



Performances of conventional activated carbon and low-cost adsorbent from clay and mineral coal in decolorization of AO7 solution

Ahmed Hammami^a, Catherine Charcosset^b, Raja Ben Amar^{a,*}

^aLaboratoire Sciences des Matériaux et Environnement, Faculté des Sciences de Sfax, Université de Sfax, Route de Soukra Km 4, 3038 Sfax, Tunisia, emails: benamar.raja@yahoo.com (R.B. Amar), a_hammami@outlook.fr (A. Hammami)

^bLaboratoire d'Automatique et de Génie des Procédés (LAGEP), UMR 5007 CNRS, Université de Lyon 1, 43 Boulevard de 11 Novembre 1918, 69622 Villeurbanne, France, email: catherine.charcosset@univ-lyon1.fr

Received 9 August 2017; Accepted 6 January 2018

ABSTRACT

The adsorption of acid orange 7 (AO7) from aqueous solution by activated carbon (AC) as a commercial adsorbent, and mineral coal (MC) and natural clay (Cl) as a low-cost and natural adsorbent was investigated. The study was carried out under various conditions, such as the average adsorbent particle size, adsorbent dosage, contact time, pH, initial dye concentration, temperature and effect of surfactant. The adsorption was particle size dependent with a high adsorption of AO7 by MC which has the smallest particle size. The variation of adsorbent dosage allowed finding the optimal dose. Adsorption kinetic data were properly fitted with the pseudo-second order kinetic model. The good fitting was obtained with the Langmuir model ($R^2 = 0.99$). It shows a maximum layer adsorption capacity of 182 mg/g by MC, 278 mg/g by AC and 403 mg/g by Cl at 25°C. The adsorption increased with an increase in the pH. From pH = 7, the equilibrium was stabilized and was unchanged in basic range using any adsorbent.

Keywords: Adsorption; AO7 dye; Activated carbon; Mineral coal; Clay

1. Introduction

Dyes are generally synthetic organic compounds that are increasingly being produced and used as colorants in many industries worldwide, including textile, cosmetics [1,2]. The wastewater generated by the processes of these industries usually contains up to around 10%–40% of used dye [3]. Accordingly, to protect humans and the receiving ecosystem from contamination, the dyes as well as other organic and inorganic pollutants should be eliminated from the dye-contained wastewaters before being released into the environment. The removal of dyes in wastewater is based on the use of the traditional methods of treatment which are composed usually of two steps: the physicochemical treatment characterized by the addition of chemical reagents (aluminum chloride, ferric chloride) [4,5] and the biological

treatment performed with activated sludge under sufficient aeration [6]. However, these processes are not always effective and need a large consumption of chemical products. In recent years, many researchers were focused on the use of natural materials as adsorbent, such as clays, zeolites, agricultural materials and industrial by-products due to their low cost and their abundance [7,9]. Additionally, the use of these natural materials reduces the generation of non-ecofriendly products since it requires simple protocols for regeneration or reuse [10]. In this context, Mustapha et al. [11] found a total decolorization of palm oil using 4% AC with 20% of hydrochloric acid. Above this dose, further increase in adsorbent dosage had no significant effect. Barka et al. [12] used dried prickly pear cactus cladodes for adsorption of Methylene Blue (MB), Eriochrome Black T (EBT) and Alizarin S (AS) from aqueous solutions. They demonstrated that the decrease in the mean particle size of adsorbent from 500 to 100 μm led to the increase of the amount adsorbed from 45 to 120 mg/g. The biosorption yield of MB increased from 37.74%

* Corresponding author.

to 68.92% when the biosorbent dosage was increased from 0.2 to 1 g/L, from 13.37% and 18.24% to 59.78% and 61.80%, respectively, for EBT and AS, when the biosorbent dosage was increased from 0.2 to 3 g/L for a particle size less than 100 μm during 90 min.

It is well known also that the surface properties of AC, that is, the structure and the surface chemistry, enable the preparation of adsorbents with appropriate characteristics for specific applications. In this context, Karanfil and Kilduff [13] studied the removal by adsorption of two organic contaminants (the trichloroethylene and the trichlorobenzene), with two types of modified adsorbents: coal-based and wood-based granular AC, modified by HNO_3 oxidation and heat treatment under N_2 inert atmosphere. It was found that increasing surface acidity increased the polarity of the surface and reduced adsorption of hydrophobic synthetic organic contaminants by granular activated carbon. The Boehm method was useful for correlating the reactivity of carbon surfaces pre-cleaned by acid washing and heat treatment, and subsequently modified with a single oxidant.

More recently, some authors started to study the effect of AC surface chemistry on the removal of dyes from textile effluents [14,15]. Hazza and Hussein [16] used agriculture solid waste as low-cost adsorbents: raw olive stone (OS) and AC prepared from Egyptian olive stones (OSAC) for MB removal. The determination of the pH effect showed that the adsorption of MB by OSAC increased from 6.4 to 8.3 mg/g at pH of 2 and 9, respectively, and reached its maximum value of 9.5 mg/g at pH 5. The increase of the temperature from 25°C to 45°C leads to increase of the removal percentage of MB from 93% to 97% by OSAC and from 80% to 90% by OS, respectively. Al-Degs et al. [14] studied the adsorption of three reactive dyes on a Filtrasorb 400 AC. They attributed the high adsorption capacity of this adsorbent to its net positive surface charge during the adsorption process. In this case, the AC was tested to remove an anionic dye. For this, the equilibrium adsorption data were found to be fitted with both Langmuir and Freundlich models.

Our work is focused on the decolorization of AO7 solution by adsorption using three adsorbents, commercial AC, low-cost mineral coal (MC) and natural clay (Cl). A comparison study was performed taking into account the operating parameters and the adsorption conditions. The determination of kinetics and adsorption equilibrium was also achieved.

2. Materials and methods

2.1. Characterization of AO7

The AO7 dye corresponds to acid orange 7 ($\text{C}_{16}\text{H}_{11}\text{N}_2\text{NaO}_4\text{S}$, MW = 350.32 g/mol, $\lambda_{\text{max}} = 483 \text{ nm}$, zeta potential = -15.3 mV) commercialized by Sigma-Aldrich, France.

The molecular structure of this dye is presented in Fig. 1.

