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Adsorption characteristics of Congo Red on coal-based mesoporous activated carbon

Ewa Lorenc-Grabowska, Grażyna Gryglewicz*

Faculty of Chemistry, Division of Polymer and Carbonaceous Materials, Wrocław University of Technology, ul. Gdańska 7/9, 50-344 Wrocław, Poland

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Abstract

Adsorption of Congo Red dye (CR) on bituminous coal-based mesoporous activated carbon (AC) from aqueous solutions was studied. The ACs used differed significantly in terms of total surface area, pore volume distribution and surface charge properties. The mesopore contribution to the total pore volume ranged from 52 to 83%. The adsorption tests were performed under static conditions at solution pH 7.8–8.3. The pH at the point of zero charge (pH_{PZC}) for ACs used was over 10. It was found that the higher the fraction of mesopores with a size between 10 and 50 nm, the shorter the time to achieve the equilibrium stage for CR adsorption. The kinetics of adsorption in view of three kinetic models, i.e. the first-order Lagergren model, the pseudo-second-order model and the intraparticle diffusion model, was discussed. The pseudo-second-order kinetic model describes the adsorption of CR on mesoporous activated carbon very well. The correlation coefficients ranged from 0.980 to 0.991. The intraparticle diffusion into small mesopores was found to be the rate-limiting step in the adsorption process. The equilibrium adsorption data were interpreted using Langmuir and Freundlich models. The adsorption of CR was better represented by the Langmuir equation. The monolayer adsorption capacity of ACs was found to increase with increasing both the mesopore volume and the mesopore contribution to their porous texture. The effect of solution ionic strength on the uptake of CR by two different mesoporous carbons was also investigated.

Keywords: Congo Red; Adsorption; Activated carbon; Porous texture; Kinetics

1. Introduction

The introduction of waste products in the environment is a world wide problem that has been highlighted by various environmentalist groups. Colored organic effluent is produced in industries such as textiles, rubber, paper, plastic, cosmetics, etc. Discharging of dyes into water resources even in a small amount can affect the aquatic life and food web. Dyes can also cause allergic dermatitis and skin irritation. Some of them have been reported to be carcinogenic and mutagenic for aquatic organisms.

The treatment of dyes in industrial wastewater possesses several problems since dyes are generally difficult to biodegradate and photodegradate. Many different techniques including cloud point extraction, oxidation processes, nanofiltration, ozonation and coagulation have been used for the removal of colored dyes from wastewater [1–4]. However, adsorption is the most popular physicochemical treatment for the removal of dissolved organics from waters. A number of non-conventional, low cost adsorbents have been tested for dye removal. These include peat [5], red mud [6], coir pith [7], Neem leaf [8], activated sludge [9], waste organic peel [10], tree fern [11] and minerals [12]. Moreover, the removal of dye by activated carbon produced from non-conventional sources such as coir pith [13], sawdust and rice-husk [14], pinewood [15] and others has also been investigated. However, the adsorption capacity of the above adsorbents is not large.

The adsorption capacity of activated carbon depends on various factors such as surface area, pore size distribution and surface functional groups of adsorbent; polarity, solubility and molecule size of adsorbate; solution pH and the presence of other ions in solution and so on [16]. The most widely used

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* Corresponding author. Tel.: +48 71 48 3206398; fax: +48 71 3221580. *E-mail address:* grazyna.gryglewicz@pwr.wroc.pl (G. Gryglewicz).

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activated carbon is microporous and has high surface area, and as a consequence, showing a high efficiency for the adsorption of low molecular weight compounds and low for giant molecules. The adsorption of bigger size compounds such as dyes, dextrines or natural organic materials, requires a material with high mesopore contribution to the total pore volume of adsorbent [17–19]. Even if the adsorbate size is in the micropore range, an enhanced mesoporosity positively influences on the extent of adsorption [20,21].

Mesoporous activated carbons are mainly produced from costly synthetic resins. It seems to be interesting to use the mesoporous carbon produced from the coal as a raw material due to its low cost and accessibility. Poland is known for its big resources of the coal. Highly mesoporous carbons were prepared by steam activation of coal or pitch modified with a small amount of organo rare-earth metal complexes [17,22]. Recently we have elaborated the method of producing mesoporous activated carbon from calcium and iron loaded sub-bituminous and bituminous coals [23]. So far there has been no report in the literature of the study of dye adsorption using coal-based activated carbon with well developed mesoporosity.

The objective of this work was to investigate the adsorption of Congo Red dye on coal-based mesoporous carbon of different porous texture and surface charge properties. CR is commonly used in textile industry to give wool and silk red color with yellow fluorescence. The factors determining the efficiency in the CR removal from aqueous solutions such as pore size distribution of activated carbon, pH_{PZC} and ionic strength of the solution have been discussed.

2. Experimental

2.1. Materials

Four coal-based mesoporous activated carbons were used for this study. The ACs were produced from sub-bituminous coal from Kazimierz-Juliusz mine (KJA series) and high-volatile bituminous coal from Szczygłowice mine (SA). More details about the carbon preparation are given elsewhere [24]. Briefly, the KJA/Ti carbon was produced from the KJ coal impregnated with titanium oxide acetylacetonate. KJA/N/CaFe, SA/N/CaFe and KJA/S/CaFe carbons were produced from Ca- and Fe-exchanged coals. Prior to ion-exchange, the raw coals were treated with nitric acid (N) or sulfuric acid (S) to generate the ion-exchangeable groups on the coal surface. The final stage of activated carbon preparation included carbonization and activation with steam at 850 °C up to 50% of burn off.

