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Adsorption of dyes from aqueous solution onto activated carbons prepared from date pits: The effect of adsorbents pore size distribution

Naima Bouchemal*, Fatima Addoun

Labortoire d'étude physico-chimique des matériaux et application à l'environnement, Faculté de Chimie, USTHB,
B.P. 32, El Alia, 16111 Bab-Ezzouar, Algiers, Algeria
Tel./Fax +213 (21) 24 73 11; email: naima1usthb@yahoo.fr

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ABSTRACT

Several active carbons were prepared starting from Algerian date pits by chemical activation with the $ZnCl_2$, by physical activation with the CO_2, and by a method combined in the presence of $ZnCl_2/CO_2$. The active carbons obtained were followed by the evaluation of the yield and the physisorption of nitrogen at 77 K. Activated carbon particles were analyzed by scanning electron microscope (SEM). Indeed, it showed that mesoporous active carbon can be obtained at a lower cost by chemical impregnation in $ZnCl_2$ with 800°C followed by activation with CO_2. Thus, techniques combining the chemical method ($ZnCl_2$) and the physical method (CO_2) help to widen the pores allowing the conversion of the micropores into mesopores. Dye contamination in wastewater can lead to a variety of environmental problems. Colored water can affect plant life and thus an entire ecosystem can be destroyed by contamination of various dyes in water. The produced AC was tested against methylene blue and Congo red. This test was conducted to check the ability of the produced activated carbon. The mesoporous carbons showed high adsorption capacity of methylene blue and Congo red.

Keywords: Activated carbon; BET surface area; Porosity; Activation; Zinc chloride

1. Introduction

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 once dates are eaten. The generated pits can be reused to produce activated carbon that can be used for treating polluted water. The importance of this lies in 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.

The production of activated carbon appears to be one of the most important phases of this study. Different permutation combinations were investigated to achieve activated carbons with optimum physical characteristics.

Mostly microporous in nature (with pore diameters less than 2 nm) [1] activated carbons occupy an important position as adsorbent materials and are extensively employed for purification of gases, water and in chemical processing. Conventional activated carbons also contain mesopores (pore diameter in the range of 2–50 nm). Application of porous carbon materials as catalytic supports, battery electrodes, capacitors and in biomedical engineering often involves large molecules or macromolecules as adsorbates [2]. For these and similar applications, the carbon materials should possess not only high surface areas, but also high mesopore or macropore (pore di-

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* Corresponding author.

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ameters above 50 nm) content. Besides contributing to adsorption, mesopores are the main transport arteries for the adsorbate.

Dyes are widely used in industries such as textiles, rubber, paper, plastics, cosmetics etc. to color their products; these dyes are invariably left in the industrial wastes. Dyes even in low concentrations affect the aquatic life and food web. Since many organic dyes are harmful to human beings, the removal of color from process or waste effluents becomes environmentally important. Due to the large degree of organics present in these molecules and the stability of modern dyes, conventional physicochemical and biological treatment methods are ineffective for their removal [3,4]. This led to the study of other effective methods. The adsorption process is one of the efficient methods to remove dyes from effluent [5]. The process of adsorption has an edge over the other methods due to its sludge free clean operation and complete removal of dyes even from dilute solutions. Activated carbon is the most widely used adsorbent for this purpose because of its extended surface area, microporous structure, high adsorption capacity and high degree of surface reactivity.

2. Materials and methods

2.1. Carbon preparation

Carbon preparation process is presented in Fig. 1.

2.2. Carbon characterization

N_2 adsorption at –196°C was utilized to determine specific surface areas and porosities of these carbon samples. An automated adsorption apparatus (Micromeritics, ASAP 2010) was employed for these measurements. The external surface areas and the micropore volume of the samples (S_{Ext} and V_{mic}, respectively) were determined through the *t*-plot method [6]. The amount of N_2 adsorbed at relative pressures near unity (0.99 here) corresponds to the total amount adsorbed (V_T) in both the micropores and the mesopores. The mesopore volume (V_{me}) was obtained by subtracting the micropore volume from the total pore volume.

Surface images of the granular activated carbon were captured by SEM. The SEM used was Model JSM-35 CF by JOEL, Tokyo, Japan.

2.3. Adsorption studies

Adsorption from the liquid phase was carried out to verify the nature the porosity and the capacities of the samples. Methylene blue (MB) and Congo red (CR) were employed as the adsorbates in the adsorption experiments. An aqueous solution with a concentration of 500 mg/l was prepared by mixing an appropriate amount of MB or CR with distilled water adsorption experiments were conducted by placing 0.05 g of the carbon samples and 50 ml of the aqueous solution in a 250 ml glass-stoppered flash. The flask was then put in a constant-temperature shaker bath with a shaker speed of 100 rpm. The isothermal adsorption experiments were performed at 25 ±2°C.

