

Adsorption of a Textile Dye on Commercial Activated Carbon: A Simple Experiment To Explore the Role of Surface Chemistry and Ionic Strength

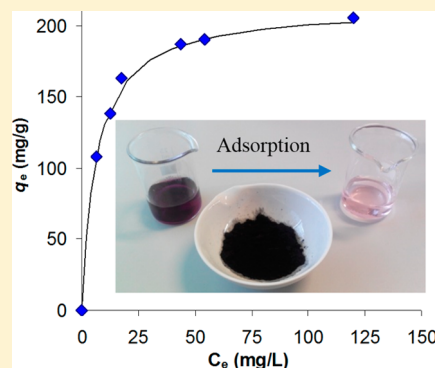
Angela Martins* and Nelson Nunes

Área Departamental de Engenharia Química and CIEQB, Instituto Superior de Engenharia de Lisboa, Rua Conselheiro Emídio Navarro, 1, 1959-007 Lisboa, Portugal

CQB, Faculdade de Ciências, Universidade de Lisboa, Campo Grande C8, 1749-016 Lisboa, Portugal

Supporting Information

ABSTRACT: In this study, an adsorption experiment is proposed using commercial activated carbon as adsorbent and a textile azo dye, Mordant Blue-9, as adsorbate. The surface chemistry of the activated carbon is changed through a simple oxidation treatment and the ionic strength of the dye solution is also modified, simulating distinct conditions of water hardness. The purpose of this experimental work, directed to undergraduate (second-year) students is to allow them to understand the influence of surface chemistry and ionic strength on the interaction between the carbon surface and the dye molecule.



KEYWORDS: Second-Year Undergraduate, Physical Chemistry, Environmental Chemistry, Hands-On Learning/Manipulatives, Surface Science, UV-vis Spectroscopy, Laboratory Instruction

THEORETICAL CONCEPTS

Adsorption and adsorption processes are a key topic included in most physical chemistry undergraduate courses and textbooks.^{1,2} The interaction between adsorbed molecules (adsorbate) and the solid surface (adsorbent) can be typified into two categories: physisorption, when the adsorbed molecules are weakly connected to the surface by electrostatic type bonds, and chemisorption, when molecules are strongly bonded, as a consequence of chemical reactions taking place at the solid surface. Adsorption is the background for several applications such as heterogeneous catalysis, wastewater contaminant removal, chromatographic analysis and textile dyeing, among others. The importance of this phenomenon and its application, led to the publication of a significant number of papers in this Journal^{3–6} as well as the inclusion of several adsorption experiments in many chemistry laboratory textbooks.^{7,8}

Activated carbons are excellent adsorbent materials, with particular application in the clarification of effluents, including the removal of coloring matter from various sources like textile, printing, cosmetics, and food coloring. However, the high costs of activated carbon, especially in some developing countries led to the search of alternative sources to obtain activated carbon from inexpensive waste materials such as coconut coir, olive stone, sawdust, and so forth.^{9–11}

Mordant Blue-9 (MB-9), is a cationic synthetic dye that belongs to the category of azo dyes due to the presence of one

or more azo linkages ($-\text{N}=\text{N}-$) and aromatic rings. The molecular structure of MB-9 is represented in Figure 1. The azo

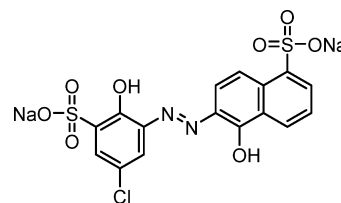


Figure 1. Molecular structure of Mordant Blue-9 ($\text{C}_{16}\text{H}_9\text{ClN}_2\text{Na}_2\text{O}_8\text{S}_2$).

dyes represent the most common group of synthetic dyes used in textile industry (60–70%) and are known to be toxic to living organisms. Therefore, the treatment of wastewater containing dyes with simple and low-cost technologies is a challenging goal.

