake of dyes due to its impact on both the surface binding-sites of the adsorbent and the ionization process of the dye molecule (Singh et al., 2003; Oliveira et al., 2008). Many authors reported that adsorption increases in higher pH’s values for basic dyes adsorption onto some adsorbents like different materials based activated carbon as fly ash (Qada et al., 2007; Jãnos et al., 2003; Kannan and Sundaram., 2001; Allen and Koumanova, 2005). This effect is called “pH adsorption edge”. It can be explained by considering a zero point of charge of the adsorbent (pH_{PZC}). Above the zero point of charge, the negative charge density on the surface increases, thus favoring the sorption of basic (cationic) dyes. The sorption of acid (anionic) dyes, on the other hand, decreased at higher pH values for the same reason (Jãnos et al., 2003). The pH_{PZC} is characterized by the pH in which the negative charges on the surface of the adsorbent are exactly counterbalanced by the positive charges. It is an important parameter used in the characterization of adsorbent, mainly activated carbons, since it will dictate its performance when electrostatic forces are relevant to the adsorption process. The determination of the pH_{PZC} of a carbon is of utmost relevance to adsorption applications where the target sorbate is either in a cationic or an anionic state (Oliveira and Franca, 2008). Nevertheless, there are some cases that pH do not strongly affects the adsorption process. Nunes et al. (2008) studied the pH effect for values between 3 and 11 and reported no significant differences after 5h of adsorption of methylene blue onto defective coffee beans activated carbon. They pointed that, even though the positively charged surface sites of the adsorbent do not favor dye adsorption in lower pH values for basic dyes, due to electrostatic repulsion, dye removal was still efficient, hence suggesting that π–π dispersion interactions between adsorbent and adsorbate are dominant in this case.

3.3.1 Adsorption isotherms

After a certain period of contact between the adsorbent and a fluid phase containing the adsorbate molecules, the adsorption process tends to end and the equilibrium is reached. The relation between the amount of substance adsorbed and the equilibrium concentration of fluid phase at a constant temperature is named adsorption isotherm (Suzuki, 1990).

The assessment of the equilibrium adsorption isotherm is very important in the design of adsorption systems (Wang et al., 2006). The adsorption isotherm is, as well, an important tool to predict thermodynamic parameters, such as adsorption free energy, heat and entropy. Several isotherm equations are available and the most common isotherms which are considered in many studies are the Langmuir and Freundlich isotherms.

The Langmuir adsorption isotherm, based on a theoretical model (Gibbs equation), assumes monolayer adsorption over an energetically and structurally homogeneous adsorbent surface and does not take into account interactions between adsorbed molecules. It has found successful application for many sorption processes of monolayer adsorption (Wang et al., 2006). The Langmuir isotherm is given by:

$$q_e = \frac{q_{\max} K_L C_e}{1 + K_L C_e} \qquad (3.1)$$

where q_e (mg.g^{-1}) is the amount adsorbed per gram of adsorbent, and C_e (mg.L^{-1}) is the solute concentration in the aqueous solution after equilibrium was reached. The constants q_{max} and K_L are related to the maximum adsorption capacity (mg.g^{-1}) and the adsorption energy (L.mg^{-1}), respectively. Another characteristic parameter of the Langmuir isotherm is the dimensionless factor r, called separation factor:

$$r = \frac{1}{1 + K_L C_0} \qquad (3.2)$$

where C_0 corresponds to the highest value for initial sorbate concentration (mg.L^{-1}). The value of r is related to the type of the isotherm, and it can indicate either unfavorable ($r > 1$), linear ($r = 1$), favorable ($0 < r < 1$) or irreversible ($r = 0$) adsorption. The relationship between the separation factor and the isotherm type can be visualized on Figure 3.1.

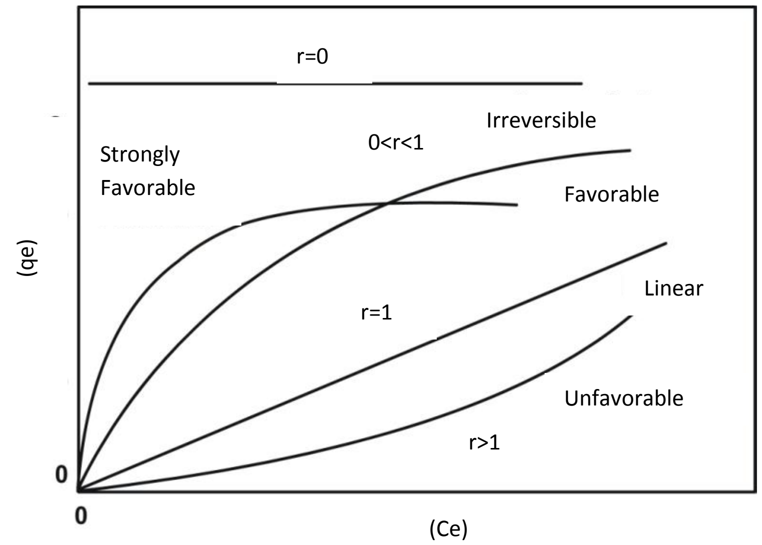

Figure 3.1 - Adsorption isotherm shapes (Adapted from McCabe et al., 1993).

Other important isotherms derived from Gibbs equation are linear equation based on Henry law, Volmer, Fowler-Guggeneim, Harkins-Jura and Hill-deBoer. These models are theoretical equations based on pure component equilibria.

The Freundlich equation is one of the earliest empirical equations used to describe equilibria adsorption data. The Freundlich equation is given by:

$$q_e = K_F C_e^{1/n} \tag{3.3}$$

where K_F represents the relative adsorption capacity ($mg^{1-(1/n)}L^{1/n}g^{-1}$) and n is related to the intensity of adsorption, with values of $n > 1$ indicating favorable adsorption. The larger is this value, the adsorption isotherm becomes more nonlinear as its behavior deviates further away from the linear isotherm (Do, 1998).

The Freundlich equation is popularly used in the description of adsorption of organics species from aqueous streams onto activated carbon. It is also applicable in gas phase systems having heterogeneous surfaces, provided the range of pressure is not too wide as this isotherm equation does not have a proper Henry law behavior at low pressure and it also does not have a finite limit when pressure is sufficiently high. Therefore, it is generally valid in the narrow range of the adsorption data (Do, 1998). There are other empirical and semi-empirical models for describing adsorption equilibria. Some of these equations are useful to describe adsorption of gases and vapors below the capillary condensation region, for example, Langmuir-Freundlich (Sips equation), Toth, Unilan and Dubinin-Radushkevich. Others are used to describe equilibrium data in the region of multilayering adsorption like the classical equation BET, which is the most important equation for the characterization of mesoporous solids and from which parameters like surface area of adsorbents can be obtained (Do, 1998).

3.3.2 Kinetic modeling

The study of adsorption kinetics in wastewater treatment is essential as it provides understanding of the reaction pathways and the mechanisms of adsorption reactions. Furthermore, identifying the rate-determining step in adsorption processes is important as it provides information on rate parameters for design purposes. Specifically, the kinetics of adsorption processes is concerned with intermolecular forces between adsorption sites and adsorbate molecules and forms an important area of surface chemistry (Qada et al., 2007).

In general, adsorption theory is based on the principle that three steps are involved in the process, any of which could be the rate-controlling factor. The three steps are as follows: external mass transport across the external boundary layer, internal mass transport within the particle by pore and/or surface diffusion, and adsorption at a site. The final step is assumed to be rapid with respect to the first two steps and it is, thus, not considered in kinetic analysis (Qada et al., 2007). The most used models to predict rate-limiting step in many adsorption processes are the pseudo-first order, the pseudo-second order models and the intraparticle diffusion model.

The pseudo-first order model is based on Lagergren equation. In most of cases, the first-order equation can not be applied at all the time range and it is usually applied for the first minutes of the adsorption process (Azizian, 2004). The pseudo-first order model is given by:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{3.4}$$

where k_1 is the rate constant of the pseudo-first order adsorption (h^{-1}), and q_e and q_t are the amount absorbed at equilibrium and at time t, respectively.

The pseudo-second order model assumes that the adsorption process is a pseudo-chemical reaction process with the driving force being the difference between the average solid concentration and the equilibrium concentration with the overall adsorption rate proportional to the square of the driving force (Qada et al., 2007). Ho and McKay (2000) assumed that the adsorption capacity is proportional to the number of active sites occupied in the adsorbent (Qada et al., 2007). The kinetic rate equation can be represented by:

$$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2 \qquad (3.5)$$

where k_2 is the rate constant of the pseudo-second order adsorption (g. mg^{-1}.h), and q_e and q_t are the amount absorbed at equilibrium and time t, respectively.

Intraparticle diffusion plays a significant role in many adsorption processes and assumes that diffusion of adsorbate occurs within the pore structure of the adsorbent. Kannan and Sundaram (2001) considered that the adsorbate species are most probably transferred from the exterior to the interior surface of the solid through an intraparticle diffusion/transport process, which is often the rate-limiting step in many adsorption processes, especially in a rapidly stirred batch reactor. According to Guibal et al. (1998) a plot of fraction of solute adsorbed against $t^{1/2}$ can be used to estimate the intraparticle diffusion rate in the linear range. This mathematical dependence of concentration in the solid with $t^{1/2}$ has been deduced by considering the adsorption mechanism to be controlled by diffusion in the adsorbent (as spherical particles) and by convective diffusion in the solution. The following equation represents the intraparticle-diffusion model (Qada et al., 2007):

$$q_t = K_p . t^{1/2} + C \qquad (3.6)$$

where k_p is the intraparticle diffusion rate constant, evaluated as the slope of the curve q_t versus $t^{1/2}$ (Weber et al., 1963).

3.4 Adsorbents

An adsorbent is a natural or synthetic substance having a microcrystalline or amorphous structure, usually porous in nature, thus presenting a high surface area. Its porous internal structure is accessible to a selective combination between the solute and the solid (Suzuki, 1990). The most important observed attributes of an adsorbent for any application are capacity and kinetics.

Adsorption capacity or loading is the most important characteristic of an adsorbent. Simply stated, it is the amount of adsorbate taken up by the adsorbent, per unit mass (volume) of the adsorbent, for example $mg.g^{-1}$. Adsorption capacity is of great importance to the capital cost because it dictates the amount of adsorbent required, which also fixes the size of the adsorber vessels.

Adsorption kinetics is important because it controls the cycle time of a fixed bed adsorption process. Fast kinetics provides a sharp breakthrough curve, while slow kinetics yields a distended breakthrough curve. The effect of a distended breakthrough can be overcome by adding adsorbent at the product end, or by increasing the cycle time, which reduces the throughput per unit of adsorbent (Knabel, 2008).

Thus, a good solid is the one that provides, at least, good adsorptive capacity as well as good kinetics. To satisfy these requirements, the solid must have reasonably high surface area or micropore volume (small pore size with a reasonable porosity), in order to provide good adsorptive capacity.

A good solid adsorbent must have a combination of two pore ranges: the micropore and the macropore range (Do, 1998). The classification of pore size as recommended by IUPAC (Sing et al., 1985; Do, 1998) is often used to delineate the range of pore size (see Table III.6).

Table III.6 - Classification of pore size as recommended by IUPAC (Sing et al., 1985; Do, 1998).

Type of porous	Average diameter (nm)
Microporous	$d < 2$
Mesoporous	$2 < d < 50$
Macroporous	$d > 50$

Other important attributes of a solid adsorbent are selectivity, regenerability, compatibility and cost.

All cyclic adsorption applications rely on regenerability, so that the adsorbent can operate in sequential cycles with uniform performance. This means that each adsorbable component must be relatively weakly adsorbed. The heat of adsorption provides a measure of the energy required for regeneration, and in that regard low values are desirable in order to provide a lower cost.

Selectivity is related to the preferential capacity for a given solute. The simplest definition of selectivity is the ratio of the capacity for a given component instead of another, at a given fluid concentration. An ideal situation occurs when the major component is not adsorbed much, which leads to a very large selectivity. Compatibility covers various possible modes of chemical and physical attack that could reduce the life expectancy of the adsorbent (Knabel, 2008). These two properties are related to the adsorbent superficial chemical structure.

There is a wide range of adsorbents with a wide variety of applications. Among them are included activated carbons, inorganic materials, biosorbents and some natural and synthetic polymers. This work focus on non-conventional low cost adsorbents from agricultural waste materials (biosorbents and activated carbons), so these adsorbents are discussed separately on itens 3.5 and 3.6.

3.4.1 Inorganic materials

A brief citation of inorganic adsorbent materials and their usage are given as follows. Alumina and silica gel are used for drying (Do, 1998); siliceous sorbents such as silica beads, glasses, alunite, perlite and dolomite are used for wastewater treatments, specially removal of acid dyes, natural and synthetic zeolites are used as alternative materials in areas where sorptive applications are required (on removing trace quantities of pollutants such as heavy metal ions and phenols) and, finally, natural clays such as smectites (montmorillonite, saponite), mica (illite), kaolinite, serpentine, pylophyllite (talc), vermiculite and sepiolite are classically used to adsorb inorganic molecules and most recently to adsorb dyes (Crini, 2006).

3.4.2 Biosorbents

A biosorption process is commonly defined as a passive physicochemical uptake of a sorbate from a solution by living or dead biomass cells (biosorbents) without the occurrence of metabolic transformation/accumulation of the sorbate, i.e., it is strictly a function of the chemical makeup of the cell wall (Volesky, 1990). As stated by Oliveira and Franca (2008), although this definition does not impose any restrictions to the nature of the biomass, the terminology "biosorption" is almost exclusively used when the biomass is comprised of living or dead microorganisms, such as bacteria, fungi, yeasts and algae (Volesky, 1990; Davis et al., 2003; Aksu, 2005), sometimes subjected to mild chemical and thermal treatments.

Crini (2006) itemizes a list of biological biosorbents by living or dead biomass cells such as chitin, chitosan, peat, yeasts, fungi and bacterial biomass, which are used as chelating and complexing agents in order to concentrate and/or to remove dyes from solutions.

