Kinetics of the Adsorption of Anionic and Cationic Dyes in Aqueous Solution by Low-Cost Activated Carbons Prepared from Sea Cake and Cotton Cake

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Authors' contributions

This work was carried out in collaboration between all authors. Authors BLM and DBG designed and supervised the study and the manuscript writing. Author TI performed the research and managed the analyses of the study. He was helped by authors DKV and NP. Protocol, Statistical analysis and literature research were performed by authors TI and KT. Authors TI and KT wrote the manuscript and all authors read and approved the final manuscript.

Research Article

ABSTRACT

Activated carbons prepared from shea cake (CA-K) and cotton cake (CA-C) were investigated for removal of four dyes in aqueous solutions (0 – 200 mg/L): Reactive Black 5 (RB5), Methylene blue (BM), Reactive Orange 16 (RO16) and Methyl Orange (MO) from water by adsorption. The activated carbons were prepared by chemical activation using phosphoric acid as activation agent. Chemical characteristics of these activated carbons was monitored by Bohem titration and the method of Lopez-Ramon et al. while surface areas of the samples were determined by nitrogen adsorption/desorption isotherm measurement. Activated carbons CA-K and CA-C have the following characteristics: BET surface and the pore volumes are respectively 1148 m^2/g and 0.607 cm^3/g for CA-K, 584 m^2/g and 0.298 cm^3/g for CA-C. The two activated carbons synthesized are microporous

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activated carbon with micropores volume representing more than 70% of the total pore volume. The removal of dyes was studied using batch reactor. The nature of the activated carbon and the dyes are the key factors influencing the contact time. At the equilibrium times (35 to 270 min for CA-K and 60 to 300 min for CA-C), the removal of BM, MO and RO16 was quasi-total while for RB5 the amount adsorbed was about 83%. Based on the adsorption capacity, it was shown that CA-K was more effective than CA-C. Various kinetic models such as pseudo first-order, pseudo second-order and intraparticle diffusion were used to evaluate the mechanism of dyes adsorption on activated carbons. BM, RO16, and MO removal process was found to be governed by second-order kinetic while pseudo-first order kinetic is suitable for RB5 adsorption study. The pHs of the solutions and the amount of activated carbon have strong effect on the adsorption capacity of these dyes. An acid pH (for anionic dyes) and basic pH (for cationic dyes) were favorable for the maximum adsorption of dyes. The isotherm data could be well described by the Freundlich and Langmuir equations in the concentration range of 0–80 mg/L. For the present adsorption process intraparticle diffusion of dyes within the particle was identified to be rate limiting. Both activated carbons were shown to be promising materials for adsorption removal of dyes from aqueous solutions.

1. INTRODUCTION

Water pollution by dyes is an environmental problem that the variation of aspects and scope depend to development level of the country. These wastewaters are usually bad treated in most countries, especially in developing countries. These effluents are characterized by strong colors, strong variations of pH, high chemical oxygen demand (COD) and high biotoxicity against bacteria [1-3]. Most dyes have been identified as toxic or carcinogenic towards aquatic organisms as well as human [4]. In addition, the dyes can cause allergic dermatitis and irritation of the skin [5]. It is therefore necessary to treat dyes because of their dangerousness.

To avoid this situation, several decontamination methods have been developed. For example, adsorption on activated carbon [6,7], photocatalysis [8], precipitation (coagulation, flocculation, sedimentation), the reverse osmosis, Incineration, Aerobic, and Anaerobic Treatment etc. Among these methods, adsorption on activated carbon has been used extensively due to the efficiency and high adsorption capacity [4,9-12]. However, the commercial activated carbons are quite expensive and their application is limited. The research of alternative precursors for the preparation of activated carbons from carbonated organic waste is particularly encouraged. Activated carbons synthesized by food waste are low cost [13]. They are obtained by stage of synthesis: carbonization of precursor characterized by a large proportion of carbon and a low percentage of inorganic and then activation of the result material [14]. Various studies have been devoted to preparation and characterization of activated carbons from different precursor like cores date [11,15], rice straw [16-19], the hull coco nut [20] coconut [21], grain of sorghum [22], skin of cassava [23], the almond shell [24], the shell of apricot [25], pod of bean [26] pod of rice [27] and the stone of cherry [28]. In addition, the conversion of agricultural waste into activated carbons will decrease their disposal.

The purpose of this work was to test the possibility of using activated carbon CA-K and CA-C, for adsorption removal of various dyes: Reactive black 5 (RB5) Methylene blue (BM), Reactive Orange 16 (RO16) and Methyl Orange (MO) from water. The amounts of

equilibrium adsorption were then evaluated and were finally correlated with process variables such as dye concentration, contact time, amount of activated carbons and solution pH.

2. MATERIALS AND METHODS

2.1 Activated Carbons

2.1.1 Preparation of activated carbon

Activated carbons CA-K and CA-C were prepared from shea cake and cotton cake respectively. The synthesis of activated carbon was performed as follows: the precursors were riddled to have particles which diameter was less or equal to 0.8 mm, then, the particles obtained were impregnated for 6 hours in phosphoric acid solution of ca. 40%. The ratio of impregnating (Mass of Acid/Mass of precursor) was 1.5. The activated carbon was obtained by carbonization of the impregnated material at 450ºC for 2 hours [29].

2.1.2 Characterization of activated carbons

Chemical characteristics (chemical surfaces functions, pH of zero charge) of synthesized activated carbon were determined by Boehm titrations [30-31] and the method of Lopez-Ramon et al. respectively [32].