The adsorptive properties of activated carbon are determined not only by its porous structure but also by its chemical composition. Oxygen surface groups (OSG) are formed by reaction with oxygen during the carbon preparation steps, they can also result from the interaction with many oxidizing gases

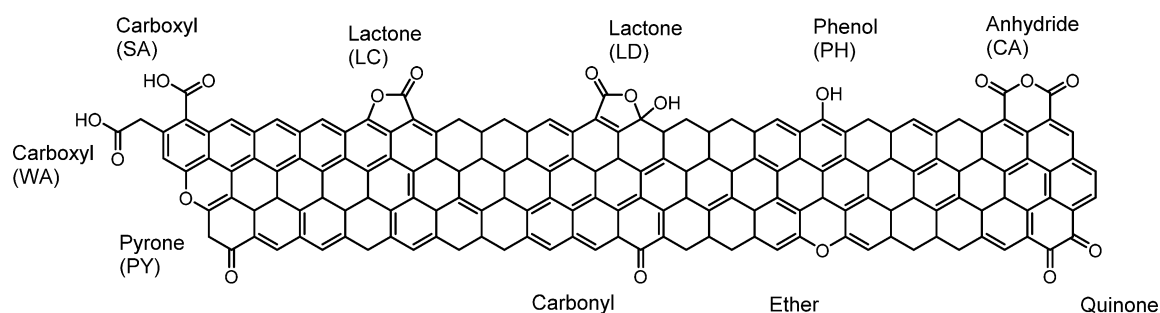


Figure 2. Types of oxygen surface groups (OSG) commonly present on activated carbon.

such as ozone, nitrous oxide, among others or oxidizing solutions like nitric acid, hydrogen peroxide, and so forth.¹²

There are several types of oxygen surface groups, as can be observed in Figure 2. The nature of these groups is responsible for the basic or acid character of the carbon, which is a key parameter for an efficient interaction between the adsorbent and the adsorbate. The amount and type of OSG present on the carbon surface is also responsible for the negative or positive charged surfaces when the carbon is placed in aqueous solutions, depending on the pH. For a particular value of pH the net of overall surface charge will be zero. On the basis of the previous reasons, this point is called point of zero charge, pH_{pzc} , an important parameter to evaluate the presence of positive or negative surface charge; at $\text{pH} > \text{pH}_{\text{pzc}}$ the carbon surface will attract cations from solution; on the other hand, if $\text{pH} < \text{pH}_{\text{pzc}}$ it will attract anions.

In this work, we propose an adsorption experiment directed to undergraduate (second-year) students using activated carbon as adsorbent and a textile azo dye, Mordant Blue 9 (MB-9), as adsorbate. The surface chemistry of the adsorbent material is modified through a simple oxidation treatment and the ionic strength of the dye solution is also modified, simulating distinct conditions of water hardness. The purpose of this experimental work is to allow students understand the effect of the surface chemistry and the ionic strength on the interaction between the carbon surface and the dye molecule.

UV-vis spectroscopy is used for determining the concentration of dye molecules in solution after contact with the solid adsorbent. The dye concentration is simply determined by absorbance measurement of an aliquot at appropriate wavelength, preceded by separation of the solution dye from the adsorbent through filtration or centrifugation. The difference in optical density between the initial and equilibrium solutions provides an easy way to measure the amount of dye adsorbed.

■ PEDAGOGICAL STRATEGY

When second year undergraduate students face the study of adsorption phenomena, they are generally instructed to determine experimentally an adsorption isotherm, followed by the application of a model, such as Langmuir or BET, estimating the adsorption capacity and specific surface area of the porous sample. The proposed experiment follows this approach but goes further by exploring the role of oxygenated surface groups at the activated carbon surface and their possible interaction with the dye molecule. Also, the effect of water characteristics (water hardness) is considered, placing students with a hypothetical wastewater treatment situation and how this parameter could influence the efficiency in the contaminant removal.