There is another concept of biomass presented by Stout (1984) and cited by Oliveira and Franca (2008). Biomass, hence biosorbents, could be defined as "all renewable organic matter including plant material, whether grown on land or water; animal products and manure; food processing, forestry by-products and urban wastes". Among this kind of materials, attention has been focused on various natural solid wastes, which are able to remove pollutants from contaminated water: the so mentioned non-conventional low-cost adsorbents. They can be used as raw materials on biosorption or as precursor for activated carbons.

3.5 Non-conventional low-cost adsorbents

According to Bailey et al. (1999), a sorbent can be considered low-cost if it requires little processing, is abundant in nature or is a by-product or waste material from another industry. Certain waste products from industrial and agricultural operations, natural materials and biosorbents represent potentially economical alternative sorbents.

3.5.1 Agricultural solid wastes

A wide variety of raw agricultural solid wastes and waste materials from forest industries has been recently investigated for textile effluents treatment. Among them, there are some materials with a great potential as adsorbents, mainly because of their low-cost and physical and chemical characteristics. They are usually lignocellulosic materials with a variable chemical composition. Some examples are bark, rice husk an tree fern which presented the highest sorption capacities for basic dyes in comparison to other waste materials sorption capacities (Table III.7). A complete review of agricultural solid adsorbent materials for dyes and their sorption capacity can be found in Crini (2006).

Table III.7 - Reported adsorption capacities (q_{max}) for agricultural and industrial waste materiais (Adapted from Crini, 2006).

Adsorbent	Dye	q_{max} (mg.g^{-1})
Bark	Basic red 2	1119
Bark	Basic blue 9	914
Rice	Basic red 2	838
Sugar-industry-mud	Basic red 22	519
Tree fern	Basic red 13	408
Pine sawdust	Acid yellow 132	398.8
Palm-fruit bunch	Basic yellow	327
Rice husk	Basic blue 9	312
Pine sawdust	Acid blue 256	280.3
Vine	Basic red 22	210
Rice hull ash	Direct red 28	171
Egyptian bagasse	Basic blue 69	168
Vine	Basic yellow 21	160
Egyptian bagasse pith	Basic blue 69	152
Coir pith	Basic blue 9	120.43
Coir pith	Basic violet 10	94.73
Eucalyptus bark	Remazol BB	90
Raw date pits	Basic blue 9	80.3
Fly ash	Basic blue 9	75.52
Egyptian bagasse pith	Basic red 22	75
Treated sawdust	Basic green 4	74.5
Wood sawdust	Basic blue 69	74.4
Metal hydroxide sludge	Reactive red 2	62.5
Metal hydroxide sludge	Reactive red 141	56.18
Metal hydroxide sludge	Reactive red 120	48.31
Treated sawdust	Basic green 4	26.9
Fe(III)/Cr(III) hydroxide	Basic blue 9	22.8
Banana peel	Methyl orange	21
Banana peel	Basic blue 9	20.8
Banana peel	Basic violet 10	20.6
Orange peel	Methyl orange	20.5
Egyptian bagasse pith	Acid red 114	20
Orange peel	Acid violet	19.88
Orange peel	Basic blue 9	18.6
Egyptian bagasse pith	Acid blue 25	17.5
Egyptian bagasse pith	Acid blue 25	14.4
Orange peel	Basic violet 10	14.3
Fly ash	Alizarin sulfonic	11.21
Coir pith	Acid violet	7.34
Wood sawdust	Acid blue 25	5.99
Sugar cane dust	Basic green 4	4.88
Banana pith	Direct red	5.92

3.5.2 Industrial by-products

Because of their low cost and local availability, industrial solid wastes are candidates to be used as adsorbents. Its importance is due to two reasons: wastewater treatment and minimization of solid wastes discharge. Some important examples of this type of adsorbent for dye removal are metal hydroxide sludge, which is produced by precipitation of metal ions in wastewater in the electroplating industry, fly ash which is a waste material in combustion processes and red mud, a bauxite processing residue discarded in alumina (Crini, 2006). Their sorption capacities are also shown in Table III.7.

Other materials that can be considered very important industrial by-products for dye removing from wasterwaters are chitin and chitosan. They are extracted from crustaceans (crab, krill, and crayfish) exoskeleton available as a by-product of food processing. The annual worldwide crustacean shells production has been estimated to be 1.2 x 10^6 ton (Crini, 2006). The performance of chitosan as an adsorbent to remove acid dyes has been demonstrated by Wong et al. (2004). They found that the maximum adsorption capacities of chitosan for acid orange 12, acid orange 10, acid red 73 and acid red 18 were 973.3, 922.9, 728.2, and 693.2 $mg.g^{-1}$, respectively.

3.6 Activated carbons

Activated carbons can be generally described as highly microporous carbons which, after carbonization and activation of the precursor material, are comprised of microcrystalline graphite layers interspersed with non-graphitic aromatic carbon structures containing heteroatoms such as oxygen and hydrogen, and in which many carbon-carbon bounds are left incomplete, thus creating chemically active sites which are responsible for specific physical and chemical interactions with an assortment of sorbates of great relevance in adsorption processes (Rodriguez-Reinoso and Molina-Sabio, 1998).

Activated carbons are some of the most widespread agents for the treatment and purification of water. Their high porosities, from macro to microporous structures, make them efficient adsorbents to trap low molecular weight chemicals such as metal ions, dyes and other organic compounds. This is achieved through adsorption processes, where the atoms and molecules are fixed to the carbon surface via physical interactions or chemical bonds (Hernandez-Ramirez and Holmes, 2008). They can be used in many applications as purification, decolorization, deodorization, dechlorination, defluoridation, separation and concentration of products in diverse areas (Oliveira and Franca, 2008).

Although the microporosity is the main reason for the large adsorptive capacity of porous carbons such as activated carbon, the chemical composition of the surface also plays an important role in the adsorption behavior. Activated carbon is invariably associated with appreciable amounts of heteroatoms such as oxygen and hydrogen chemically bonded to the structure, and with inorganic ash components. Oxygen surface groups are by far the most important ones in influencing the surface characteristics and adsorption behavior of activated carbon.

Commercially available activated carbons are usually derived from natural materials such as wood, coconut shell, lignite or coal, but almost any carbonaceous material may be used as precursor for the preparation of carbon adsorbents (Crini, 2006). These materials are used to obtain a series of activated carbon types, which will offer a variety of properties depending on their final application (Rodriguez-Reinoso and Molina-Sabio, 1998).

The major drawback of commercial activated carbon is its high cost, which makes it impractical for the treatment of the current high volumes of waste produced by industry and society. This problem has been addressed through two lines of investigation: finding cheap alternative sources of precursor materials and enhancing the efficiency of the existing materials (Hernandez-Ramirez and Holmes, 2008).

3.6.1 Activated carbons from agricultural wastes

Ioannidou and Zabaniotou (2007) stated that agricultural by-products have proved to be promising raw materials for the production of activated carbons because of their availability at a low price and that activated carbon produced from these materials presents high adsorption capacity, considerable mechanical strength, and low ash content. They also pointed out many attempts to obtain low-cost activated carbon or adsorbent from agricultural wastes such as wheat, corn straw, olive stones, bagasse, birch wood, miscanthus, sunflower shell, pinecone, rapeseed, cotton residues, olive residues, pine rayed, eucalyptus maculata, sugar cane bagasse, almond shells, peach stones, grape seeds, straw, oat hulls, corn stover, apricot stones, cotton stalk, cherry stones, peanut hull, nut shells, rice hulls, corn cob, corn hulls, hazelnut shells, pecan shells, rice husks and rice straw.

In his review, Crini (2006) presented a wide variety of carbons prepared from agricultural and wood wastes which can be used for dye removal from textile effluents. It was pointed that non-conventional activated carbons exhibit high sorption properties, for example: activated carbons made from corncob have very large values of 1060–790 mg of dye per g of carbon. Table III.8 synthesizes reported adsorption capacities in mg.g^{-1} for carbon materials made from solid wastes and compare it with coal-based sorbents (commercial activated carbon precursors) performance.

However, the adsorption capacities of a carbon depend also on the different sources of raw materials, the history of its preparation, treatment conditions such as pyrolysis temperature and activation time, surface chemistry (heteroatom content), surface charge and pore structure (Crini, 2006).

Table III.8 - Reported adsorption capacities (q_{max}) for carbon materials made from solid wastes and coal-based sorbents (Adapted from Crini, 2006).

Adsorbent	Dye	q_{max} (mg.g^{-1})
Pinewood	Acid blue 264	1176
Pinewood	Basic blue 69	1119
Corncob	Acid blue 25	1060
Bagasse	Basic red 22	942
Cane pith	Basic red 22	941.7
Corncob	Basic red 22	790
Bagasse	Acid blue 25	674
Cane pith	Acid blue 25	673.6
Pinewood	Basic blue 9	556
Rice husk	Basic green 4	511
Bagasse	Acid blue 80	391
Waste newspaper	Basic blue 9	390
Coal	Basic blue 9	250
Waste carbon slurries	Acid blue 113	219
Waste carbon slurries	Acid yellow 36	211
Waste carbon slurries	Ethyl orange	198
Sewage sludge	Basic red 46	188
Mahogany sawdust	Acid yellow 36	183.8
Coal	Basic red 2	120
Sewage sludge	Basic blue 9 et al.	114.94
Charcoal	Acid red 114	101
Rice husk	Acid yellow 36	86.9
Rice husk	Acid blue	50
Charfines	Acid red 88	33.3
Lignite coal	Basic blue 9	32
Lignite coal	Acid red	30.8
Bituminous coal	Acid red 88	26.1
Rice husk	Basic blue 9	19.83
Straw	Basic blue 9	19.82
Date pits	Basic blue 9	17.3
Hazelnut shell	Basic blue 9	8.82
Coir pith	Acid violet	8.06
Charfines	Direct brown 1	6.4
Coir pith	Direct red 28	6.72
Sugarcane bagasse	Acid orange	5.78
Coir pith	Basic violet 10	2.56

3.7 Activated carbon production

Basically, there are two main steps for the preparation and manufacture of activated carbon (Ioannidou and Zabaniotou, 2007):

(1) Carbonization (pyrolysis) of the carbonaceous raw material below 800 ^{0}C, in the absence of oxygen or in an inert atmosphere (usually nitrogen).

(2) Activation of the carbonized product (char), which is either physical or chemical.

During the carbonization step, most of the non-carbon elements (mainly volatiles) are removed, leaving a char with high carbon content and slight porosity. In addition, a large number of repaired electrons are trapped in the microcrystallite structure of activated carbon due to bond breakage at the edge of the planar structure. Foreign atoms such as oxygen and hydrogen interact with these electrons to form surface complexes or functional groups (Qada et al., 2008).

Physical activation is a two-step process. It involves carbonization of a carbonaceous material followed by the activation of the resulting char at elevated temperature in the presence of suitable oxidizing gases such as carbon dioxide, steam, air or their mixtures. The activation gas is usually CO_2, since it is clean, easy to handle and it facilitates control of the activation process due to the slow reaction rate at temperatures around 800°C (Ioannidou and Zabaniotou, 2007). In general, considering lignocellulosic precursors, activation with CO_2 leads to the creation and widening of small micropores, whereas activation with steam only promotes widening of the existing micropores in the char structure (Rodríguez-Reinoso and Molina-Sabio, 1998). The final properties of the activated carbon are strongly influenced by the activation temperature and duration. A complete review about carbonization and activation conditions for various agricultural residues can be found at Ioannidou and Zabaniotou (2007).

Chemical activation is a single-step process including the impregnation of the carbonaceous material with dehydrating agent prior to carbonization. The significance of the impregnation is to enhance the pore structure of precursor and hence increases its surface area (Qada et al., 2008). Chemical activation offers several advantages since it is carried out in a single step, combining carbonization and activation, performed at lower temperatures and therefore resulting in the development of a better porous structure, although the environmental concerns of using chemical agents for activation could be developed (Ioannidou and Zabaniotou, 2007). The chemical agents used in the chemical process are normally alkali and alkaline earth metal containing substances and some acids such as KOH, K_2CO_3, NaOH, Na_2CO_3, $ZnCl_2$, $MgCl_2$ and H_3PO_4. Although, phosphoric acid is shown to be the most environmentally sound chemical for the activation processes, most studies have used zinc chloride due to its effective activating capability (Qada et al., 2008).

Chemical activation also modifies the chemical make up of the adsorbent surface, thus altering its functionality in regard to its affinity to specific sorbates (Oliveira and Franca, 2008). Activated carbon is invariably associated with appreciable amounts of heteroatoms such as oxygen and hydrogen chemically bonded to the structure, and with inorganic ash components. Oxygen surface groups are by far the most important in influencing the surface characteristics and adsorption behavior of activated carbon. The precise nature of carbon-oxygen structures is not entirely established but the results of many studies using different experimental techniques conclude that there may be several types of oxygen functional groups, as carbonyl, lactone, phenol, carboxyl, ether, pyrone and chromene. The presence of these surface groups gives activated carbons an acid-base character (Rodríguez-Reinoso and Molina-Sabio, 1998).

Oliveira and Franca (2008) point out some methods for preparation of lignocellulosic material-based activated carbon, described in the literature. They can be conducted in a diversity of equipments such as common lab muffle (Gupta et al., 2005; Sathishkumar et al., 2007; Malik et al., 2007; Rao et al., 2008), tube furnaces (Gergova and Eser, 1996; Savova et al., 2001), domestic microwave oven (Hirata et al., 2002), benchscale fixed and fluidized bed reactors (Guerrero et al., 2008) and industrial pyrolyser (Zabaniotou et al., 2008).

