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Studies on Sorption of Congo Red from Aqueous Solution onto Soil

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ABSTRACT: The aim of this study was to investigate the Congo red sorption on soil from the region of Iasi (NE of Romania). The effects of contact time, temperature, sorbent dose and initial dye concentration on soil sorption were investigated. The results show that the amount adsorbed of Congo red on soil increase with increasing dye concentration, temperature and contact time. The experimental data were analyzed using the pseudo-first order Lagergren model, the pseudo-second order model and intraparticle diffusion model. Experimental results show that the dye sorption process follows the pseudo-second-order kinetic model. Intraparticle diffusion studies indicated that the adsorption mechanism was not exclusively controlled by the diffusion step. The equilibrium sorption data were interpreted using Langmuir, Freundlich and Tempkin models and the results were best described by Freundlich isotherm. It was indicative of the heterogeneity of the sorption sites on the soil particle. Thermodynamic analysis of the Congo red sorption on studied soil indicates that the system is spontaneous and exothermic in nature.

Key words: Congo red, Sorption, Kinetic models, Langmuir, Freundlich and Tempkin isotherms, Sorption thermodynamic

INTRODUCTION

Widespread contamination of soil and groundwater by synthetic organic chemicals (e.g. pesticides, dyes etc.) has been recognized as an issue of growing importance in recent years (Shahidi Bonjar, 2007; Onwurah *et al.,* 2007; Akoto *et al.,* 2008). Dyes are extensively used in many industries such as textile, food, leather, rubber, plastic, tannery, paints, cosmetic, paper and dye manufacturing etc. At present, more than 10 000 of different types of commercial dyes and pigments are available on the market (Tan *et al.,* 2007), and more than 700 000 tons per year are produced world wide (Kannan and Meenakshisundaran, 2002). Two percent of produced dyes are discharged from textile industry directly in environment, especially in aqueous effluents. Wong et al. (2008) estimate that 10-20% of dyes used are lost in effluents during application and manufacture, of which about 50 percent may reach the environment even after treatment.

These compounds can generate serious problems to the environment, not only by aesthetically displeasing, but they also contribute to high organic loading and ecotoxicity of water bodies. Presence of very small concentrations of dyes in water (less than 1 ppm for some dyes) are highly visible and undesirable because these compounds are persistent in natural environments (Zille, 2005) and can absorb and reflect sunlight, retard photosynthetic activity and inhibit the growth of biota (Vimonses *et al.,* 2009). Some of them can sometimes form toxic, carcinogenic or mutagenic compounds under the action of anaerobic reductive bacteria (Pinheiro *et al.,* 2004).

The most challenging are anionic dyes because they are bright colored, water soluble reactive and show acidic properties. Congo red is an example of anionic diazo dyes discharged in wastewater from textiles, printing and dying, paper and plastic industries (Purkait *et al.,* 2007). Also, Congo red is used for microscopic preparations, in biochemistry and histology (Vijayakumar *et al.,* 2009). The treatment of contaminated Congo red in wastewater is not easy, since the dye is generally present in sodium salt form giving it very good water solubility. Also, the high stability of its structure makes it difficult to biodegrade and

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photo degrades (Vimonses *et al.,* 2009). Due to its properties and because it has a very complex and stabile structure, Congo red can persist in environment (Gharbani *et al.,* 2008).

There are many studies concerning sorption of Congo red on various sorbents such as: rice husk (Han *et al.,* 2008), kaolin (Vimonses *et al.,* 2009), activated carbon (Kannan and Meenakshisundaram, 2002), seed coat (Oladoja and Akinlabi, 2009), mycelial biomass (Binupriya *et al.,* 2008), biogas waste slurry (Namasivayam and Yamuna, 2007), waste red mud (Namasivayam and Arasi, 1997), perlite (Vijayakumar *et al.,* 2009). On the other hand, many studies were performed using soils as sorbent for heavy metals sorption (Bradl, 2004; Covelo *et al.,* 2007; Anagu *et al.,* 2009; Yong *et al*., 2007), some with dyes sorption onto soils (Mon *et al.,* 2006; Miyamoto and Tram, 1979), but only a few deal with Congo red sorption on soil (Krishnasamy *et al.,* 2002; Vimonses *et al.,* 2009).

The aim of this study was to investigate the sorption of Congo red from aqueous solution onto soil in batch system, in order to quantify the quantities that could be sorbed in soil in different experimental conditions. This information is useful for analyzing the bioavailability in soil as well as to establish the best way to remediate soils contaminated with Congo red.

MATERIALS & METHODS

The soil samples were collected from the region of Iasi (Romania) from the depth 0-25 cm. The soils were classified as cambic chernozem upon Romanian System of Soil Taxonomy (SRTS-2003). The collected soil was silty clay loam with a composition of 32 % clay, 62 % silt, 6 % sand and a content of organic matter of 3.37%.

Soil samples were dried in an oven at 105°C for a period of 3 hours. After drying, the soil was milled for 30 minute at 800 rpm in order to obtain a ≤ 0.02 mm size fraction. The soil pH natural value was 7.11, determined by a potentiometric method (soil: bidistilled water, 1/5 w/v; size fraction < 0.01 mm; contact time – 30 minutes), using a multimeter Cornning Pinnacle Model 555. The redox potential was determined by direct method with a pair of platinum-calomel electrodes. Physical and chemical characteristics of soil are presented in Table 1.