2.2. Characterization of adsorbents

AC was purchased from the Norit, USA. The density, molasses number, average particle size and surface area of the adsorbent were 0.37 g/mL, 180 g/mol, 37 μm and 1,400 m^2/g , respectively (obtained from the manufacturer).

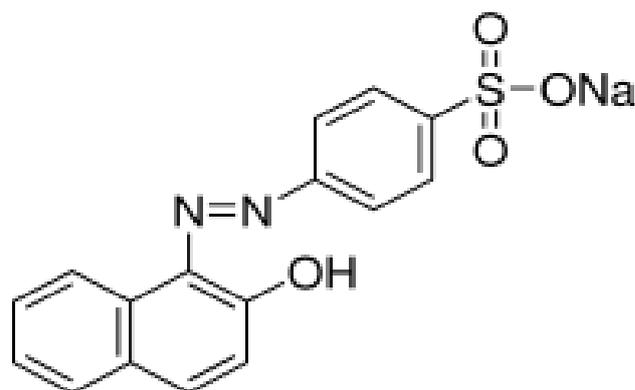


Fig. 1. Molecular structure of AO7.

MC is a natural product from Tunisia. In our case, the carbon powder was prepared by the crushing–sieving technique. Three powders differing by their mean particle size were ground in a planetary crusher at 300 rpm during 30 min, 2 h and 15 h, respectively. Then, these powders were activated under air at a temperature of 800°C.

The adsorbent clay used in this work is from Northeastern Tunisia. This clay is predominantly composed of kaolinite and illite. This clay was thermally activated at 700°C after grinding and sieving.

The pH at zero point of charge (pHpzc) is defined as the pH of the solution in which the solid exists under a neutral electric potential. It is determined for all AC, MC and Cl using the method of Lopez-Ramon et al. [17].

2.3. Experimental procedures

A stock solution of 35 mg/L of AO7 dye was prepared by dissolving the amount of dye in distilled water and the used concentration was obtained by dilution. Adsorptions experiments were conducted in 1 L reactor at a constant stirring rate of 300 rpm using a solution volume of 500 mL.

The suspension was then decanted and the dye concentration in the supernatant was measured with a UV-visible spectrophotometer at 483 nm wavelength.

The color removal was determined by the following equation:

$$R (\%) = (1 - C_e/C_0) \times 100 \quad (1)$$

where C_0 and C_e are the initial concentration of dye (mg/L) and concentration of dye (mg/L) after adsorption, respectively.

The amount of adsorbed dye per unit mass of adsorbent at time t , Q (mg/g), was then determined by the following equation:

$$Q = (C_0 - C_e) \cdot V/m \quad (2)$$

where Q is the amount of dye adsorbed (mg/g), C_0 is the initial concentration of dye (mg/L), C_e is the concentration of dye after adsorption (mg/L), V is the volume of the solution (mL) and m is the mass of the adsorbent (g).

The effect of adsorbent particle size was studied using the three MC powders at different doses at the following

conditions: pH of 7, ambient temperature of 25°C and initial dye concentration of 35 mg/L (0.1 mM). The temperature was controlled using a thermostatically controlled incubator.

The effect of the initial pH on the amount of adsorbed dye was also studied under similar conditions over a range of pH from 4 to 10.

To reach the same conditions than those of real textile waste water effluent, different surfactants differing by their functional charge: dodecyl trimethylammonium bromide C12TAB (cationic surfactant), sodium dodecyl sulfate SDS (anionic surfactant) and Brij 35 (nonionic surfactant) were added. The critical micelle concentration of these surfactants are 15.2, 8, and 0.09 mM, respectively, for C12TAB [17], SDS [18] and Brij 35 [19].

The AO7 concentration in the supernatant was measured by UV-visible spectrophotometer at 483 nm. The pH was adjusted to a given value by adding a few drops of diluted 0.1 N NaOH or 0.1 N HCl solutions before each experiment and then measured using a pH meter (Mettler Toledo, France).

The adsorption isotherms were obtained by considering different solution concentrations (25 to 150 mg/L) at different temperatures (25°C, 40°C, 50°C and 60°C). The time of contacting was set to 4 h time beyond which it is ensured that there was no significant variation in the concentration of dye at equilibrium.

The adsorption isotherms obtained in this work were interpreted using the adsorption models: Langmuir, Toth and Freundlich.

Langmuir model: The Langmuir model was linearized to the following:

$$C_e/Q = f(C_e). \quad (3)$$

The Langmuir equation can be represented as follows [20]:

$$Q = (q_m \cdot b \cdot C_e) / (1 + b \cdot C_e) \quad (4)$$

where C_e (mg/L) is the equilibrium concentration of dye in solution, Q (mg/g) is the amount of dye adsorbed at equilibrium, q_m (mg/g) is the amount of dye adsorbed at complete monolayer coverage, b (l/mg) is a constant that is related to the heat of adsorption [21].

Toth model: If the Langmuir model derives from fundamental principles of thermodynamics and kinetics, most adsorbent/adsorbate pairs cannot be described by these theoretical models and therefore require the use of other hypotheses and mathematical models to represent the studied system. Other models, more empirical, tend to better represent the real phenomena observed including that of Toth [22]:

$$q_e = C_e \cdot Q_m / (1/K + C_e^m)^{1/m} \quad (5)$$

K_T is the Toth's equilibrium constant; C_e is the equilibrium concentration (mg/L); Q_m is the maximum capacity of Toth (mg/g); m is the exponent of the Toth model.

This empirical equation (Eq. (5)) proposed by Toth is based on that of Langmuir but allows a better adequation with the experimental points, in particular in the inflection of isotherms. The parameters are identical to those of the

Langmuir equation, to which a coefficient C is added. These parameters and in particular the coefficient m make it possible to take into account the lateral interactions, the heterogeneity of the surface within the system as well as other deviations from ideality.

Freundlich model: The Freundlich model was linearized as:

$$\ln(Q) = \ln(C_e). \quad (6)$$

The Freundlich equation can take the following form [20]:

$$Q = K \cdot C_e^n \quad (7)$$

where K (L/g) represents the adsorption capacity when dye equilibrium concentration (C_e), n represents the degree of dependence of adsorption on equilibrium concentration (heterogeneity factor) [20].