The pedagogical strategy proposed in this study is the collaborative learning of all students in the class. The proposed activity was carried out by second year students with basic knowledge of adsorption previously lectured on Physical Chemistry theoretical classes. The laboratory classes took place in three weekly periods the first session took 2 h in a regular classroom equipped with computers. In the first 30 min, the instructor presented the theme of the work including the theoretic background and mathematical treatment, emphasizing the key parameters to be explored. Then the students formed groups of two or three elements and briefly searched for information in the literature.

In the end of this session, the instructor coordinated the equilibrated distribution of experimental work, ensuring that each group would work with different pair adsorbent/adsorbate or different experimental conditions. The second session consumed 4 h of laboratory work. Because some steps of the experimental work are very time-consuming, such as the preparation of: oxidized carbon samples, stock solution of MB-9 dye and hard water solutions, these operations were previously performed by the instructor.

Student's experimental procedure and instructor guidelines are detailed in Supporting Information. The third session took about 2 h in a regular classroom equipped with computers. In this session, each student group processed the data and made a short presentation of the most relevant results for the whole class followed by debate, involving the whole class and supervised by the instructor.

■ EXPERIMENTAL PROCEDURE

Mordant Blue-9 (MB-9) dye ($\text{C}_{16}\text{H}_9\text{ClN}_2\text{Na}_2\text{O}_8\text{S}_2$, 502.81 g/mol) was purchased from Sigma-Aldrich and used as received (Figure 1). A concentrated solution of MB-9 dye (200 mg/L) was prepared by dissolving the powder in deionized water and used as a stock solution, MB9.

Two synthetic water samples were prepared using $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (Sigma-Aldrich, 99%) and $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (Aldrich, 99.95%) in such proportions (detailed procedure described in Supporting Information) to obtain two different hardness levels: 80 and 200 mg/L of equivalent CaCO_3 , as described. These solutions were used as solvent to prepare the stock solution MB9-80 or MB9-200, following the procedures described above.

Two commercial samples of activated carbon were used in this study: Panreac (Lot 0000115091) and Fagron (Lot 11090097). The samples were used as received or after being submitted to an oxidant acid treatment in order to change the amount of oxygen surface groups (OSG). To perform this operation 20 mL of 4.6 M HNO_3 solution (Sigma-Aldrich, ACS 70%) were added to 2 g of each activated carbon sample. The

suspensions were heated at 60 °C on a heating plate (IKA C-MagHS7) until a paste was obtained. The paste was filtered (using typical laboratory folded filter paper) and washed several times with deionized water until the pH of the filtrate is identical to that of deionized water and left to dry at room temperature for about 24 h.

To shorten the experimental time all the stock solutions were previously prepared as well as the oxidation treatment of the activated carbons.

The students started their laboratory work by preparing diluted solutions from one of the stock solutions MB9, MB9-80, and MB9-200, according to their previous choice. Six to eight solutions were prepared with concentration ranging from 20 to 110 mg/L in order to obtain absorbances from 0.05 to 1.5.

For the adsorption studies, 10 mg of carbon samples were accurately weighed and placed in 100 mL stoppered flasks. Then, 80 mL of dye solution solutions previously prepared were added to the flasks and stoppered. The flasks are then immersed on a thermostatic bath at 30 °C (Julabo MP), which is placed on a multiposition magnetic stirrer (Multimatic 9-S, Selecta) for 2 h to reach equilibrium. The 2 h equilibration time can be used by each group of students to perform two operations following the instructor guidance: (i) calibration curve using the previously prepared dye solutions and (ii) preparation of the carbon samples for pH_{pzc} determination. For building the calibration curve, each solution was scanned in the visible region (400 to 600 nm) using a double beam spectrophotometer (Jasco V530), taking deionized water as reference. The wavelength for maximum adsorbance (λ_{max}) was 420 nm. For this concentration range and using a standard cell of 1 cm optical length, the dye solutions obey the Beer–Lambert law.

For measuring the point of zero charge (pH_{pzc}) 1 g of the selected carbon sample was added to 20 mL of deionized water (preferentially, this water should be previously boiled for about 1 h to remove CO₂ and then cooled to room temperature). The slurries were left under stirring until nearly the end of the experimental session and then the pH of the slurry was measured by each group of students using a glass electrode (Crison, GLP22 pH meter).