Table 1. Physical and chemical characteristics of soil

Physical property	**Value**
Deep (cm)	0 - 25
pH (in water)	7.11
Particle size (mesh)	200
E_h(mV)	535.21
CTSC	25.63
Chemical compound	Percentage by weight (%)
SiO_2	59.67
Al_2O_3	20.63
Fe_2O_3	1.17
TiO_2	0.1
Na_2O	2.25
K_2O	3.41
MgO	1.13
CaO	4.84
P_2O_5	0.19
SO_3	0.21
CO_2	2.94
Cd^x	0.06
Cr^{x*}	6.44
Pb^x	10.59
As^x	0.83
Zn^x	57.55
Cu^x	20.15
Mn^x	72.03

E_h – redox potential (mV).
CTSC – total cation exchange capacity (milligram equivalents/100 g soil)
* Total concentration.
^{x} The values measured as µg /g.

Congo red was supplied by Sigma Aldrich and used as a model reactive dye in the present work (C.I. = 22120; molecular formula $C_{32}H_{22}N_6Na_2O_6S_2$ and molecular weight of 696.66 g/mol, without further purification). The chemical structure of the dye molecule is shown in Fig. 1. Congo red (CR) or 1-naphthalenesulfonic acid, 3,32-(4,42-biphenylenebis (azo)) bis (4-amino-) disodium salt is a benzidine-based anionic diazo dye prepared by coupling tetrazotised benzidine with two molecules of napthionic acid (Purkait *et al.,* 2007; Vimonses *et al.,* 2009). Congo red has two sulphonate groups, which have negative charges in aqueous solution (Binupriya *et al.,* 2007).

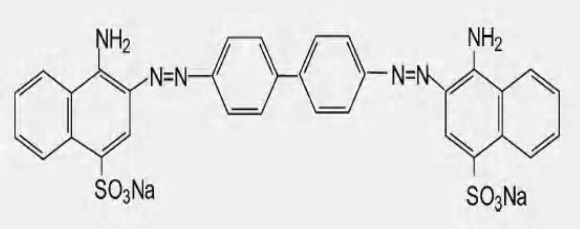

Fig. 1. The molecular structure of the Congo Red

The sorption experiments were carried out in batch mode. A stock solution of Congo red (1000 mg/L) was prepared by dissolving 1g of the dye in distilled water. The experimental dye solutions with different concentration were obtained by diluting the stock solution. For the kinetic study, 20 mg/L, 50mg/L and 100 mg/L dye solutions and natural pH of solution, were stirred together with 2.5 g of soil at 30 °C for predetermined intervals of time. Equilibrium studies involved fifty milliliters of Congo red solution with known initial concentration, ranging from 20 to 400 mg L^{-1} added to an accurately weighted mass of soil (2.5 g) in conical flasks and agitated in a thermostatic shaker (IKA KS 4000 IC Control, Germany) at 150 rpm and 30°C. The experiments were carried out for 24 hours to ensure that equilibrium was obtained. At the end of the sorption period, the dye solution was separated from the adsorbent by centrifugation at 6000 g for 20 minutes (Hettich EBA 20 Centrifuge, Germany). The supernatant was filtered through 0.45 µm filter (OlimPeak) and the dye concentration in the filtrate was determined by measuring absorbance at 497.5 nm (maximum absorbance) using a UV-VIS spectrophotometer (CamSpec M501, UK). The sorption studies were carried out at different temperature for determining the influence of temperature on process and to evaluate de thermodynamic parameters.

The amount of dye adsorbed on soil (*q* in mg/g) and efficiency of dye removed (*P*) were calculated using the relationships (1, 2):

$$P\% = \frac{(C_i - C_e)}{C_i} x100 \qquad (1)$$

$$q = \frac{(C_i - C_e)V}{m} \qquad (2)$$

RESULTS & DISCUSSION

The effect of contact time and initial dye concentration on the sorption process was studied for three different concentrations of dye in solution: 20 mg/L, 50 mg/L, 100 mg/L. The results obtained at 30^0 C and natural pH of solution is presented in Fig. 2. The amount of dye sorbed per unit of mass of soil (mg/g) enhances with contact time increasing and reached the equilibrium after 40 minutes. Very rapid sorption process was observed during the first two minutes, when the removal efficiency was about 63% (for 100 mg/L initial dye concentration in solution), and after ten minutes, a removal efficiency of about 91% was determined. Also, a rapid rate of sorption of Congo red on soil was reported by Krishnasamy et al. (2002).

The sorption capacity at equilibrium (q_e) increased from 0.92 mg/g to 2.23 mg /g with the increase of dye concentration from 20 to 100 mg/L. In addition, the percent of dye removal at equilibrium decreased when the dye concentration increased from 20 to 100 mg/L, probably as a result of the effect of increasing competition for active sites. It is evident that for lower initial concentration of dye the adsorption process is very fast, while for higher concentrations the available adsorption sites become fewer. Comparable results were obtained for sorption of Congo red on soil (Krishnasamy *et al.,* 2002), fly ash (Acemioglu, 2004), anilinepropylsilica xerogel (Pavan *et al.,* 2008) or on perlite (Vijayakumar *et al.,* 2009). Similar results were also reported by Tan *et al.,* (2007) for the classical sorption on activated carbon of methylene blue. Therefore, it is demonstrated that the sorption efficiency on soil of the dye depends on its concentration of the dye in solution and the contact time. The removal curves are distinct, smooth and continuous indicating monolayer coverage of soil surface by dye (Namasivayam and Arasi, 1997).