The modeling of adsorption kinetics was investigated using two models: pseudo-first order and pseudo-second order to predict the adsorption kinetics of AO7 by AC and MC and CI.

The adsorption rate constant of the first order is inferred from the model established by Tóth [23]. In the context, Yaneva and Koumanova [24] have opted instead for a kinetic model of order two.

For the pseudo-first order rate constant k is given by the following equation:

$$d(q_t)/dt = k(q_e - q_t) \quad (8)$$

The pseudo-second order rate constant is given by the following equation:

$$d(q_t)/dt = k(q_e - q_t)^2 \quad (9)$$

with q_e , the amount of adsorbate at equilibrium (mg/g), t , the contact time (min), k , the rate constants of adsorption, respectively, for the pseudo-first order (min^{-1}) and the pseudo-second order (g min/mg).

3. Results and discussion

3.1. Effect of mineral coal particle size

The adsorption of AO7 dye has been performed for 4 h using three coal mineral powders differing by their particle sizes of 278 μm (C1), 158 μm (C2) and 67 μm (C3) at different doses (100, 300, 500, 700 and 900 mg/L) under the following conditions: pH = 7 and $T = 25^\circ\text{C}$.

Fig. 2 shows that the colorant retention increases when the particles sizes decrease for adsorbent doses below 700 mg/L. Beyond, this value, that is, for 900 mg/L, a maximum retention of 100% was obtained and was independent of adsorbent particle sizes. The best retention of almost 100% was achieved for mean particle size of 67 μm . The porosity of MC increases with increasing surface area. It can be noticed that the decrease of the particle size resulting in the increase of the porosity, which makes it possible to fix more AO7 molecules [25]. According to Nai [26], the high specific surface

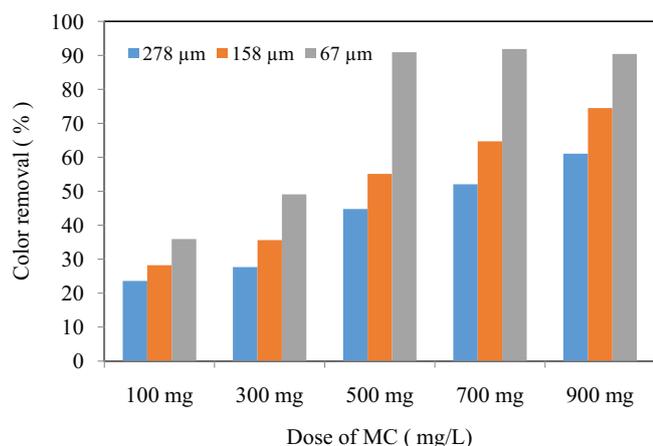


Fig. 2. Effect of MC dose on color removal after 4 h adsorption (initial AO7 concentration = 35 mg/L, $T = 25^{\circ}\text{C}$, $\text{pH} = 7$).

of 499 m^2/g achieved by 67 μm particle sizes can explain the high retention obtained in comparison with that provided by 158 and 278 μm particles sizes of 225.5 and 128.7 m^2/g , respectively. This result has been previously shown by Barka et al. [12] who found that the removal of methylene blue depended on the variation of the particle sizes dried to dried prickly pear cactus cladodes used as adsorbent. At equilibrium, the amount of dye adsorbed increased from 54.91 to 118.8 mg/g when particle sizes decreased from 500 to less than 100 μm .

3.2. Effect of adsorbent dose

To determine the optimal dose of adsorbent, tests were conducted considering the removal of colorant by adding different doses of AC, MC and CI (100, 200, 300, 400, 500 and 600 mg/L) during 4 h at a pH value of 7 and a temperature of 25°C . Fig. 3 shows that the best retention of AO7 by CI, AC and MC was obtained at a dose of 200, 300 and 500 mg/L which correspond to more than 99% of AO7 removal.

The total decolorization obtained at the optimum adsorbent dose explains that there are enough active sites located at the adsorbent surface which could retain the entire quantity of dye. In this context, Aksu [27] showed that increasing the dose of cactus-based biomaterials as adsorbent from 0.25 to 1 g leads to a total removal of color from MB aqueous solution. Beyond this dose, the addition of adsorbent has no effect on the color removal. Some authors have shown that as the amount of adsorbent added to the dye solution is low, the dye molecules can easily access the adsorption sites. The increase in porosity has a considerable effect on increasing the adsorption capacity (Table 1). In this context, Sakr et al. [28] have shown that for large pores, a satisfactory capacity of adsorption was obtained compared with narrow pores.

3.3. Effect of contact time

The variation of the kinetics of dye adsorption in presence of aqueous AO7 solution at a concentration of 35 mg/L by adding the optimal doses of CI, AC and MC is illustrated in Fig. 4. The kinetics of AO7 adsorption using the MC was slower than the kinetics of adsorption by AC and CI. The stabilization was

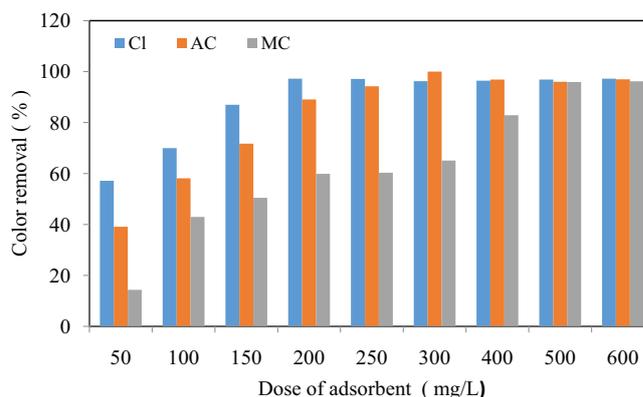


Fig. 3. Variation of color removal with adsorbent dose after 4 h adsorption in presence of CI, AC, MC as adsorbent (initial dye concentration = 35 mg/L, $T = 25^{\circ}\text{C}$, $\text{pH} = 7$).

