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Removal of Methylene Blue by Adsorption on Mesoporous Carbon from Peach Stones

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The objective of this work was to evaluate the efficiency of a synthesized activated carbon for the removal of methylene blue from aqueous solution. Activated carbons synthesized from lignocellulosic precursors are an interesting alternative for their use as adsorbents and catalyst supports in the wastewater treatment field. In this work a micro-mesoporous activated carbon was synthesized from peach stones by chemical activation. The textural, morphological and chemical characterization of the material was carried out, revealing the acidic nature of the solid. Adsorption isotherms were conducted at several solution temperatures, obtaining the largest methylene blue adsorption capacity value, 444.3 $mg.g^{-1}$, at the highest temperature, 333 ° C. The equilibrium adsorption data were tested by four isotherm models, i.e. Langmuir, Freundlich, Tóth and Redlich-Peterson, finding that the models best fitting the experimental adsorption data were Tóth and Redlich-Peterson equations. The calculated thermodynamic parameters suggested that an endothermic and spontaneous adsorption process is occurring.

1. Introduction

Dyes and pigments are present in textile, leather, paper, plastic, and other industries effluents. These streams are characterized by containing color, a fluctuating pH, a large load of suspended organic/inorganic solids (salts and high amounts of surfactants), dissolved solids, possibly heavy metals such as Cr, Ni and Cu, and high values of COD. In industrial water pollution, the color produced by amounts of organic dyes in water is considered of very concern due to its possible harmful effects. Many dyes and pigments have toxic as well as carcinogenic, mutagenic and teratogenic effects on aquatic life and also possibly on humans, specifically those containing benzidine group in their structure (Gregory et al., 1991). Therefore, many studies have been conducted on the toxicity of dyes and their impact on the ecosystems, as well as the environmental issues associated to the manufacture and subsequent usage and disposal of dyes (Saha, 1996). Methylene Blue, $C_{16}H_{18}N_3SCl.3H_2O$, is a cationic dye with large molecular structure, used as a model compound for the adsorption of organic dyes from aqueous solution (Hamdaoui, 2006).It has been used as a dye for leather and cellulosic fibres, redox indicator and ISO test pollutant in semiconductor photocatalysis (Mills et al., 2011). It can have several harmful effects on aquatic ecosystems and it can be considered as potentially carcinogenic (Sandoval González & Silva Martínez, 2008).
The conventional biological wastewater treatments cannot efficiently remove these compounds, and it is necessary to found new emerging alternatives to reduce the presence of these substances in surface waters. Adsorption processes using carbon materials have been considered as effective techniques to remove organic compounds, such as dyes, but especially dynamic mode operation could be reach expensive. Adsorption on activated carbons prepared from biomass materials has revealed as an efficient methodology to treat the secondary effluents in wastewater treatment plants. The synthesis of activated carbons from lignocellulosic precursors are a very interesting alternative versus the conventional commercial carbons due to a selection of

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the appropriate textural and chemical properties is possible by the optimization of the synthesis conditions, i.e. type of precursor and activation method (Khalfaoui et al., 2014). However, from our knowledge, few studies in the literature report the removal of methylene blue from water by an activated carbon synthesized from peach stones, it is worth mention the work of Attia and col. (Attia et al., 2008), who study the removal of MB by H_3PO_4-activated carbons in static and dynamic adsorption experiments. The novelty of the present work is the study of the MB adsorption equilibrium at different temperatures, investigating the thermodynamic parameters of the system.

2. Materials and Methods

2.1 Reactants

Methylene Blue was purchased from Sigma-Aldrich (Steinheim, Germany); orto-phosphoric acid (85 wt %) was obtained from Panreac. For the preparation of buffer solutions, citric acid 1-hydrate (purity > 99 %, from Sigma-Aldrich), hydrochloric acid (37 wt%, from Carlo Erba), sodium hydroxide (purity > 99 %, from Sigma-Aldrich), boric acid (purity > 99.97 %, from Sigma-Aldrich) and potassium chloride (purity > 99 %, from Sigma-Aldrich) were used.

