Adsorption properties of modified date pits activated carbons

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Abstract — Equilibrium adsorption isotherm for the removal of Methylene Blue (MB) from aqueous solution using modified activated carbons has been investigated. The activated carbon was prepared by physical activation of date pits using CO_2 . The surface chemistry of the activated carbon was modified by appropriate treatments (Oxidation with $(NH_4)_2S_2O_8$ and heat treatment) in order to obtain two additional samples, with different chemical surface properties. The three carbons have been characterized by adsorption of N_2 (-196°C) and CO_2 (0°C). The changes in surface chemistry were studied by temperature programmed decomposition (TPD). Freundlich, Langmuir and Redlich-Peterson equations were tested for modelling the adsorption isotherms at equilibrium. Influence of temperatures of the adsorption of MB onto activated carbons has been considered too. The thermodynamic parameters such as standard enthalpy $\Delta H°$, standard entropy $\Delta S°$ and standard free energy $\Delta G°$ were evaluated. The adsorption of MB on activated carbons is a spontaneous process.

Keywords — Activation, microporous carbons, oxidation, adsorption

1 INTRODUCTION

Synthetic organic dyes present hazards and environmental problems. Dye effluent are aesthetic pollutants that contain chemicals that exhibit toxic effects toward microbial populations and can be toxic and or/ carcinogenic to organisms and mammals[1].

Activated carbons are the most popular adsorbents used for the removal of toxic substances from water. The carbon precursors may be of botanical origin (wood, coconut shells, fruit seeds), mineral origin (coal, peat), or polymeric materials (rubber tyres, plastics). About 50% of industrially available activated carbons are derived from precursors of botanical origin [2]. These precursors are usually low-cost agricultural residues with no notable applications except as fuels for energy generation. Numerous agro-waste biomaterials have been used for the production of activated carbons, including coconut shells, almond shells, peach stones, apricot stones, plum stones, cherry stones, apple pulp, and nutshells . Date pits have received less consideration as a source material for the preparation of activated carbon [3].

Algeria is one of the leading countries engaged in planting several millions of palm-date trees. Huge quantities of date pits are generated as wastes. The generated pits can be used to produce activated carbon. The importance of this lies on utilizing the generated waste, which is the palm-date pits, in the form of activated carbon as a medium for wastewater treatment purposes. Thus, it will have an advantage from environmental and economical aspects.

In the present work, the activated carbon was prepared from date pits by thermal activation, then, the sample was modified by appropriate treatments in order to obtain two additional activated carbons with different surface chemical properties but with no important differences in their textural properties. The adsorbents prepared are subsequently tested in the removal of Methylene blue from aqueous solution.

2 EXPERIMENTAL

2.1 Materials

The activation was carried out in two stages: pyrolysis and activation. The carbonization was made with N_2 (150 mL min^{-1}) at 825 °C during 120 min, based in previous work [4]. The activation process was carried out at the same temperature of activation during 270 min under a flow of CO_2(80 mL min^{-1}), which corresponded to a burn off of 50%. This sample was labelled DS followed by the burn off 50.

In order to study the effect of surface functional groups in the adsorption process, sample DS50 was submitted in a subsequent step to an oxidation treatment with a saturated solution of $(NH_4)_2S_2O_8$

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during 4 hours at 25 °C. The oxidized sample (DS50Ox) was washed with distilled water and subsequently heat treated under N_2 (80 mL min^{-1}) at 700°C in order to remove the less stable of the oxygen surface groups (sample DS50OxH).

The N_2 adsorption isotherms were used to calculate: (1) the value of the BET specific surface (S_{BET}) [5] , (2) the volume of micropores (V_{mi}) through the Dubinin–Radushkevich equation [6], and (3) the mesopore volume (V_{me}), which was determined from the difference between the pore volume at P/P0=0.95 and the calculated V_{mi}.

The pore volume corresponding to the narrow microporosity (Vn) was obtained after application of the DR equation to the CO_2 adsorption data [7].

Temperature programmed desorption (TPD) experiments were done in a U-shaped quartz reactor on-line coupled to a mass spectrometer ((Balzer MSC200), to characterize the surface chemistry of all samples. In these experiments, 10 mg of the sample were heated up to 1000°C (heating rate 10 °C/min) under a helium flow rate of 50 ml/min. The amount of CO and CO_2 evolved were quantified after calibration with calcium oxalate (CaC_2O_4-H_2O).