Upon equilibration, all samples were filtered through nylon filters prior to analysis in order to minimize interference of the carbon fines with the analysis. The concentrations of the adsorbates in the residual solutions were determined spectrophotometrically using ultraviolet spectrophotometry (JASCO model 8543). A previously established linear Beer–Lambert relationship was used in the concentration analysis. For the solutions with high concentrations, dilution was needed to operate the analysis in the linear Beer–Lambert region. The equilibrium adsorption capacities (*Q*) at different dyes concentrations were determined according to the mass balance on the adsorbate:

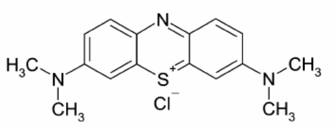
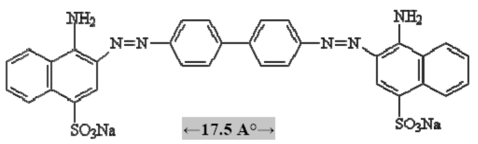
$$Q = \left(C_0 - C_r\right) V / m \qquad (1)$$

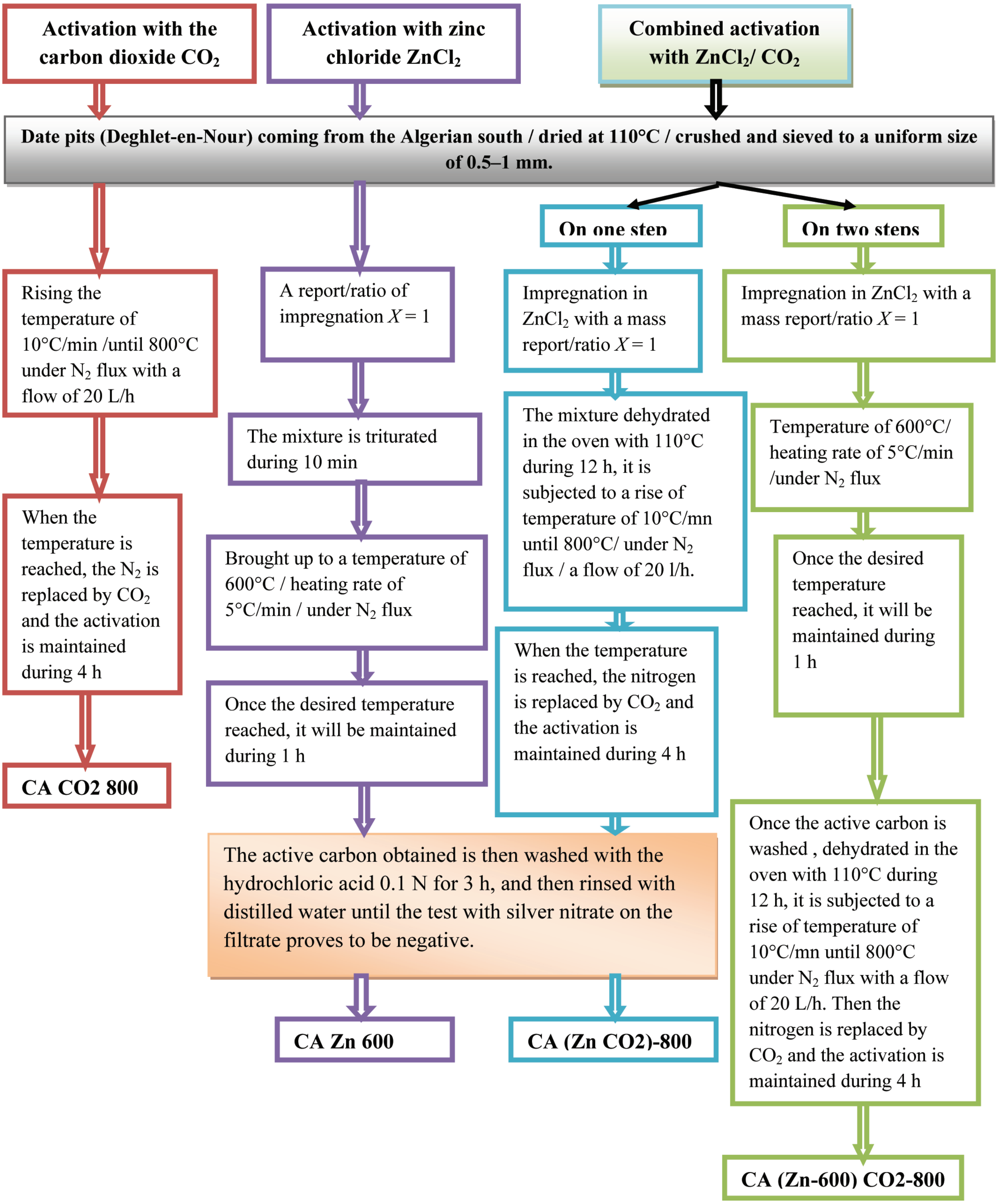
where C_0 is the initial concentration, C_r is the residual or equilibrium concentration, V is the volume of the liquid phase, and m is the mass of the activated carbon.

The effect of contact time on the amount of dye adsorbed was investigated at the optimum initial concentration of dyes. The initial concentrations were 200 mg/l.

Table 1 shows some characteristics of the chosen dyes for the present study.