Table 1
Characteristics of the different adsorbents

Adsorbent	Average particle size (μm)	Specific area (m^2/g)	Porosity (%)	pHpzc
AC	37	1,400	61	7.8
MC 1	278	129	8	5.3
MC 2	158	226	32	5.3
MC 3	67	499	43	5.3
CI	100	78	76	9

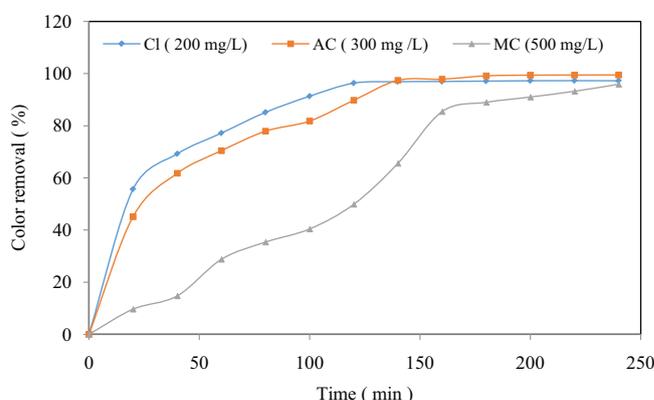


Fig. 4. Kinetic study of adsorption at optimal adsorbent doses (initial dye concentration = 35 mg/L, $T = 25^{\circ}\text{C}$, $\text{pH} = 7$).

obtained after 3 h of adsorption. As the porosity is related to the pore size distribution, it reflects the internal structure of the microporous adsorbents from where each adsorbent has its adsorption capacity. The rapid kinetics of adsorption can be interpreted by the fact that at the beginning, the number of active sites available on the surface of the adsorbent material is much larger than that remaining after a certain operating time [29,30]. According to Ho and Mc Kay [31], it has been shown that the fast kinetics step corresponds to the transfer of external mass while the stabilized step is related to the transfer of internal mass. The textures of AC, MC and CI before and after adsorption were characterized by scanning electron

microscopy (SEM). As shown in Figs. 5(a)–(c), there is a difference in structure morphology between the three types of the raw adsorbents. The CI shows the most irregular structure resulting in a rougher surface, while MC seems having to most regular structure. The SEM photos provide that CI is more porous than AC and MC which explains the noticeable adsorption capacity achieved by this adsorbent. After adsorption, the pores seem to be totally covered by the pollutants due to the saturation of the active sites by AO7 molecules.

3.4. Effect of pH

The effect of initial pH on the removal of AO7 by AC, MC and CI was investigated in the pH range of 4–10 and the results are shown in Fig. 6. The adsorption performance varies according to the pH of the solution. The dye adsorption was constant at pH 7–10 and it was unfavorable at pH < 7. In the presence of H^+ ions, substitution takes place between the ions H^+ and Na^+ , after removal of the sulfone groups responsible of electrostatic attraction may have places by releasing a molecule of sulfuric acid. The release of sulfone group leads to absence of van der Waals bonds that make the molecular interactions between the dye and the adsorbent [32]. At neutral and alkaline pH, nothing happens to the adsorption or remains unchanged. Furthermore, the behavior of the different

adsorbents in color removal at different pHs of solution can be explained on the basis of their pH_{pzc} evaluated to be 9, 8 and 5, respectively, for CI, AC and MC (Fig. 7; section 2.2). It, therefore, follows that the surface of adsorbent was negatively charged in solutions at which the equilibrium pH was greater than pH_{pzc} and positively charged at pH solution lower than pH_{pzc}. Color removal would be ion-exchange between the negatively charged ions at the surface and the positively charged AO7 dyes. Therefore, molecules removal at pH > pH_{pzc} was most probable.

3.5. Effect of surfactants

The effect of surfactants on dye adsorption was studied at pH 7, dye concentration 35 mg/L and optimal doses of AC, MC and CI for 2 h (Figs. 8(a)–(c)). The addition of anionic surfactants leads to significant reduction of adsorption performance. This can be explained by the increase in the electrostatic repulsion between the dye and the surface of the adsorbent used hydrophilic head [33].

The nonionic surfactants result in to a decline of the adsorption performance. This is due to steric hinderance or competition between AO7 molecules and the nonionic surfactants (Brij 35) [34].

The cationic surfactant leads to the improvement of the performances of adsorption of MC and AC. However, a slight improvement of the performances was observed for the CI. The addition of a cationic surfactant results in the change of the

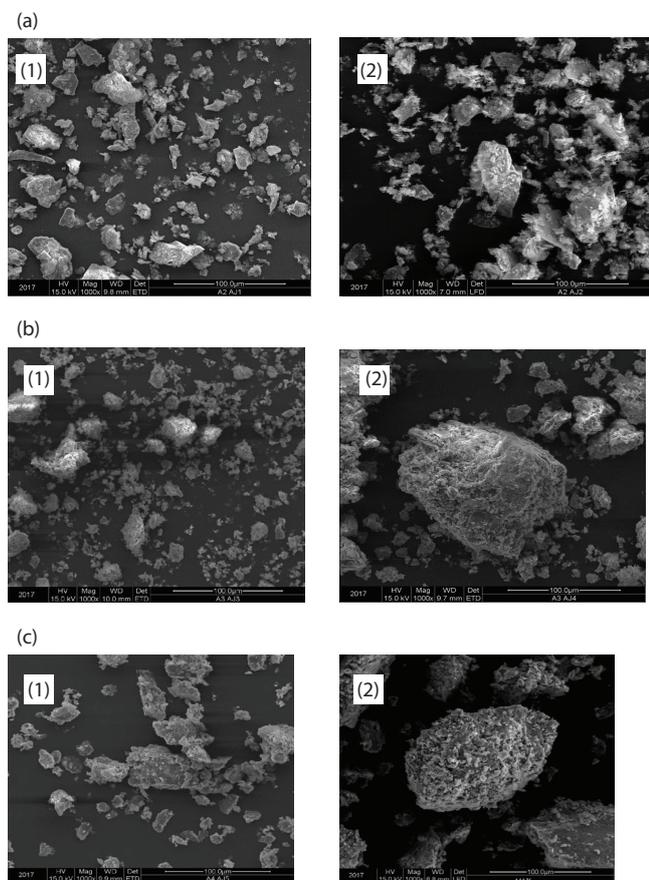


Fig. 5. (a) SEM photographs of AC: (1) before and (2) after adsorption; (b) SEM photographs of MC: (1) before and (2) after adsorption; (c) SEM photographs of CI: (1) before and (2) after adsorption.