When 2 h equilibration time was reached, the activated carbon samples were separated from the dye solutions by centrifugation (Hermle Z206 A). Aliquots of each solution were taken and their adsorbance at 420 nm was measured. Each data point resulted from the average of at least three individual aliquots/scans assuring a relative standard deviation below 5%.

Experimental details and alternative equipment's/procedures are available for students and instructor at Supporting Information.

HAZARDS

HNO₃ should be handled with the utmost caution because it is corrosive and flammable. Due to the high concentration of HNO₃ solutions, it is advisable that the oxidation treatment is performed by the instructor in a well-ventilated hood.

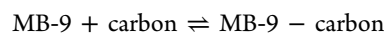
Because the experiment involves the manipulation of fine powders, such as the activated carbon samples or Mordant Blue-9 dye, all students and the instructor must wear individual safety equipment: dust mask, goggles, and gloves.

TREATMENT OF THE RESULTS

The concentrations of MB-9 dye present on the solutions were calculated using the Beer–Lambert law, which relates the measured absorbances (*A*) with the solutions concentrations (*C*) and the extinction molar coefficient at 420 nm (ϵ_{420}), the linear relation was valid in the concentration range of 20 to 110 mg/L and for a standard path length (*l*) of 1 cm

$$A = \epsilon_{420}lC \quad (1)$$

The adsorption isotherms were obtained as described above. After 2 h of contact between the dye solutions and the carbon samples, the equilibrium is reached between the two phases



As the experimental values obtained through the measures of absorbances only allow determining the concentration of the dye present in the solutions, the amount of dye adsorbed on the surface of activated carbon, q_e , expressed in milligrams of dye adsorbed per gram of carbon (mg/g) is calculated using the relation

$$q_e = \frac{C_0 - C_e}{W} \times V \quad (2)$$

where $C_0 - C_e$ is the difference between the initial and equilibrium concentration of the dye in solution (mg/L), respectively, *W* is the mass of activated carbon (mg), and *V* is the volume of solution that was in contact with the activated carbon (L).

The relation between the amount of dye adsorbed on the carbon and the equilibrium concentration of the dye solution is described in the Langmuir isotherm equation

$$q_e = \frac{q_m \cdot K_L \cdot C_e}{1 + K_L \cdot C_e} \quad (3)$$

where q_m is the adsorption capacity (mg/g), K_L is the Langmuir constant (L/mg), which can be related with the affinity between the adsorbent and the adsorbate. The parameters K_L and q_m are characteristic of each adsorbent/adsorbate system and can be determined from the linearization of eq 3

$$\frac{C_e}{q_e} = \frac{1}{q_m \cdot K_L} + \frac{C_e}{q_m} \quad (4)$$

The process of turning a hyperbolic graph (eq 3) into a linear graph (eq 4) is a common procedure applied in several disciplines such as biochemistry (Michaelis–Menten enzyme kinetics).

By representing C_e/q_e as a function of C_e a straight line is obtained (if the adsorbent/adsorbate system obeys the behavior predicted by the Langmuir equation), allowing obtaining K_L and q_m taken from the slope and the intercept, respectively.

RESULTS AND DISCUSSION

The adsorption capacity of porous materials is strongly dependent from their textural properties. Table 1 displays the

Table 1. Textural Parameters of the Commercial Activated Carbons

Carbon sample	V_{micro} (cm ³ /g)	V_{meso} (cm ³ /g)	A_{ext} (m ² /g)
Fagron	0.33	0.66	514
Panreac	0.19	0.35	296

textural characteristic of the commercial activated carbons used in this work: microporous volumes, V_{micro} (voids with average pore diameter lower than 2 nm), mesoporous volume, V_{mesop} (average pore diameter comprised between 2 and 50 nm) and external surface area, A_{ext} . The textural parameters were determined from the N_2 desorption isotherms obtained from an automatic gas adsorption apparatus (Micromeritics ASAP 2010), performed at the Adsorption Laboratory–CQB/FCUL, Lisbon, Portugal. Detailed information concerning the determination of the textural parameters from N_2 adsorption data can be found on ref 13. Despite the fact that carbon textural characterization is not usually done in students laboratories because is a very long essay, these data are generally given by the suppliers of activated carbons or, alternatively, some data can be found on the literature.