Table 1
List of dyes chosen for the present study

	Methylene blue (MB)	Congo red (CR)
Molecular structure		
λ_{max}, nm	664	497
M (molar mass), g/mol	320	650.6
Size (A°)	15 (diameter)	17.5×5.0×2.8



Rising the temperature of 10°C/min /until 800°C under N_2 flux with a flow of 20 L/h

When the temperature is reached, the N_2 is replaced by CO_2 and the activation is maintained during 4 h

A report/ratio of impregnation $X = 1$

The mixture is triturated during 10 min

Brought up to a temperature of 600°C / heating rate of 5°C/min / under N_2 flux

Once the desired temperature reached, it will be maintained during 1 h

Impregnation in $ZnCl_2$ with a mass report/ratio $X = 1$

The mixture dehydrated in the oven with 110°C during 12 h, it is subjected to a rise of temperature of 10°C/mn until 800°C/ under N_2 flux / a flow of 20 l/h.

When the temperature is reached, the nitrogen is replaced by CO_2 and the activation is maintained during 4 h

The active carbon obtained is then washed with the hydrochloric acid 0.1 N for 3 h, and then rinsed with distilled water until the test with silver nitrate on the filtrate proves to be negative.

Impregnation in $ZnCl_2$ with a mass report/ratio $X = 1$

Temperature of 600°C/ heating rate of 5°C/min /under N_2 flux

Once the desired temperature reached, it will be maintained during 1 h

Once the active carbon is washed , dehydrated in the oven with 110°C during 12 h, it is subjected to a rise of temperature of 10°C/mn until 800°C under N_2 flux with a flow of 20 L/h. Then the nitrogen is replaced by CO_2 and the activation is maintained during 4 h

Fig. 1. Carbon preparation.

3. Results and discussion

Fig. 2 shows the nitrogen adsorption isotherms obtained at 77 K for activated carbons prepared with different methods. The four carbons prepared exhibit steep type 1 isotherms [1], indicative of highly micropous materials. For the samples CA (Zn CO2)-800 and CA (Zn-600) CO2-800 the isotherms take a shape resembling a combination of type 1 and II.

Additionally, development of mesoporosity is indicated by the pronounced desorption hysteresis loops.

Parameters calculated by the Brunauer–Emmett–Teller (BET) equation [16] and the *t*-plot method [17] from N_2 sorption isotherms are shown in Table 2. Samples CA (Zn CO2)-800 possess mesopore volumes greater than 0.9 cm^3/g and BET surface area greater than 1500 m^2/g; the effect of adding $ZnCl_2$ is felt in terms of tow competing mechanisms–micropore formation and pore widening [7]. For the sample CA Zn 600 micropore formation is the dominating mechanism.

Table 2 also shows the results obtained for sample CA CO2 800 is essentially a microporous carbons, the micropore content reaches a value of 75%. While yields (calculated on the basis of raw material dried at 110°C prior to $ZnCl_2$ impregnation) tend to decrease for a sample with larger surface area, Table 2 shows that it is possible to obtained mesoporous activated carbons having high surface area with the yield of 20%.

These results suggest that it is feasible to control the nature and extent of porosity by means of the experimental parameters.

Conventionally, chemical activation with $ZnCl_2$ is conducted in an inert N_2 atmosphere at 500–700°C. Most of the $ZnCl_2$ remains in the carbon during activation and is removed by washing after activation. In the present study, it was found that replacement of N_2 with CO_2 in the soaking stage coupled with the high temperature used in the activation process resulted in release of a significant amount of $ZnCl_2$ as observed from the condensation on the quartz tube. This would have resulted in releasing of blocked pores and aided penetration of CO_2 into the adsorbent and further oxidation of pore wall.

The rationale for this study involving combination of chemical activation and physical activation (combined activation) is that the $ZnCl_2$ impregnation ensures widening of pores and development of mesoporosity. Gasification,