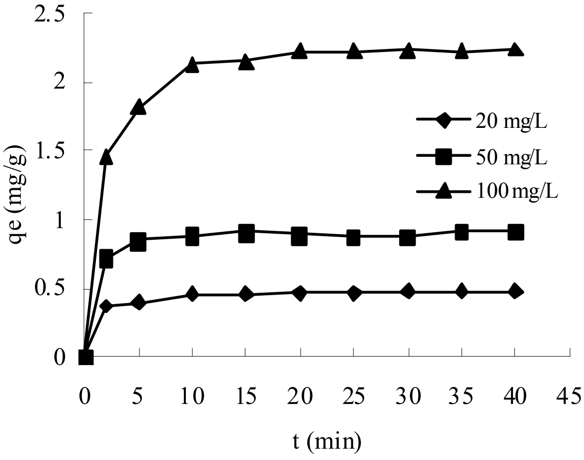

Fig. 2. Effect of contact time and initial Congo red concentration on sorption of dye onto soil (sorbent dose 2.5g/50mL; initial dye concentration in solution: 20mg/L; 50mg/L; 100 mg/L; temperature 30°C)

The effect of sorbent dose on sorption process was studied by varying the sorbent dose from 0.1 to 10 g at a constant dye concentration (50 mg/L), temperature (30^0C) and constant pH=6.8-6.9. The results are presented in Fig. 3. The percent of dye removal increased with the sorbent dosage and this effect can be explained though an increase in sorption surface area of micro pores and the availability of sorption sites (Vimonses *et al.,* 2009). The increase of soil concentration caused a decline in the amount of Congo red sorbed at the equilibrium. The highest dye removal capacity was attained at 2.5 g, when 94 % of dye was sorbed on soil. The further increase of the sorbent dose did not make any important change concerning the sorption capacity. In this way, for all experiments 2.5 g adsorbent dose at 50 mL dye solution was found suitable.

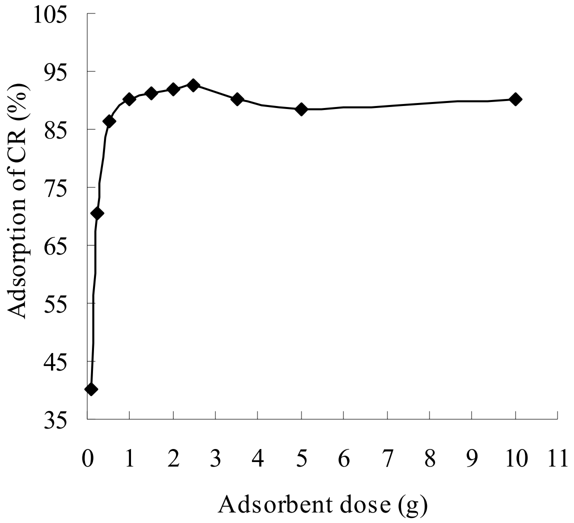

Fig. 3. Effect of adsorbent dosage on Congo red sorption on soil (adsorbent dose range 0.1-10 g/50mL; dye concentration 50mg/L; temperature 30°C).

The effect of temperature on sorption capacity of soil was investigated at 30, 40, and 50^0 C, and the results are shown in Fig. 4. It can be observed that the amount of Congo red sorbed by soil rises with an increase of temperature from 30^0 C to 50^0 C. The amount of dye sorbed per unit of sorbent increases from 0.90 mg/g to 0.94 mg/g, indicating that the temperature raising facilitate very slow increase of soil sorption capacity. Probably, higher temperature has as effect a good mobility of dye molecules, which interact more effectively with adsorbent (Vijayakumar *et al.,* 2009). Increasing the temperature may produce a swelling effect of sorbent, and the large dye molecules further penetrate into pores. In addition, the sorption capacity should largely depend on the chemical interaction between the functional groups on the sorbent surface and the sorbate, and should increase as the temperature rises. This can be explained by an increase in the diffusion rate of the sorbate into the pores (Annadurai *et al.,* 2008).

Similar results were reported on sorption studies of Congo red on activated carbon prepared from coir pith (Namasivayam and Kavitha, 2002), on calcium-rich fly ash (Acemioðlu *et al.,* 2004), on perlite (Vijayakumar *et al.,* 2009), on organo-attapulgite (Chen and Zhao, 2009).