2.3 Equilibrium sorption test

The isotherm studies have been undertaken to assess of the adsorbent to remove Methylene Blue dye from aqueous solution. Batch adsorption experiments were carried out by shaking constant mass (0.02 g) of adsorbent with constant volume (20 ml) of Methylene Blue solutions of increasing initial dye concentration. Upon equilibrium, the samples were filtered and analysed using UV/VIS spectrophotometer (Unicam helios δ). All the measurements were made at a wavelength corresponding to the maximum absorbance of 665 nm. Dilution were undertaken when absorbance exceed 1.0. The amount of dye adsorbed onto the activated carbon was measured by subtracting the remaining concentrations of the dye solution from the initial concentration.

3 RESULTS AND DISCUSSION

3.1 Characterization of activated carbons

The textural and chemical characterizations of the activated carbons can be seen in Tables 1 and 2. As it can be seen from Table 1, carbons are essentially microporous and present a certain contribution of mesoporosity. It may be concluded that the liquid oxidation with $(NH_4)_2S_2O_8$ has no significant impact on the texture of the carbon. It is generally reported that the liquid phase oxidations do not change significantly the texture of the activated carbons

[4,8,9]. However, this treatment increases the oxygen surface groups evolved as CO and CO_2 (see Table 2). The subsequent thermal treatment at temperature 700°C produces the removal of the more acidic and less stable oxygen groups, which is clearly reflected by the increase in the CO/CO_2 ratio. In the other hand, the specific surface area and micropore volume increase with the heat treatment and recover the adsorption properties of the original activated carbon.

Table 1. Textural characterisation of the activated carbons

Sample	S_{BET} (m²/g)	V_{mi} (m³/g)	V_{me} (m³/g)	V_n (m³/g)
DS48	1325	0.56	0.16	0.40
DS48Ox	1246	0.52	0.15	0.38
DS48OxT	1380	0.57	0.16	0.41

Table 2. Chemical characterisation of the activated carbons by TPD experiments

Sample	CO (mmol/g)	CO_2 (mmol/g)	CO/CO_2
DS48	1.19	0.29	4.1
DS48Ox	2.32	0.95	2.4
DS48OxT	0.90	0.11	8.1

3.2 Adsorption equilibrium modeling

The adsorption isotherms of MB at 25°C onto the three activated carbons (DS48, DS48Ox and DS48OxT) are shown in Fig. 1. The isotherms are of the L type according to Giles classification. These isotherms express the adsorption amount as a function of equilibrium concentration. Three isotherm equations are used to describe experimental adsorption data, two-parameter model, Langmuir, Freundlich and three parameter model, Redlich-Peterson equations [10-12]. The fitting curves from these three isotherm model are also illustrated in Fig.2 using non linear regression.

Langmuir model is the most widely used isotherm equation, which has the form as follows

$$q_e = \frac{Q_L K_L C_e}{1 + K_L C_e} \qquad (1)$$

where qe (mg/g) and Ce (mg/l) are the amounts of adsorbed dye per unit weight of activated carbon and equilibrium dye concentration in solution. Q (mg/g) is the maximum amount of adsorbed dye per unit weight of adsorbent and K_L (l/mg) is the adsorption equilibrium constant. Q represents a practical

limiting adsorption capacity when the surface of adsorbent is fully covered with dye molecules.
The Freundlich isotherm is an empirical equation that is also often used to correlate adsorption experimental data. The Freundlich isotherm equation has the following form

$$q_e = K_F \cdot C_e^{1/n_F} \tag{2}$$

K_F and n are the Freundlich constants. K_F and n are indicators of adsorption capacity and adsorption intensity, respectively.

Redlich-Peterson (R-P) model has three constants and it has been proposed to improve the fit by Langmuir and Freunlich models. Eq. (3) reduces to a linear isotherm at low surface coverage, to the Freundlich isotherm at high adsorbate concentration and to the Langmuir isotherm when β = 1

$$q_e = \frac{K_{RP} C_e}{1 + a_R C_e^{\beta}} \tag{3}$$

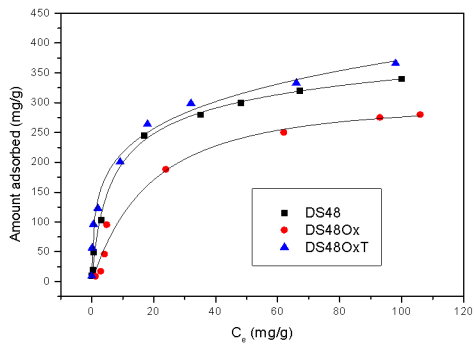where K_{RP} and β are the R–P constants.