3.8 Activated carbon characterization methods

In the past, most of the characterization of activated carbons was focused on the physical structure, mainly the porosity which was determined by adsorption techniques using gases with molecules of known sizes and properties such as N_2 and CO_2 in the BET (Brunauer, Emmett-Teller) method. For a rough estimate of the porosity, and internal surface area, adsorption of other molecules of known sizes and properties (such as iodine, methylene blue, rhodamine B and others) are also used for the characterization of the carbon texture. The porosity is the major property responsible for the carbon texture and consequently it will dictate its mechanical properties, which are fundamental to the design and selection of the type of equipment to be employed in large-scale adsorption processes (Oliveira and Franca, 2008).

It is now widely accepted that a complete characterization of adsorbent carbons must include their chemical characteristics of the adsorbent surface. The chemical composition of the surface also plays an important role in the adsorption behavior (Rodríguez-Reinoso and Molina-Sabio, 1998). Emphasis should be placed in the determination of the types of oxygenated functional groups present which play a major role in influencing the surface characteristics and consequently the adsorption as a whole (Oliveira and Franca, 2008).

3.8.1 Physical and textural characterization

Adsorption of gases and vapors is perhaps the most widely used technique for the characterization of microporous carbons. Firstly, the adsorption isotherm is obtained, and then different methods such as Dubinin-Radushkevich or BET are applied to quantify the pore volume or surface area. Alternatively a technique such as n-nonane pre-adsorption can also be used. However, the determination of the micropore volume is not straightforward since results are a function of both the method used to analyze the adsorption isotherm and the adsorbate selected, because the micropore filling mechanism is conditioned by the pore width/molecular dimension ratio ($d\rho/\sigma$) and not by the absolute value of the pore width. Consequently, a good approach would be to use the adsorption of various adsorbate and to apply different approximations to a series of microporous carbons with gradual evolution of pore dimension (Rodríguez-Reinoso and Molina-Sabio, 1998).

The surface area determined by the adsorption of small gaseous molecules (e.g. N_2, Ar, CO) is not necessarily equal to the surface area accessible to larger dissolved or solvent molecules. Nevertheless, the determination of the surface area from the N_2 gas adsorption data by the BET equation is one of the standard methods for porous solids characterization. The change in the BET surface area and the shape of the gas adsorption and desorption isotherms are representative indicators of the surface area and the pore structure that was developed during the activation process (László et al., 1997).

Another important parameter on the physical characterization of activated carbon is the pore size distribution which can be determined by the BJH (Barrett-Joyner-Halenda) method. BJH is also used to determine the mesopores radius, calculated by the Kelvin equation on the desorption region of the gas isotherm (higher pressures). In order to determine larger size porosity of activated carbons, it is necessary to employ the mercury porosimetry technique (Rodríguez-Reinoso and Molina-Sabio, 1998). It consists on applying pressure to a recipient containing mercury which involves the adsorbent sample. Due to this procedure, mercury penetrates into the adsorbent pores. The intrusion pressure which is related to the intrusion volume is measured and the diameter of pores is calculated.

The structure of a carbonaceous material is understood to be closely linked with the porosity of the material. The building block in carbons is primarily graphitic sheets, which are characterized by strong covalent bonding in the basal plane to three adjacent carbons, and weak van der Waals bonding between the basal planes. However, the structure of activated carbon is thought to be much less ordered than that of graphite. It is generally believed that two generic structural types exist. The first type consists of elementary crystallites, which are two-dimensional and analogous to graphite, with parallel layers of hexagonally-ordered carbon atoms. The second type is described as disordered, cross-linked space lattice of the carbon hexagons, which results from their deflection from the planes of the graphitic lattice (Haghseresht et al., 1999).

In order to estimate activated carbon structural data, two important methods can be cited: Raman spectroscopy and X-ray diffraction (Kastening et al., 1997).

Raman spectroscopy is a very useful tool in investigating structural variations of carbonaceous materials on adsorbents preparation. It is established that there are five structure-sensitive lines in Raman spectra of various carbonaceous materials. The graphite line (G band) is found at 1580 cm^{-1}. The disorder line (D band) as the result of condensed aromatic hydrocarbons is found at 1360 cm^{-1}. At 1620 cm^{-1}, the line responsible for the broadening and shifting of the graphite band is visible; and the two other bands are found at 2700 and 2735 cm^{-1} (Haghseresht at al., 1999). They obtained information such as the ratio of aromatic carbon to aliphatic carbon, and oxygen content (C–O) groups for most precursors. Raman spectroscopy also gives information of the degree of variation of the structure of a carbonaceous material when an adsorbate is present.

X-ray diffraction technique is a powerful tool to analyze the crystalline nature of materials. If the material under investigation is crystalline, well-defined peaks are observed while non-crystalline or amorphous systems show a hallow instead of well-defined peak. Adsorption reaction may lead to change in molecular and crystalline structure of the adsorbent and hence an understanding of the molecular structure and crystalline structure of the adsorbent and the resulting changes therefore would provide valuable information regarding adsorption reaction (Namasivayam and Kavitha, 2006).

Morphology is also an important aspect to be studied on the characterization of the adsorbent. Scanning electron micrograph studies (SEM) is widely used to study the morphological features and surface characteristics of the adsorbent materials. It is usual to study the morphological changes in the carbon surfaces following adsorption of dyes and phenol molecules. Scanning electron micrographs of unloaded and loaded adsorbents can indicate changes on the morphological features (Namasivayam and Kavitha, 2006).

3.8.2 Chemical characterization

The chemical characterization of a carbon surface is mainly concerned with the determination of the amount of heteroatoms and their type of bonding to the carbon skeleton, i.e. the nature of the surface groups. Oxygen is the more common heteroatom in porous carbons and there is a series of oxygen surface groups of interest for their adsorption properties. Since most activated carbons are prepared by a thermal process (i.e., gasification of a char at high temperature in the presence of carbon dioxide, steam or a mixture of them), the resultanting product usually possesses a low amount of oxygen surface groups mostly originated by chemisorption of oxygen from air, and it is usual practice to increase their amount by oxidation of the carbon in air or with solutions of nitric acid, hydrogen peroxide, without essentially modifying the porous texture (Rodríguez-Reinoso and Molina-Sabio, 1998).

The presence of oxygenated functional groups on the surface of an activated carbon provides an acid-base character. The identification of main chemical groups of these carbon surfaces is frequently carried out using indirect methods, such as selective neutralization by titration methods. The selective neutralization studies carried out by Boehm (1994) on several carbons suggested that $NaHCO_3$ neutralized carboxylic acid functionalities, Na_2CO_3 neutralized both carboxylic acids and lactones, and NaOH neutralized carboxylic acids, lactone and phenols (Rodríguez-Reinoso and Molina-Sabio, 1998). Surface functional groups can also be identified by spectroscopic methods such as temperature-programmed desorption (TPD), X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FT-IR) or diffuse reflectance Fourier transform infrared (DRIFTS) (Jung et al., 2001).

Temperature programmed desorption (TPD) can be utilized to determine the strength of the surface active groups, quantity, and type of activated carbon. Temperature programmed desorption carried out on carbons shows that the oxygen surface groups decompose upon heating and the evolved gases consist mainly of CO_2 at lower temperatures and predominantly CO at higher temperatures. Tremblay et al. (1978) suggested that CO_2 evolution is due to the decomposition of surface carboxyl and lactone, while decomposition of carbonyl, quinone and anhydride groups is responsible for CO evolution (Rodríguez-Reinoso and Molina-Sabio, 1998).

IR analysis permits spectrophotometric observation of the adsorbent surface in the range 400–4000 cm^{-1} spectra, and serves as a direct means for the identification of the organic functional groups on the surface. An examination of the adsorbent surface before and after adsorption reaction possibly provides information regarding the surface groups that might have participated in the adsorption reaction and also indicates the surface site(s) on which adsorption has taken place. IR studies indicate the participation of the specific functional groups in adsorption interaction (Namasivayam and Kavitha, 2006). The use of solely IR spectroscopy to investigate adsorbents is not satisfactory because of the strong absorption of IR by carbon, so improvements on the technique have been accomplished by FT (Fourier Transform) spectrometers (Boehm, 1994).

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4. PERFORMANCE OF COLD-PRESSED CAKE FROM *RAPHANUS SATIVUS (L. VAR.)* OILSEEDS, A SOLID RESIDUE FROM BIODIESEL PRODUCTION, AS ADSORBENT FOR BASIC DYES

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Abstract

Cold-pressed cake from *Raphanus sativus (L. Var.)* seeds, a solid residue from biodiesel production, was evaluated as an adsorbent for removal of methylene blue (MB) from aqueous solution. Batch adsorption tests were performed at room temperature (25°C) and the effects of particle size, contact time, adsorbent dosage and pH were investigated. Adsorption kinetics was determined by fitting first and second-order kinetic models to the experimental data, with the second-order model providing the best description of MB adsorption onto the prepared adsorbent. The experimental adsorption equilibrium data were fitted to Langmuir and Freundlich adsorption models, with Langmuir providing the best fit. Langmuir based maximum MB uptake capacity was 19.8 mg g^{-1}, higher than other adsorbents employing similar types of residues, such as sunflower oil cake, coffee seeds press cake and date pits.

Keywords: *adsorption; biodiesel solid waste; dye removal.*

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4.1 Introduction

Wastewaters generated by the textile, leather, paper, and plastics industries constitute hazardous materials that may cause severe negative environmental impact when discharged without adequate treatment. Such effluents are primarily characterized by parameters as BOD (biochemical oxygen demand), COD (chemical oxygen demand), DO (dissolved oxygen), turbidity, color, heavy metals, and total dissolved and suspended solids. Conventionally, wastewater treatment processes include primary and secondary steps, with an advanced treatment step usually required in order to comply with strict environmental regulations. The main recalcitrant compounds present in textile effluents are the synthetic dyes which are used during fiber dying processes (Asad et al., 2007). Aside from aesthetic aspects, the majority of such compounds are of significant health concern even at low concentrations in water. Thus, widespread contamination of soil and groundwater by dyes has been recognized as an issue of growing importance in recent years. In this aspect, environmental regulations in most countries have made it mandatory to decolorize wastewaters prior to discharge in natural water streams.

Decoloration of aqueous solutions is carried out by one or more of the following methods: coagulation, adsorption, chemical degradation, ultrafiltration, photodegradation with ozone, electrochemical flotation and biodegradation (Robinson et al., 2001). The main drawback with these technologies is that they generally lack the broad scope treatment efficiency required to simultaneously reduce the multitude of pollutants present in textile wastewater. Furthermore, for most of these processes, the capital and/or operating costs often become prohibitive when applied to the large scale water treatment requirements of this type of industries. Regardless of the performance presented by the available techniques for color removal from textile effluents, efficient and yet cost effective technologies for remediation of dyes in these effluents have been recently extensively investigated (Asad et al., 2007; Crini, 2006).

Particularly in the case of adsorption onto activated carbon, the main disadvantages of the treatment process are associated to the high cost of the adsorbent, as well as the high initial capital investment, long residence times, and the need for frequent and/or expensive regeneration processes. The adsorbent cost is usually high due to the use of non-renewable and relatively expensive precursor materials such as coal, which is not justifiable in pollution control applications (Martin et al., 2003). Even with such limitations, adsorption has been proven a suitable method to reduce BOD, COD and color from textile effluents, thus it becomes a competitive method for effluent treatment if renewable and cheaper adsorbents prepared from alternative precursor materials are used (Padmesh et al., 2006; Bhattacharya et al., 2008). In recent years, this insight has prompted a growing research interest in the production of activated carbons from renewable and low-cost precursors which are mostly industrial and agricultural by-products such as silk cotton hull and maize (Kadirvelu et al., 2003), jute fiber (Senthilkumaar et al., 2005), groundnut shell (Kannan and Sundaram, 2001), bamboo (Hameed et al., 2007), coconut husk (Tan et al., 2008), coffee husks (Oliveira et al., 2008), agricultural wastes (Demirbas et al., 2004), and many other alternative materials. Comprehensive reviews on preparation and application of low-cost sorbents from agri-food wastes have been recently published (Ioannidou and Zabaniotou, 2007; Crini and Badot, 2008; Oliveira and Franca, 2008; Demirbas, 2008). According to Oliveira and Franca (2008), low-cost adsorbents prepared from agricultural and food wastes may be the most promising type of biomaterials that will lead to a globalized bio-based economy. The production and applicability of such sorbents has been several times proven economical and effective. In this regard, a few recent studies have shown that adsorbents prepared from seed press cakes can be employed for adsorption of dyes. Examples include oil palm fiber (Tan et al., 2007), sunflower oil cake (Karagöz et al., 2008), and defective coffee beans press cake (Nunes et al., 2008).

In view of the aforementioned, the objective of this work was to evaluate the feasibility of using cold-pressed cake from *Raphanus sativus (L. Var.)* seeds, a solid residue from the biodiesel production industry, as precursor for the preparation of adsorbents for the removal of methylene blue (MB) from dilute aqueous solutions. Methylene blue ($C_{16}H_{18}N_3SCl$) was chosen as a model dye due to its wide use for dying cotton, wood and silk. This study, conducted in lab scale batch conditions, also aimed at evaluating the performance of the prepared sorbents by means of studying the equilibrium and kinetic behavior of MB adsorption process onto them, thus converting biodiesel solid waste into an inexpensive adsorbent for removal of dyes from textile wastewaters.