Sorption isotherms are very important because indicates how molecules of sorbate interact with sorbent surface. The sorption process is usually described by the Langmuir and the Freundlich isotherms. The Langmuir equation assumes that there is no interaction between the sorbate molecules and that the sorption is localized in a monolayer (Wong *et al.,* 2008). It is then assumed that once a dye molecule occupies a site, no further sorption can take place at that site. The linear form of Langmuir equation is expressed by Eq. (3):

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \qquad (3)$$

where C_e is the equilibrium concentration of dye solution (mg /L), q_e is the amount of dye sorbed per unit mass of sorbent (mg/g), Q_0 is the monolayer sorption capacity of the sorbent (mg/g), and b represents the Langmuir sorption constants (L/mg) and are related to the maxim monolayer sorption capacity and energy of sorption (Gupta *et al.,* 2007). The Langmuir constants can be determined from the linear plot of C_e/q_e versus C_e. The Langmuir isotherm for Congo red sorption on soil is presented in Fig. 5. Values of the Q_0 and b were calculated from the slope and the intercept of the linear plots and are presented in Table 2.The essential characteristics of the Langmuir isotherm can be expressed by a dimensionless constant - separation factor R_L. The separation factor or equilibrium parameter R_L is described by Equation (4) (Namasivayam and Kavitha, 2002; Bulut *et al.,* 2008; Vimonses *et al.,* 2009):

$$R_L = \frac{1}{1 + bC_0} \qquad (4)$$

where b is the Langmuir constant and C_0 is the initial dye concentration (mg/L). The value parameter indicates the shape of the isotherm and the nature of the adsorption process. If $R_L > 1$ the process is unfavorable, favorable ($0 < R_L < 1$), linear ($R_L = 1$) or irreversible ($R_L = 0$). The calculated R_L values at different initial Congo red concentrations are presented in Fig. 6. The R_L values were found to be between 0 and 1, indicating that adsorption of dye onto soil is favorable.

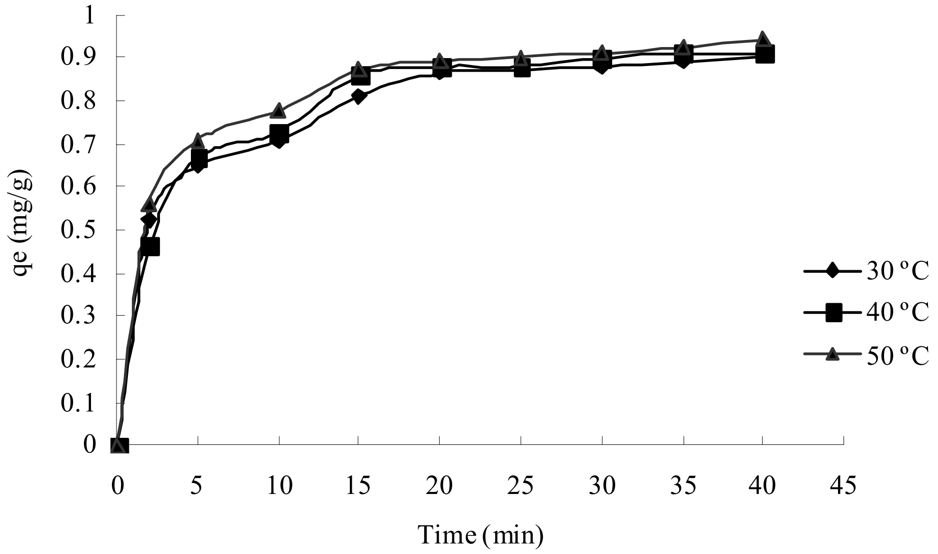

Fig.4. Effect of temperature on Congo red sorption on soil (initial dye concentration 50 mg/L; sorbent dose 2.5g/50mL; temperature 30-50^{0}C)