Nitrogen isotherms were measured using an ASAP 2010 (Micromeritics) at 77 K. The Brunauer, Emmett and Teller (BET) surface areas of the samples were determined by nitrogen adsorption–desorption isotherm measurement. These isotherms were then used to calculate total pore volume (V_p). The size distribution of pores, the micropore and mesopore volumes were obtained by Density Functional Theory (DFT). The size distribution of pores was also obtained by Barrett-Joyner and Halenda (BJH) model.

2.2 Dyes Characteristics and their Analysis

The model pollutants were Reactive Black 5 (RB5: $C_{26}H_{25}N_5O_{19}S_6$ 4Na), Methylene Blue (BM: $C_{14}H_{18}ClN_3S$ $3H_2O$), Reactive orange 16 (RO16: $C_{20}H_{19}N_3O_{11}S_3$, 2Na) and Methyl Orange (MO: $C_{14}H_{14}N_3NaO_3S$). They were supplied by Sigma Aldrich and where used without any purification. Fig. 1 shows the chemical structures of these dyes.
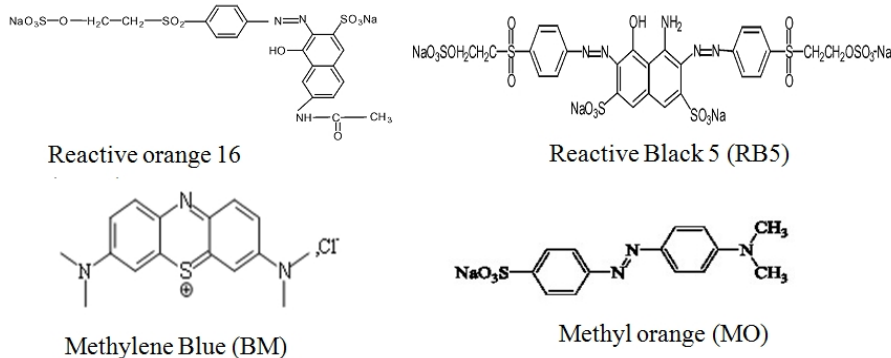

Fig. 1. Chemical structure of dyes (RB5, RO16, MO and BM)

Distillated water (Conductivity: 1-3 μS/cm) was used to prepare the solutions of each dye. The concentration of each dye before adsorption studies and the concentration of the same dye remaining in solution after the adsorption were measured using a UV–Vis spectrometer (Shimazu). The measurement was performed at specific wavelength: MB (λ_{max} = 660 nm), RO16 (λ_{max} = 495 nm), MO (λ_{max} = 440 nm for pH > 4.4 and λ_{max} = 520 nm for pH < 4.4) and RB5 (λ_{max} = 599 nm). Residual concentrations were determined from the calibration lines established.

2.3 Dye Adsorption Studies

The adsorption of RB5, BM, MO and RO16 on activated carbons was carried out in batch mode using Erlenmeyer flasks with 100 mL volume at room temperature (29 ± 2 ° C). Each flask was magnetically stirred at 300 rmp. The effects of contact time, the amount of activated carbon and the initial pH of the solution have been studied. After equilibration, the solution was filtered through a membrane filter (pore size 0.45 μm) and the filtrate was used for absorbance measurement. The amount adsorbed of each dye, Q_e (mg/g), was calculated from the formula

$$Q_e = \frac{(C_0 - C_e) \cdot V}{m} \qquad (1)$$

where Q_e is the amount adsorbed, *V(mL)* is the volume of the liquid phase, C_0 (mg/L) is the concentration of solute in the bulk phase before it comes in contact with the adsorbent, C_e is the concentration of the solute in the bulk phase at equilibrium, and *m (g)* is the amount of the adsorbent.

2.3.1 Influence of contact time

0.20 g of each activated carbon was used to study the effect of contact time during the adsorption of the target pollutants. 100 mL of the dye solution at a concentration of 100 mg/L were prepared for this experiment. The flask provided with dyes and activated carbon was kept in constant agitation at room temperature. At regular intervals, sample was taken for absorbance measurement. The adsorption capacity at every time, Qt (mg/g) of each dye was calculated using the relation:

$$Q_t = \frac{(C_0 - C_t) \cdot V}{m} \qquad (2)$$

where C_t (mg/L) represents the concentration of the dye at each time t (min), *V(mL)* is the volume of the liquid phase, C_0 (mg/L) is the concentration of solute in the bulk phase before it comes in contact with the adsorbent, and *m (g)* is the amount of the adsorbent.

2.3.2 Effect of pH

The effect of pH on the adsorption process of RB5, BM, RO16 and MO has been studied by varying the initial pH of the solution from 2 to 12. The pH was adjusted by addition of aqueous solution of NaOH (0.1 M) or HCl (0.1 M). The pH meter WTW 330i/SET was used for the measurement of pH. The initial concentration of each dye solution is set at 200 mg/L

and the adsorbent amount was 2 g/L. The percentage adsorption of each dye was calculated using the equation:

$$Adsorption\ (\%) = \frac{(C_0 - C_e)}{C_0} \times 100 \qquad (3)$$

2.3.3 Effect of amount of activated carbon

Different amounts of activated carbon (0 to 2 g) were dispersed in 100 mL of the dye which concentration was the same in each flask (200 mg/L). The pH was adjusted to be the same at the beginning. The mixture was stirred until equilibrium time and then, a sample was taken for analysis.

3. RESULTS

3.1 Physico-Chemical Characteristics of Activated Carbons

The characterization conducted on activated carbon shows that the pHs of zero charge (pHZC), slightly acid, were 6.8 and 5.3 respectively for CA-K and CA-C. According to Bohem titration, the surface function groups are more acid than basic. The result revealed that the concentration of acid functions were 6.2 meq/g for CA-K and 7.5 meq/g for CA-C) while the basic functions were 1.2 meq/g for CA-K and 0.95 meq/g for CA-C). The structural parameters calculated from nitrogen adsorption isotherms are presented in Table 1.