4.2 Experimental

4.2.1 Materials

Raphanus sativus (L. Var.) seeds were screw-pressed (Ecirtec, Brazil) for oil removal. The press cake (PC) was then submitted to the following treatments: (i) excess oil removal by Sohxlet extraction at 60°C for 6h (PCOR); (ii) one-step physical activation procedure at 800°C (PCAC): the samples, in ceramic containers, were placed in an electric muffle furnace at 100°C (temperature held for 10 min), heated to 300°C at a rate of 10°C min^{-1} and then heated to 800°C at a rate of 10°C min^{-1} under N_2 flow (0.5 L min^{-1} flow rate). This temperature was maintained for 40 min and the samples were then cooled for production of the activated carbon (PCAC). The thermal activation procedure was established based on preliminary tests and literature data on production of activated carbons by thermal activation of coffee beans press cake (Nunes et al., 2008). The cationic dye used as target adsorbate was methylene blue (MB - C.I. 52015), 15% hydrated, 95% purity, purchased from Labsynth Lab Products (São Paulo, Brazil). Evaluation of the Point of Zero Charge (pH_{PZC}) was based on a potentiometric titration procedure (Valdés et al., 2002). The morphological characteristics of the adsorbent surface, before and after carbonization, were investigated by scanning electron microscopy – SEM (JSM-6360LV Scanning Electron Microscope), with samples been covered with a thin layer of gold. The samples were also analyzed in an Autosorb-1 MP (Quantachrome, USA) by measuring N_2 isotherms at 77 K for the determination of such textural properties as surface area, total pore volume and average pore diameter. For such studies, the samples were outgassed at 473 K under vacuum for 3 h. The specific surface area value was calculated according to the Brunauer–Emmett–Teller (BET) equation and pore parameters (pore volume and pore diameter) were evaluated based on Barrett–Joyner–Halenda (BJH) model.

4.2.2 Adsorption

Batch adsorption experiments were performed in 250 mL agitated Erlenmeyer flasks (100 rpm) for pre-established time intervals. The flasks were covered with aluminum foil to prevent photodegradation (Nunes et al., 2008). In all sets of experiments, a pre-determined amount of adsorbent was thoroughly mixed with 100 mL of methylene blue

(MB) solution. Preliminary adsorption tests were conducted employing the following fixed parameters: initial MB concentration = 100 mg L^{-1}, initial pH = 5, and adsorbent concentration = 10 g L^{-1}. Effect of particle size (diameter = D) was evaluated in the following ranges: $D< 0.425$ mm; 0.425 mm $\leq D \leq$ 0.850 mm; $D \geq 0.850$ mm. Effects of pH and adsorbent concentration were studied in the respective ranges of 3 to 11 and of 5 to 50 g L^{-1} at a fixed initial dye concentration (200 mg L^{-1}). Effect of contact time was evaluated at time periods ranging from 15 min to 72 hours and initial dye concentrations ranging from 100 to 500 mg L^{-1} at a fixed adsorbent concentration (10 g L^{-1}). All tests were performed in duplicates.

4.3. Results and discussion

4.3.1. Adsorption

The Preliminary adsorption tests were performed in order to verify the effects of thermal treatment and presence of residual oil on adsorption performance. Results are displayed in Figure 4.1. removal of residual oil provided a slight increase in adsorption capacity (61 to 67%), whereas carbonization resulted on a significant improvement in the adsorbent performance (100%). The effect of carbonization on increasing adsorption capacity is probably due to an increase in porosity as can be observed in the SEM pictures (Figure 4.2), coupled to a change in surface chemical composition. Similar behavior has been reported by other studies (Bouchelta et al., 2008). Considering that adsorption capacity practically doubled as a consequence of the thermal treatment, the remaining tests of the present study were conducted solely with the activated carbon (PCAC). The initial MB concentration was increased to 200 mg L^{-1} in order to better verify the effect of adsorption parameters, given the quite high adsorption efficiency at 100 mg L^{-1}. It is noteworthy to mention that, given the reasonable adsorption capacity of the agricultural residue itself (PC and PCOR), adsorption tests will also be considered for future studies. Results from BET tests for the activated carbon were the following: specific surface area = 236.3 m^2g^{-1}; total pore volume = 0.06 cm^3g^{-1}; average pore diameter = 1.4 nm.

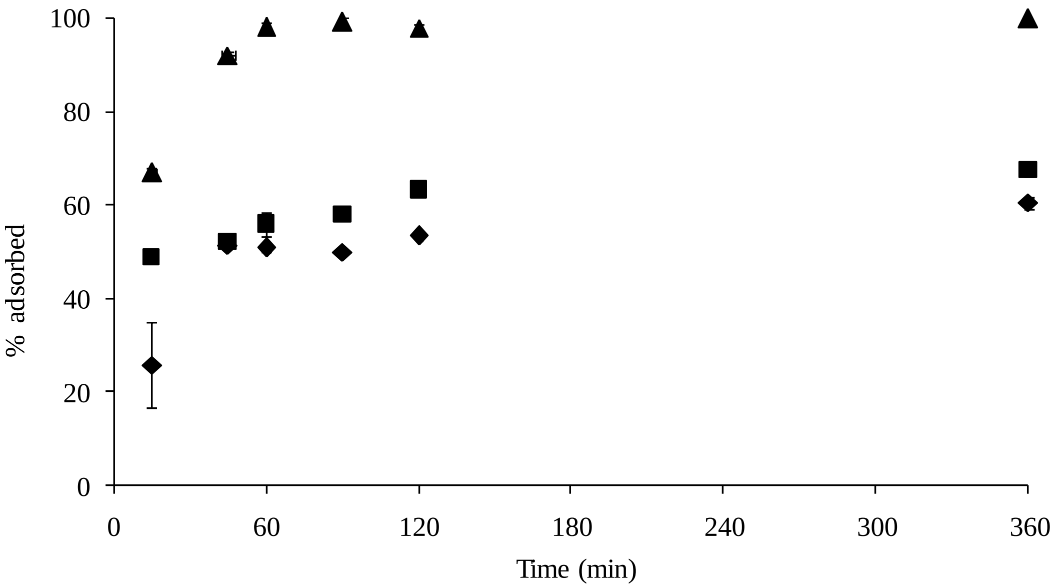
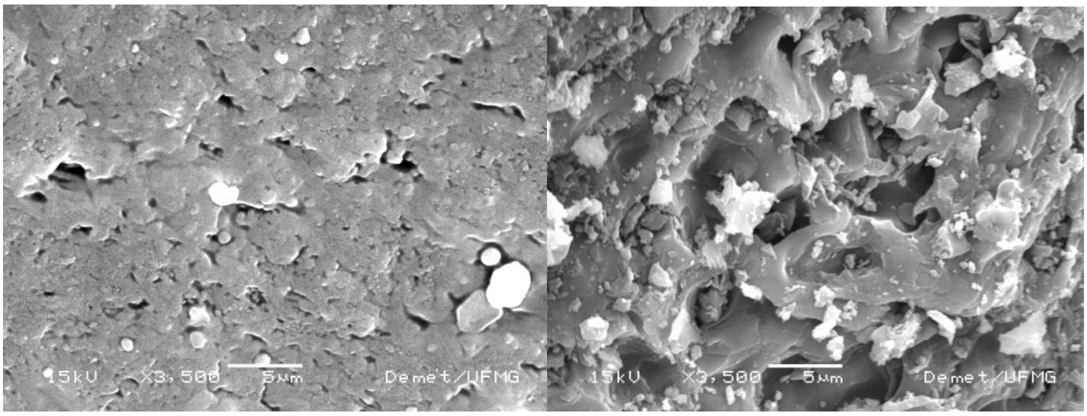


Figure 4.1 – Preliminary adsorption tests (initial pH 5, initial MB concentration 100 mg L^{-1}, adsorbent dosage 10 g L^{-1}): ◆PC, ■PCOR, ▲PCAC.



(a) (b)

Figure 4.2 – SEM images showing surface morphologies of the adsorbent (a) before (PC) and (b) after carbonization (PCAC).

The results obtained for varying contact time and initial dye concentration are displayed in Figure 4.3. Experiments were conducted employing the following parameters: adsorbent dosage of 10 g L^{-1}, pH 5 and D < 0.425 mm. A detailed discussion on the effect of such parameters on the adsorption performance is presented in section 4.3.2. The results displayed in Figure 4.3 indicate that, for MB adsorption by PCAC, a contact time of 12 hours assured attainment of equilibrium conditions for an initial dye concentration of 100 mg L^{-1}. Equilibrium could not be observed for higher initial MB concentrations, even after 72h adsorption (data not shown). Regardless of the initial MB concentration, the adsorption process can be described by a two-stage kinetic behavior, with a rapid initial adsorption during the first 6 hours, followed by a much slower rate afterwards. A similar behavior has been reported for MB adsorption by activated date pits (Banat et al., 2003) and spent coffee grounds (Franca et al., 2008). The faster adsorption of methylene blue at the lower concentration indicates that adsorption occurs mainly on the surface of the adsorbent. This was expected given the measured average pore size being smaller than the size of the MB molecule, ~1.5 nm (Xun et al., 2007). As the initial MB concentration increases, the adsorption is separated into two phases: (i) fast adsorption resulting from the rapid attachment of the MB molecule onto the adsorbent surface; (ii) slow adsorption inside the pores as a function of the small fraction of adsorbent pores with a greater diameter compared with MB molecule diameter (Banat et al., 2003). Results presented in Figure 4.3 also show that adsorption of MB by PCAC presents a strong dependency of MB initial concentration. An increase in the initial MB concentration from 100 to 500 mg L^{-1} resulted on a respective increase in the amount adsorbed after 72h from 7.3 to 21.2 mg g^{-1}. This is attributed to the increase in driving force (concentration gradient) with the increase in the initial dye concentration (Oliveira et al., 2008). However, adsorption efficiency (% adsorbed) decreased as MB initial concentrations increased as expected. An increase in the initial MB concentration from 100 to 500 mg L^{-1} led to a respective decrease in adsorption capacity from 99 to 53%, indicating external surface saturation. Also, no significant differences in the amount adsorbed were observed when the initial MB concentration was raised above 300 mg L^{-1}, confirming that adsorbent saturation was attained.

The controlling mechanism of MB adsorption by PCAC was investigated by fitting first and second-order models, with the rate equations defined as:

$$\frac{dq_t}{dt} = k_n (q_e - q_t)^n \tag{4.1}$$

where q_e and q_t correspond to the amount of MB adsorbed per unit mass of adsorbent (mg g^{-1}) at equilibrium and at time t, respectively; k_n is the rate constant for n^{th} order adsorption (k_n units are h^{-1} for n=1 and g h mg^{-1} for n=2).

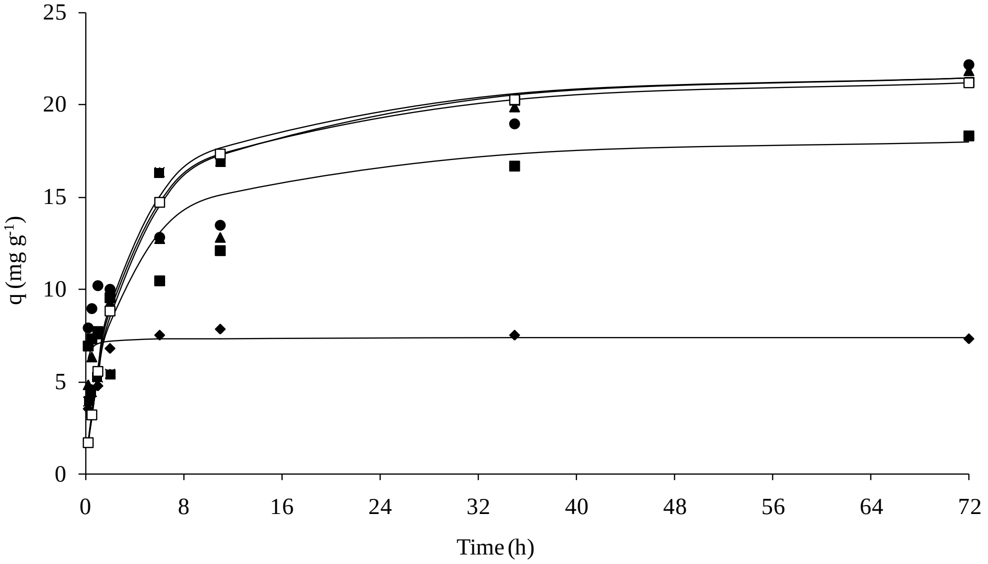


Figure 4.3 – Effect of contact time on MB adsorption by PCAC (initial solution pH = 5; adsorbent dosage = 10 g L^{-1}; adsorbent particle size ≤0,425mm; T = 25°C). Initial MB concentration: ◆100 mg L^{-1}, ■ 200 mg L^{-1}, ▲300 mg L^{-1}, ●400 mg L^{-1}, □500 mg L^{-1}. Solid lines correspond to pseudo-second order kinetics model fits.

The results of the kinetic parameters are displayed in Table IV.1. The first-order model did not provide a good fit, with q_e values being significantly underestimated compared to the experimental values. An evaluation of both the correlation coefficients and estimated q_e values indicates that MB adsorption by PCAC can be satisfactorily described by the pseudo second-order model (maximum error between estimated and experimental q_e was 4%). Thus, it can be inferred the rate limiting step may be chemisorption promoted by either valency forces, through sharing of electrons between adsorbent and sorbate, or covalent forces, through the exchange of electrons between the parties involved (Oliveira et al., 2008). The values of the rate constant decreased with increasing initial MB concentration, without significant differences at higher concentrations (≥ 300 mg L^{-1}).

Table IV.1 – Kinetic parameters for MB adsorption by PCAC.