2.2 Synthesis of the activated carbon

Peach stones, a lignocellulosic waste generated in agricultural companies, is the precursor considered in this work. Prior to the treatment, raw materials were crushed and sieved in a range from 0.883 to 1.0 mm. Then, peach stones were impregnated with a 12 M H_3PO_4 solution during 6 h at 85 ºC. After that, the impregnated material was vacuum filtered and then carbonized at 400 ºC for 4 h, under air volumetric flow of 50 mL.min^{-1} and at a heating rate of 5 ºC min^{-1}. The thermal treatment was developed in a quartz reactor (i.d. 7 cm and length 100 cm) placed in a vertical furnace. The control of the gas volumetric flow was carried out using mass controls. Finally, the solid was washed until neutral pH in order to remove the excess of phosphoric acid and it was dried in oven at 110 ºC during 24 h.

2.3 Adsorbent Characterization

The textural properties of the adsorbent were studied by the N_2 adsorption-desorption isotherms at -196 ºC, using a Micromeritics ASAP 2010 adsorption apparatus. The morphology of the material were analyzed by scanning electronic microscopy (SEM) by a JEOL JSM 6400 equipment at 22 keV.

The study of surface functional groups of the adsorbent was carried out by infra-red spectrometry, recorded at 400-4600 cm^{-1} using a Thermo Nicolet FTIR spectrophotometer. Finally, the isoelectric point (pH_{IEP}), determined by the graphical representation of zeta potential measurements versus pH solution, was obtained using a Zetasizer Nano ZS equipment. In this case, the zeta potential measurements were carried out using 0.05 g of sample suspended in 20 mL of deionized water, and adjusting the pH with either 0.1 M HCl or 0.1 M NaOH solutions.

2.4 Batch Adsorption Experiments

The adsorption tests were carried out using different experimental conditions, in order to study their influence on the adsorption capacity. All adsorption experiments were performed in a LabMate orbital shaker, using 50 mL-vessels and a constant shaking rate (250 r.p.m.). In the adsorption tests different operational conditions: initial methylene blue concentration (25-200 mg·L^{-1}), pH of the solution (4-10), adsorbent dosage (0.4-1.6 g.L^{-1}) and temperature solution (30-60 ºC) were varied. The evolution of the concentration of adsorbate in aqueous phase versus time was studied; then, when the adsorption equilibrium was reached, the sample was filtered and the methylene blue concentration was analyzed using a Shimadzu UV-2401PC UV-Vis spectrophotometer.

3. Results and Discussion

3.1 Characterization of adsorbent

The results regarding to the textural characterization of the synthesized activated carbon are shown in Figures 1 a-b. N_2 adsorption-desorption isotherms at -196 º C of the activated carbon (Figure 1a) reveals the microporous structure of the material, suggesting an acceptable percentage of mesoporosity. The specific surface area of the adsorbent has been determined in 1521 m^2.g^{-1}. The pore size distribution of the material is depicted in Figure 1b, showing a bimodal distribution in the micro and mesopores range: from 1.2 to 2.7 nm.

