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Dicolouration of Congo Red Dye by Activated Carbon in Aqueous Medium

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Congo red an azoïque dye could be fixed on activated carbon. Batch experiments conducted in aqueous medium, at room temperature (20 ± 2ºC) and pH 6.55, have showed a low affinity of this compound towards this adsorbent mainly at elevated concentrations (100 ppm and more). This fact might be attributed to its azoique structure. However, at relatively feeble concentrations, we noticed a better fixation since *ca.* 70 % of the substrate was retained over activated carbon (1 g/L) for a reaction time of 80 min. Change in initial concentration of dye has led to variation in the retention capacity. The influence of salt such as, NaCl, Na_2SO_4 and $NaHCO_3$, at various concentrations have showed no significant effect on rate and capacity of adsorption. The experimental results indicated that temperature affect rate and retention capacity. Adsorption isotherms have been correctly represented by Langmuir and Freundlich. The kinetics of adsorption was found to obey to the Lagergrein model, demonstrating that there is a mass transfer at the interface liquid/solid which is however slow since the apparent rate constant was equal about to 40 min^{-1}.

Key Words: Decolouration, Congo red, Activated carbon, Dyes, Aqueous medium, Salts.

INTRODUCTION

The release of coloured wastewaters in receiving natural waters is a crucial problem since it conducts to a severe threat to aquatic and human life[1,2]. Therefore it is important to remove colour before their discharge in environment. To reach this objective different chemical and physical treatments have been utilized[3-10]. Among these techniques, the elimination by

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activated carbon can be considered as the most used one since this adsorbent presents a high retention capacity due to its structure (surface and microporous structure)[11-14]. However, it should be mentioned that some of these techniques cannot be efficient, particularly in the case of pollutant having no affinity towards the support (adsorbent or exchanger).

The aim of this work was to study the adsorption of Congo red on activated carbon. Capacity of retention will be determined and will allow us to estimate the degree of affinity of this dye towards active carbon. The influences of initial concentrations of the substrate, temperature and salts have been investigated in order to see the impact on the capacity and rate of adsorption. Kinetic models like those of Langmuir and Freundlich will be studied in order to obtain, mainly, the maximal capacity *via* the adsorption isotherm experiments whereas that of Lagergrein will permit to estimate the degree of this mass transfer process *via* its rate constant at the interface solid/liquid.

EXPERIMENTAL

Material and compounds: Activated carbon was ground to powder prior to use. The resulting material, analyzed by granulometry technique, has a particle size ranging from 0.08 to 0.1 mm and a surface area around 700-1500 m^2/g. All Congo red solutions were prepared by dilution with distilled water from a stock solution of known concentration of this dye. All reagents used in this work were analytical grade purity.

Kinetic experiments: Experiments were conducted in batch technique using dye solutions at different concentrations. Thus, 100 mL of samples were put in contact with the adsorbent (0.1 g/100 mL), at constant temperature through circulating thermostated water at 20 ± 2ºC and stirred at 300 rpm. Solutions were filtered through a 0.22 µm membrane filter prior to any spectrophotometer measurement.

Analysis procedure: The UV-Vis absorption spectra was recorded on double beam spectrophotometer "Unicam Helios α". Kinetics studies and adsorption isotherm, were monitored by measuring the absorption of all residuals concentrations.

Isotherm adsorption: Experiments were carried out by *via* same experimental procedure outlined above. 100 mL of the dye at various concentrations were put in contact with activated carbon (0.1 g/100 mL) during a time corresponding to saturation or equilibrium state (*i.e.* contacting time) at constant temperature and a permanent stirring. After that, all solutions were filtered and then analyzed by spectrophotometer at the appropriate wavelength (498 nm).

RESULTS AND DISCUSSION

Structure and UV-Vis spectrum of Congo red: The absorption spectrum of the Congo red (5×10^{-5} M and pH = 6.55) in aqueous medium, exhibits three bands where the most intense is located at 498 nm (ε = 21200 L mol^{-1} cm^{-1}). It should be mentioned the pH affects the UV-visible spectrum mainly in acidic medium (pH = 2.5) where one observes a shift of the most intense band to higher wavelength: 565 nm (ε = 10400 L mol^{-1} cm^{-1}) (Fig. 2).

