SYNTHESIS AND CHARACTERIZATION OF AN ACTIVATED CARBON FROM PEACH STONES FOR ADSORPTION OF DYES

S. Álvarez-Torrellas[1], G. Ovejero[1], R. García-Lovera[2], A. Rodríguez[1], J. García[1]

[1]Grupo de Catálisis y Procesos de Separación (CyPS), Departamento de Ingeniería Química, Facultad de Ciencias Químicas, Universidad Complutense de Madrid, Avda. Complutense s/n, 28040 Madrid, Spain
satorrellas@ucm.es; jgarciar@ucm.es

[2]Laboratorio de Materiales Microporosos en Catálisis y Adsorción, Departamento de Físico-Química, Facultad de Ciencias Químicas, Universidad de Concepción, Edmundo Larenas 129, Concepción, Región del Biobío, Chile.

ABSTRACT

Activated carbons synthesized from agricultural wastes precursors are an interesting alternative for their use as adsorbents and catalyst supports in the wastewater treatment field, and represent an important ecological benefit. The objective of this work was to evaluate the efficiency of a synthesized activated carbon from peach stones for the removal of methylene blue from aqueous solution. The textural, morphological and chemical characterization of the material was carried out, revealing the acidic nature of the solid. The effect of different experimental conditions on the adsorption capacity: initial methylene blue concentration, pH solution, adsorbent dosage and temperature have been investigated. The kinetic experimental data followed the pseudo-second order model. Adsorption isotherms were conducted at several operation temperatures, obtaining the largest methylene blue adsorption capacity value, 444.3 $mg.g^{-1}$, at the highest temperature, 333 K. The calculated thermodynamic parameters suggested that an endothermic and spontaneous process is occurring.

Keywords: Adsorption, Chemical activation, Dyes, Modelling, Thermodynamic parameters

1. INTRODUCTION.

The analysis of industrial effluents from textile, leather, paper, plastic, etc. reveals the presence of dyes, pigments and coloured organic compounds. In this context, it has been established that these compounds could possibly cause hazardous environmental pollution due to their toxic character and in addition they could inhibit the photosynthesis processes of the aqueous flora. There are evidence of the biotoxic, carcinogenic and genotoxic effects of many dyes and pigments, specifically those containing benzidine groups in their structure. Therefore, many studies have been conducted in order to demonstrate the potential mutagenic and carcinogenic effects of dyes on human health [1].

Methylene Blue, $C_{16}H_{18}N_3SCl.3H_2O$, is a cationic dye with a large molecular structure, used as a model compound for the adsorption of organic dyes from aqueous solution. It is usually used as a dye for leather and cellulosic fibres. Several harmful effects of methylene blue on aquatic ecosystems and a potentially carcinogenic behavior have been reported [2].

The conventional biological wastewater treatments cannot efficiently remove these compounds, which could reach drinking water sources and WWTPs sludge. So it is necessary to found new emerging alternatives to reduce the presence of these substances in surface waters. Various technologies such as adsorption, advanced oxidation processes, coagulation/flocculation, membrane and ion exchange techniques have been extensively carried out.

Adsorption on activated carbons prepared from biomass materials has revealed as an efficient methodology to treat 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 the appropriate textural and chemical properties, which is possible by the optimization of the synthesis conditions, i.e. type of precursor and activation method [3].

From our knowledge, few works in the literature report the removal of methylene blue from water by an activated carbon synthesized from peach stones. The effects of the initial methylene blue concentration, pH solution, adsorbent dosage and temperature on the methylene blue adsorption behavior were studied. In addition, the equilibrium of the system and the thermodynamic of the adsorption process were investigated in order to establish the more proper adsorption mechanism.

2. MATERIALS AND METHODS.

2.1. Reactants.

Methylene Blue were 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 (37wt%, 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. Ultrapure water was used in all the experiments.