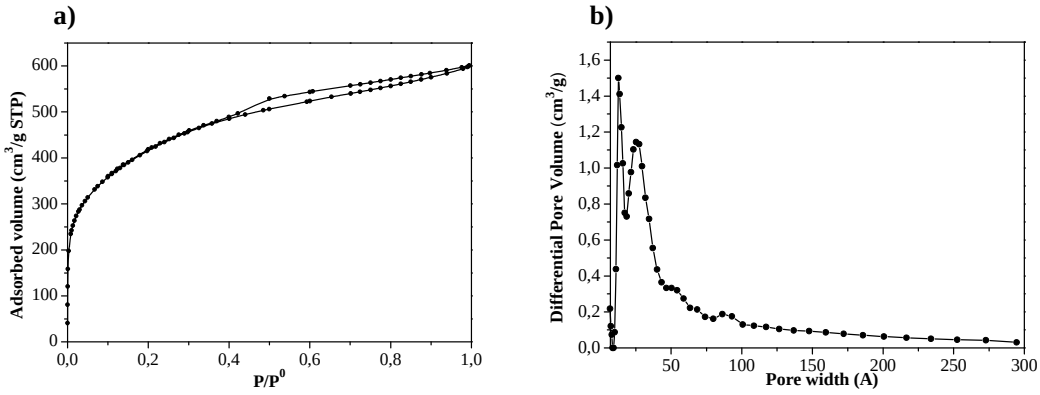

Figure 1: (a) N2 adsorption isotherm at -196 ºC (b) Pore size distribution of the synthesized activated carbon

Infrared spectra of the synthesized activated carbon is shown in Figure 2. The material showed a typical vibration at 3400 cm^{-1}, associated to hydroxylic groups; 2,850-2,920 cm^{-1}, indicative of aliphatic groups $–CH_2-$; 1,629 cm^{-1}, indicating the presence of C=C vibrations or systems like as diketone, ketoester and quinone (Fanning & Vannice, 1993); 1,558 to 1,461 cm^{-1}, attributed to both carboxyl C=O and non-aromatic carboxylic acid and lactone structures, and 1,118 cm^{-1} is associated with C-O stretching vibrations, and O-H modes of phenol structures (Biniak et al., 1997). Zeta potential changes as a function of pH solution range from 2.5 to 9.8 were investigated, determining that the isoelectric point (pH_{IEP}) of the activated carbon occurred at pH = 3.0 ± 0.25, being the activated carbon surface positively charged at below of this pH and negatively charged at above of it.

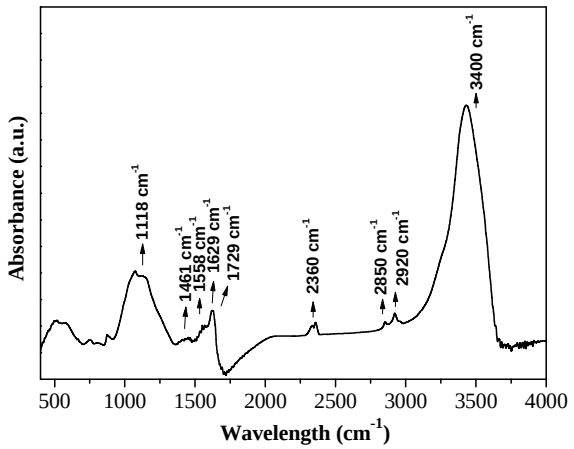

Figure 2: FT-IR spectra of the synthesized activated carbon

Additionally, the scanning electron microscope (SEM) images of the activated carbon are shown in Figure 3 a-b. The micrographs show a well-developed and homogeneous porous structure.

3.2 Adsorption isotherms.

3.2.1 Thermodynamic studies

The adsorption equilibrium of the methylene blue uptake onto the activated carbon at different temperatures was studied. The adsorption isotherms at temperatures from 30 to 60 ºCare depicted in Figure 4. It is clear that the acidic nature of the adsorbent favours the methylene blue adsorption, since electron donor-acceptor interactions are occurring between the aromatic ring and the oxygenated surface groups. Therefore, the activated carbon surface at the working pH range is negatively charged due to deprotonated acidic groups, enhancing the methylene blue uptake. Similar behaviour has been found in the removal of methylene blue and phenol onto chemical-activated carbon from vetiver roots (Altenor et al., 2009).