The data presented in Table 1 show that the textural properties of the two commercial activated carbon samples are distinct.

In fact, Fagron carbon shows a more developed porosity, both V_{micro} and V_{meso} , along with a higher external surface area, A_{ext} , when compared with Panreac carbon.

The values of pH_{pzc} , determined for commercial and oxidized samples, are displayed in Table 2, where the

Table 2. Parameters Determined from the Linearized Langmuir Equation, Statistical Parameters of Fit and pH_{pzc} Values

Sample	q_m (mg/g)	K_L (dm ³ /mg)	R^2	sd_{fit}	F	pH_{pzc}
Fagron	221	0.126	0.97	0.030	199	6.9
Fagron-80	300	0.330	0.98	0.012	300	
Fagron-200	490	0.418	0.98	0.004	332	
Fagron-Ox	180	0.005	0.90	0.061	28	2.9
Panreac	213	0.157	0.99	0.003	4423	6.7
Panreac-Ox	93	0.032	0.92	0.083	60	2.8

designation “-Ox” is used after the commercial names of the activated carbons to name the oxidized samples. The two commercial activated carbons present similar pH_{pzc} values, close to neutrality, which is common for commercial activated carbons. Upon oxidative treatment with HNO_3 solution, both carbons samples show a low value of pH_{pzc} , which indicates that a higher concentration of oxygenated surface groups does not improve the interaction between the activated carbon surface and MB-9 dye molecule. If a deeper exploration of the effect of the surface chemistry is desired, a larger set of oxidized carbons can be given to the students, prepared with solutions of HNO_3 or H_2O_2 with several concentrations, which allow obtain a wider range of pH_{pzc} values. On the other hand, alternative dye molecules can be used, with distinct interactions with the carbon surface. In some cases, the enrichment of oxygenated surface groups can improve the adsorbent/adsorbate interaction.

Figure 3 shows the adsorption isotherms for the two commercial activated carbons as well as the effect of the oxidative treatments.

The effect of the ionic strength of the dye solution, aiming to simulate the hardness of the water, was studied for Fagron carbon and the respective isotherms are presented in Figure 4, where the designation “-80” or “-200” was used after the commercial names of the carbon to label the samples in contact with medium hard and hard water, respectively.

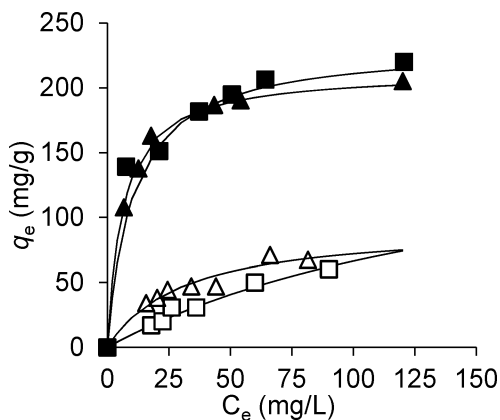


Figure 3. Adsorption isotherms of MB-9 dye at commercial activated carbon samples Fagron (■) and Panreac (▲) and oxidized samples Fagron-Ox (□) and Panreac-Ox (Δ).

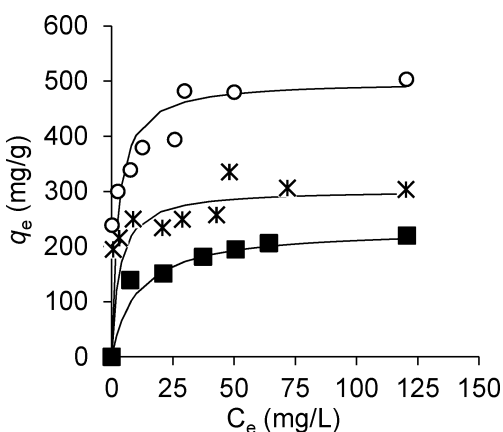


Figure 4. Effect of water hardness on the adsorption isotherms of MB-9 at Fagron commercial activated carbon. Fagron (■), medium hard water Fagron-80 (*) and hard water Fagron-200 (○).