Table 1. Structural parameters of activated carbons calculated from Nitrogen adsorption/desorption

Parameters	CA-K	CA-C
Yield (%)	32.5	29.8
Surface area (S_{BET}) m^2/g	1148	584
Micro-pore surface area (S_{mic}) m^2/g	1005	528
Total pore volume (V_p) cm^3/g	0.607	0.298
Micropore Volume cm^3/g	0.435	0.223
Meso-pore Volume cm^3/g	0.172	0.075
Average diameter of pore by BET $Å$	21.16	20.37
Average diameter of pore by BJH $Å$	29.15	29.59

The data clearly shows that sample CA-K has larger surface area and bigger volume of micropores than sample CA-C. Based on the ratio of the volume of micropores to the total pore volume, both samples can be described as predominantly microporous about 70%.

Both activated carbons have average diameters of pores (by BET) relatively small, almost at the limit of the microporosity.

3.2 Influence of Contact Time

Fig. 2 shows the effect of time on the adsorption of BM, RB5, RO16 and MO on activated carbon CA-K and CA-C. The adsorption of these dyes is fast in the first 50 minutes, and then gradually slows until equilibrium is reached.
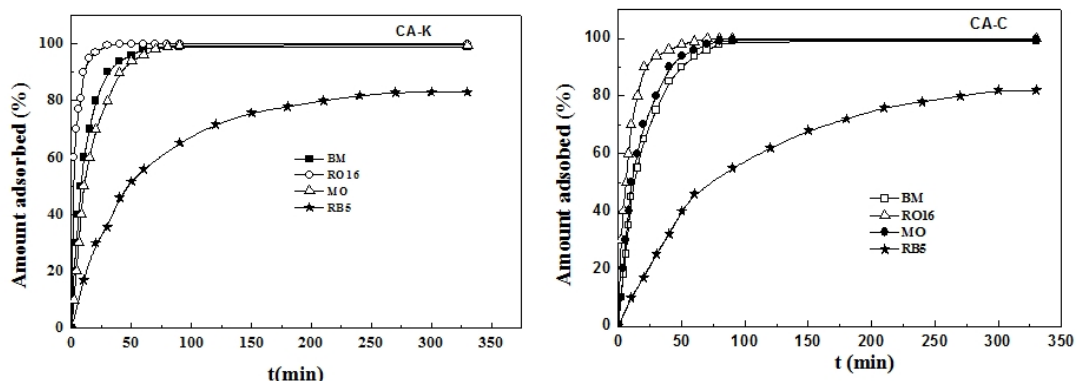
Fig. 2. Effect of contact time on adsorption of RB5, RO16, MO and BM onto activated carbon CA-K and CA-C (C = 100 mg/L, V = 100 mL, natural pH, m_{CA} = 0.2 g)

The equilibrium time obtained depends on the nature of the dye and also activated carbon (Table 2).

Table 2. Equilibrium time of adsorption of dyes

Dyes	CA-K	CA-C
	Equilibrium time (min)	Equilibrium time (min)
BM	40	70
RB5	270	300
RO16	35	60
MO	60	90

At the equilibrium times, the removal of MB, MO and RO16 was quasi-total while for RB5 the amount adsorbed was about 83%.

3.3 Adsorption Kinetics

The kinetics of adsorption of dyes RB5, RO16, BM and MO was examined using kinetic models of pseudo-first order and pseudo-second order. The kinetic equation of pseudo-first order is usually expressed as follows [33-37]:

$$\ln(q_e - q) = \ln q_e - k_1 t \tag{4}$$

where q_e (mg/g) represents the amount of dye adsorbed at equilibrium, q (mg/g) is the amount of dye adsorbed at time t, and k_1 (min^{-1}) represents the pseudo-first order constant. The values of k_1 are determined from the slopes of the straight line obtained when plotting $\ln(q_e-q)$ versus time t. The obtained values of k_1, q_e and r_1^2 (coefficient of correlation) are presented in Table 3. The values of the coefficients of correlation obtained for the four dyes are greater than 0.96.

Table 3. Pseudo-first order kinetic constants of adsorption of dyes on CA-K and CA-C

Samples	Dyes	$q_{e,\ exp}$ (mg/g)	$q_{e,\ cal}$ (mg/g)	k_1 (min^{-1})	r_1^2
	BM	33.27	23.96	0.135	0.994
CA-K	RO16	33.33	21.17	0.162	0.988
	MO	33.33	20.69	0.115	0.961
	RB5	27.93	26.63	0.019	0.984
	BM	32.33	22.57	0.055	0.993
	RO16	33.33	26.81	0.074	0.976
CA-C	MO	32.16	27.69	0.056	0.996
	RB5	27.93	28.40	0.013	0.993

Despite these very high values, the experimental values of q_e are not in agreement with the calculated values of q_e, except for the RB5 where experimental values of q_e and those calculated are similar. The values of the pseudo-first order constants k_1 are between 0.019 and 0.162 min^{-1} with activated carbon CA-K and it varies from 0.013 to 0.074 min^{-1} for CA-C.

The equation of the kinetic model of pseudo-second order is expressed as [38]:

$$\frac{t}{q} = \frac{1}{k_2 \cdot q_e^2} + \frac{1}{q_e} \cdot t \tag{5}$$

where k_2 (g/mg.min) is the pseudo-second order constant.

The value of k_2 is determined from the intercept of the straight line obtained by plotting t/q versus time (t).

The kinetic constants of the adsorption reaction of the pseudo-second-order k_2, the amount of RB5, RO16, MO and BM adsorbed at equilibrium q_e, and the correlation coefficients are given in Table 4.