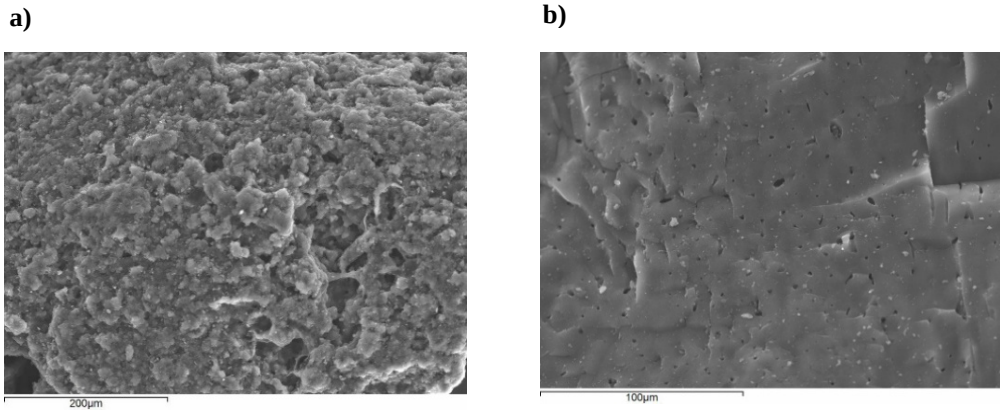

*Figure 3: SEM micrographs of the synthesized activated carbon **(a)** 200 µm **(b)** 100 µm*

From the Figure 4 it can be observed that the adsorption capacity highly increased from 275.7 to 444.3 $mg \cdot g^{-1}$ when the temperature increased from 30 to 60 ºC. This behaviour is indicative of endothermic processes. Since generally adsorption processes are defined as exothermic nature, many examples of endothermic processes in aqueous phase adsorption are usually found in the literature (Mahmoodi et al., 2011). According to some authors, this behavior could be attributed to an increase in the mobility of the adsorbate, to a decrease in the diffusion pore resistances by other works (Fontecha-Cámara et al., 2006) or even it might be a consequence of the increase in the chemical interactions between the adsorbate and the surface functionalities of the adsorbent when the temperature increases (Li et al., 2009). .

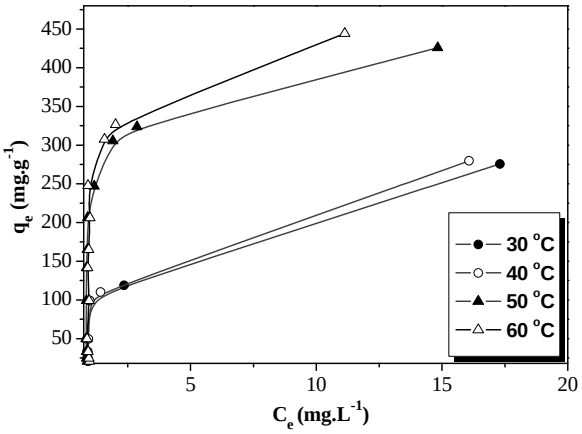

Figure 4: Adsorption isotherms of methylene blue onto the synthesized activated carbon at several temperatures

The thermodynamic parameters can be determined from the equilibrium experimental data of the adsorption of methylene blue onto the synthesized activated carbon. Gibbs free energy (ΔG^0, kJ.mol^{-1}) was evaluated and the change in the standard enthalpy (ΔH^0, kJ.mol^{-1}) and entropy (ΔS^0, J.mol^{-1}.K^{-1}) values were determined by van't Hoff equation. The thermodynamic parameters for the tested temperatures are shown in Table 1.
The positive ΔH^0 value is indicative of an endothermic process, as it was expected. Deng and coworkers (Deng et al., 2012) proposed a range of enthalpy values from 80 to 450 kJ.mol^{-1} for chemisorption processes and values lower than 80 kJ.mol^{-1} when physical adsorption is occurring. In this study, a value of 6.12 kJ.mol^{-1} was obtained, so it could be supposed that only physisorption mechanism, attributed to electrostatic interactions, is involved. Therefore, the positive value of AS^0 indicates an increasing in the randomness at the solid-liquid interface during the adsorption processes with the increase in the solution temperature. This behaviour is associated to physical adsorption phenomenon. Other authors have reported positive values of change of standard entropy, as in the adsorption of Direct Red 23 onto corn stalks (Fathi et al., 2015), or the removal of Rhodamine-B using treated rice husk-based activated carbon (Ding et al., 2014). Finally, all the

ΔG^0 values are negative, indicating that the adsorption of methylene blue onto the synthesized activated carbon was spontaneous and thermodynamically favourable.