By some other means, this change of colour (the compound becoming blue violet in acidic medium) could indicate the formation of protonated species thanks to the basic groups NH_2, according the following equation:

$$R\cdots NH_2 \rightleftharpoons R—NH_3^+$$

Thus, because of these variations of absorbance with pH, all experiments have been carried out at the pH 6.55 of the dye, since we noticed no change in its spectrum and therefore in its structure.

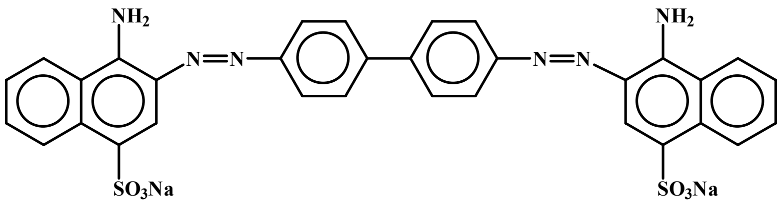


Fig. 1. Structure of the Congo red

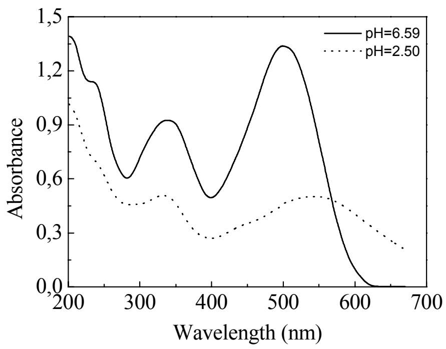


Fig. 2. Structure and UV-Vis spectrum of Congo red in at pH = 6.55 and acidic medium (pH = 2.5)

Contacting time (T): The determination of this parameter has consisted by putting in contact 50 ppm of dye with activated carbon (1 g/L) according the experimental procedure outlined above. It has been observed that equilibrium state has been reached around 80 min with a maximum adsorption capacity of 40 mg/g of the solid support (Fig. 3). This value has been derived by means of the following equation:

$$Q = \frac{C_o - C_t}{m}.V$$

where, Q: Quantity of dye adsorbed at instant time per mass of support (mg/g), Co: Initial concentration of dye (ppm), Ct: Concentration of dye at instant time (ppm), m: Mass of solid support (g), V: Volume of the sample (L).

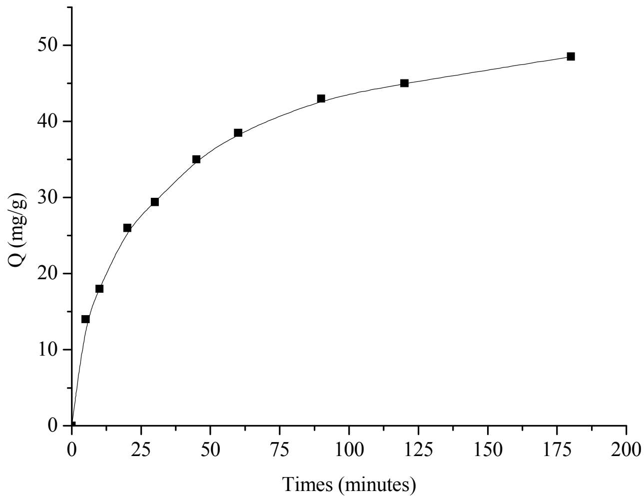


Fig. 3. Kinetic adsorption of Congo red on active carbon: $[CR]_o$ = 50 mg/L; r = 1 g/L; t = 20 ± 2ºC; pH = 6.55 and 0.08 ≤ d < 0.1 mm

However this time could be taken as an equilibrium state since the retention capacity increased only by about 4 mg/g, which is an insignificant amount for an extended time of 3 h. One can deduce that Congo red has not a good affinity toward activated carbon.

By looking at the retention curve, one can observe two steps. The first one corresponding to a very short time (10 min) showing a good elimination of present substrate with respect to the solid support and the second corresponding to a long time, is indicating a slow elimination of the dye and the equilibrium state. On the basis of these results, one can confirm that Congo red has a relative weak affinity toward activated carbon. This important result will allow setting up the adsorption isotherm; r: being the concentration of the adsorbent and d: the diameter of adsorbent particles of activated carbon. The obtained results indicate a moderate affinity of this dye for activated carbon.