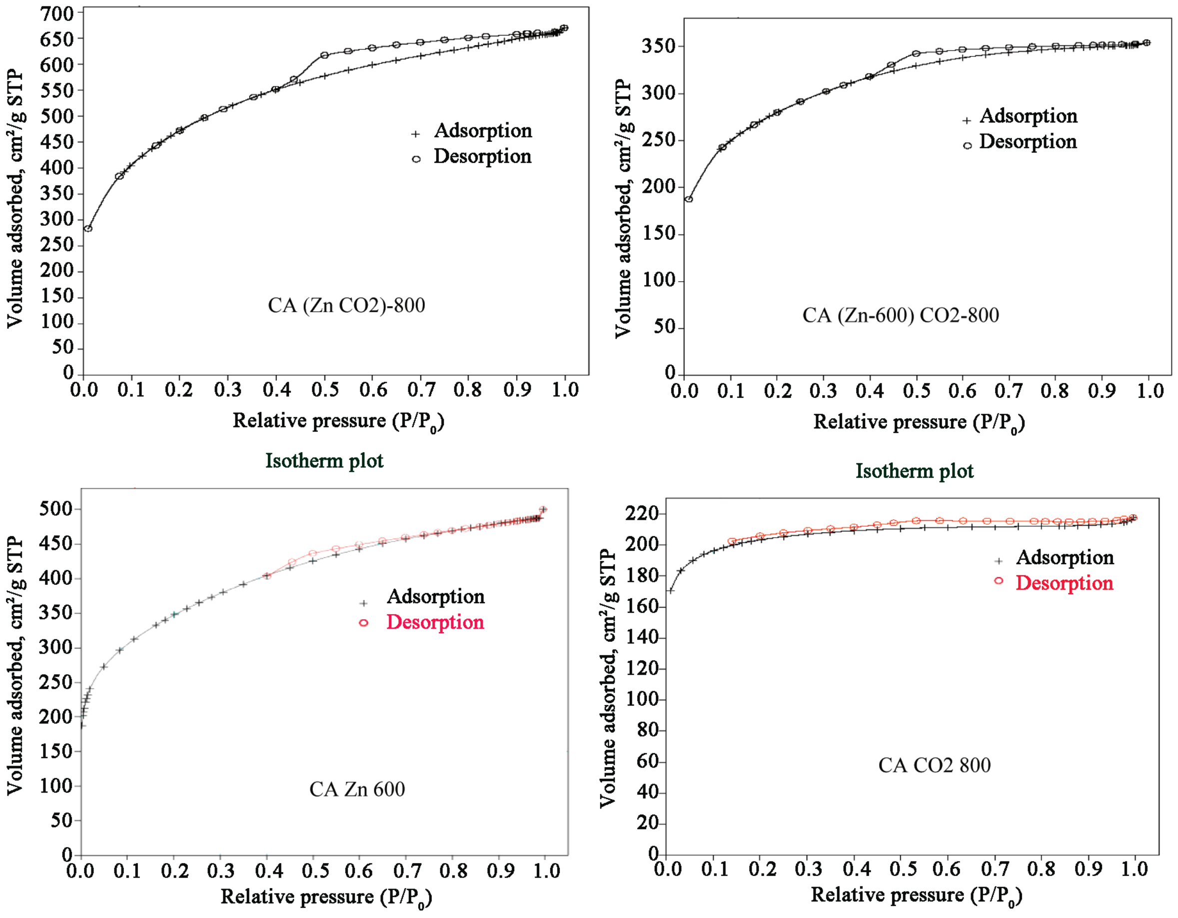


Fig. 2. Isotherms of adsorption and desorption of nitrogen at 77 K on the prepared activated carbons.

Table 2
Characteristics of activated carbons calculated from BET model and *t*-plot

Samples	Yield (%)	V_T (cm^3/g)	V_{me} (cm^3/g)	V_{mi} (cm^3/g)	S_{BET} ±10 (m^2/g)	S_{Ext} (m^2/g)	S_{mic} (m^2/g)	V_{me}/V_T (%)
CA (Zn CO2)-800	21	1.01	0.91	0.1	1587	1419	168	90.09
CA (Zn-600 CO2-800)	—	0.54	0.39	0.15	914	632	281	72.22
CA Zn 600	30	0.81	0.15	0.66	1322	237	1084	18.51
CA CO2 800	24	0.32	0.08	0.24	688	151	537	25.00

S_{BET}: BET surface area; S_{Ext}: external surface area; S_{mic}: micropore surface area ($S_{BET} = S_{Ext} + S_{mic}$); V_T: total volume; V_{mi}: micropore volume; V_{me}: mesopore volume.

known to further develop the surface area and porosity, works in combination with $ZnCl_2$ impregnation to yield adsorbents with highly developed mesoporosity. Since the $ZnCl_2$ impregnated raw material is subjected to activation temperatures above the boiling point of $ZnCl_2$ (732°C), a plausible sequence is that $ZnCl_2$ evaporation takes place, and simultaneously and thereafter, oxidation of the pore walls by CO_2 occurs.

The SEM micrographs of some adsorbents derived from date pits are presented in Fig. 3.

Scanning electron microscopy (SEM) showed that carbons obtained from date pits gave rougher textures with heterogeneous surfaces and a greater variety of randomly distributed cavities size. A comparison between carbons did not show major differences in their external surface characteristics.

The effect of contact time on the amount of dyes adsorbed was investigated at the optimum initial concentration of dyes and the data are presented in Figs. 4 and 5.

The extent of removal (in terms of *Q*) of dyes by these activated carbons were found to increase, reach a maximum value with the increase in contact time. The relative increase in the extent of removal of dyes after 360 min of contact time is not significant and hence it is fixed as the optimum contact time. Similar results have been reported in literature for the removal of dyes [8, 9].

In batch type adsorption systems, a monolayer of adsorbate is normally formed on the surface of the adsorbent [10] and the rate of removal of adsorbate species from aqueous solution is controlled primarily by the rate of transport of the adsorbate species form the exterior/outer sites to the interior sites of the adsorbent particles [11,12].