Table 1: Thermodynamic parameters of methylene blue adsorption by the synthesized activated carbon

T (K)	ΔH^0 (kJ.mol^{-1})	ΔS^0 (J.mol^{-1}.K^{-1})	ΔG^0 (kJ.mol^{-1})
303	6.12	51.64	-9.59
313			-9.79
323			-10.91
333			-10.93

3.2.2 Adsorption Equilibrium Modelling

The equilibrium adsorption data were analyzed using several adsorption isotherm models: Langmuir, Freundlich, Tóth and Redlich-Peterson equations, in order to obtain an empirical model predicting the adsorption process. The obtained results (Tables 2 and 3) allow to conclude that the three-parameter models, i.e. Tóth and Redlich-Peterson equations, showed the best fitting to the experimental data, with similar standard error of estimate values. Therefore, the Langmuir model can well describe the experimental data. Thus the Langmuir constant affinity, b, depends on the adsorbed quantity; from Table 2 a slight increasing tendency of b could be appreciated when the adsorption capacity increased. In addition, the monolayer adsorption capacity, q_{sat}, increased when the temperature was increased, suggesting that the isosteric adsorption heat depends on the saturation percentage of the active sites within the solid surface. According to the literature, this behavior could also mean that the solid surface is heterogeneous, that is the surface is composed of sites having different energy of adsorption. Molecules prefer to adsorb onto sites having the highest energy of adsorption, and as the process proceeds molecules then adsorb within sites of progressively lower adsorption energy (Do, 1998).

Table 2: Langmuir and Freundlich models parameters for the adsorption of methylene blue onto activated carbon at several temperatures

	Langmuir			Freundlich		
T (K)	q_{sat} (mg.g^{-1})	b , (L.mg^{-1})	SE	k_F (L.g^{-1})	n_F	SE
303	355.35	0.22	30.25	95.07	22.91	87.51
313	357.69	0.23	39.88	311.76	16.70	62.42
323	528.78	0.38	79.64	290.85	8.05	140.69
333	600.20	0.31	84.14	430.17	8.49	131.80

Table 3: Tóth and Redlich-Peterson models parameters for the adsorption of methylene blue onto activated carbon at several temperatures

	Tóth				Redlich-Peterson			
T (K)	k_T (mg.g^{-1})	a_T (mg.L^{-1})	t	SE	k_R , (L.g^{-1})	a_R (L.mg^{-1}) x 10^{-4}	β	SE
303	275.69	3.31	8.47	25.47	61.56	1.31	3.51	25.50
313	279.71	1.96	7.16	37.52	70.18	2.11	3.45	37.54
323	421.71	41.42	3.48	74.80	146.35	3.36	1.78	75.38
333	444.58	1.69	12.62	76.91	142.85	2.10	3.91	76.96

4. Conclusions

In this work an activated carbon from peach stones by chemical activation using phosphoric acid was synthesized. The electron donor-acceptor interactions between adsorbate and adsorbent surface seem to be the responsible of the excellent behavior in the removal of methylene blue from aqueous solution. The equilibrium experimental data were more adequately fitted by the three-parameter adsorption models, Tóth

and Redlich-Peterson. Therefore, the determination of the thermodynamic parameters (ΔG^0, ΔH^0, ΔS^0) suggests the spontaneous and endothermic nature of the adsorption process. The process implicated in the adsorption of methylene blue from solution is based on the electrostatic interactions between the oxygenated surface groups on the carbon structure and the charged surface of the dye in solution. The results of this study suggest that the laboratory made-activated carbon could be successfully applied for the removal of wastewater in the textile industry.

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