Pseudo first-order

MB initial concentration (mg L^{-1})	$q_{e\ calc}$	K (h^{-1})	% diff.*	R^2
100	5.37	1.076	26.4	0.936
200	10.99	0.054	40.0	0.993
300	15.35	0.058	29.8	0.980
400	13.17	0.041	40.5	0.986
500	14.72	0.083	30.5	0.907

Pseudo second-order

MB initial concentration (mg L^{-1})	$q_{e,\ calc}$	K (g.h.mg^{-1})	% diff.*	R^2
100	7.35	3.045	0.7	0.999
200	18.61	0.021	-1.6	0.994
300	22.41	0.045	-2.6	0.991
400	22.31	0.045	-0.8	0.989
500	22.03	0.045	-4.0	0.997

Intraparticle diffusion

MB initial concentration (mg L^{-1})	k_p (mg g^{-1} $h^{-1/2}$)	C (mg g^{-1})	R^2
100	0.389	5.052	0.438
200	1.489	6.691	0.970
300	2.120	5.597	0.948
400	1.761	7.806	0.986
500	2.368	4.646	0.788

*percent difference between calculated and experimental q_e values

The effect of diffusion as the rate controlling step in the adsorption was evaluated according to the intraparticle diffusion model (Weber and Morris, 1963) given by:

$$q = k_p t^{1/2} + C \tag{4.2}$$

where k_p is the intraparticle diffusion rate constant, evaluated as the slope of the curve q_t vs. $t^{1/2}$ (see Figure 4.4). Curves for 300 and 500 mg L^{-1} were not presented in order to provide better visualization, since they did not present significant differences in comparison to the concentration of 400 mg L^{-1}. Model coefficients are displayed in Table IV.1. A comparison of the curves from figure 4.4 and the parameters displayed in Table IV.1 clearly demonstrates the difference in adsorption mechanism between the 100 mg L^{-1} curve and the ones for higher initial MB concentration, indicating that diffusion is of significance only for initial MB concentrations ≥ 200 mg L^{-1}. If the line pass through the origin (C=0), then intraparticle diffusion should be the rate-controlling step (Weber and Morris, 1963). An evaluation of the C coefficients in Table IV.1 indicates that, although of significance for the adsorption process, intraparticle diffusion is not the rate-controlling mechanism, even for the highest initial MB concentration.

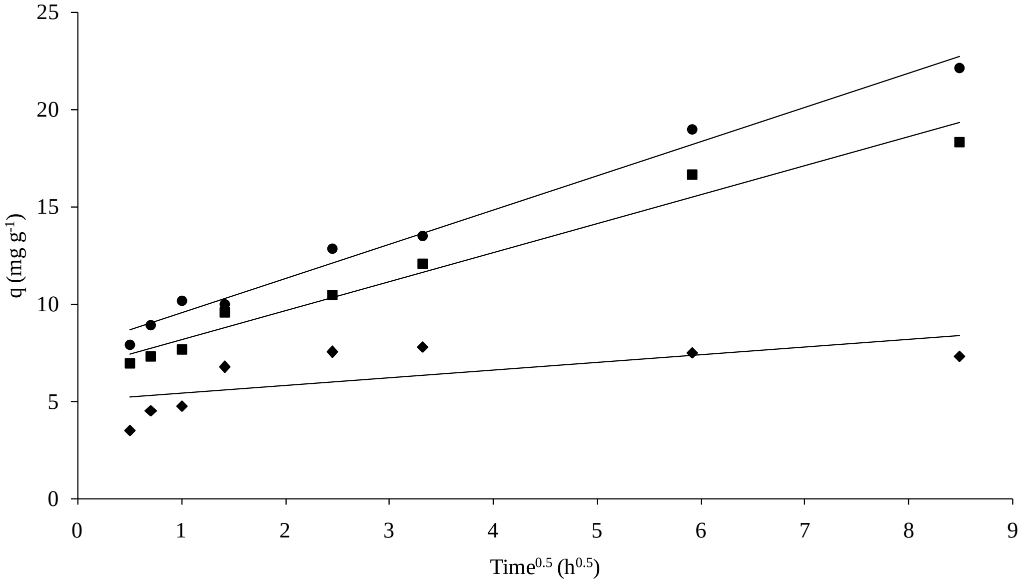


Figure 4.4 – Evaluation of intraparticle diffusion model for MB adsorption by PCAC. Initial MB concentration: ◆100 mg L^{-1}, ■ 200 mg L^{-1}, ●400 mg L^{-1}. Solid lines correspond to linear fits.

The adsorption isotherm after 72h at 25°C is presented in Figure 4.5. The shape of the curve indicates favorable adsorption. Langmuir and Freundlich adsorption models were evaluated for description of the MB sorption isotherm. Langmuir isotherm, based on a theoretical model, assumes monolayer adsorption over an energetically and structurally homogeneous adsorbent surface and does not take into account interactions between adsorbed molecules. It can be represented by the following equation:

$$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e} \tag{4.3}$$

where q_e (mg g^{-1}) is the amount adsorbed per gram of adsorbent and C_e (mg L^{-1}) is the solute concentration in the aqueous solution after equilibrium was reached. q_{max} and K_L are constants related to the maximum adsorption capacity (mg g^{-1}) and the adsorption energy (L mg^{-1}), respectively. Another characteristic parameter of the Langmuir isotherm is the dimensionless factor r, called separation factor:

$$r = (1 + K_L C_0)^{-1} \tag{4.4}$$

where C_0 corresponds to the highest value for initial sorbate concentration (mg L^{-1}). The value of r is related to the type of the isotherm, and can indicate either unfavorable ($r > 1$), linear ($r = 1$), favorable ($0 < r < 1$) or irreversible ($r = 0$) adsorption.

Freundlich´s equation, an empirical model based on heterogeneous adsorption over independent sites, can be written as:

$$q_e = K_F C_e^{1/n} \tag{4.5}$$

where K_F represents the relative adsorption capacity ($mg^{1-(1/n)} L^{1/n}$ g^{-1}) and n is related to the intensity of adsorption, with values of $n > 1$ indicating favorable adsorption.

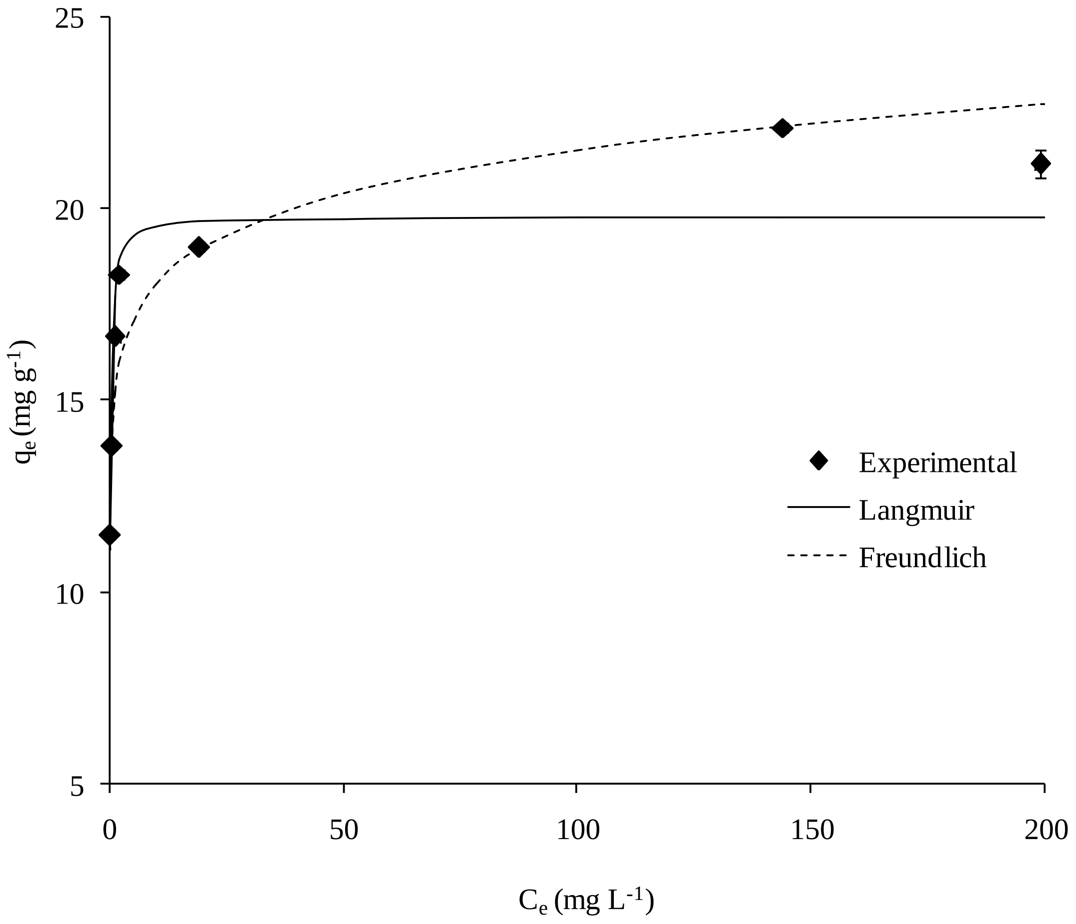


Figure 4.5 – Adsorption isotherm of MB by PCAC (Initial solution pH = 5; adsorbent dosage = 10 g L^{-1}; adsorbent particle size ≤0,425mm; T = 25°C; t = 72 h).

Langmuir and Freundlich coefficients are shown in Table IV.2. MB adsorption from aqueous solutions by PCAC was better described by Langmuir equation in comparison to Freundlich. An evaluation of r (separation factor) value presented in Table IV.2 corroborates the statement of favorable and irreversible adsorption. Maximum MB uptake capacity, represented by q_{max} in Langmuir equation, was 19.8 mg g^{-1}, a higher value in comparison to other adsorbents employing similar types of residues, such as apricot stones, coffee seeds press cake and date pits (Table IV.3). Regarding Freundlich isotherm, the slope 1/*n* ranging between 0 and 1 is a measure of adsorption intensity. A value for 1/*n* below one indicates a normal Langmuir isotherm while 1/*n* above one is indicative of cooperative adsorption. An average value of 0.077 was observed for 1/*n*, corroborating the homogeneous nature of the adsorbent surface also consistent with the Langmuir fit.

Table IV.2 – Langmuir and Freundlich isotherm constants for MB adsorption by PCAC.

	Constants
Langmuir	
K_L (L mg^{-1})	7.414
q_{max} (mg g^{-1})	19.81
R	0.0003
R^2	0.9326
Freundlich	
K_F	15.090
1/n	0.077
R^2	0.8517

Table IV.3 – Langmuir based maximum adsorption capacity of several adsorbents for MB adsorption near room temperature.

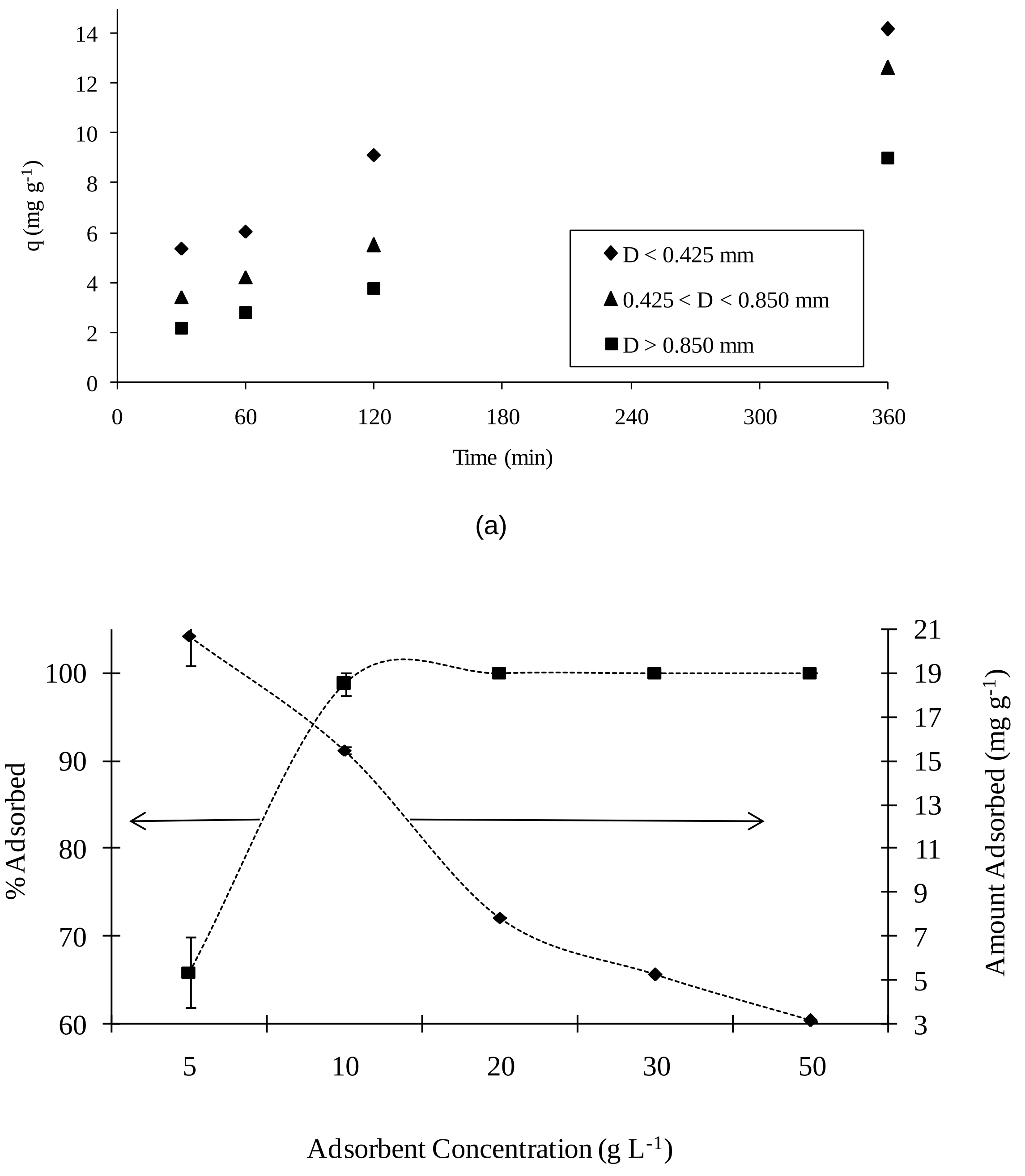
Residue (Activation Temp. °C)	**q_{max} (mg g^{-1})**	**Reference**
Fly ash* (140 °C)	19.9	Wang et al., 2006
PCAC* (800 °C)	19.8	This study
Date pits* (900°C)	17.3	Banat et al., 2003
Sunflower oil cake** (600°C)	16.4	Karagöz et al., 2008
Defective coffee beans press cake* (800°C)	14.9	Nunes et al., 2008
Date pits* (500°C)	12.9	Banat et al., 2003
Apricot stones** (750 °C)	4.1	Aygun et al., 2003

*thermal activation only; **thermal/chemical activation

4.3.2. Parameters

Particle size: To evaluate the effect of particle size on the adsorption process, the activated carbon was ground and sieved into three different size fractions: $D < 0.425$ mm; 0.425 mm $\leq D \leq$ 0.850 mm; $D \geq 0.850$ mm. Adsorption results are shown in Figure 4.6(a). These results show that MB uptake increased with the decrease in particle size, as a result of the corresponding increase in surface area and better accessibility to the pores (Nunes et al., 2008). Similar results on particle size effect have been reported for other residues including jute fibers (Senthilkumaar et al., 2005), date pits (Banat et al., 2003) and coffee beans press cake (Nunes et al., 2008).