2.2. Synthesis of the activated carbon.

Peach stones, a lignocellulosic waste widely generated in agricultural environments, are 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, 60 g of peach stones were impregnated by using a 12 M H_3PO_4 solution in a round bottom flask immersed in an oil bath during 6 hours at 85 ºC. After that, the impregnated material was vacuum filtered and then carbonized at 400 ºC for 4 hours, under an 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. At the end, the solid was thoroughly washed with de-ionized water until neutral pH of the rinsing waters and it was dried in oven at 110 ºC during 24 h.

2.3. Characterization of the activated carbon.

The textural properties of the adsorbent were studied by N_2 adsorption-desorption isotherms at -196 ºC, using a Micromeritics ASAP 2020 adsorption apparatus. The morphology of the material was analyzed by scanning electronic microscopy (SEM) by a JEOL JSM 6400 equipment at 22 keV.

The study of the surface functional groups of the adsorbent was carried out by infra-red spectrometry, recorded at 400-4600 cm^{-1} using a Thermo Nicolet FT-IR spectrophotometer. Finally, the isoelectric point (pH$_{IEP}$) was obtained using a Zeta sizer Nano ZS equipment. In this case, the zeta potential measurements were carried out with 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 studies.

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 rpm). In the adsorption tests different operational conditions, e.g., 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. Samples were filtered in 0.45 μm nylon filters and the methylene blue concentration was analyzed using a Shimadzu UV-2401PC UV-Vis spectrophotometer.

3. RESULTS AND DISCUSSION.

3.1. Characterization of the activated carbon.

The shape of the N_2 adsorption-desorption isotherm at -196 ºC of the activated carbon (Fig. 1a) reveals the microporous structure of the material, suggesting an acceptable percentage of mesoporosity. A significant desorption hysteresis was observed at P/P^0 values from

1.0 to 0.4. The specific surface area of the solid, determined by using BET equation was of 1521 m^2.g^{-1}. The pore size distribution of the material is depicted in Fig. 1b, showing a bimodal distribution in the micro and mesopore range.
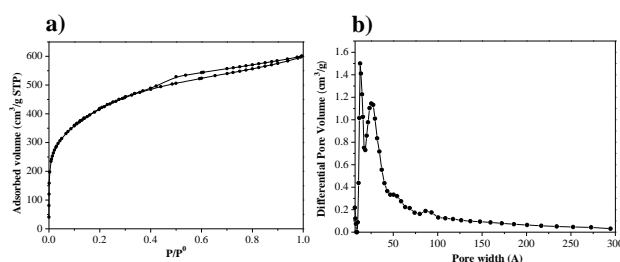

Figure 1. (a) N_2 adsorption-desorption isotherms at -196 ºC; (b) Pore size distribution of the synthesized activated carbon.

Infrared spectrum of the synthesized activated carbon is shown in Figure 2. The material showed a typical broad peak at around 3400 cm^{-1} which is associated to hydroxylic groups. The solid also shows peaks at 2850-2920 cm^{-1} which are indicative of the stretching vibrations of aliphatic groups –CH$_2$-. The band at 1629 cm^{-1} suggested the presence of C=C stretching vibrations or systems like as diketone, ketoester and quinone. The peaks observed from 1558 to 1461 cm^{-1} can be attributed to both carboxyl C=O stretching and non-aromatic carboxylic acid and lactone structures. The intensity of the peak at around 1118 cm^{-1} is associated with C-O stretching vibrations, and the bending O-H modes of phenol structures.
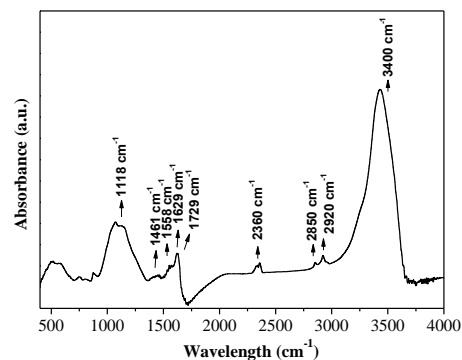

Figure 2. FT-IR spectra of the synthesized activated carbon.