Table 4. Pseudo-second Order Kinetic constants of adsorption of dye on CA-K and CA-C

	Dyes	$q_{e,\ exp}$ (mg/g)	$q_{e,\ cal}$ (mg/g)	k_2 (g/mg.min)	r_2^2
	BM	33.27	33.67	0.014	0.999
CA-K	RO16	33.33	34.45	0.018	0.999
	MO	33.33	32.76	0.024	0.985
	RB5	27.93	17,68	0.004	0.853
	BM	32.33	33.95	0.001	0.987
CA-C	RO16	33.33	33.84	0.005	0.998
	MO	32.16	32.96	0.001	0.983
	RB5	27.93	64.22	0.00001	0.790

The values of the correlation coefficients obtained for RO16, MO and BM is high than 0.98. However, it value is less than 0.86 for RB5. On the contrary of the previous model, experimental values of q_e for BM, RO16 and MO are much closer to the values of q_e

calculated from the linear forms of the pseudo-second order kinetic. On the other hand, experimental values of q_e are not in agreement with those calculated for RB5.

3.4 Adsorption Mechanism

The adsorption mechanism can be examined using the intra particle diffusion model whose equation can be expressed as [39]:

$$q = k_i \cdot t^{1/2} + C \tag{6}$$

where k_i is intra particle diffusion constant. The representation of q versus $t^{1/2}$ has several linear parts (Fig. 3). However, k_i was determined from the slopes of straight linear parts of the curves presented in Fig. 4.
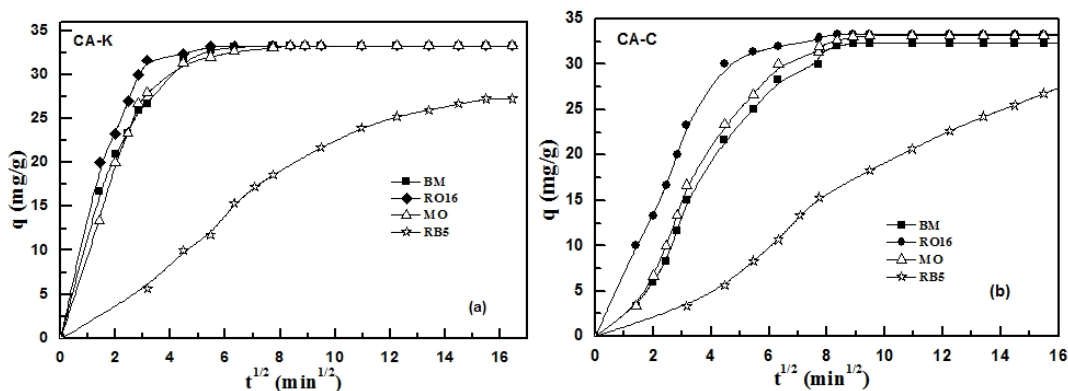

Fig. 3. Intra particle diffusion kinetic of adsorption of BM, RO16 and MO, RB5 onto activated carbons
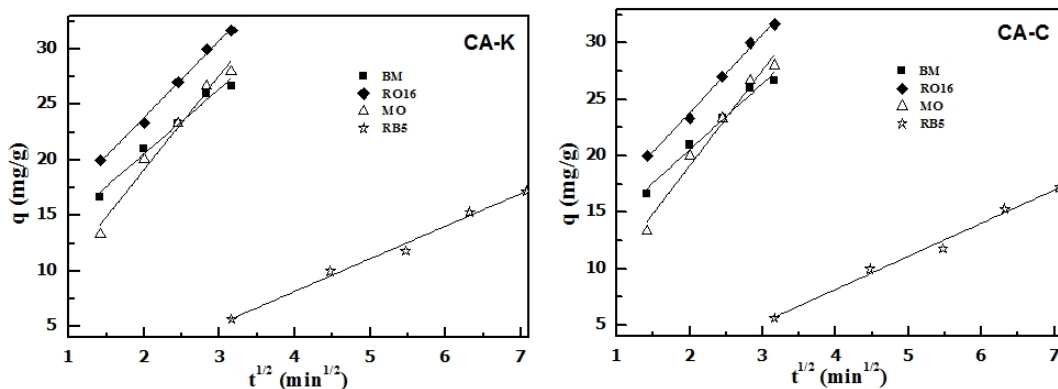

Fig. 4. Intra particle diffusion kinetic of adsorption of BM, RO16 and MO, RB5 onto activated carbons, determination of k_i from the slope of straight line

The values of the constants k_i as well as correlation coefficients are shown in Table 5. The values of intra particle diffusion constants vary from 2.549 mg/g.min$^{1/2}$ to 8.468 mg/g.min$^{1/2}$

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and from 2.549 mg/g.min^{½} to 7.614 mg/g.min^{½} with activated carbons CA-K and CA-C respectively. The correlation coefficients of linear equations are above 0.97.

Table 5. Parameters of Intra-particle diffusion and Pore diffusion coefficient

	Dyes	Constants of intra particules diffusion			Pore diffusion coefficients
		k_i (mg/g.min^{½})	C	r^2	D (cm^2/s)
CA-K	BM	5.867	8.832	0.975	$10.00×10^{-8}$
	RO16	6.935	9.962	0.992	$13.33×10^{-8}$
	MO	8.468	2.196	0.973	$6.00×10^{-8}$
	RB5	2.935	-3.550	0.987	$0.44×10^{-8}$
CA-C	BM	6.578	-6.730	0.970	$2.00×10^{-8}$
	RO16	7.614	-1.383	0.981	$3.33×10^{-8}$
	MO	7.614	-8.050	0.980	$2.00×10^{-8}$
	RB5	2.549	-5.240	0.979	$0.33×10^{-8}$

When analyzing the figure 3a, one can clearly see that the curve of BM, RO16 and MO presents a linear portion between 0 and 30 min which indicates intra particle diffusion phenomenon and after 30 min a plateau characterizing the equilibrium adsorption. The curve of RB5 presents several linear parts indicating three different diffusion phenomena. The slightly concave between the first parts (0-40 min) characterizes the phenomenon of diffusion at the external surface of the activated carbon CA-K (instantaneous adsorption). The second linear portion from 40 to 260 min characterizes the gradual adsorption step. The third, a plateau beyond 260 min, characterized the step of adsorption equilibrium.