Adsorbent dosage: The influence of adsorbent dosage on the efficiency of MB removal can be viewed in Figure 4.6(b). It can be observed that MB removal efficiency presented a significant improvement with the increase in adsorbent dosage. After 24h, the percent removal of MB varied from 66 to 100% with an increase in adsorbent concentration from 5 to 50 g L^{-1}. This is due to the increase in the adsorbent mass. However, the amount of dye adsorbed per unit mass of adsorbent decreased with increasing adsorbent mass, as expected. Similar behavior for the effect of adsorbent concentrations on MB sorption capacity was reported in the literature for other types of adsorbents (Oliveira and Franca, 2008; Banat et al., 2003). Based on the results presented in Figure 4.6, the kinetics and equilibrium experiments were conducted for an adsorbent dosage of 10 g L^{-1} and $D < 0.425$ mm.

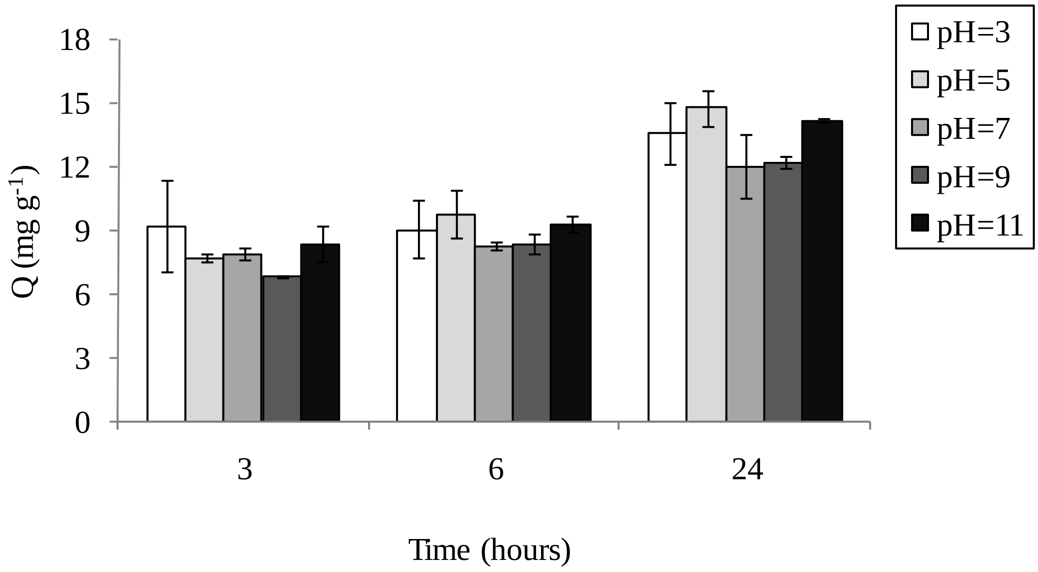


(a)

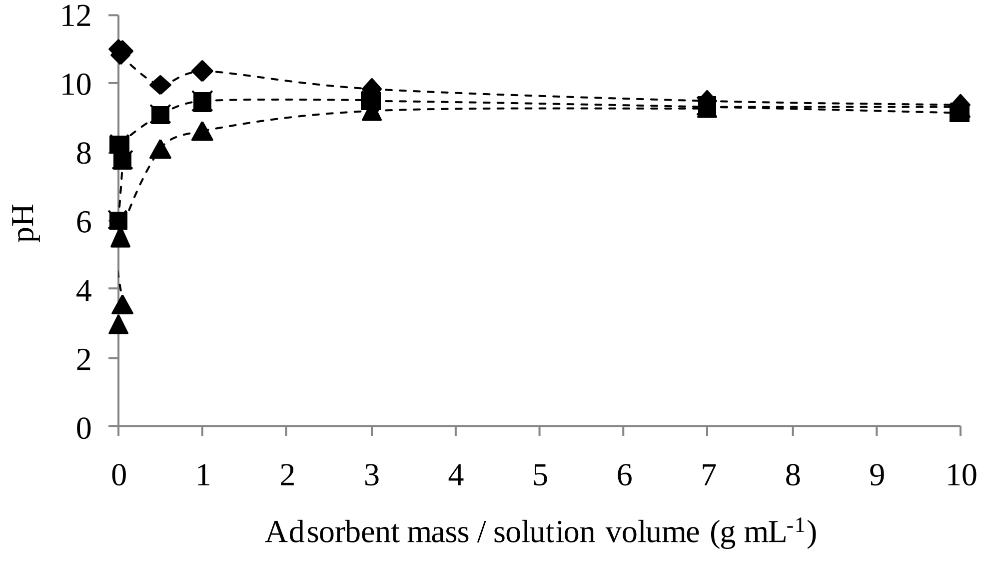
(b)

Figure 4.6 – Effect of (a) particle diameter (D) and (b) adsorbent dosage on MB adsorption by PCAC (initial MB concentration 200 mg L^{-1}, initial pH 5).

Initial solution pH: The initial solution pH should affect the adsorptive uptake of dyes due to its effect on the ionization process of the dye molecule (Oliveira and Franca, 2008; Nunes et al., 2008). In the present study, the effect of pH was investigated for values between 3 and 11 and the results are displayed in Figure 4.7(a). These results indicate that a small difference in adsorption capacities were observed, for a given adsorption time. Similar results are reported in the literature for MB adsorption (Nunes et al., 2008; Kavitha and Namasivayam, 2007). Also, the pH of the solutions was measured after all adsorption tests, and pH values varied during adsorption towards the pH_{PZC} (Figure 4.7(b)). In this study, at pH values below the pH_{PZC} (~9), even though the positively charged surface sites of the adsorbent do not favor dye adsorption due to electrostatic repulsion, dye removal was still efficient. This behavior suggests that π-π interactions between adsorbent and adsorbate are dominant in this case. Considering the high value of the activation temperature employed (800^0C), no acidic groups are expected to be present after carbonization (Nunes et al., 2008; Chun et al., 2004). The basic groups at the adsorbent surface are π electron donors. Since there were no significant differences in adsorption efficiency for pH values above and below the pH_{PZC}, hydration effects of protons interacting with carbon surface basic groups can be considered nearly non-existent (Nunes et al., 2008; Terzyk, 2004). Given that the initial solution pH did not present a significant effect on adsorption capacity, remaining tests were conducted at pH = 5, since it is the natural pH of the aqueous MB solution.



(a)



(b)

Figure 4.7 – (a) Effect of initial solution pH on MB adsorption by PCAC (initial MB concentration 200 mg L^{-1}, adsorbent dosage 10 g L^{-1}). (b) Experimental curves for pH_{PZC} determination (▲ Initial pH = 3, ■ Initial pH = 6, ◆ Initial pH = 11).

4.4 Conclusions

Experiments were conducted in order to investigate the potential of cold-pressed cake from *Raphanus sativus (L. Var.)* seeds, a residue from biodiesel production, as raw material for production of adsorbents. Adsorption kinetics was better described by a pseudo second-order model. Equilibrium data demonstrated favorable adsorption and were better described by the Langmuir model, in comparison to Freundlich, thus indicating homogeneous adsorption. The maximum value of uptake capacity obtained for the PCAC/MB system (19.8 $mg.g^{-1}$) was slightly higher in comparison to values encountered in the literature for other similar residue based activated carbons.

4.5 Acknowledgements

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5. CHARACTERIZATION OF THE ACTIVATED CARBON PRODUCED FROM *RAPHANUS SATIVUS (L. VAR.)*, A RESIDUE FROM THE BIODIESEL INDUSTRY, BEFORE AND AFTER METHYLENE BLUE ADSORPTION

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Abstract

In this study, activated carbon produced from *Raphanus sativus (L. Var.)*, a residue from the biodiesel industry, was characterized by SEM-EDS microscopy gas adsorption and Raman spectroscopy methods in order to understand the methylene blue (MB) adsorption behavior. Raman spectroscopy was found to be a potential method to characterize carbons as physical parameters obtained by BET, BJH and SEM analyses were corroborated by the Raman analysis on the regard of the porous structure and adsorption capacity of the studied carbon. It was verified that MB adsorption onto *Raphanus sativus (L. Var.)* activated carbon probably occurs by MB monomer species bonding through the central nitrogen atom of the MB molecule or also through the sulfur atom that may occur but at a lower intensity; MB bonding through the amino nitrogen atom was found to be not probable.

Key-words: adsorption; methylene blue; carbon characterization; Raman spectroscopy.

5.1. Introduction

The removal of synthetic dyes from textile wastewaters is extremely important to allow the reuse of water and/or the final discharge of effluent because most of such dyes are toxic, mutagenic and carcinogenic. Several methods have been developed to remove dyes from aqueous solutions in order to decrease their impact on the environment. A comparative survey of technologies including adsorption, coagulation, chemical degradation, ultrafiltration, photodegradation with ozone, electrochemical flotation and biodegradation is found elsewhere (Banat et al., 1996; Slokar and Le Marechal, 1998; Robinson et al., 2001; Crini, 2006; Santos et al., 2007; Lázaro et al., 2008).

As long as there is no universal method available for color removal from aquatic systems, some technologies have been extensively investigated for the remediation of dyes using non-conventional low-cost sorbents based on waste materials generated by industrial and/or agricultural activities such as wheat, corn straw, olive stones, bagasse, birch wood, miscanthus, sunflower shell, pinecone, rapeseed, cotton residues, olive residues, pine rayed, eucalyptus maculata, sugar cane bagasse and many others (Ioannidou and Zabaniotou, 2007). Recently the removal of methylene blue (MB) using activated carbons based on the pressed cake of *Raphanus sativus (L. Var.)*, which is a residue from the biodiesel industry, was found to be technically feasible (Lázaro et al., 2008).

In this context, the aim of this paper is to characterize the activated carbon produced from *Raphanus sativus (L. Var.)* using SEM-EDS (Scanning Electron Microscopy coupled with X-ray Energy Dispersive Spectrometry), gas adsorption and Raman spectroscopy methods in order to better understand the adsorption behavior of MB from aqueous solutions as those produced by textile industries.

5.2. Experimental

5.2.1. Preparation of the carbon from *Raphanus sativus (L. Var.)*

Activated carbon from *Raphanus sativus (L. Var.)* was prepared according to the following procedure. Firstly, seeds of *Raphanus sativus (L. Var.)* were screw-pressed (Ecirtec, Brazil) for oil extraction followed by Sohxlet extraction procedure at 60^{o}C for 6h to remove the excess of oil still present in the cake. Samples of the cake were weighted (20 g), placed in ceramic containers and then submitted to one-step thermal activation procedure (carbonization) using an electric muffle furnace.

During the carbonization, samples were initially burned at 100^{o}C for 10 min. Temperature was then raised at the rate of 10^{o}C min^{-1} to 800^{o}C; N_2 gas was injected into the furnace (N_2 flowrate = 0.5 L min^{-1}) when $T \geq 300^oC$ in order to create an inert atmosphere. Finally, temperature was maintained constant at 800^{o}C for 40 min. After carbonization samples were cooled down and submitted to the characterization testes described as follows. The carbonization procedure was based on preliminary tests and also on literature data for the production of carbons using coffee beans pressed cake as precursor material (Nunes et al., 2009).

5.2.2. Morphological analysis and determination of textural properties

Morphological characteristics of the adsorbent surface study (before and after carbonization) were carried out by Scanning Electron Microscopy (SEM) using a JEOL microscopy (model JSM6360LV). Due to the non-conductive nature of the material, samples were covered with a thin layer of gold. The qualitative composition at surface of some particles was obtained by SEM coupled with X-ray Energy Dispersive Spectrometry (EDS) using a Thermo Noram spectrometer (model Quest).

Surface area, total pore volume and average pore diameter were assessed by measuring multipoint N_2 isotherms at 77 K in an Autosorb-1 MP (Quantachrome). For such analysis, samples were outgassed at 473 K under vacuum for 3 h. The specific surface area value was calculated according to the Brunauer–Emmett–Teller (BET) equation and pore parameters (pore volume and pore diameter) were evaluated based on Barrett–Joyner–Halenda (BJH) model.