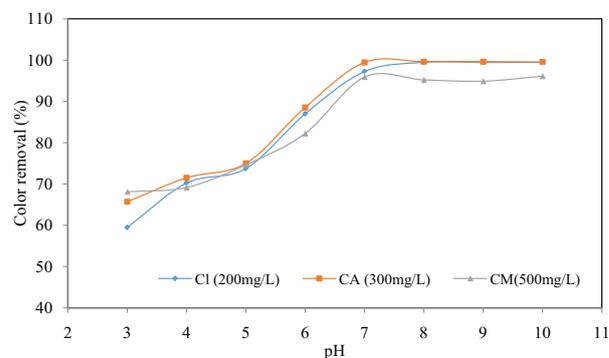


Fig. 6. Effect of pH on color removal of AO7 (initial dye concentration = 35 mg/L, $T = 25^{\circ}C$).

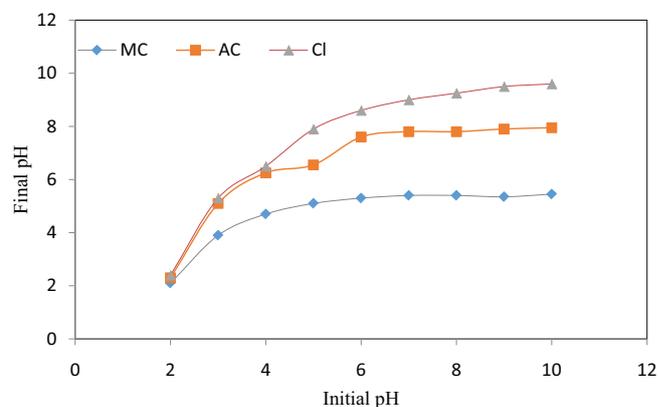


Fig. 7. Determination of pH_{pzc}.

surface of MC and AC, this modification increases the interaction forces between the dye and the adsorbent and improves the efficiency of the process [35,36]. Moreover, adding the cationic surfactant allows to reduce the optimal doses for MC and AC (Fig. 9). The molecules of cationic surfactant can activate more adsorbent by fixing alkyl chains located in the molecules of cationic surfactants. When the adsorbent becomes more active, we can use the doses less than the optimal doses found. Alkyl chains increase the contribution entropy of adsorption energy and develop more van der Waals interactions [37].

3.6. Adsorption isotherms

The amount of dye rapidly increases at low concentrations in solution, and then this increase is reduced more and more until the early appearance of a bearing corresponding to the saturation of adsorption sites (Figs. 10(a)–(c)).

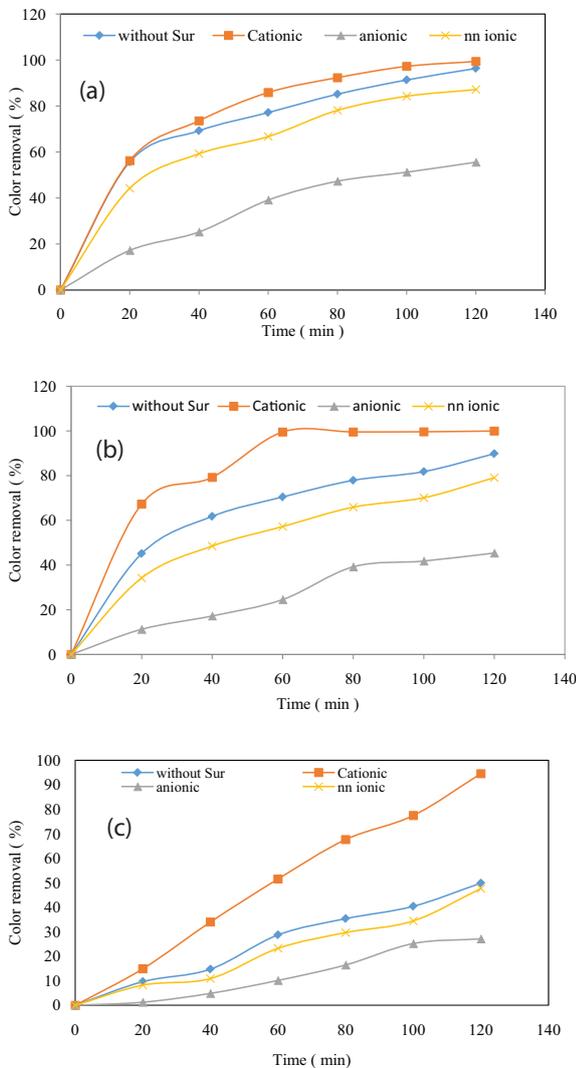


Fig. 8. Effect of surfactant on the adsorption by (a) Cl (initial dye concentration = 35 mg/L, M_{Cl} = 200 mg/L, T = 25°C, pH = 7); (b) AC (initial dye concentration = 35 mg/L, M_{AC} = 300 mg/L, T = 25°C, pH = 7) and (c) MC (initial dye concentration = 35 mg/L, M_{MC} = 500 mg/L, T = 25°C, pH = 7).

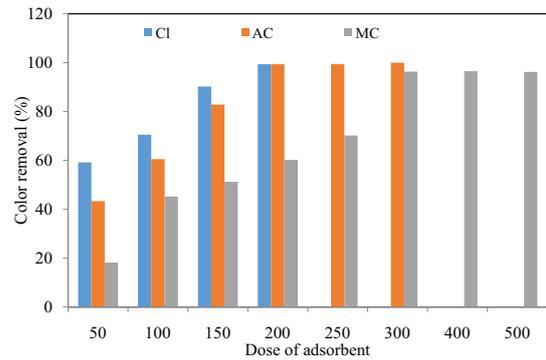


Fig. 9. Effect of adsorbent dose on color retention in the presence of surfactant.