According to figure 3b, the adsorption graphs of RO16 and RB5 present the similar characteristics as in figure 3a. On the other hand, adsorption graphs of BM and MO reveal three different parts:

The first portion slightly concave between 0 to 9 min characterizes instantaneous adsorption, the second step between 9 to 50 min characterizes the gradual adsorption and a third part beyond 50 min corresponds to adsorption equilibrium.

Moreover, the diffusion coefficient of pores D can be calculated using the equation:

$$t_{1/2} = 0,03 \cdot \frac{r_0^2}{D} \tag{7}$$

where $t_{1/2}$ (s) is the half time-reaction, r_0 (cm) is diameter of the adsorbent particles and D (cm^2 s^{-1}) is the diffusion coefficient of intra-particle.

The calculated values of D vary from $6.00×10^{-8}$ cm^2/s to $13.33×10^{-8}$ cm^2/s and from $0.33×10^{-8}$ cm^2/s to $3.33×10^{-8}$ cm^2/s for CA-K and CA-C respectively.

3.5 Effect of pH of the Solution

Acid or anionic dyes (RO16, MO and RB5) have the same behavior on both activated carbons when pH varies from 2 to 12 (Fig. 5).
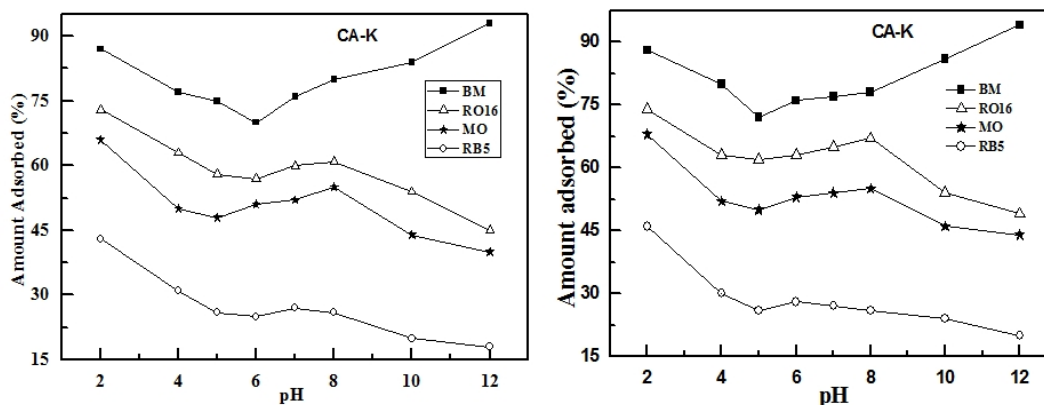
Fig. 5. Influence of pH on removal by adsorption of BM, RO16, MO and RB5 onto activated carbons (C = 200 mg/L, V = 100 mL, m_{CA} = 0.2 g)

For example, the removal percentages decreased from 74% to 62% (RO16), 68% to 51% (MO) and 45% to 26% (RB5) when the pH increases from 2 to 5. From pH 5 to 8, adsorption rate did not vary significantly and the removal percentage was steady around 65% (RO16), 54% (MO) and 27% (RB5). When the pH increases from 8 to 12, we observed a decrement of adsorption rate with a variation of dye amount adsorbed from 65% to 50% (RO16), from 54% to 44% (MO) and from 27% to 20% (RB5).

The result of basic or cationic dye, Methylene Blue, shows different behavior. When the pH of the solution ranges from 2 to 5 its percentage removal decreases from 88% to 70%, and then increases continuously from 70% to 95% when the pH ranges from 5 to 12.

3.6 Effect of Amount of Activated Carbon

The amount of activated carbon was varied from 0 to 2 g and the concentration of each dye was fixed at 200 mg/L. The Fig. 6 shows the effect of the mass of activated carbon on the percentage removal of these dyes.
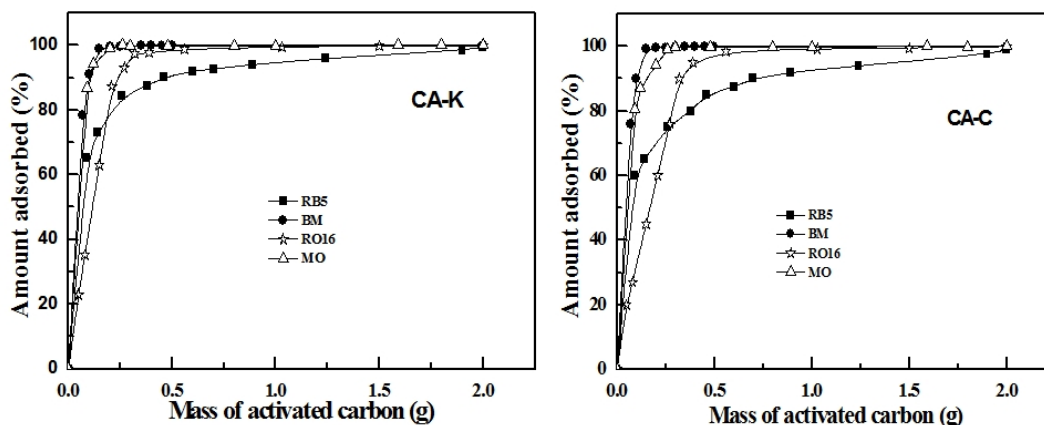

Fig. 6. Influence of mass of adsorbent on adsorption of BM, RO16, MO and RB5 (C = 200 mg/L, V = 100 mL, free pH)

The result shows that removal percentages increase as the amount of activated carbon increases. For both active carbons we have a quasi total removal of MB, RO16 and MO for amount 0.2 g, 0.6 g and 1 g respectively. With 2 g of each activated carbon, the removal of RB5 was about 98%.