The mechanism for the removal of dye by adsorption may be assumed to involve the following four steps [13]:

- Migration of dye from bulk of the solution to the surface of the adsorbent (AC)
- Diffusion of dye through the boundary layer to the surface of the adsorbent.
- Adsorption of dye at active site on the surface of AC, and
- Intra-particle diffusion of dye into the interior pores of the AC particle.

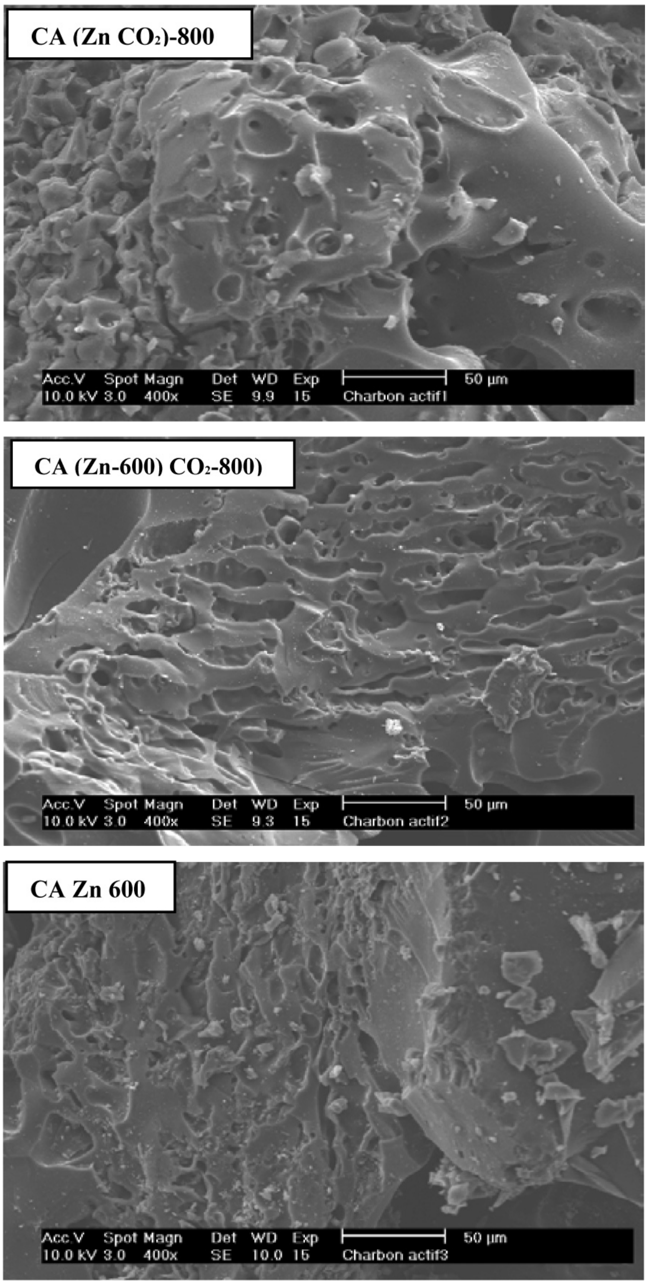


Fig. 3. SEM micrographs of the activated carbons prepared.

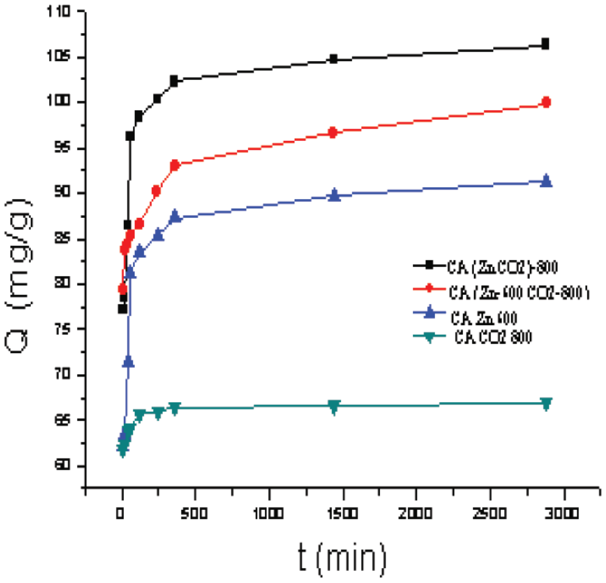


Fig. 4. Effects of contact time on adsorption of MB by activated carbon at 25±2°C.

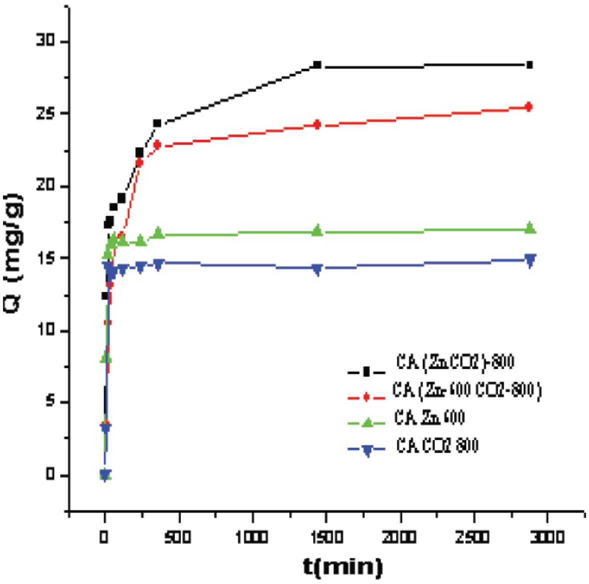


Fig. 5. Effects of contact time on adsorption CR by activated carbon at 25±2°C.