The application of the linearized Langmuir equation (eq 4) is exemplified in Figure 5 for Fagron carbon, using common deionized water and Fagron-80 and 200 for synthetic medium hard and hard water. The equations obtained from the linear regression and the correspondent coefficients of determination (R^2), along with other relevant statistical information can be

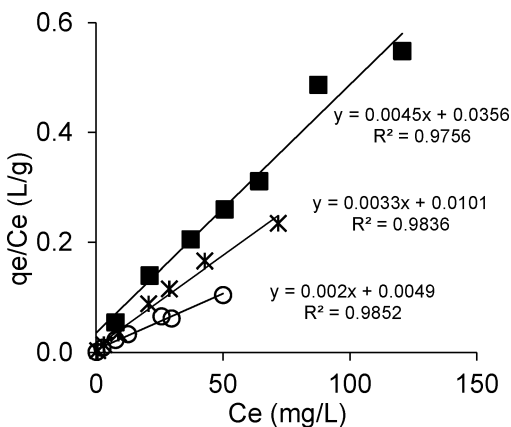


Figure 5. Application of the Langmuir isotherm (linearized form) to the experimental data points determined for the adsorption of MB-9 at Fagron (■), Fagron-80 (*), and Fagron-200 (○).

easily obtained by students using Microsoft Excel or other statistical software.

Table 2 summarizes the parameters K_L and q_m taken from the linearized Langmuir equation (eq 4), as well as statistical parameters: determination coefficient (R^2), standard deviation of the fit (sd_{fit}) and Fisher statistics (F). The multiple statistical values indicate how well data points fit the linearized Langmuir equation and all studied experimental conditions are predicted with the obtained equation, meaning that the Langmuir equation can be applied for this adsorbent/adsorbate systems.

Table 2 analysis of allows a direct comparison between the two commercial samples, with Fagron carbon presenting a higher adsorption capacity (q_m), in accordance with the textural properties of this carbon (see Table 1). However, the Langmuir constant, K_L , is lower, indicating a higher affinity between the dye and the surface of Panreac carbon. The effect of the hardness of the water was investigated on commercial Fagron carbon and the results obtained (Figure 3 and Table 2) showed that the raise of the ionic strength promotes the interaction between the dye molecules and the carbon surface, being advantageous for removing MB-9 contaminant from the effluent. On the other hand, the oxidative treatment performed on the carbon samples has a negative impact on dye retention in both carbons (Figure 4 and Table 2), showing that the presence of a higher concentration of oxygenated surface groups is not beneficial for the retention of this particular dye molecule.

CONCLUSIONS

This laboratory activity led second year undergraduate student to understand and apply concepts and equations related to adsorption and adsorbent materials and, simultaneously, allowed the introduction of some topics concerning water pollutants and wastewater treatments technologies.

However, the main purpose of this activity was to lead student understanding the role of important parameters that affect adsorbent/adsorbate systems such as (i) the surface chemistry of the carbons and (ii) the importance of ionic strength of the water where the dye is dissolved.

This experimental activity is reasonably versatile and, depending on the number of students in the class and available equipment other types of dyes, carbon samples with distinct degrees of oxidation and water with distinct levels of hardness can be studied and discussed.

The experimental work can be carried out with equipment and material present on a typical Physical Chemistry undergraduate laboratory and several options are given in Supporting Information section.

ASSOCIATED CONTENT

Supporting Information

Instructions for students and notes for instructors are available in this issue of JCE online. This material is available via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

*E-mail: amartins@deq.isel.ipl.pt.

Notes

The authors declare no competing financial interest.

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