Influence of initial concentration on retention capacity: Fig. 4 showed that retention capacity increased as the initial concentration increased in present experimental conditions. This might be credited to the important available sites of the solid support which are still available for adsorption. It is noticed that rate of retention has been very fast at the beginning during the first 10 min and became sluggish after this time. This fact could be attributed to a difficult diffusion of the molecules of the substrate into the solid support. The contacting time has been around 80 min except for the weakest concentration Therefore the contacting time might decrease as the concentration of the dye decreases. These kind of results have been found with methylene blue[15].

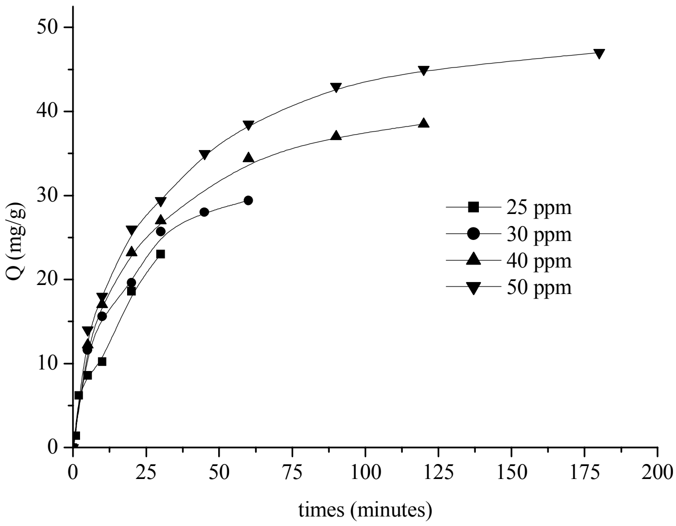


Fig. 4. Kinetic adsorption of Congo red on active carbon at various concentration of the dye: r = 1 g/L; t = 20 ± 2ºC; pH = 6.55 and $0.08 \leq d < 0.1$ mm

Influence of temperature on retention capacity: Fig. 5 represents the influence of the temperature in the process of the dye adsorption. The obtained results proved that this parameter can affect positively this process since we observed an important improvement of the capacity and rate of retention as the temperature augmented. This feature could be due to the high contribution of thermique energy allowing surpassing all repulsive forces which are located at the interface solid/liquid but to a certain limit where we noticed a decrease of this contribution. This means that retention could be endothermic ($\Delta H > 0$) thus leading to a chemisorption. Same behaviour of this parameter has been reported in the literature[16].

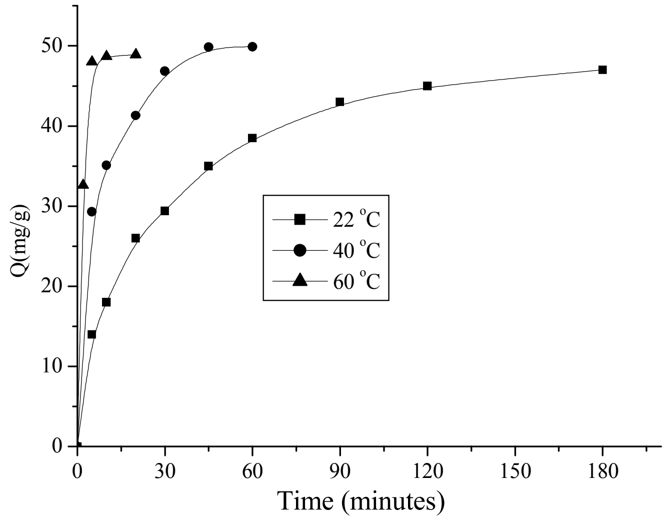


Fig. 5. Influence of temperature on retention process of Congo red on activated carbon r = 1 g/L; t = 20 ± 2ºC; pH = 6.55 and 0.08 ≤ d < 0.1 mm

Influence of salts on retention capacity: It is known that natural and polluted water contain inorganic ions at variable concentrations. Thus it is necessary to study their impact on rate and capacity of adsorption. For this reason experiments have been conducted in presence of salts such as NaCl, Na_2SO_4 and $NaHCO_3$.