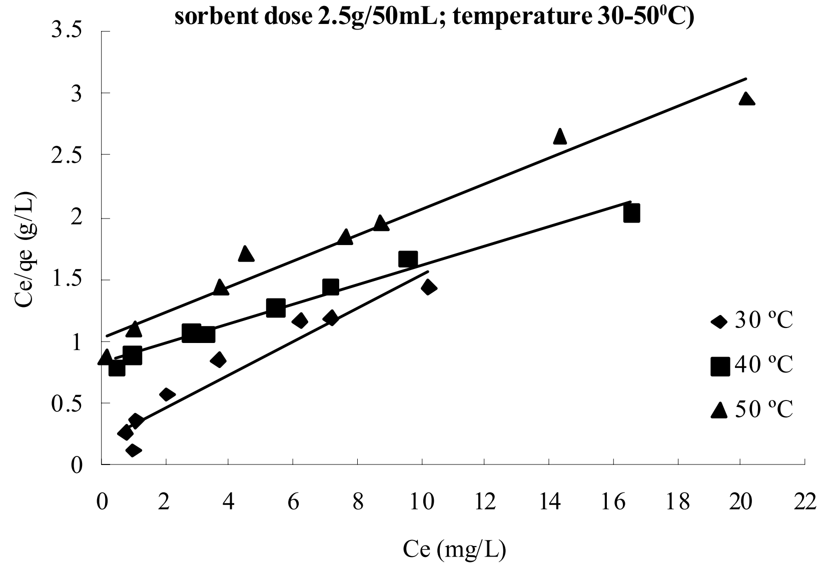

Fig. 5. Langmuir isotherms for the sorption of Congo red on soil

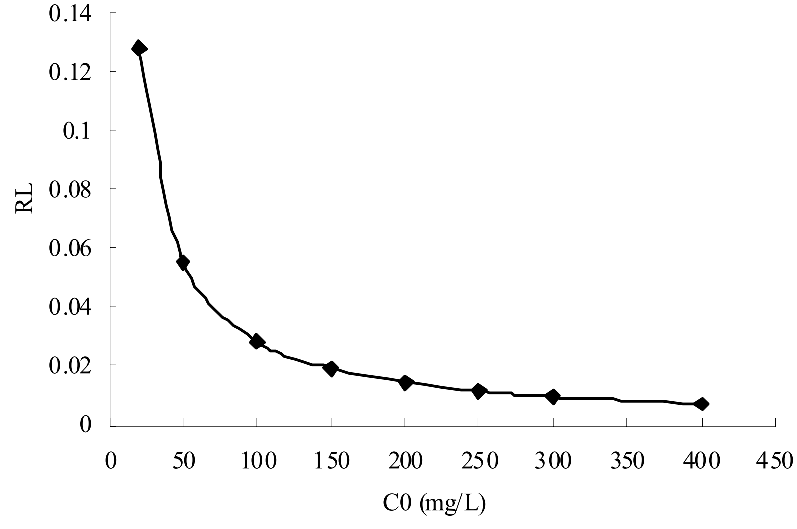

Fig. 6. Plot of separation factor R_L versus initial dye concentration C_0 for Congo red sorption onto soil (temperature 30^{0}C, adsorbent dose 2.5 g)

The Freundlich sorption model was also applied for the sorption of Congo red on soil. The empirical equation can be written as (Equation 5):

$$q_e = K_F C_e^{1/n} \qquad (5)$$

A linear form of the Freundlich expression can be obtained taking logarithms of Equation (5), resulting Equation (6):

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \qquad (6)$$

where q_e is the amount of dye adsorbed at equilibrium time (mg/g), C_e is the concentration of dye solution at adsorption equilibrium (mg/L). K_F (L/g) and n are the Freundlich adsorption isotherm constants witch indicate the capacity and intensity of the sorption process (Acemioglu, 2004) or surface heterogeneity (Gupta *et al.,* 2007). A plot of log q_e versus log C_e is given by Fig. 7, and the empirical constants K_F and n were determined from the intercept and slope of the linear regression.

The isotherm constants and correlation coefficients were calculated and listed in Table 2. The values of n ranging from 1 to 10 indicated a good adsorption process. For the adsorption of Congo red onto soil, the *n* values were above 1for all temperature studied, therefore the adsorption is favorable. The values of K_F and n determined from the model are increasing slightly with the increase of temperature (Han *et al.,* 2005).The Tempkin isotherm takes into accounts the effects of interaction of sorbate and sorbing species. The heat of sorption of all the molecules on the sorbent surface layer would decrease linearly with coverage due to sorbate–sorbate interactions. The Tempkin isotherm can be expressed in its linear form as Equation 7:

$$q_e = B\ lnA + B\ ln\ C_e \qquad (7)$$

The parameter B can be calculated using Equation (8):

$$B = \frac{RT}{b} \qquad (8)$$

where A (L/g) is the Tempkin isotherm constant, b (J/mol) is a constant related to the heat of sorption, R is the gas constant (8.314 J/mol) and T is the absolute temperature (K). A plot of q_e versus ln C_e enables the determination of isotherm constants A, B from the slope and intercept (Han *et al.,* 2005).The values of the Tempkin constants and correlation coefficients are presented in Table 2 and the plot of this isotherm is shown in Fig. 8. The correlation coefficient values showed a good agreement with the experimental data.

Table 2. Adsorption isotherms constants for the adsorption of Congo red on soil

Temperature (^{0}C)	**Langmuir isotherm**			**Freundlich isotherm**			**Tempkin isotherm**		
	Q_0 (mg/g)	**b (L/mg)**	**R_L^2**	**K_F (mg/g)**	**n**	**R_F^2**	**A**	**B**	**R_T^2**
30	8.6505	0.3404	0.9557	1.022	1.251	0.9759	0.096	3.140	0.9498
40	12.953	0.0918	0.9789	1.081	1.528	0.9883	0.732	1.937	0.9099
50	9.7181	0.0997	0.9820	1.133	1.669	0.9860	2.428	1.259	0.7805

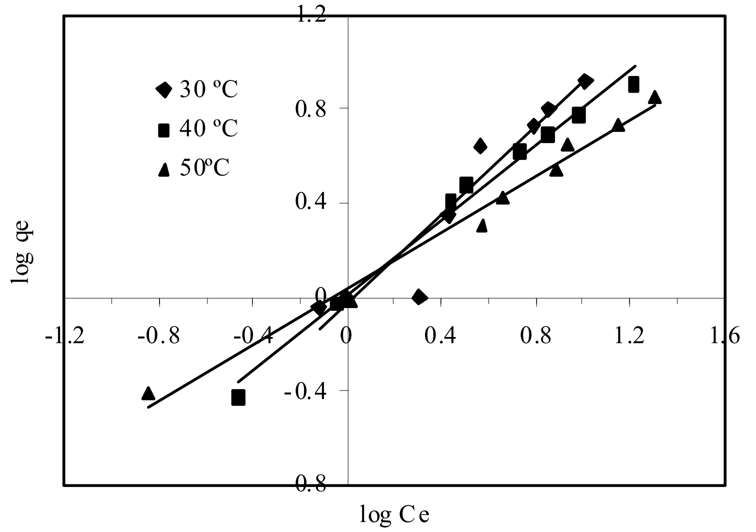

Fig. 7. Freundlich isotherms for the adsorption of Congo red onto soil at 30, 40 and 50^{0}C