The boundary layer resistance will be affected by the rate of adsorption and an increase in contact time, which will reduce the resistance and increase the mobility of dye during adsorption. Since, the uptake of dye at the active sites of AC is a rapid process; the rate of adsorption is mainly governed by either liquid phase mass transfer rate [13].

Figs. 6 and 7 show the adsorption isotherms for MB and CR on carbons for experimental situations wherein the chemical and gaseous environments were varied.

CA CO2 800 refers to the isotherm for the case where activation was performed with CO_2 without the $ZnCl_2$ treatment, while micropore development would have taken place certainly [14]. Since only pores larger than the size of the adsorbate molecule are accessible to the adsorbate, Figs. 6 and 7 clearly show that CA (Zn CO2)-800 have a much larger amount of mesopores compared to CA Zn 600 and CA CO2 800. CA (Zn-600) CO2-800 was obtained by a two-step process: the raw material was impregnated with $ZnCl_2$ (with a mass report/ratio $X = 1$) carbonized in a nitrogen atmosphere and the product was washed with water to remove $ZnCl_2$. Subsequently, the sample was activated in CO_2 under the same conditions as for the simultaneous treatment. The uptake of

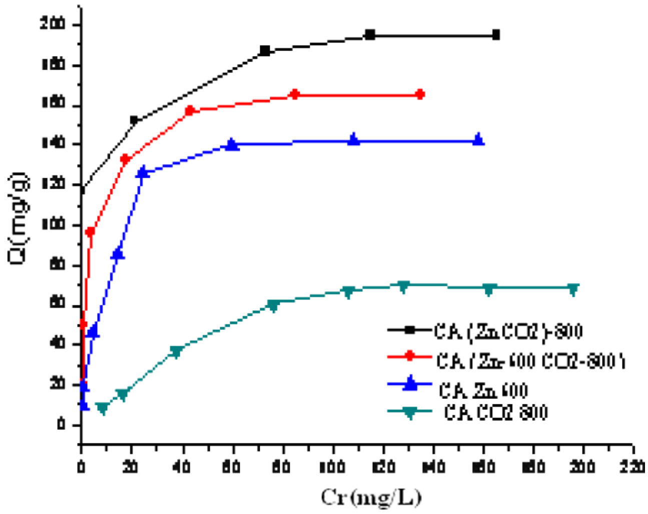


Fig. 6. Adsorption isotherms of MB from aqueous solution.

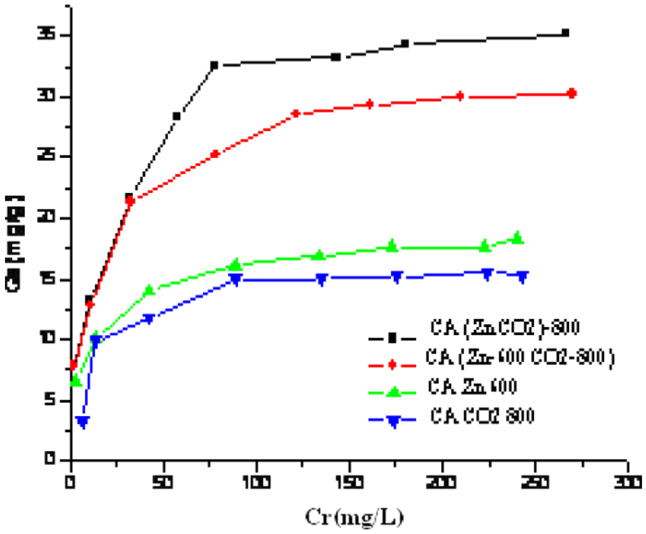


Fig. 7. Adsorption isotherms of CR from aqueous solution.

erythrosine for this case is comparable to that observed for CA (Zn CO2)-800

The difference in uptakes for MB is not as marked as for CR. The difference in the uptake between the various carbons becomes significant with increasing size of the adsorbate molecule. On comparing pore volumes (Table 1) and the uptakes, it can be seen that the adsorption isotherms conform to the nitrogen adsorption and pore size results.

Fig. 8 shows the correlation between the amounts adsorbed of dyes and the mesoporous volumes of activated carbons.

In Fig. 8 the largest amount was adsorbed among all the samples due to its largest mesoporous volume. Congo red with a larger molecular volume cannot be efficiently adsorbed on all the pores of activated carbons. Since MB has relatively small molecules, its adsorption would be mainly in the micropores.