However prior to this study experiences have been carried out in absence of activated carbon for mixture constituted for example by NaCl (10^{-1} M) and Congo red (50 ppm) in order to reveal if any reaction could occur between these two components. Thus one might allow situating the proper efficiency of the activated carbon in the retention process of this dye.

The results represented in Fig. 6 showed a decrease by 20 % of the absorption, mainly, in the principal band located at 498 nm indicating thus, an interaction between both compounds. Similar behaviour has been observed for the two others salts. Same results have been obtained with methylene blue[15].

Thus experiments conducted in presence of these salts for various concentrations (10^{-1} M) showed on the whole a negligible effect on rate and capacity of adsorption mainly at 10^{-2} M and 10^{-3} M signifying therefore, that no competition can occur for sites between molecules of dye and salts. Moreover, for these latter, ionic charge (Na_2SO_4) did not affect the retention capacity (Fig. 7).

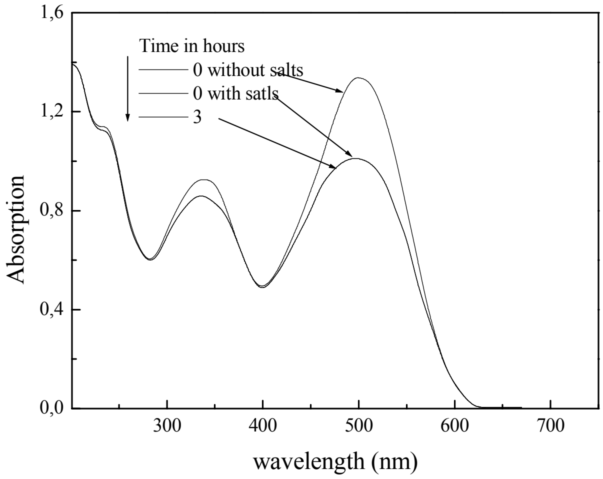
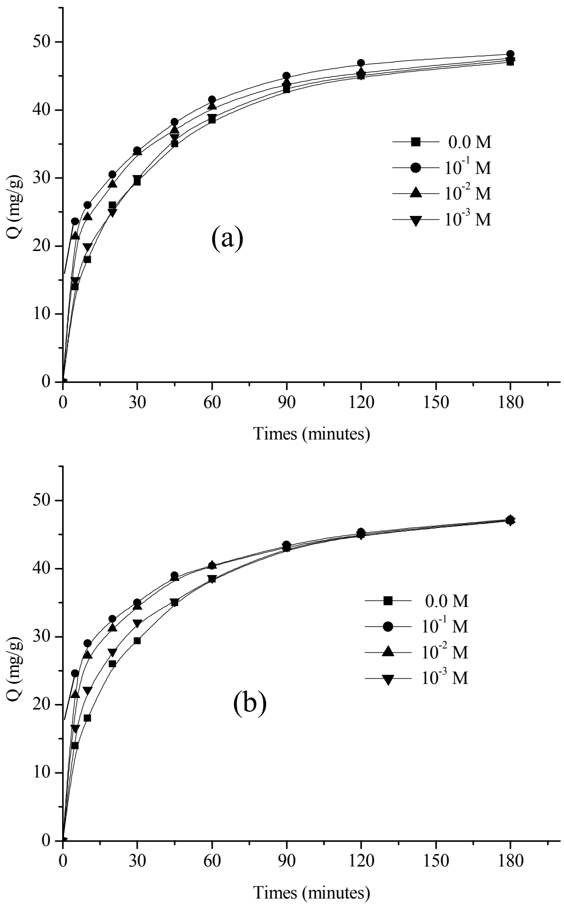


Fig. 6. Thermal Evolution of the mixture NaCl (10^{-1} M) + RC (50 ppm) *vs.* of time.