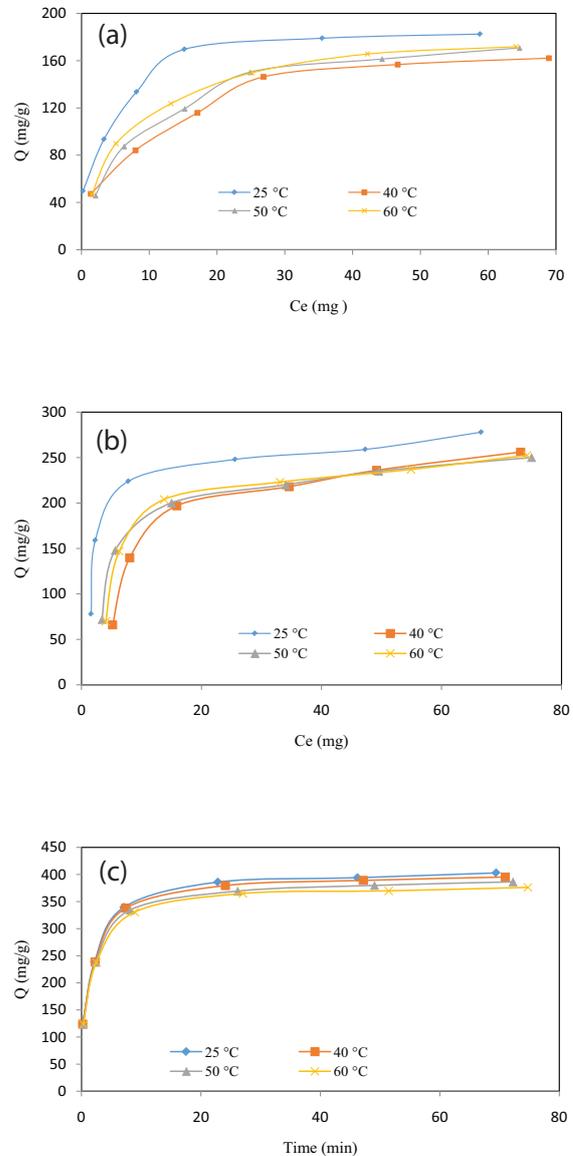


Fig. 10. Isotherms adsorption of AO7 at different temperatures by (a) MC (pH = 7, T = 25°C, M_{MC} = 500 mg/L); (b) AC (pH = 7, T = 25°C, M_{AC} = 300 mg/L) and (c) Cl (pH = 7, T = 25°C, M_{Cl} = 200 mg/L).

The best results were obtained at 25°C, for a higher temperature, the results were similar and the performances seem unchanged when the temperature increased from 40°C to 60°C. The good fitting was obtained with the Langmuir model ($R^2 = 0.99$). It shows a maximum layer adsorption capacity of 182 mg/g by MC, 278 mg/g by AC and 403 mg/g by CI at 25°C.

3.6.1. Langmuir model

According to Fig. 11(a), we note that the linearization of the adsorption isotherms of AC, MC and CI is satisfactory with good correlation coefficients for all temperatures. We can say that the Langmuir model is adequate for a good description of adsorption isotherms. The values of parameters, Q_m , b and R^2 , are presented in Table 2.

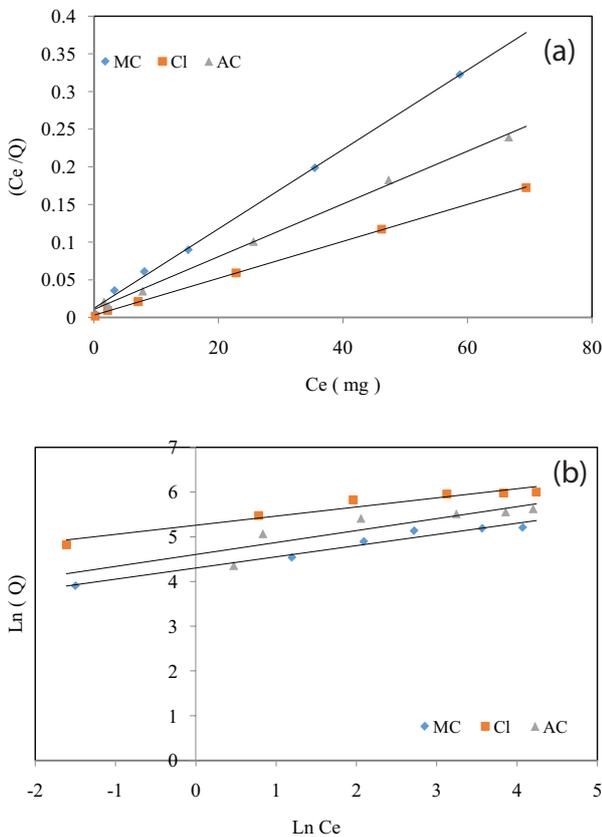


Fig. 11. Modeling of adsorption isotherms of AO7 by MC, AC and CI at 25°C according to the (a) Langmuir model and (b) Freundlich model.

Table 2
Langmuir constants at 25°C in presence of MC, AC and CI

Adsorbent	R^2	b (L/mg)	Q_m (mg/g)
MC	0.99	0.416	188.679
AC	0.99	0.3	333.333
CI	0.99	1	500

3.6.2. Freundlich model

The test results of the modeling of AO7 adsorption on AC, MC and CI according to the Freundlich model are shown in Fig. 11(b). Based on the correlation coefficients R^2 shown in Table 3 (0.95 for MC, 0.75 for AC and 0.93 for CI), we deduce that the Freundlich model was not adequate to model the adsorption isotherms of AO7 on AC and MC throughout the concentration range studied and for all temperatures.

3.7. Adsorption kinetics

Kinetic constants of dye adsorption on AC, MC and CI for the pseudo-first order and the pseudo-second order are determined graphically from the lines obtained (Figs. 12(a) and (b)).