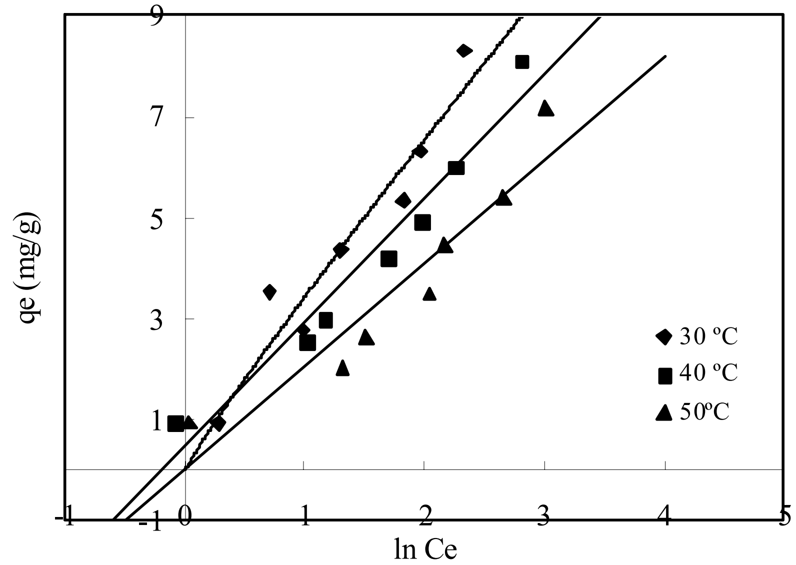

Fig. 8. Tempkin adsorption isotherm for Congo red onto soil at 30, 40 and 50 ^{0}C

By comparing the correlation coefficients R^2 calculated to Langmuir, Freundlich and Tempkin isotherms can be deduced that the experimental equilibrium sorption data are well described by the Freundlich model, when the correlation coefficients were 0.9759, 0.9883 and 0.9860 at 30, 40 and 50^{0}C, respectively. Also, the Langmuir isotherm fits the experimental data well. This result is in agreement with Qu et al. (2008), who reported a good correlation of Freundlich equation with experimental data obtained for the sorption Acid red 14 on soil.

The Freundlich isotherm assumes that there is a continuously varying energy of sorption as the most actively energetic sites are occupied first and the surface is continually occupied until the lowest energy sites are filled at the end of the process.

Sorption kinetics show large dependence on the physical and/or chemical characteristics of the sorbent material, and sorbate species which also influence the sorption mechanism. In order to examine the controlling mechanism of sorption processes such as mass transfer and chemical reaction, several models have been proposed: pseudo first-order kinetic, pseudo second-order and intraparticle diffusion kinetic (Ho and McKay, 1998). The pseudo-first-order kinetic model was suggested by Lagergren for the sorption of solid/liquid systems and its formula is given according to Equation (9):

$$log(q_e - q_t) = log\ q_e - \frac{k_1}{2.303}t \qquad (9)$$

where q_e and q_t (mg/g) are the amounts of Congo red sorbed at equilibrium and time t and k_1 (1/min) is the rate constant of the pseudo-first order adsorption. A plot of log (q_e-q_t) against t was made and values of k_1 and q_e were obtained from the slope and intercept, respectively. The plot of log (q_e-q_t) versus t gives a straight line for first order sorption kinetics and is presented in Fig. 9.

The pseudo-second-order equation proposed by Ho and Mackay (1999) is expressed in the following form (Equation 10):

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (10)$$

where k_2 (g/mg min) is the rate constant of pseudo-second order adsorption, q_e (mg/g) is the amount of dye adsorbed on soil at time t. *The pseudo second order rate constants can be de-termined by plotting t/q versus t, and* k_2 and q_e can be calculated from the slopes and intercepts. The constant k_2 can be used to calculate the initial sorption rate h using the equation (Maximova and Koumanova, 2007):

$$h = k_2 q_e^2 \qquad (11)$$

where k_2 is the rate constant of pseudo second order kinetics, q_e is the amount of dye adsorbed at equilibrium and at time t. The initial rate of sorption for 20, 50 and 100 mg/L are listed in Table 3. Comparing these kinetic parameters can be observed that the initial sorption rate is increasing with the increase of the initial dye concentration.

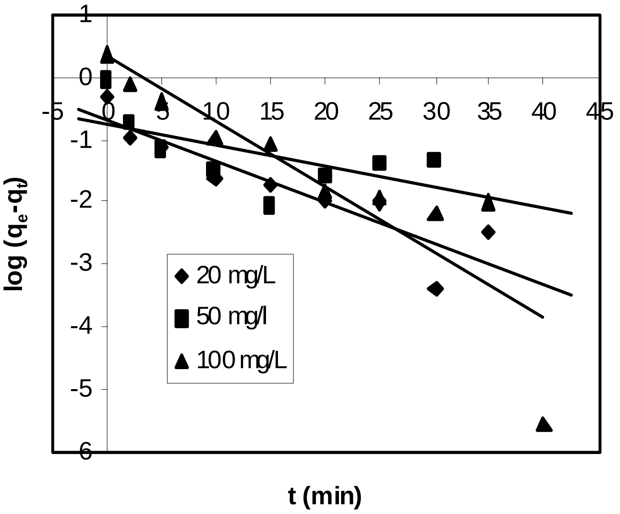

Fig. 9. The pseudo first order kinetic for adsorption of Congo red on soil (dye concentration 20, 50, 100mg/L; adsorbent dose 2.5g/50mL; temperature 30 ⁰C)