3.7 Study of Adsorption Isotherms

Adsorptions isotherms are obtained by plotting Q_e versus C_e (Fig. 7).
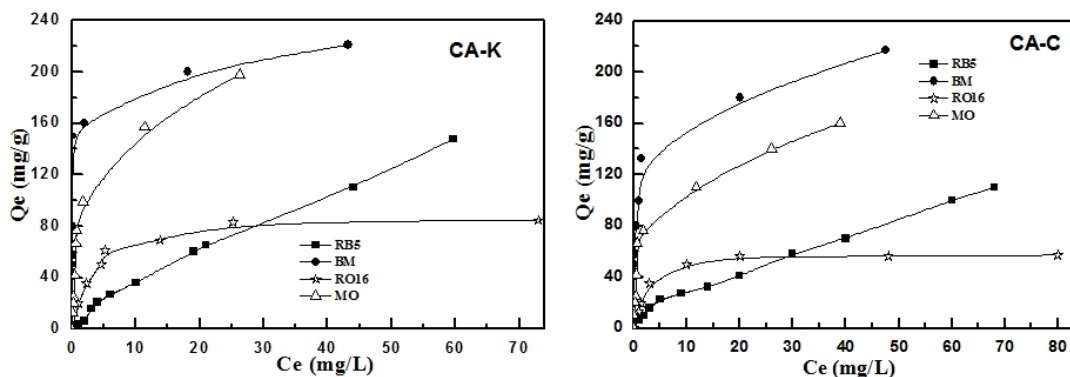
Fig. 7. Isotherms of dyes (RO16, RB5, MO and BM) adsorption from solution (C = 200 mg/L, V = 100 mL, Free pH)

Langmuir Isotherm and Freundlich Isotherm are used to describe the nature of the adsorption equilibrium.

The model of Langmuir is most frequently used for the adsorption of pollutants in solution. The Langmuir isotherm can be modeled by the equation:

$$Q_e = \frac{Q_0 K_L C_e}{1 + K_L C_e} \qquad (8)$$

where Q_e is the amount of dye adsorbed at equilibrium per unit mass of the adsorbent (mg/g), Q_0 is the adsorption capacity at saturation (mg/g), C_e is the concentration of dye at equilibrium and K_L (L/mg) is the adsorption equilibrium constant.

The linear form of the model of Langmuir is written by:

$$\frac{C_e}{Q_e} = \frac{(1 + K_L C_e) \cdot C_e}{Q_0 K_L C_e} = \frac{1}{Q_0 K_L} + \frac{C_e}{Q_0} \qquad (9)$$

The Langmuir model is characterized by the separation factor, RL, which is given by the equation below [40-42]:

$$R_L = \frac{1}{(1 + K_L \cdot C_0)} \qquad (10)$$

where C_0 (mg/L) is the initial concentration of the pollutant and K_L (L/mg) is Langmuir constant.

In the case of an adsorbent with a heterogeneous adsorption surface (adsorption sites energetically different), Freundlich model is used to characterize the adsorption [43]. The Freundlich equation is given by:

$$Q_e = K_F C_e^{1/n} \tag{11}$$

where Q_e *(mg/g)* is an amount adsorbed, C_e *(mg/L)* is the equilibrium solution phase concentration recalculated per unit mass of carbon, *n* (dimensionless) is the empirical parameter that represents the heterogeneity of the site energies, and K_F is the so-called unit capacity factor.

K_F and 1/n can be determined by the linearization of the Freundlich equation which corresponds to:

$$\ln Q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{12}$$

The Tables 6 and 7 present the parameters of fitting our experimental data (figure not shown here) to the Langmuir and Freundlich equation.

Table 6. Parameters resulting from fitting of experimental data of Freundlich isotherm and Langmuir Isotherm

	Dyes	Freundlich			Langmuir		
		n	K_F (mg/g)	r^2	Q_0 (mg/g)	K_L	r^2
	RB5	1.36	6.9	0.991	125.00	0.049	0.997
	BM	6.25	125.5	0.989	333.33	0.750	0.998
CA-K	RO16	4.37	34.7	0.767	111.11	0.209	0.993
	MO	2.21	49.4	0.990	166.67	0.193	0.994
	RB5	1.59	7.1	0.987	90.91	0.067	0.991
	BM	4.55	94.5	0.994	250.00	0.570	0.991
CA-C	RO16	2.77	17.7	0.887	66.67	0.280	0.998
	MO	2.67	43.3	0.981	200.00	0.130	0.994

Table 7. Values of separation factor, R_L, determined from Langmuir Isotherm

Dyes	CA-K	CA-C
RB5	0.092	0.068
BM	0.007	0.009
RO16	0.023	0.018
MO	0.025	0.037

The values of separation factors (R_L) calculated for all dyes are between 0.007 and 0.092 for CA-K and they vary from 0.009 to 0.068 for CA-C. K_F values are between 4.9 mg/g and 125 mg/g when activated carbon CA-K is used while K_F values vary from 7.1 mg/g to 94.5 mg/g

when adsorbent CA-C is used. Average energy of sites, n, oscillates between 1.36 and 6.25 for CA-K and between 1.59 and 4.55 for CA-C.