Table 3
Freundlich constants at 25°C in presence of MC, AC and CI

Adsorbent	R^2	n (L/mg)	K (mg/g)
MC	0.96	0.25	73.84
AC	0.757	0.267	99.78
CI	0.93	0.203	191

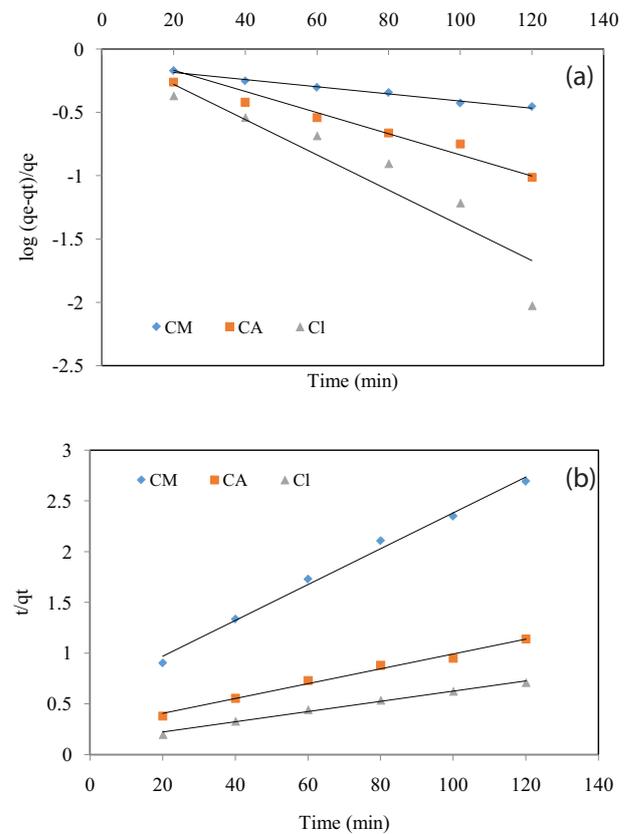


Fig. 12. Determination of the rate constants of the (a) pseudo-first order adsorption of AO7 by the different adsorbents (AC, MC, CI) and (b) pseudo-second order adsorption of AO7 by the different adsorbents (AC, MC, CI).

Table 4
Pseudo-first order, pseudo-second order for AO7 removal by AC, MC and CI

	Pseudo-first order	Pseudo-second order
Rate constant AC	193.2×10^{-4} (min^{-1})	2.05×10^{-4} ($\text{min} \cdot \text{g}/\text{mg}$)
Factor of correlation (R^2)	0.92	0.99
Rate constant MC	98.9×10^{-4} (min^{-1})	5.08×10^{-4} ($\text{min} \cdot \text{g}/\text{mg}$)
Factor of correlation (R^2)	0.65	0.98
Rate constant CI	56.5×10^{-4} (min^{-1})	3.45×10^{-5} ($\text{min} \cdot \text{g}/\text{mg}$)
Factor of correlation (R^2)	0.87	0.99

According to the results shown in Table 4 ($R^2 = 0.99$ in pseudo-second order for MC, AC and CI), we note that the pseudo-second order model is the most reliable way to determine the order of kinetic dye adsorption by our adsorbents and that is a high correlation coefficient ($R^2 = 0.98$). A number of studies [38,39] found that the kinetics of adsorption of dyes on clay materials correspond to the pseudo-second order. For adsorption on AC, the models of pseudo-first order and the pseudo-second order are reliable to the kinetic order, they have a correlation factor of 0.99 [40].

4. Conclusion

AC, MC and CI that were used in this work have shown to be effective in reducing the amount of dye in water in two ways: kinetics and equilibrium. The MC that has the smallest average particle size, with a higher surface area, contains more adsorbent sites and therefore can retain more dye molecules. The increase in adsorbent dosage leads to increase in the dye adsorption due to increase in number of adsorbent sites. The adsorption capacity of dye increased in basic solutions, but decreased in acidic solutions. Molecular interactions exchanged by the sulfonate groups of the dye and carbon sites of the adsorbent is the main adsorption mechanism. The addition of cationic surfactants promotes interaction. The adsorption isotherms of AO7 dye by AC, MC and CI are described satisfactorily by the Langmuir model, while the Freundlich model can describe our results throughout the experimental concentration range studied.

Acknowledgement

The authors wish to gratefully acknowledge the financial support from the PHC-UTIQUE program (code CMCU 13G1111).