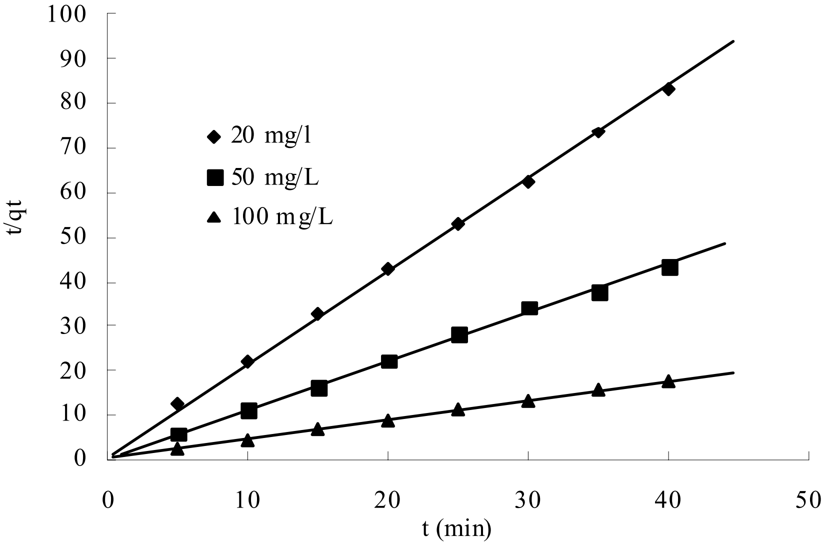

Fig. 10. The pseudo second-order kinetics for adsorption of Congo red on soil (dye concentration 20, 50, 100 mg/L; adsorbent dose 2.5g/50mL; temperature 30 ⁰C)

The plots of the linearized form of the pseudo-second-order kinetic model for the adsorption of Congo red on soil are shown in Fig.10.

The sorption rate constant k_1, k_2 and q_e with correlation coefficients for the pseudo-first-order and pseudo-second-order models are presented in Table 3. With increasing dye concentration from 20 to 100 mg / L at 30^0 C, the rate constant of pseudo-first-order, k_1, increases from 0.1484 to 0.237 and the pseudo-second-order constant k_2, decreases from 2.4148 to 0.4168 (g/mg min). For pseudo-first order kinetic model, the values of calculated q_e increased with the initial concentration and did not have a good correlation with the experimental q_e.

The correlation coefficients (R^2) obtained for the Lagergren model are relatively small. From the Table 3 it was observed that the correlation coefficients were found to be higher for pseudo second order model, in the range of 0.9982 to 0.9998. The higher values confirm that the sorption process follows a pseudo-second-order mechanism. The value of the equilibrium sorption capacity is very close to the value of the experimental sorption capacity, for an initial dye concentration of 100 mg/L the q_e calculated from the model is 0.9214 mg/g and the q_e experimental is 0.9213 mg/g. Therefore, the sorption can be approximated more appropriately by the pseudo-second-order kinetic model for the sorption of Congo red onto soil. Similar kinetic

Table 3. Sorption kinetic parameters for sorption of Congo red on soil

Initial dye concentration (mg/L)	Pseudo first order kinetic model			Experimental q_e (mg/g)	Pseudo second order kinetic model			
	k_1 (min^{-1})	q_e (mg/g)	R^2		k_2 (g/mg min)	q_e (mg/g)	R^2	h (mg/g min)
20	0.1484	0.194	0.8663	0,47992	2.4148	0.4894	0.9998	0.5783
50	0.0774	0.175	0.6165	0,9213	1.9849	0.9214	0.9982	1.685
100	0.2371	2.045	0.7821	2,23972	0.4168	2.3068	0.9996	2.2179

results have also been reported for the adsorption of CR onto calcium-rich fly ash (Acemioglu, 2004), coir pith carbon (Namasivayam and Kavitha, 2002), clay (Vimonses *et al.,* 2009) and xerogel (Pavan *et al.,* 2008) The intra-particle diffusion model, proposed by Weber and Morris (Vimonses *et al.,* 2009), has been applied to identify diffusion mechanisms of adsorption process. The effect of intra-particle diffusion resistance on adsorption can be determined by the following relationship (eq. 12):

$$q_t = k_{id} t^{1/2} + C \qquad (12)$$

where q_t is the amount of dye adsorbed on soil at various times t, k_{id} is the intraparticle diffusion rate constant (mg/g $min^{1/2}$) and C is the intercept. The values of intercept (C) give information about the thickness of the boundary layer, i.e. the larger intercept the greater is the boundary layer effect (Kannan and Meenakshisundaram, 2002; Ayoob *et al.,* 2008).