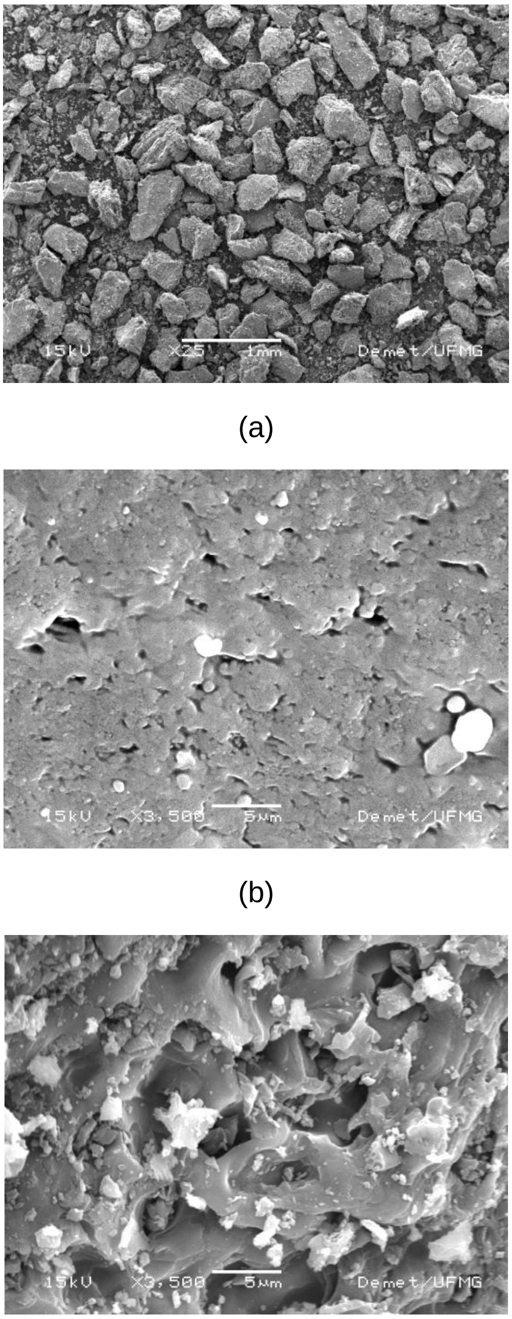
5.2.3. Raman spectroscopy analysis

Raman analysis was carried out in order to evaluate the structural change of the activated carbon due to the adsorption of MB using a Jobin-Yvon/Horiba Raman laser system (model Labran HR) coupled with a transference optic microscopy. Samples of carbon (unloaded and MB loaded samples) were analyzed under the following conditions: lens 100x, laser power < 1 mW, laser acquisition time = 20 s (acquisitions 5x), red laser wavelength = 632.8 nm, analysis in two points (1 μm). MB loaded carbon samples were obtaining by contacting MB solutions in 250 mL agitated Erlenmeyer flasks (100 rpm) at following conditions (Lázaro et al., 2008): Initial MB concentration = 500 mg L^{-1}; initial solution pH = 5; adsorbent dosage = 10 g L^{-1}; adsorbent particle size ≤0,425mm; T = 25°C; t = 72 h. The flasks were covered with aluminum foil to prevent photodegradation. As it was not possible to get the Raman spectra for MB solutions in concentrations as those commonly used in the adsorption tests (an intense fluorescence was obtained probably due to the color of solution), the solid MB reagent was evaluated for comparative analysis under the following conditions: laser power = 0.08 mW (power was raised to reduce signal noise), wavelength = 632.8 nm, laser acquisition time = 10_ s. Analytical MB, 15% hydrated, (95% purity, Labsynth, Brazil) was used to load carbon for Raman analysis.

5.3. Results and discussion

5.3.1. Morphological analysis and determination of textural properties

A typical view of the activated carbon from *Raphanus sativus* (L. var.) is shown in Figure 5.1(a) (SEM micrographs at resolution of 25x). It can be seen that particles of homogeneous color, highly irregular shapes and different sizes were obtained; in fact, particles are smaller than 1 mm size and they could be classified into fine and coarse fractions due to low mechanical resistance of the material. In addition, particles seem to be not too porous, so adsorption is expected to occur predominantly at the surface of the carbon. Such evidence is corroborated by analyzing SEM micrographs at resolution of 3,500x as shown in Figures 5.1(b) and 5.1(c). As expected, an increase on the porosity of *Raphanus sativus (L. Var.)* is visibly verified, comparing SEM micrographs before 5.1(b) and after 5.1(c) carbonization.



(a)

(b)

(c)

Figure 5.1 - Typical surface morphology of *Raphanus sativus (L. Var.)* and its activated carbon at different SEM micrograph resolutions: (a) Activated carbon at SEM resolution of 25x, (b) *Raphanus sativus (L. Var.)* at SEM resolution of 3,500x, and (c) Activated carbon at SEM resolution of 3,500x

The qualitative composition given by EDS as shown in Figure 5.2 reveals that particles contain predominantly carbon, as well as phosphorous, calcium, magnesium and potassium. Metals such as zinc and copper were found at very low quantities while presence of gold in the carbon is due to the thin layer of metal which covered the sample to carry out SEM analysis. The presence of oxygen was found to be quite low as well.

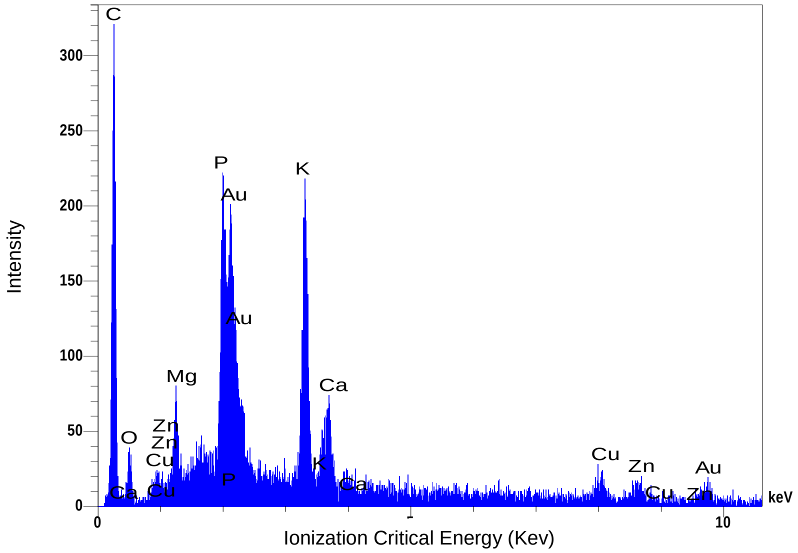


Figure 5.2. Qualitative composition of the activated carbon surface of *Raphanus sativus (L. Var.)* by EDS analysis

The following properties of the activated carbon of *Raphanus sativus (L. Var.)* were estimated by N_2 gas adsorption: specific surface area = 236.3 m^2 g^{-1} (Multipoint BET equation, R^2 = 0.998), total pore volume = 0.06 cm^3 g^{-1} (BJH method) and average pore size = 1.4 nm (BJH method). Such results reveal that specific surface area and total pore volume of *Raphanus sativus (L. Var.)* activated carbon are low if compared to other carbons from agricultural residues. Ioannidou and Zabaniotou (2007), for instance, pointed out the surface area of apricot stones activated carbon is 1190 m^2 g^{-1} (similar to some commercial activated carbons) with total pore volume of 0.5 cm^3 g^{-1} while the carbon from oat hulls has surface area ranging from 349 to 625 m^2 g^{-1} with total pore volume from 84.2 to 91.4 cm^3 g^{-1}. Such results, however, do not guarantee satisfactory MB adsorption. Ferrero (2007) reported that although hazelnut shells activated carbon achieved high surface area due to thermal treatment (793 m_2 g^{-1}), the maximum adsorption capacity at equilibrium was q_{max} = 8.82 mg g^{-1}.

The Langmuir isotherm was also obtained in the BET test (R^2 = 0.999) thus giving Langmuir surface area = 366.4 m² g^{-1} and Langmuir constant K = 98.795. The adsorption (A) and desorption (D) isotherms for the activated carbon of *Raphanus sativus (L. Var.)* shown in Figure 5.3 reveal that an IUPAC type I isotherm was obtained. Such curves are normally encountered when adsorption is limited to at most only a few molecular layers and to microporous carbons whose pore size does not exceed a few adsorbate molecular diameters so, once the micropores are filled there is only a small fraction of the original surface exposed for continued adsorption (Lowell and Shields, 1991).

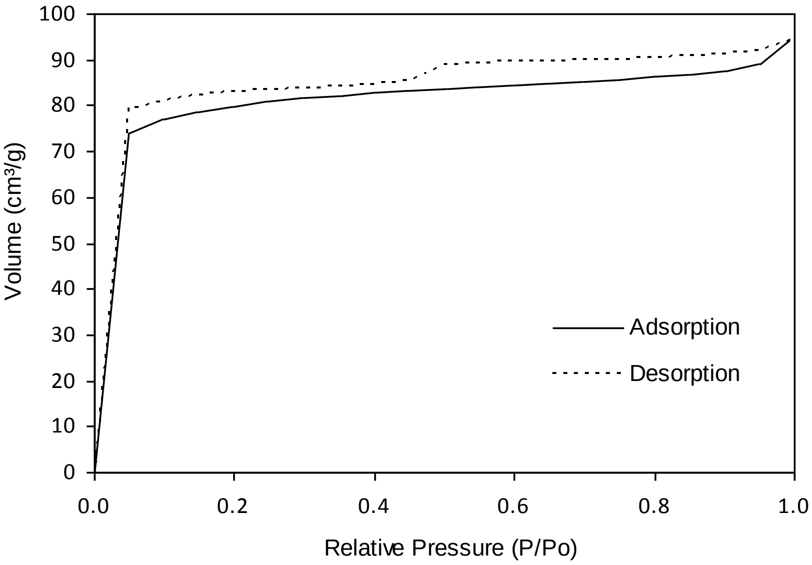


Figure 5.3. Adsorption (A) and desorption (D) isotherms of *Raphanus sativus (L. Var.)* activated carbon of BET test.

5.3.2. Raman spectroscopy analysis

Raman spectra of the activated carbon of *Raphanus sativus (L. Var.)* before (unloaded carbon) and after MB adsorption (loaded carbon) are shown in Figure 5.4.

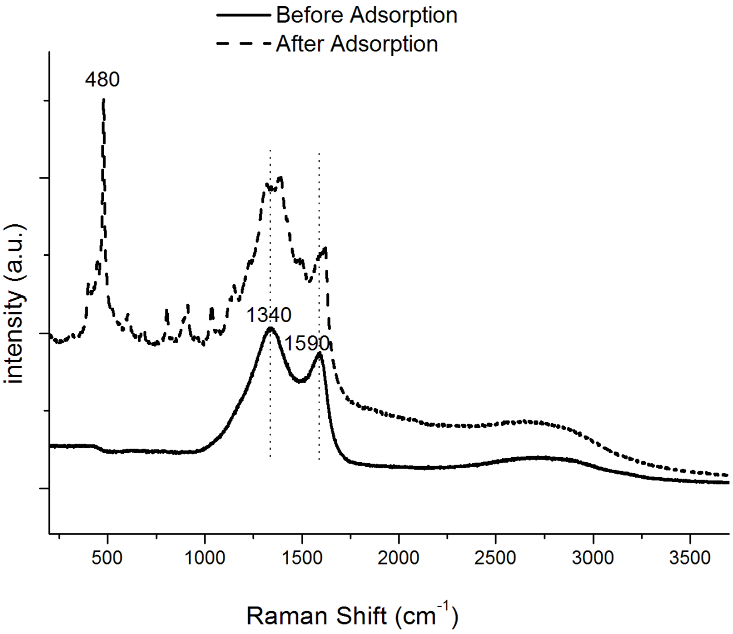
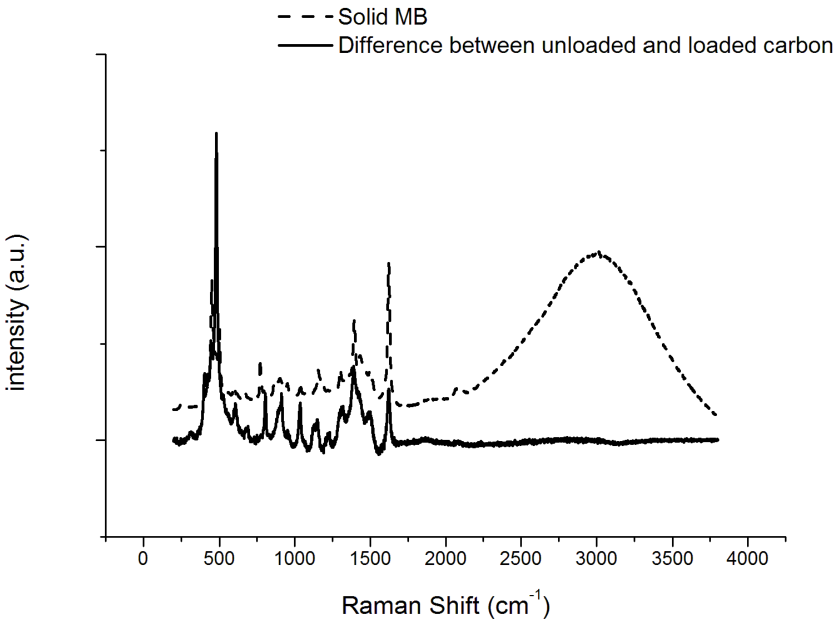


Figure 5.4. Raman spectra of activated carbon of *Raphanus sativus (L. Var.)* before and after MB adsorption.

Two characteristic bands which are typical of carbonaceous materials used as precursors for activated carbons were found at 1340 and 1590 cm^{-1} in the unloaded carbon, thus corresponding to the disorder line (D band) and the graphite line (G band), respectively; another characteristic band was identified at 2793 cm^{-1} but much softer than D and G bands. The intensity of D and G bands is an indicative of the structure of the carbon. In fact, the amount of disorganized carbons which is characterized by the intensity ratio of D to G bands (hereafter named I_D/I_G ratio) will affect both the pore structure and the adsorption properties of the adsorbent. Haghseresht et al. (1999) evaluated the relationship between I_D/I_G ratio with total BET surface area, total pore volumes, micropore volumes, mesopore volumes and other parameters for a number of microporous carbonaceous adsorbents prepared by oxidation of coal reject in various conditions prior to heat treatment at 600^{0}C. They verified an increase on the adsorption capacity of the resulting carbons for organic compounds with the increase of I_D/I_G ratio. Also, higher amount of disorganized carbons (which is related to the increase on the amount of aromatic compounds in comparison with aliphatic carbons) indicates lesser space between the clusters of aromatic compounds, hence smaller micropores are obtained. For *Raphanus sativus (L. Var.)* activated carbon shown in Figure 5.4, I_D/I_G =

1.20 for the unloaded carbon, thus indicating that pores are probably too small (microporous) and corroborating previous BET observations. Figure 5.4 shows also an intense peak in the MB loaded curve at 480 cm^{-1} as well as other less intense peaks that are related to the adsorption of MB; the interaction between MB and the carbon of *Raphanus sativus (L. Var.)* is discussed as follows.