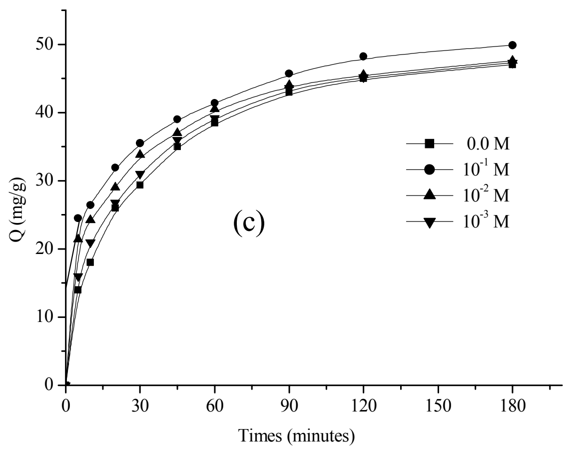


Fig. 7. Influence of salts on adsorption of Congo red on activated carbon (a) NaCl, (b) Na_2SO_4 and (c) $NaHCO_3$. Conditions r = 1 g/l; T = 20 ± 2ºC; pH = 6.55 $[CR]_o$ = 50 mg/L and 0.08 ≤ d < 0.1 mm

Adsorption isotherm: The adsorption isotherms play an important role in the determination of the maximal capacity and rate of retention at a given equilibrium state and also in the identification of the type of adsorption which has to take place. Further, they are based on the contacting time. The resulting isotherm found experimentally, is on one part an L-shape according to the classification of Giles *et al.*[17] indicating a moderate competition between the solvent and the solute and on the other part a monolayer type of adsorption (Fig. 8).

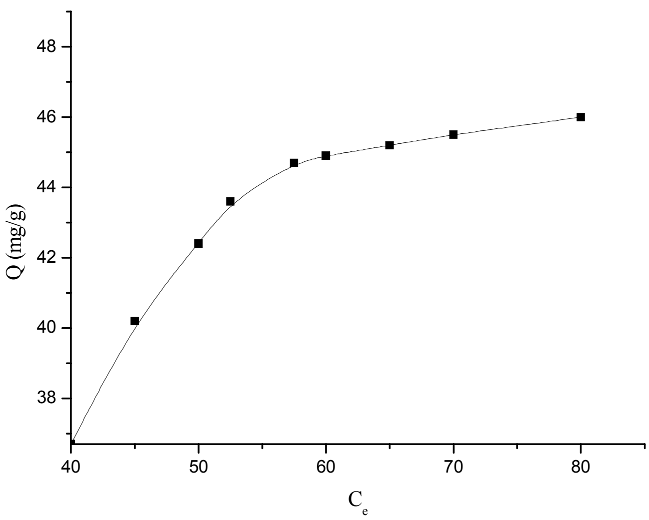


Fig. 8. Adsorption isotherm of Congo red at 20 ± 2ºC

The two most current kinetic models which describe the process of adsorption were those of Langmuir (represented by the following equation: $Q_e = \frac{abC_e}{1+C_e}$ with its linearized form which is, $\frac{1}{Q_e} = \frac{1}{a} + \frac{1}{abC_e}$) and Freundlich (represented by the following equation: $Q = K_F C_e^{1/n}$ with its linearized form which is, $\log Q_e = \log K_F + 1/n \log C_e$). The results in presented Fig. 9 proved that retention of Congo red onto activated carbon is well represented by the two linearized forms of both models. All kinetics constants are reported in Table-1.