According to this model, the plot of uptake, q_t versus the square root of time, $t^{1/2}$ should be linear if intraparticle diffusion is involved in the sorption process and if these lines pass through the origin, then intraparticle diffusion is the rate controlling step (Lian *et al.,* 2009). If the line does not pass trough the origin, the process is very complex with more than one mechanism limiting the rate of sorption (Ayoob *et al.,* 2008). Usually, the plot q_t versus $t^{1/2}$ presents a multi-linearity, which can be explained by the presence of two or more steps occur during the process (Lorenc-Grabowska and Gryglewicz, 2007). The first stage is associated with the external mass transfer or instantaneous sorption stage. The second stage illustrates the gradual sorption stage, when the intraparticle diffusion is the rate controlling of the phenomena. The third stage is the final equilibrium stage where the intraparticle diffusion starts to slow down due to the low sorbate concentration left in the solution (Noroozi *et al.,* 2007).

The plots for the intraparticle diffusion of Congo red on soil are not linear to the whole time range (fig. not shown), resulting that more than one process affects the dye sorption on soil. The sorption process tends to be followed by two phases. The initial curve portion between $t = 2$ to 10 minutes could be due to intraparticle diffusion effects.

The intra-particle diffusion model constants are calculated and given in Table 4. The correlation coefficients (R^2) for the intraparticle diffusion model present values ranging from 0.8913 to 0.9946, which are lower than the pseudo-second-order model, but it indicates that adsorption of Congo red on soil may be followed by an intraparticle diffusion model. Also, the intraparticle diffusion plots do not pass through the origin and C“"0, these indicated the presence of intraparticle diffusion process, but this is not the only rate controlling step and other mechanisms such as complexation or ion exchange play an important role in the process (Bulut *et al.,* 2008). Similar results were reported by Vadivelan and Kumar (2005) for methylene blue adsorption onto rice husk, Vijayakumar *et al.,* (2009) for Congo red adsorption by perlite.
For better understanding the effect of temperature on the sorption, it is important to study the thermodynamic parameters such as standard Gibbs free energy change ΔG^0, standard enthalpy ΔH^0, and standard entropy ΔS^0. The Gibbs free energy change represents the fundamental criterion of spontaneity (Han *et al.,* 2005).
The Gibbs free energy of sorption by using equilibrium constant (K_c) is calculated from Equation (13):

$$\Delta G^0 = \text{“}RT \ln K_c \qquad (13)$$

Standard enthalpy ΔH^0, and standard entropy, ΔS^0, of sorption can be estimated from van’t Hoff equation given as Equation (14):

$$\ln K_c = \frac{-\Delta H^0}{RT} + \frac{\Delta S^0}{R} \qquad (14)$$

Table 4. Intraparticle diffusion parameters for Congo red

Initial dye concentration (mg/L)	Intraparticle diffusion model		
	k_{id} (mg/g min^{-1})	C	R^2
20	0.0481	0.3005	0.9872
50	0.0915	0.6132	0.8913
100	0.3833	0.9367	0.9946

Table 5. Thermodynamic parameters for the adsorption of Congo red on soil

T (^{0}K)	Δ G^0 (kJ/mol)	ΔS^0 (J/mol K)	ΔH^0 (KJ/mol)
303	-29.0012	-19.9236	- 36.95271
313	-26.9563		
323	-29.9378		

where R is the universal gas constant (8.314 J/mol K), K_c is the adsorption equilibrium constant, T is absolute temperature (K). The value of ΔH^0 and ΔS^0 can be obtained from the slope and intercept of the plot of ln K_c against $1/T$ (in Kelvin). The values of the thermodynamic parameters obtained by above mentioned equations are summarized in Table 5.

The negative values of free energy changes (ΔG^0) for all studied temperatures revealed that a spontaneous process occurred. The enthalpy change was found -36.95 kJ/mol, this negative enthalpy value indicates that the sorption process was exothermic physisorption. Generally, the change in adsorption enthalpy for physisorption is in the range of -20 to -40 kJ/mol. In many studies, the adsorption of dye is described as an exothermic phenomenon (Oladoja *et al.,* 2009; Tan *et al.,* 2008). The negative value of ΔS^0 confirms the decreased randomness at the solid-liquid interface during sorption of CR onto soil particles. Similar results were reported by Vimonses et al. (2009) for the sorption of Congo red on Australian kaolin clay and Han et al. (2005) for adsorption of lead on chaff.

CONCLUSION

The sorption process of Congo red from aqueous solution onto soil was studied under different experimental conditions, in batch modes. The percent of sorbed dye increased with the contact time, initial dye concentration, sorbent dose and temperature. The experimental results were analyzed using two-parameter adsorption isotherm models - the Langmuir, Freundlich and Temkin isotherms. The analytical data showed that the Freundlich isotherm offers the best fit of the data, and also the Langmuir isotherm described the data more appropriate than Temkin isotherm. The pseudo second order kinetic model agrees very well with the dynamic behaviour for the adsorption of Congo red on soil. Isotherms have also been used to get the thermodynamic parameters such as free energy, enthalpy and entropy of sorption. The negative value of free energy confirm the spontaneous nature of the CR sorption on studied soil and the negative value of enthalpy leads to exothermic nature of sorption process whereas the negative ΔS^0 value showed the decreased randomness at the solid-liquid interface during sorption of CR onto soil particles.

Desorption studies will follow to these experiments, which should further help to elucidate the mechanism of sorption and also in the recovery of dye, using an economical and environmentally friendly treatment process.

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