In order to evaluate how MB molecules are adsorbed in the *Raphanus sativus (L. Var.)* carbon and also to identify the predominant adsorption mechanism involved in this separation, the MB loaded carbon spectra was subtracted from the unloaded carbon spectra; a comparison between this curve and that of solid MB spectra is shown in Figure 5.5(a) as the Raman spectra of MB aqueous solutions was not possible to be carried out. In fact, the bonding between MB and carbon can be identified according to changes verified in the peak positions of both curves. In order to obtain a better visualization of the Raman spectra, the curves shown in Figure 5.5(a) were split into regions according to Raman shift interval of 200 to 700 cm^{-1} and 700 to 1700 cm^{-1}, shown respectively in Figures 5.5(b) and 5.5(c).



(a)

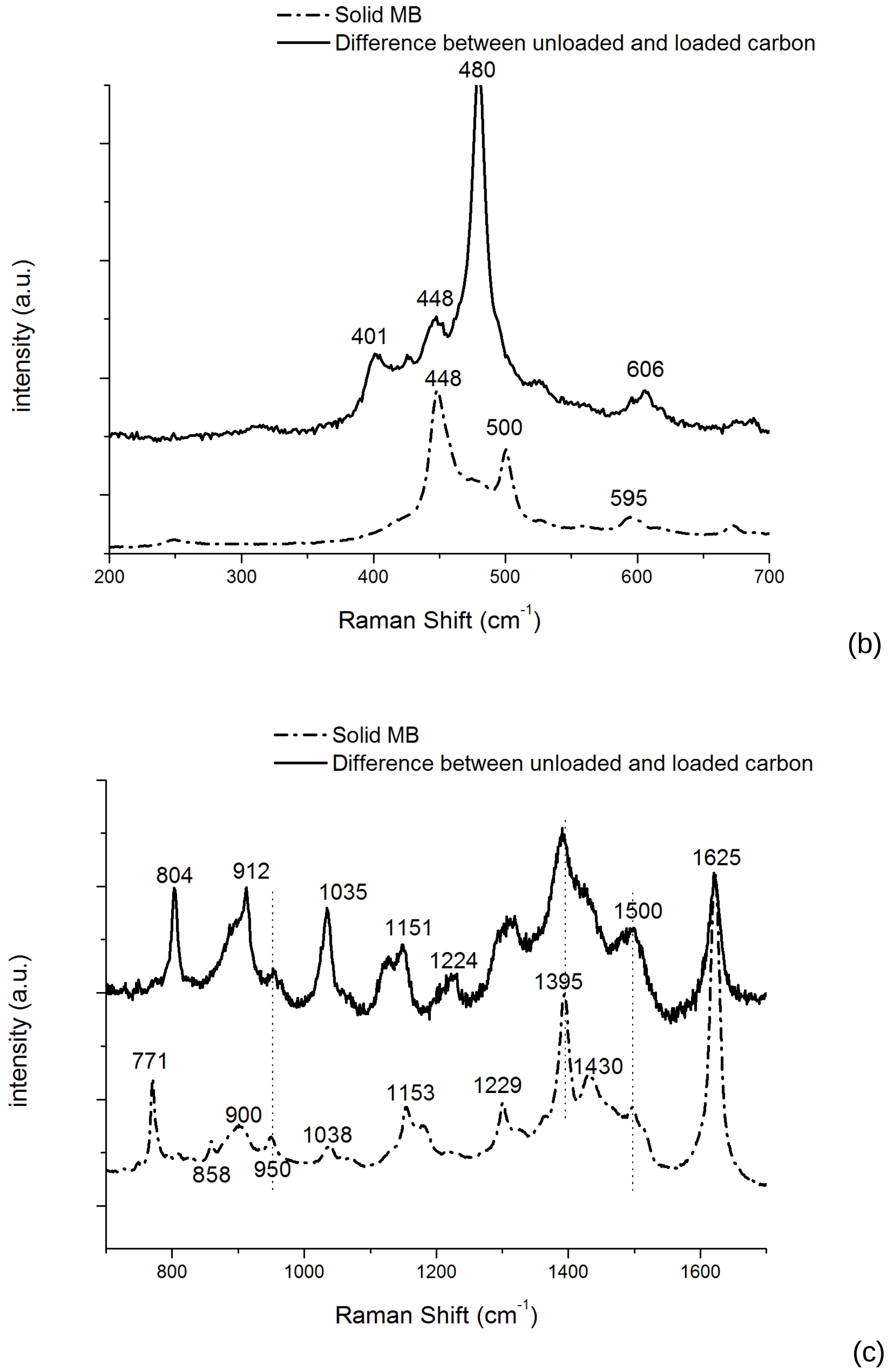


Figure 5.5. Raman spectra of solid MB and the spectra difference between unloaded and MB loaded carbon: (a) 0 to 4000 cm^{-1}, (b) 200 to 700 cm^{-1} and (c) 700 to 1700 cm^{-1}

According to Rubim et al. (2001), the bands identified at 448, 480 and 500 cm^{-1} as shown in Figure 5.5(b) are associated to the aggregation state of the MB molecules that might change due to the contact with the carbon surface or even with pH of the aqueous solution. The presence of dimmer-MB species is evidenced by peaks around 448 and 500 cm^{-1} while the monomer-MB species can be identified at 485 cm^{-1} (δ(CNC) skeletal deformation mode). Therefore, according to Figure 5.5(b), MB molecules are predominantly found as dimmers in the solid but they are adsorbed as monomer in the *Raphanus sativus (L. Var.)* carbon. Recently, UV-vis analysis of aqueous solutions containing MB carried out by Tafulo et al. (2009) pointed to the non existence of dimmers in the aqueous solution as referred by several authors and that changes on the position and shape of bands obtained by them are in fact influenced by the ionic strength of the solution. The chemical structure of MB and its possible dimerization reaction in solution is shown in Figure 5.6. The peak at 401 cm^{-1} can be attributed to some deformation in the C-S-C bond of the MB species (Tognalli et al., 2006) and no significant change in the intensity of peaks nearby 600 cm^{-1} was considered.

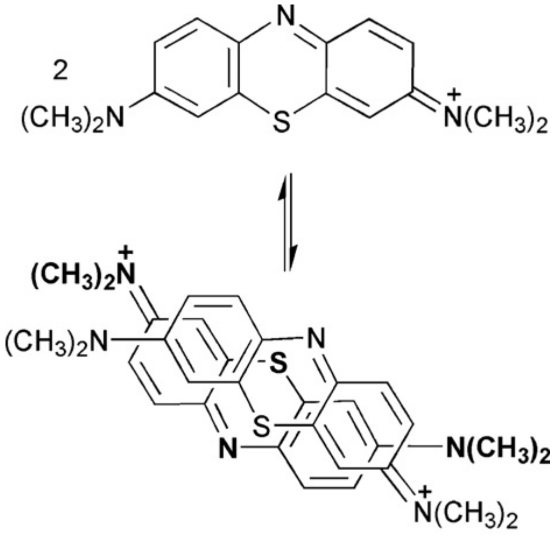


Figure 5.6. MB chemical structure and its possible dimmer (Tafulo et al., 2009).

Some peaks related to atoms deformation in the molecules of solid MB and adsorbed MB are shown in Figure 5.5(c). Firstly, peaks related to the CH bond deformation β(C-H) are found at 1030 and 1151 cm^{-1} (Naujok et al., 1993). One peak was identified at 1038 cm^{-1}, showing low intensity in the solid MB spectra but being quite significant when MB molecules are adsorbed in the *Raphanus sativus (L. Var.)* carbon; the other peak occurred at 1153 cm^{-1} for both curves with quite similar intensities. Other deformation on the atoms of MB molecules is related to the symmetric and asymmetric stretch of C-N bond that are found at 1390 and 1430 cm^{-1}, respectively (Naujok et al., 1993). According to Figure 5.5(c), the symmetric stretch of C-N bond occurs in both solid and MB loaded carbon, but the asymmetric stretch of C-N bond has been identified in the solid only. And finally a typical large MB peak was found at 1625 cm^{-1} for both spectra which is related to the C-C bond stretch of the benzene ring of MB molecule (Hutchinson and Hester, 1984; Naujok et al., 1993). It was considerably more intense in the solid MB spectra. Other non identified peaks occurred at 771, 858, 900, 950 and 1229 cm^{-1} for the solid MB spectra and at 804, 912, 1224 and 1500 cm^{-1} for the MB adsorbed in the carbon.

The identification of bands that have appeared, disappeared or just shifted after adsorption of MB molecules in comparison with those bands of solid MB may help to elucidate how MB can possibly be linked to the activated carbon of *Raphanus sativus (L. Var.)*. Hutchinson and Hester (1984), studying the structure of the surface coat of a thionine-modified gold electrode, suggested that the coat occurred basically by thionine units linked via an amino nitrogen in a secondary amine structure. According to the molecule of MB shown in Figure 5.6, there are three probable sites for this bonding: the central nitrogen atom, the central sulfur atom and/or the amino nitrogen atoms. MB bonding as monomer species through the central nitrogen atom seems to be the most probable mechanism to occur during adsorption of MB molecules onto *Raphanus sativus (L. Var.)* carbon because a very high intensity peak at 480 cm^{-1} was identified, which is assigned to a δ(CNC) skeletal deformation mode. MB bonding through the sulfur atom seems to occur as well but at lesser amount because intensity of peak near 405 cm^{-1}, attributed to some deformation in the C-S-C bond of the MB species, has also appeared. However, bonding through an amino nitrogen atom to a carbon atom seems less probable because symmetric stretch of C-N bond 1395 cm^{-1} was found to be not affected and the asymmetric stretch at 1430 cm^{-1} just vanished at the MB loaded curve.

5.4. Conclusions

The characterization of carbons is an important step for the design of adsorption processes. Main results on MB adsorption onto activated carbon made of *Raphanus sativus (L. Var.)* are:

- A microporous structure was verified qualitatively (SEM and Raman analysis) indicating that MB adsorption occurs predominantly at the surface of the adsorbent (surface area = 236.3 $m^2.g^{-1}$, pore volume = 0.06 $cm^3.g^{-1}$; pore size = 1.4 nm; MB diameter ≈ 1.5 nm (Xun et al., 2007).
- Adsorption probably occurs by MB bonding of monomer species through central nitrogen atom; MB bonding through sulfur atom may occur while MB bonding through amino nitrogen atom seems improbable.

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6. FINAL CONSIDERATIONS AND SUGESTION FOR FUTURE WORKS

Experiments were conducted in order to investigate the potential of cold-pressed cake of *Raphanus sativus (L. Var.)* seeds, a residue from biodiesel production, as raw material for the production of adsorbents for the removal of dyes from textile effluents. In this work, adsorption of methylene blue (MB) from synthetic aqueous solutions onto prepared activated carbon was investigated regarding to adsorption aspects such as equilibrium, kinetic, characterization and operational parameters (particle size, adsorbent dosage and initial pH of the aqueous solution) behavior.

The adsorption of MB onto *Raphanus sativus (L. Var.)* activated carbon was satisfactory considering that a residue was used as precursor for the given carbon. Equilibrium analysis evidenced that the maximum value of uptake capacity of MB was nearly 20 mg.g^{-1}; such value is higher than other activated carbons from similar wastes used for MB removal like sunflower oil cake (16.4 mg.g^{-1}) (Karagöz et al., 2008), defective coffee seeds pressed cake (14.9 mg.g^{-1}) (Nunes et al., 2009) and date pits (12.9 mg.g^{-1}) (Banat et al., 2003), but it is comparatively low when compared to commercial adsorbents or even other carbons produced from agricultural solid wastes or industrial by-products (see Table III.7). Such result may be attributed to the fact that average pore size of the *Raphanus sativus (L. Var.)* carbon was smaller than the size of the MB molecule. In fact, MB adsorption was superficial only, so better results could be obtained if adsorbate of smaller size were considered. Such evidence was corroborated by the fact that equilibrium data were better described by the Langmuir model, in comparison to Freundlich, thus indicating homogeneous adsorption. It was corroborated by the kinetics results: pseudo-second order model providing the best fit - maximum error between estimated and experimental q_e was 4%), as well as by characterization analysis (Raman, BET, SEM and EDS).

Characterization studies using Raman spectroscopy evidenced this methodology as a potential method for further studies in order to investigate structural variation of carbonaceous adsorbent materials before/after adsorption and through chemical characterization of carbon and solution. The method was useful to better comprehension of MB adsorption mechanism onto *Raphanus sativus* (L. Var.) carbon, and further investigations on characterization seems necessary to fully understand it.

On regard to such final considerations and given the results obtained so far with this work, the following aspects are suggested for future investigations:

1) Evaluate the performance of *Raphanus sativus (L. Var.)* activated carbon as an adsorbent for metals such as chromium, mercury and arsenic which are serious pollutant for aqueous systems. The possibility of using it as a molecular sieving method to other separation processes could be suggested as well given its cost and surface characteristics.

2) Evaluate the potential of *Raphanus sativus (L. Var.)* as a biosorbent for removing dyes from dilute solutions, mainly as a second step of textile wastewater treatments due to results presented in Chapter 4.

3) Investigate the chemical characterization of *Raphanus sativus (L. Var.)* activated carbon through Raman spectroscopic study and complement it with other techniques like FT-IR and Boehm method to make a comparative study.

4) Evaluate the performance of *Raphanus sativus (L. Var.)* activated carbon chemical activation. Chemical activation could improve the adsorption capacity through the increase of adsorbent pores size and functional groups on adsorbent surface.

5) Evaluate *Raphanus sativus (L. Var.)* activated carbon macro, meso and micro pore distribution.