In our work, we have shown that simultaneous activation with zinc chloride and carbon dioxide yields activated carbon with both higher surface area and high mesopore content. It is not clear at present how simultaneous application of the activation methods yields much higher mesoporosity in contrast to sequential application of the same activation methods; the results suggest that evaporation of $ZnCl_2$ is more effective in removing $ZnCl_2$ than is washing. Nevertheless, the combined effect of $ZnCl_2$-mediated reactions and gasification in a CO_2 atmosphere do contribute to producing large surface areas and high mesopore content.

The adsorption data were analysed with the help of the following isotherms [15]:

Freundlich isotherm:

$$\log Q = \log K_F + 1/n \log C_r \tag{2}$$

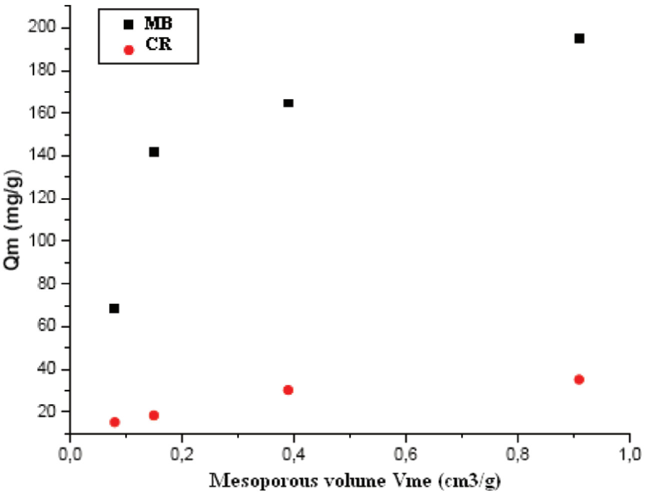


Fig. 8. Correlation between the amounts adsorbed of dyes and the mesoporous volumes of activated carbons .

Langmuir isotherm:

$$1/Q = 1/Q_m + 1/Q_m K C_r \tag{3}$$

where Q is the amount of dye adsorbed per unit mass of adsorbent (in mg/g) and C_r is the equilibrium concentration of dye (in mg/L); Q_m and K are the Langmuir constants, which are the measures of a monolayer (maximum) adsorption capacity (in mg/g) and energy of adsorption (in g/L), respectively; K_F and n are the Freundlich constants, which are the measure of the adsorption capacity and indicator of adsorption effectiveness.

The linear correlations between the values of log Q and log C_r (Freundlich) and $1/Q$ and $1/C_r$ (Langmuir) are shown in Figs. 9–12.

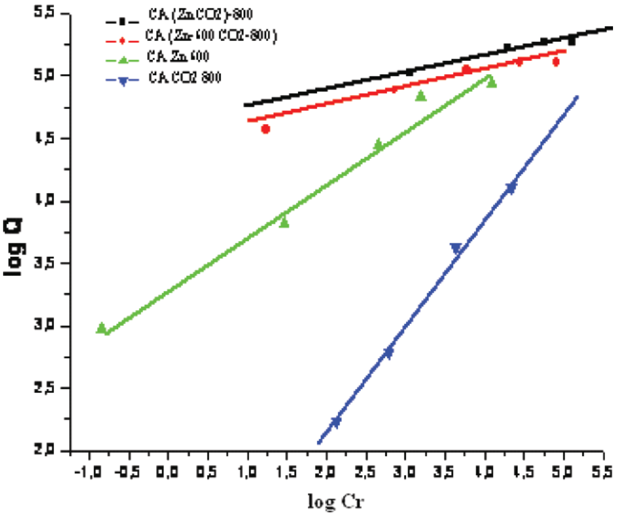


Fig. 9. Freudlich isotherms for the removal of MB by adsorption on various ACs.

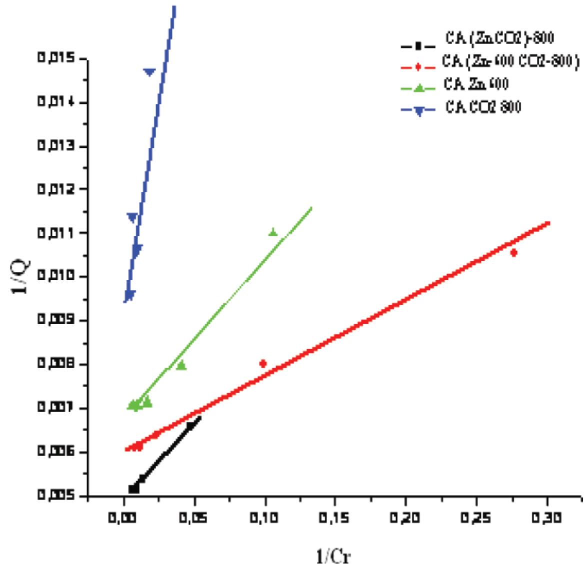


Fig. 10. Langmuir isotherms for the removal of MB by adsorption on various ACs.