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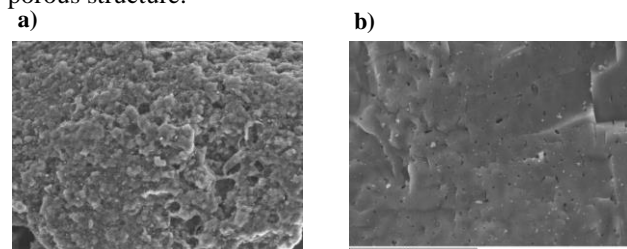

Figure 3. SEM micrographs of the synthesized activated carbon.

Finally, 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 material occurred at pH = 3.0±0.25.

3.2. Effect of initial concentration on adsorption process.

The amount of methylene blue adsorbed (q, $mg.g^{-1}$) at different initial concentrations onto the lignocellulosic-activated carbon is depicted in Figure 4a. It was observed that the adsorption of methylene blue gradually increased with the time and then attained the equilibrium at about 50 hours; although, the kinetic plot shows a fast increasing in the adsorption capacity achieved during the first 1 hour. The fast adsorption at the initial stage is due to the relatively high contribution of mesoporous in the porous structure of the activated carbon.

As it was expected, for the variation of the initial concentration from 25 to 200 $mg.L^{-1}$, the adsorption capacity increased from 29 to 239 $mg.g^{-1}$, showing that the removal of dye depends on the initial concentration.

3.2. Effect of pH solution on adsorption process.

The evolution of methylene blue adsorption capacity versus time at different pH solution values is shown in Figure 4b. The adsorption capacity increased at initial times and it gradually reached the equilibrium stage. The equilibrium time obtained for all the tested pH values was of approximately 48 hours. Appreciable changes in the adsorption capacity were not observed by changing the pH solution. This behavior could be explained taking into account that all the studied pH solution was higher than the adsorbent isoelectric point (pH_{IEP} = 3.0±0.25). This means that, at the tested pH range, the carbon surface was negatively charged, which does favor the adsorption of methylene blue cations due to electrostatic attraction forces [4].
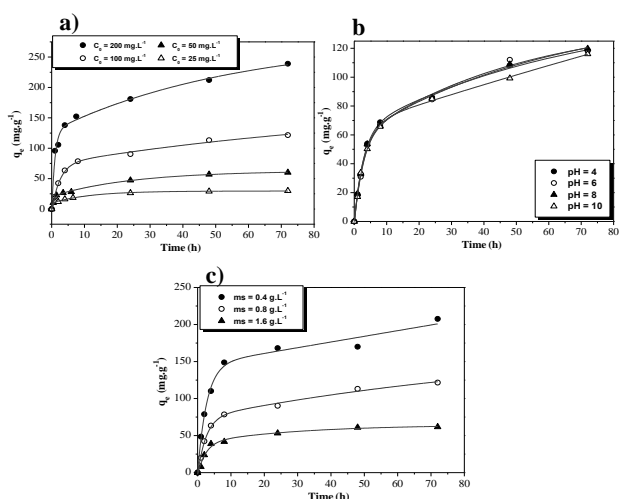

Figure 4. Effect of (a) initial methylene blue concentration, (b) pH solution, (c) adsorbent dosage on the methylene blue adsorption capacity onto activated carbon.

3.3. Effect of adsorbent dosage on adsorption process.

The effect of the adsorbent dosage on the removal of methylene blue from aqueous solutions is shown in Figure 4c, varying this parameter from 0.4 to 1.6 $g.L^{-1}$.

The adsorption capacity decreased from 207.6 to 61.7 $mg.g^{-1}$ when the adsorbent dosage increased from 0.4 to 1.6 $g.L^{-1}$. This decreasing in the adsorption capacity can be attributed to the overlapping or aggregation of the adsorption sites, which leads to a decreasing in the available adsorbent surface area and an enhancement of the diffusional resistances [5].

The prediction of the kinetic experimental results was assessed by using pseudo-first-order, pseudo-second-order and intra-particle diffusion kinetic models. This latter, known as Weber and Morris model, was used to describe the mechanism of the adsorption process.