According to these results, one can conclude that adsorption of dyes RB5, BM and MO on CA-K and CA-C obeyed both Freundlich and Langmuir adsorption isotherms when regarding the high values of correlation coefficients ($r^2 > 0.98$). However, the adsorption of RO16 on these adsorbent more follows the Langmuir isotherm ($r^2 > 0.99$) than the Freundlich isotherm ($r^2 < 0.89$).

3.8 Discussion

3.8.1 Textural properties of activated carbon

The value of the specific surface area of activated carbon CA-K obtained is similar to those obtained by Emine et al [44]. On the other hand, specific area of activated carbon CA-C is included in field of specific area found by Mohammad et al. [45] and A.H. Basta et al [16]. However, other research groups obtained the values of specific surface area of activated carbon which are much greater than our values [17,46]. Furthermore the pore volume ($V_p = 0.607$ cm^3/g) of activated carbon CA-K is two time greater than that of CA-C ($V_p = 0.298$ cm^3/g). Both activated carbons have average diameters of pores (by BET) relatively small, almost at the limit of the microporosity. This result is agreement with those obtained by some research groups [11,47], Table 8. The difference probably comes from the difference in precursor and the preparation method.

Table 8. Comparison of textural characteristic of our activated carbon (CA-K and CA-C) to those of literature

Adsorbents	T_C (°C)	Activation	S_{BET} (m^2/g)	References
Activated carbon « CA-K »	450	H_3PO_4	1148	--
Activated carbon « CA-C »	450	H_3PO_4	584	--
Mineral activated carbon of Algeria « Ménouna »	800	KOH	1241	Khelifi et al. [47]
Activated carbon prepared from stones of date	500	KOH, NaOH, H_3PO_4	1400	Cyrus et al. [46]
Activated carbon derivated from rice strow	450	KOH	1554	Basta et al. [17]
Activated carbon derivated from waste of tea	350	H_3PO_4	1157	Emine et al. [44]
Activated carbon prepared from jute sticks	750	Physical activation	452 - 724	Mohammad et al. [45]
Activated carbon prepared from rice straw and its derivatives	450	H_3PO_4	368 - 789	Basta et al. [16]

Base on the result of BET which shows that activated carbon CA-K has surface area and pore volume much higher than activated carbon CA-C, it appears that activated carbon CA-K is most potentially interesting and should have a greater capacity to adsorb a large number of molecules in the pores.

3.8.2 Adsorption

3.8.2.1 Effect of contact time

Smaller is the time to reach equilibrium with high amount adsorbed, best is the adsorbent. The result shows that equilibrium time obtained depends on the nature of dyes and also on the type of activated carbon. Indeed for:

- Methylene blue (BM): equilibrium was reached after 40 min for CA-K and 70 min for CA-C. At theses times, the total discoloration of MB was observed. For the same dye and with commercial activated carbon, Hounas et al. [48] reported that the total adsorption was obtained after 5 hours whereas for oxidized activated carbon, Khelifi et al. [47] observed that the equilibrium time of BM adsorption was reached after 48 hours. This difference in the behavior of BM versus various activated carbons is of course due to their origin, their method of preparation and their porous texture;
- Reactive black 5 (RB5): the equilibrium time corresponding to 83% of RB5 removal was 270 min for CA-K and 300 min for CA-C. With the same magnitude of removal, 200 min of equilibrium time was reported by Zeynep et al. [49] for the adsorption of Reactive black 5 (RB5) on activated carbon. 300 min of equilibrium time was reported by Dogan et al. [50] with modified zeolite. Exposing this dye a long time for it removal with activated carbon is not benefit because we observed that there is a desorption of a part of the dye beyond 10 hours of contact time;
- Reactive orange 16 (RO16): few minutes was enough to reach equilibrium. Indeed, the removal of RO16 was observed at 35 min for CA-K and 60 min for CA-C. However, more than 10 hours were necessary to remove this dye by adsorption on activated carbon according to the work of Won et al. [51];
- Methyl orange (MO) was total removed after 60 min when using CA-K and 90 min when CA-C is used.
  Moreover, the study of adsorption kinetics using pseudo first-order and pseudo-second order and the adsorption mechanism (intra particle diffusion) reveal that:
- The pseudo-first order kinetic is not suitable to describe the adsorption of Methylene blue (BM), the Reactive orange 16 (RO16) and Methyl orange (MO) on activated carbon CA-K and CA-C. Nevertheless, this model responds very well to describe the adsorption of Reactive black 5 (RB5) on our synthetic activated carbon;
- The pseudo-second order kinetic fits well for the description of adsorption of BM, RO16 and MO on both activated carbons. However, the opposite trend is observed in the case of adsorption of Reactive black 5 (RB5) on activated carbon CA-K and CA-C;
- All values of intra particle diffusion constants k_i indicate that the intra-particle diffusion is a crucial step in the adsorption of target dyes studied on activated carbon CA-K and CA-C. However, this step is two to three times determinative with Reactive black 5 compared to other dyes;
- The values of the pore diffusion coefficients D for dyes MB, RO16 and MO have slightly higher values than 10^{-8} cm^2/s indicating that the adsorption process of the three dyes is governed by the pore diffusion.

3.8.2.2 Effect of pH

pH is an important variable influencing the rate of adsorption of many dyes on activated carbon. Indeed, the experimental results indicate that the percentage removal of dyes on activated carbons CA-K and CA-C depends on the nature of the dye considered. Acidic or

anionic dyes (RO16, MO and RB5) have almost the same behavior on both activated carbons at pH ranging from 2 to 12. Strong adsorption in an acidic medium, a middle adsorption for pHs near the zero point charge (pH$_{PZC}$) of activated carbon and low adsorption in a basic medium were observed. Similar behavior of adsorption of acid dyes has been reported in the literature [52,54].