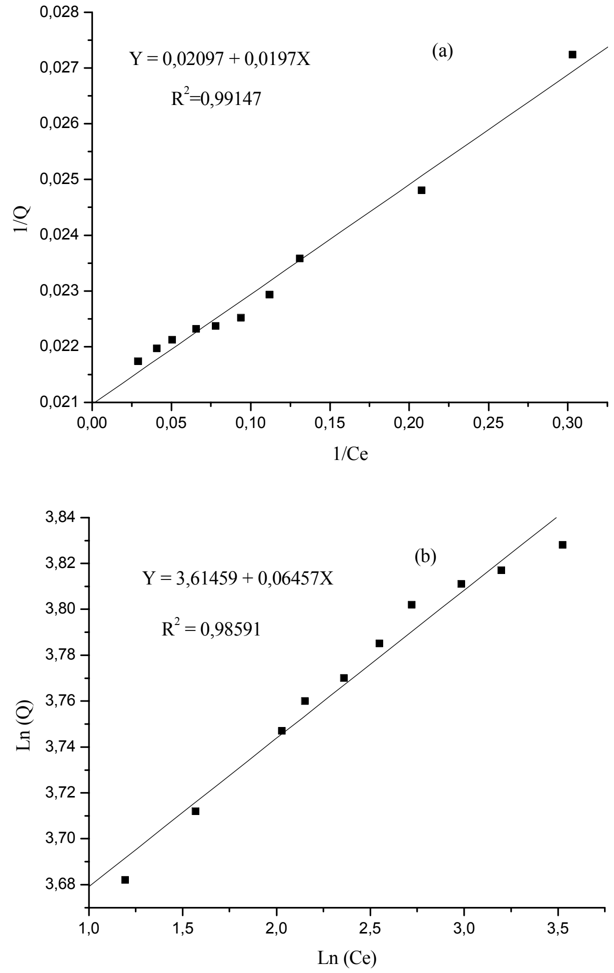


Fig. 9. Linear representation of the adsorption isotherm using: (a) the model of Langmuir ($1/Q_e$ *vs.* $1/C_e$) and (b) the model of Freundlich ($\ln Q_e$ *vs.* $\ln C_e$). $t = 20 \pm 2$ºC, pH = 6.55 and $0.08 \leq d < 0.1$ mm

TABLE-1
VALUES OF THE ADSORPTION PARAMETERS a, b, n and K_F OF CONGO RED ON ACTIVATED CARBON

Models	a (mg/g)	b (L/mg)	K_F (mg/g)	R
Langmuir $Q_e = \frac{abC_e}{1+C_e}$; $\frac{1}{Q_e} = \frac{1}{a} + \frac{1}{abC_e}$	40.1	4.31	–	0.9914
Freundlich $Q = K_F.C_e^{1/n}$; $\log Q_e = \log K_F + 1/n \log C_e$	–	–	23.4	0.9859

R: correlation coefficient; n = 8.60: heterogeneous coefficient, a = 1st constant of Langmuir, b = 2nd constant of Langmuir K_F = Adsorption constant of Freundlich.

Kinetics of adsorption: The study of the kinetic adsorption of Congo red on activated carbon is linked to its mass transfer at the liquid/solid interface, a region characterized by all resistances to this transfer. This feature could be attributed to a film established near the sites of the solid support surface. In general, the kinetic law used to describe this process was that of Lagergrein :

$$\frac{dQ}{dt} = k_{ad}(Q_e - Q_t)$$

where, k_{ad}: Kinetic constant of mass transfer; Q_e: Quantity of dye adsorbed at equilibrium; Q_t: Quantity of dye adsorbed at time t.

The integration of the above equation led to the following relation:

$$\ln(Q_e - Q_t) = -k_{ad}t + \ln(Q_e)$$

According to our experimental results, it appears that mass transfer from the liquid phase to the solid phase is described by the first-order kinetic law with respect to the various initial concentrations of the dye (Fig. 10).

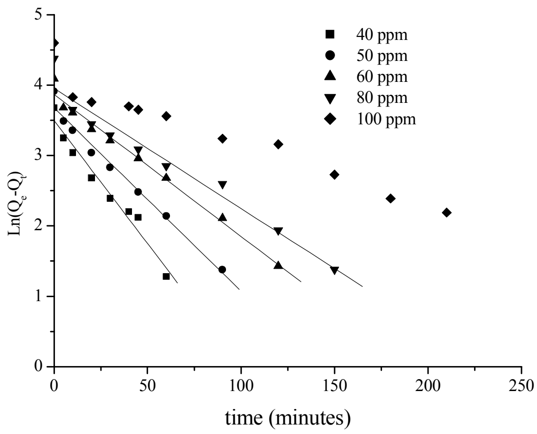


Fig. 10. Kinetics of Congo red adsorption on activated carbon $NaHCO_3$ Conditions r = 1 g/L; T = 20 ± 2ºC; pH = 6.55; $[CR]_o$ = 50 mg/L and $0.08 \leq d < 0.1$ mm

The kinetic constant k_{ad} has not varied markedly with the phenol concentrations taken in the following range: 40-80 ppm.The average value k_{ad} has been equal to 0.0247 min^{-1}. All results are reported in Table-2. By taking into account the constant time T defined by $1/k_{ad}$ in this case[18], it is concluded that the mass transfer at the interface has been slow since this constant time T has been of 40-50 min. This could confirm too, that Congo red, has a low affinity toward activated carbon, compared to methylene blue[15].