For all the tested experimental conditions, pseudo-second order model showed the best fitting to the experimental data, according to the regression coefficient values, R^2, and closer values of q_e from the experimental and the predicted by the model. It was found that the values of the rate constant, k_2, decreased when the initial concentration increased and when the adsorbent dose decreased. The pseudo-second order kinetic constant did not significantly change with the variation of the pH solution. So, it can be concluded that the kinetic of the process is highly dependent on the initial concentration and the adsorbent dosage.

Therefore, according to the intra-particle diffusion equation, i.e. Weber and Morris model, if the regression of q versus $t^{0.5}$ is linear and passes through the origin, the adsorption process is controlled only by the intra-particle diffusion. On the contrary, if the plot does not pass through the origin, both intra-particle diffusion and film diffusion are involved in the adsorption mechanism. In this work, for the tested conditions, the q versus $t^{0.5}$ graphs pass through the origin, suggesting that the intra-particle diffusion is the rate-controlling step in the adsorption process.

Through the application of the intra-particle diffusion model to the experimental data, two stages of different slope were obtained (plots not depicted here). The first one of these lines could be attributed to the surface adsorption, i.e., the transport within the macro and mesopores [6]; then, in the second stage the dye penetrates within the less accessible pores, micropores, increasing the mass transfer diffusion resistance and decreasing the diffusion rate.

3.4. Adsorption isotherms.

The adsorption equilibrium of the methylene blue uptake onto the activated carbon at different temperatures was studied. The adsorption isotherms at temperatures from 303 to 333 K are depicted in Figure 5. 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. As it was discussed above, the activated carbon surface at the working pH range is negatively charged due to deprotonated acidic groups, enhancing the methylene blue uptake.
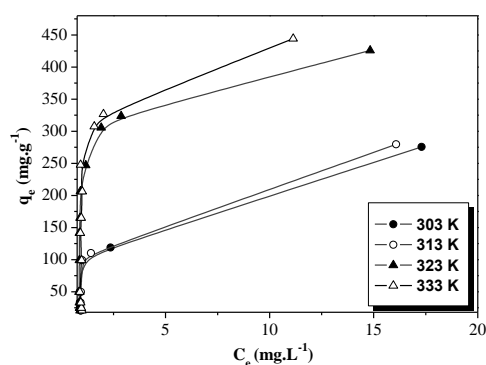
Figure 5. Adsorption isotherms of methylene blue onto activated carbon at different temperatures. Conditions: pH: 6.3; particle size: 125-250 μm; initial concentration: 100.0 mg.L^{-1}; adsorbent dosage: 0.8 g.L^{-1}.

From the Figure it can be observed that the adsorption capacity highly increased from 275.7 to 444.3 mg.g^{-1} when the temperature increased from 303 to 333 K. Since generally adsorption processes are defined as exothermic nature, many examples of endothermic processes in aqueous phase adsorption are usually found in the literature. 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 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. The thermodynamic parameters, standard enthalpy (ΔH^0, kJ.mol^{-1}), entropy (ΔS^0, J.mol^{-1}.K^{-1}) and Gibbs free energy (ΔG^0, kJ.mol^{-1}) were determined from the equilibrium experimental data of the adsorption of methylene blue onto the synthesized activated carbon.

The positive ΔH^0 value is indicative of an endothermic process, as it was observed from experimental data. Deng et al. [7] 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. The obtained positive value of AS^0, 51.64 J.mol^{-1}.K^{-1}, indicates an increasing in the randomness at the solid-liquid interface during the adsorption processes with the increase in the solution temperature. This behavior is usually associated to physical adsorption phenomenon. Finally, all the ΔG^0 values are negative, from -10.93 to -9.59 kJ.mol^{-1}, indicating that the adsorption of methylene blue onto the synthesized activated carbon was spontaneous and thermodynamically favorable.

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 lead to the excellent behavior in the removal of methylene blue from aqueous solution. The kinetic studies revealed that the initial methylene blue concentration and the

adsorbent dosage are the main tested parameters influencing on the adsorbate uptake. The equilibrium adsorption time was attained in around 50 hours. In addition, through the modelling of the experimental data, it could be concluded that the pseudo-second order model attained the best fitting to the experimental kinetic data and that the intra-particle diffusion is the only rate-controlling step in the process. 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 waste waters in the textile industry.

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