On the other hand, basic or cationic dye (BM) has a different behavior. It exhibits a high adsorption in an acidic medium and in a basic medium whereas a middle adsorption was observed when pH is close to pH$_{PZC}$ activated carbons.

It is well known that the negative surface charge of the activated carbon becomes greater with increasing pH. So for the cationic dye (BM), the attraction increases, therefore the adsorption increases. Indeed, the chemical characteristics of the activated carbon CA-K and CA-C show that they contain polar functional groups (for example carboxylic function and the carbonyl function). These functions may be involved in the formation of chemical bonds between the surface of activated carbons and the cationic dye, and therefore responsible for the high adsorption of cationic dyes. The reactions of bond formation can be represented in two ways:

Equation 1: $\quad\quad\quad -CO^- + dye^+ \rightarrow -CO\text{-}dye$

Equation 2: $\quad\quad\quad -COO^- + dye^+ \rightarrow -COO\text{-}dye$

On the other hand, for anionic dyes RB5, RO16 and MO, repulsive interactions increase as the pH increases resulting to the decrement of adsorption in basic medium. The strong adsorption in acidic media can be explained by the fact that their molecules contain amine groups that are ionized by H$^+$ fixation, which leads to an increase of the amount adsorbed.

3.8.2.3 Adsorption isotherms

Our results show that adsorption isotherms of RB5, BM and MO on CA-K and CA-C obey both Freundlich and Langmuir adsorption isotherms. The high value of the correlation coefficients ($r^2 > 0.98$) confirms these results. Similar results were obtained by Hameed B.H. and Daud F.B.M. [55] for the adsorption of Methylene blue on activated carbon prepared from the bark of rubber grains. With Basic Yellow, a similar dye, Namane A. et al. [56] reported that it adsorption on activated carbon prepared from stems of coffee fits well Freundlich and Langmuir isotherms. However, adsorption of RO16 on CA-K and CA-C longer obeys the Langmuir isotherm ($r^2 > 0.99$) than the Freundlich isotherm ($r^2 < 0.89$).

Moreover, the high values of capacity factor, K$_F$ (125.5 mg/g for CA-K and 94.5 mg/g for CA-C) during the adsorption of BM according to Freundlich model, indicate a higher affinity of this dye on both activated carbons. The values of parameter n obtained for adsorption of all dyes on both CA-K and CA-C satisfy the condition of heterogeneity ($1 < n < 10$).

Similarly, considering the values of Q$_0$ we can draw the following remarks:

- Activated carbon CA-K adsorbs well the target dyes versus activated carbon CA-C. The values of Q$_0$ are in agreement with the specific surface areas of the two activated carbons (1148 m^2/g for CA-K and 584 m^2/g for CA-C). However, the amount adsorbed is not proportional to specific surface area.

- The maximum adsorption capacity Q_0 decreases respectively from BM (333.33 mg/g and 250 mg/g), MO (166.67 mg/g and 200 mg/g), RB5 (125 mg/g and 90 91 mg/g) to RO16 (111.11 mg/g and 66.67 mg/g). The decrement can be explained by the fact that the RB5 and RO16 are large molecules than those of BM and MO. This could explain the decrease in their maximum adsorption compared to BM and MO. Maximum adsorption capacity of 227.27 mg/g, 220 mg/g and 294.12 mg/g for the adsorption of Methylene blue were reported respectively by Hameed B.H. and Daud F.B.M. [57] (for an activated carbon prepared from the bark of rubber grains), by Sheikha S.A. [11] (for an activated carbon prepared from stones of date) and Hameed B.H. et al. [58] (for an activated carbon prepared from rattan sawdust).

In addition, the RL values between 0.007 and 0.092 suggest that the adsorption of dyes RB5, BM, RO16 and MO on activated carbon CA-K and CA-C systems are favorable [58,59]. However, the adsorption of RB5 seems to be complex regarding the difference between experimental and theoretical values.

4. CONCLUSION

This study shows that activated carbons CA-K and CA-C prepared respectively from shea cake and cotton cake can be used for efficient dyes removal from water. The activated carbon prepared from shea cake (CA-K) has high surface area (1148 m^2/g) ca. two time bigger than surface area (584 m^2/g) of activated carbon CA-C prepared from cotton cake.

Equilibrium and kinetic studies were made for the adsorption of dyes from aqueous solutions onto activated carbons CA-K and CA-C in the concentration range 0- 200 mg/L.

Under the conditions tested (C_0 = 100 mg/L, V = 100 mL, free pH, dosage of adsorbent 0.2 g), the amounts of adsorption were maximized at up to 35 min (RO16), 40 min (BM), 60 min (MO) and 270 min (RB5) using (CA-K), and 60 min (RO16), 70 min (BM), 90 min (MO) and 300 min (RB5) using (CA-C). The adsorption kinetics may be considered as the pseudo second order for BM, RO16 and MO dyes, and pseudo-first order for the RB5 dye. The Langmuir equation showed a somewhat better fit than does the Freundlich equation for adsorption of dyes using both activated carbons. The intra-particle diffusion is a key step in the adsorption of the four dyes on activated carbons CA-K and CA-C. The adsorption rate depends on the pH of the solution. High adsorption is observed for the cationic dye (BM) at high pH whereas for anionic dyes (RB5, RO16 and MO), adsorption is high in acid medium. On basis of the studies reported, both activated carbon (CA-K) and (CA-C) have been successfully used as absorbents for the removal of dyes from aqueous solution. This is so an alternative of green chemistry to reduce carbon residue for useful purposes.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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