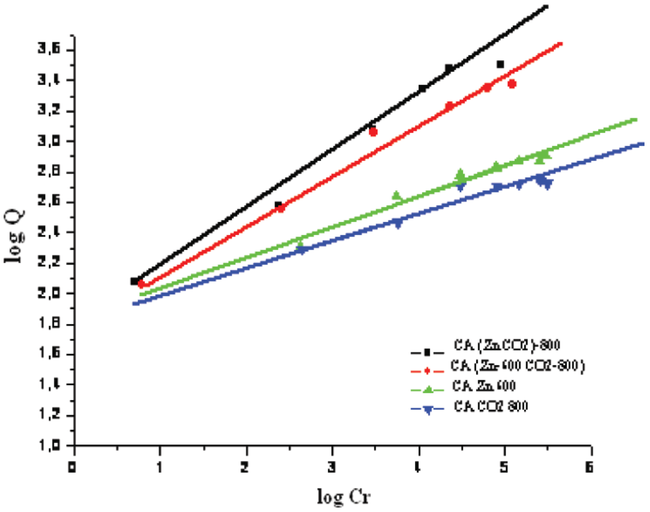


Fig. 11. Freudlich isotherms for the removal of CR by adsorption on various ACs.

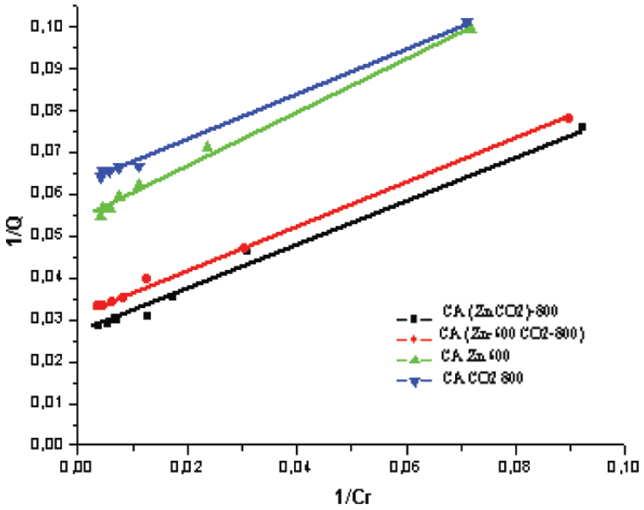


Fig. 12. Langmuir isotherms for the removal of CR by adsorption on various ACs.

The adsorption isotherms parameters along with the correlation coefficients are presented in Tables 3 and 4. The observed statistically significant (at 95% confidence level) linear relationships as evidenced by the *R*-values (close to unity) indicate the applicability of these two adsorption isotherms and the monolayer coverage on adsorbent surface.

It was found that the adsorption of MB and CR onto the prepared activated carbons from aqueous solution fits well the Freundlich and the Langmuir equations.

The monolayer adsorption capacities of the adsorbents are found to be the order:
CA (Zn CO2)-800 < CA (Zn-600 CO2-800) < CA Zn 600 < CA CO2 800.

The four activated carbon are observed to possess high adsorption capacity and hence they could be employed as adsorbents as adsorbents for the removal of dyes in general and MB, in particular.

Table 3
Parameters of Freundlich and Langmuir equations for adsorption of MB

Echantillons	Freundlich			Langmuir		
	1/*n*	K_F (L/g)	R^2	Q_m (mg/g)	*K* (L/g)	R^2
CA (Zn CO2)-800	0.1288	104.030	0.942	194.73	0.01264	0.994
CA (Zn-600 CO2-800)	0.1521	83.126	0.950	164.73	0.99407	0.969
CA Zn 600	0.4236	27.417	0.980	141.94	1.14366	0.963
CA CO2 800	0.8643	1.500	0.994	68.74	1.63453	0.999

Table 4
Parameters of Freundlich and Langmuir equations for adsorption of CR

Echantillons	Freundlich			Langmuir		
	1/*n*	K_F (L/g)	R^2	Q_m (mg/g)	*K* (L/g)	R^2
CA (Zn CO2)-800	0.161	6.6132	0.979	35.21	1.0864	0.991
CA (Zn-600 CO2-800)	0.200	6.2660	0.984	30,22	0.9988	0.997
CA Zn 600	0.318	6.2116	0.958	18.32	1.0138	0.992
CA CO2 800	0.363	6.0545	0.958	15.23	1.0546	0.996

4. Conclusion

Preparation of high surface area, granular, mesoporous activated carbons has been carried out by a simultaneous physical and chemical activation technique, using date pits as starting materials.

The surface area and the nature of the porosity can be controlled by means of the experimental parameters.

Adsorption tests in liquid media show that adsorption capacities conform to calculations based on nitrogen adsorption isotherms. The mesoporous nature of the prepared samples is confirmed by observation of large uptakes for methylene blue (MB) and congo red (CR) relative to those observed for adsorbents with less pronounced mesoporosity.

The resultant activated carbons have high adsorptive performance not only for small molecules, but also for large molecules. Because it is facile and effective, the novel activation process is an advisable method for producing high quality and high performance activated carbons.

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