TABLE-2
VALUES OF KINETICS CONSTANTS OF ADSORPTION (k_{ad})
OF CONGO RED ON ACTIVATED CARBON

Dye Concentration (ppm)	k_{ad} (min^{-1})
40	0.034, R* = 0.98339
50	0.026, R* = 0.99112
60	0.021, R* = 0.99316
80	0.018, R* = 0.97687

R* = correlation factor.

Conclusion

Congo red an anionic dye of direct class has been retained on activated carbon throughout experiments conducted in batch methods and with a moderate affinity toward this support. It has been observed that the adsorption of the substrate became more and more difficult as its concentration increased. One noticed also that the presented of salts did not affect seriously capacity and rate of adsorption, meaning therefore no competition between substrates and ions for sites of the support. By contrast, the temperature has affected both parameters and showing that this adsorption could be a chemisorption. On the other part, kinetic studies have revealed that the two used models those of Langmuir and Freundlich have represented well the process of retention. Further, the experimental results have also showed a satisfactory linearity for the kinetic model of Lagergrein which describes the process of mass transfer of the dye at the liquid/solid interface. Moreover, this way of decontamination is not sufficient, because it is a pollution transfer of one phase to another. Therefore, to finish complete destruction of the pollutant, one needs additional cost effective treatment, like burning or landfilling.

REFERENCES

1. T. Sauer, Gesconato Neto G. Jose H.J., Moreira R.F P.M., *J. Photochem. Photobiol. A*, **149**, 147 (2002).
2. N. Daneshwar, D. Salari and A.R. Khataee, *J. Photochem. Photobiol. A*, **157**, 111 (2003).
3. F. Perineau, J. Molinier and A. Gazet, *Water Res.*, **17**, 559 (1983).
4. Y. Yang, C. Ladisch and M.R. Ladisch, *Enzym. Microb. Tech.*, **10**, 632 (1988).
5. Z. Linsheng and B. Dobias, *Water Treatment*, **7**, 221 (1992).
6. W.G. Kuo, *Water Res.*, **26**, 881 (1992).
7. J.T. Sapadaro, I. Lorn and V. Renganathan, *Environ. Sci. Tech.*, **28**, 1389 (1994).
8. J.C. Milano, P. Loste-Berdot and J.L. Vernet, *Environ. Tech.*, **16**, 329 (1994).
9. S. Al-Quaradawi and R.S. Salman, *J. Photochem. Photobiol. A*, **148**, 161 (2002).
10. C.G. Da Silva and J.L. Faria, *J. Photochem. Photobiol. A*, **157**, 133 (2003).
11. G. McKay and B.A.A. Al-Duri, *Colourage*, **35**, 24 (1988).
12. V. Specchia, B. Ruggeri and A. Gianetto, *Chem. Engg. Comm.*, **68**, 99 (1988).
13. V.V. Sethuraman and B.C. Raymahashay, *Environ. Sci. Tech.*, **9**, 1139 (1975).
14. G. McKay and M.C. Otterburn, *Water, Air Soil Pollut.*, **24**, 307 (1985).
15. O. Baghriche, K. Djebbar, T. Sehili, D.A. Rouag and A. Bouchoul, *Asian J. Chem.*, **18**, 2136 (2006).
16. K. Bellir, M. Bencheikh-Lehocine, A.-H. Meniai and N. Gherbi, *Desalination*, **185**, 111 (2005).
17. C.H. Gilles, M. McEvant, S.W. Nakhawas and D.J. Smith, *J. Chem. Soc.*, 3973 (1960).
18. S. Bekkouche, M. Bouhelassa, N.H. Salah and F.Z. Meghelaoui, *Desalination*, **166**, 355 (2004).

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