References

- [1] F.-C. Wu, R.-L. Tseng, High adsorption capacity NaOH-activated carbon for dye removal from aqueous solution, *J. Hazard. Mater.*, 152 (2008) 1256–1267.
- [2] G. Crini, Non-conventional low-cost adsorbents for dye removal: a review, *Bioresour. Technol.*, 97 (2006) 1061–1085.
- [3] E. Forgacs, T. Cserhati, G. Oros, Removal of synthetic dyes from wastewaters, *Environ. Int.*, 30 (2004) 953–971.
- [4] G.S. Gupta, G. Prasad, V.N. Singh, Removal of chrome dye from aqueous solutions by mixed adsorbents fly ash and coal, *Water Res.*, 24 (1990) 45–50.
- [5] M.S. El Geundi, Adsorbents for industrial pollution control, *Adsorpt. Sci. Technol.*, 15 (1977) 777–787.
- [6] G. MC Kay, B. Alduri, Multicomponents dye adsorption onto carbon using a solid diffusion mass transfer model, *Ind. Eng. Chem. Res.*, 30 (1991) 385–395.
- [7] F. MC Convey, G. MCKay, Mass transfer model for the adsorption of basic dyes on wood meal in agitated batch adsorbents, *Chem. Eng. Process. Process Intensif.*, 19 (1985) 267–275.
- [8] G. MC Kay, Adsorption of dye stuffs from aqueous solutions with activated carbon. I. Equilibrium and batch contact-time studies, *Chem. Technol. Biotechnol.*, 32 (1982) 759–772.
- [9] C. Parfait, A. Villanova, Traitement des nuisances olfactives par photocatalyse et charbon actif dans les stations et tunnels de métro, *Rev. Gen. Chemins. Fer*, 45 (1999) 5–8.
- [10] J. De Laat, F. Bouanga, M. Dore, J. Mallevalle, Influence of bacterial growth in granular activated carbon filters on the removal of biodegradable and of non-biodegradable organic compounds, *Water Res.*, 19 (1985) 1565–1578.
- [11] S.I. Mustapha, A.A. Mohamed, A.Y. Zakari, H.A. Mohamed, Performance evaluation of local clays from northern Nigeria for the refining of palm oil, *J. Chem. Eng. Mater. Sci.*, 4 (1985) 58–66.
- [12] N. Barka, K. Ouzaouit, M. Abdennouri, M. El Makhchouf, Dried prickly pear cactus (*Opuntia ficus-indica*) cladodes as a low-cost and eco-friendly biosorbent for dyes removal from aqueous solutions, *J. Taiwan Inst. Chem. Eng.*, 44 (2013) 52–60.
- [13] T. Karanfil, J.E. Kilduff, Role of granular activated carbon surface chemistry on the adsorption of organic compounds.1. Priority pollutants, *Environ. Sci. Technol.*, 32 (1999) 17–24.
- [14] Y. Al-Degs, M. Khraisheh, S.J. Allen, M.N. Ahmad, Effect of carbon surface chemistry on the removal of reactive dyes from textile effluent, *Water Res.*, 34 (2000) 927–935.
- [15] M.F.R. Pereira, S.F. Soares, J.J.M. Orfao, J.L. Figueiredo, Adsorption of dye on activated carbons: influence of surface chemical groups, *Carbon*, 41 (2003) 811–821.
- [16] R. Hazzaa, M. Hussein, Adsorption of cationic dye from aqueous solution onto activated carbon prepared from olive stones, *Environ. Technol. Innovation*, 4 (2015) 36–51.
- [17] M.V. Lopez-Ramon, F. Stoeckli, C. Moreno-Castilla, F. Carrasco-Marin, On the characterization of acidic and basic surface sites on carbons by various techniques, *Carbon*, 37 (1999) 1215–1221.
- [18] J. Aguiar, P. Carpena, J.A. Molina-Bolívar, C. Carnero Ruiz, On the determination of the critical micelle concentration by the pyrene 1:3 ratio method, *J. Colloid Interface Sci.*, 258 (2003) 116–122.
- [19] A.M. Kahn, S.S. Shah, Determination of critical micelle concentration (cmc) of sodium dodecyl sulfate (SDS) and the effect of low concentration of pyrene on its cms using origin Software, *J. Chem. Soc. Pak.*, 30 (2008) 186–191.
- [20] A. Patist, S.S. Bhagwat, K.W. Penfield, P. Aikens, D.O. Shah, On the measurement of critical micelle concentrations of pure and technical-grade nonionic surfactants, *J. Surfactants Deterg.*, 3 (2000) 53–58.
- [21] D. Chatzopoulos, A. Varma, R. Irvine, Activated carbon adsorption and desorption of toluene in the aqueous phase, *AIChE J.*, 39 (1993) 20–27.
- [22] D.M. Ruthven, Principles of Adsorption and Adsorption Processes, John Wiley & Sons, New York, 1984.
- [23] J. Tóth, Thermodynamical correctness of gas/solid adsorption isotherm equations, *J. Colloid Interface Sci.*, 163 (1994) 299–302.
- [24] Z. Yaneva, B. Koumanova, Comparative modelling of mono- and dinitrophenols sorption on yellow bentonite from aqueous solution, *J. Colloid Interface Sci.*, 293 (2006) 303–311.
- [25] Y.S. Ho, G. Mc Kay, The kinetics of sorption of divalent metal ions onto sphagnum moss peat, *Water Res.*, 34 (2000) 735–742.
- [26] N. Nai, Etude du procédé d'adsorption du phenol sur charbon actif à base de grignon d'olive, modélisation par plan d'expérience. Mémoire de magister, université de M'hamed Bougara Boumerdes, 2006.
- [27] Z. Aksu, Application of biosorption for the removal of organic pollutants: a review, *Process Biochem.*, 40 (2005) 997–1026.

- [28] F. Sakr, A. Sennaoui, M. Elouardi, M. Tamimi, A. Assabbane, Adsorption study of Methylene Blue on biomaterial using cactus, *Mater. Environ. Sci.*, 6 (2015) 397–406.
- [29] P.R.B. Walton, N. Quirke, Modelling the phase behaviour of a fluid within a pore, *Chem. Phys. Lett.*, 129 (1986) 382–386.
- [30] A.R. Dincer, Y. Gunes, N. Karakaya, Comparison of activated carbon and bottom ash for removal of reactive dye from aqueous solution, *J. Hazard. Mater.*, 141 (2007) 529–535.
- [31] Y.S. Ho, G. Mc Kay, Pseudo-second order model for sorption processes, *Process Biochem.*, 34 (1999) 451–465.
- [32] M.E. Ouardi, S. Alahiane, S. Qourzal, A. Abaamrane, J. Douch, Removal of carbaryl pesticide from aqueous solution by adsorption on local clay in Agadir, *Am. J. Anal. Chem.*, 4 (2013) 72–79.
- [33] S. Yahya, Y. Al-Degs, I. Musa, El-Barghouthi, H. El-Seikh, M. Walker, Effect of solution pH, ionic strength, and temperature on adsorption behavior of reactive dyes on activated carbon, *J. Hazard. Mater.*, 169 (2009) 1–30.
- [34] C. Kartal, H. Akbas, Study on the interaction of anionic dye-nonionic surfactants in a mixture of anionic and nonionic surfactants by absorption spectroscopy, *Dyes Pigm.*, 65 (2005) 191–195.
- [35] J.U. Chang – Huang, C.T. Steffens, Coadsorption sur charbon actif de composés organiques dans les eaux usées, *Proc. 31 St. Ind. Waste Conf. Perdue. Unir.* 31 (1976) 107–121.
- [36] A. Ozcan, C. Omeroglu, Y. Ordugan, A.S. Oscan, Modification of bentonite with a cationic surfactant: an adsorption study of textile dye Reactive Blue 19, *J. Hazard. Mater.*, 140 (2007) 173–179.
- [37] G.M. Nabil, N. El-Mallah, M.E. Mahmoud, Enhanced decolorization of reactive black 5 dyes by active carbon sorbent-immobilized-cationic surfactant (AC-CS), *J. Ind. Eng. Chem.*, 20 (2013) 994–1002.
- [38] L. Qi, W. Liao, Z. Bi, Adsorption of conventional and gemini cationic surfactants in nonswelling and swelling layer silicate, *Colloids Surf., A*, 302 (2007) 568–572.
- [39] J. Yener, T. Kopac, G. Dogu, Adsorption of Basic Yellow 28 from aqueous solutions with clinoptilolite and amberlite, *J. Colloid Interface Sci.*, 294 (2006) 255–264.
- [40] P. Janos, P. Michakel, P. Turex, Sorption of ionic dyes onto untreated low-rank coal – oxihumolite: a kinetic study, *Dyes Pigm.*, 74 (2007) 363–370.