Fig.1 Adsorption equilibrium isotherms of methylene blue on activated carbons at 25°C
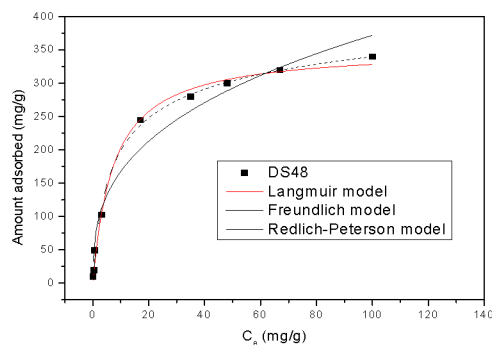

Fig.2 Model fit of Langmuir, Freundlich and Redlich-Peterson isotherms of methylene blue on activated carbon DS48

The constants of isotherms and correlation coefficients obtained from non-linear method are listed in Table 3.The comparison of parameters suggests that Redlich-Peterson and Langmuir best fit the adsorption of methylene blue on the three activated carbons according to the correlation coefficient. The high adsorption capacity is reached with DS48OxT sorbent. The maximum adsorption capacity follows this sequence: DS48OxT >DS48>DS48Ox. Values of $1/n_F$ of Freundlich model isotherm are less than unity, suggest that the dye is favorably adsorbed by all activated carbons.

Table 3 Langmuir, Freundlich and Redlich-Peterson parameters of methylene blue on activated carbons

Sample	Q	K_L	R^2
DS48	352.3	0.135	0.997
DS48Ox	333.0	0.050	0.990
DS48OxT	360.1	0.232	0.987

Sample	K_F	$1/n_F$	R^2
DS48		0.29	4.1
DS48Ox	2.32	0.95	2.4
DS48OxT	0.90	0.11	8.1

Sample	K_{RP}	a_R	β	R^2
DS48	66.8	0.296	0.921	0.998
DS48Ox	22.1	0.090	1.02	0.990
DS48OxT	44.0	0.113	0.892	0.991

3.3. Thermodynamics studies

The thermodynamic parameters like enthalpy change ($\Delta H°$) and entropy change ($\Delta S°$) were obtained from the Van't Hoff equation:

$$\log K_C = \frac{\Delta S^0}{2.303R} - \frac{\Delta H^0}{2.303RT} \tag{4}$$

Where $\Delta S°$ and $\Delta H°$ were calculated from the slope and intercept of linear plots of log K_C vs. $1/T$.
Equilibrium constant (K_C) was calculated from the following relationship:

$$K_C = \frac{C_{Ae}}{C_e} \tag{5}$$

where C_{Ae} and C_e are the equilibrium concentrations of dye (mg /L) on sorbent and in solution, respectively.
Free energy change ($\Delta G°$) was calculated from the relation

$$\Delta G° = -RT \ln K_c \tag{6}$$

Where T (K) is the absolute temperature, R (J/K mol) gas constant, $\Delta G°$ is the standard free energy change.
It is noted that all $\Delta G°$ values listed in Table 4 are negative. This suggests that the adsorption process is spontaneous with high preference of methylene blue

for activated carbon. As seen from Table 3 the positive value of adsorption enthalpy shows that the adsorption process is endothermic. Increasing temperature is known to increase the rate of diffusion of the adsorbate molecules across the external boundary layer and in the internal pores of the adsorbent particle, owing to the decrease in the viscosity of the solution. The positive value of entropy $\Delta S°$ change shows the increase in randomness at the solid/solution interface during the sorption.

Table 4
Thermodynamic parameters for the sorption of Methylene blue at different temperatures

Activated carbon	Temp. (K)	$\Delta G°$ (kJ/mol)	$\Delta H°$ (kJ/mol)	$\Delta S°$ (kJ/mol)
DS48	298	-7.29		
	313	-8.47	29.85	0.123
	333	-11.57		
DS48Ox	298	-6.81		
	313	-7.94	16.98	0.079
	333	-9.61		
DS48OxT	298	-8,20		
	313	-10,12	30.60	0.129
	333	-12.71		

4 CONCLUSIONS

Activated carbons produced from date stones by physical activation with CO_2 give good physical and chemical properties before and after treatments.
The oxidation of the activated carbon DS48 can fix a higher amount of oxygen, however the heat treatment reduces this quantity and gives basic characteristic to the sample.
The Langmuir and Redlich-Peterson best fit the isotherms data with Maximum adsorption capacity obtained from the Langmuir equation of 360mg/g.
The adsorption of methylene blue on activated carbons with different chemical surface properties is spontaneous and endothermic under the used conditions.

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