For adsorption studies Congo Red dye obtained by POCh Gliwice was used as an adsorbate. The selected properties of the adsorbate are given in Table 1. The molecular structure of CR is shown in Fig. 1.

Table 1
Selected physical properties of Congo Red

Parameter	CR[a]
Molecular weight (g/mol)	650.7
Width (nm)	2.62
Depth (nm)	0.74
Thickness (nm)	0.43
pK_a	5.5

[a] Does not include associated sodium ions [25].

2.2. Sorption of dyes

The adsorption process of CR from aqueous solution was carried out at 25 °C in a static system. A sieve fraction of activated carbon between 0.2 and 0.5 mm was used for the sorption experiments. The carbon sample was washed with deionized water and dried at 105–110 °C for 24 h before use. To establish the equilibrium time, 0.2 g of activated carbon was placed into the set of flasks which were kept in a thermostat shaker bath and agitated for 4 days. For the adsorption isotherm determination, 0.01–0.2 g of activated carbon was placed into Erlenmeyer flasks and 100 ml of adsorbate solution (50 mg/l) was added to each of the flasks. Each set of flasks included two additional flasks containing blank solution to check the adsorption of sorbate on the walls. The stoppered flasks were kept in a thermostat shaker bath and agitated for 2 days. Before and after contact, the pH of solutions was measured by a digital pH-meter (Accumet Basic, Fisher Scientific) using a glass electrode. The adsorption tests were carried out without buffer addition to avoid an influence of the additional ions on the process.

To determine the influence of the solution ionic strength on the adsorption behavior of CR, the equilibrium isotherms were obtained for KJA/Ti and SA/N/CaFe carbons at solution pH 10 using 0.01 and 0.1 M NaCl.

2.3. Analyses

The porous texture was characterized by adsorption/desorption of benzene at 25 °C in a McBain apparatus for gravimetric sorption measurements. Specific surface area S_{BET} was taken from benzene adsorption isotherms using BET equation. The Gurvitch rule and Kelvin condensation theory were used to establish the extent of microporosity (V_{mic}) and the mesopore size distribution [26]. The mesopore fraction is expressed as percentage of mesopore volume to the total pore volume (V_{mes}/V_{tot}). The pH_{PZC} of the carbons was determined according the procedure described by Moreno-Castilla et al. [27].

The concentration of solute remaining in the water phase was quantified. The CR concentration was measured using a spectrophotometer at wavelength 497 nm.

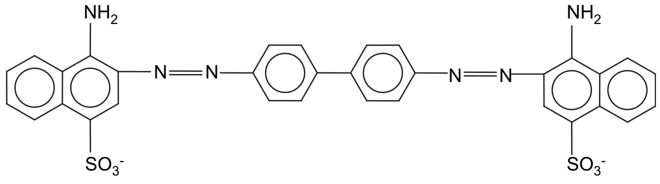

Fig. 1. Molecular structure of Congo Red dye.

3. Result and discussion

3.1. Characteristics of AC

The porous structure parameters and the results of pH_{PZC} measurements for the activated carbons are given in Table 2. The ACs used are characterized by mesopore volumes between 0.271 and 0.471 cm^3/g and high contribution of mesopores of 53.4–82.1%. The BET surface area of ACs ranges from 331 to 679 m^2/g. For KJA/Ti and KJA/S/CaFe carbons the mesopores with a pore size range of 2–10 nm constitute approximately half of their mesopore volume. Whereas bigger size mesopores, between 10 and 50 nm, are predominant in the porous texture of KJA/N/CaFe and SA/N/CaFe carbons.

The pH_{PZC} of all ACs studied is above 10. The adsorption tests were carried out at the pH of the solution between 7.8 and 8.3, thus significantly lower than the pH_{PZC} of the carbons used. When solution pH is lower than pH_{PZC} the carbon surface is charged positively [16]. Taking into account that Congo Red dye occurs in the anionic form, the attraction forces are present between the AC surface and the adsorbate molecule [28,29]. This suggests that different adsorption behavior of CR observed for ACs studied would arise from differences in their pore size distribution.

3.2. Adsorption studies

3.2.1. Effect of contact time

The results of adsorption of Congo Red on mesoporous activated carbons versus time is shown in Fig. 2. The adsorption of CR reaches the equilibrium after 30 h for the KJA/N/CaFe and SA/N/CaFe carbons and after 48 h for the remaining carbons. It can be observed that the time required to attain the equilibrium is shorter for these carbons which are characterized by higher contribution of larger in size mesopores (Table 2). A particle size of adsorbent may also affect the kinetics of adsorption [30]. However, in our case the particle size range is the same for all ACs used, hence the differences in the kinetics of adsorption are thought to be due to differences in the mesopore size distribution of the carbon.

The ACs differ in terms of the extent of CR removal with time. The equilibrium uptake increases from 90% for KJA/Ti to almost 100% for KJA/N/CaFe and SA/N/CaFe carbons. As can be seen in Table 2, the two latter adsorbents compared to KJA/Ti show higher values for both the mesopore volume and the mesopore contribution to the porous texture (over 80%). This explains their highest adsorption efficiency. Whereas the KJA/Ti carbon, which is characterized by the lowest mesopore fraction (53.4%), shows the poorer efficiency for the CR removal despite the highest BET surface area. This leads to the conclusion that mesopores act not only as transporting arteries but also contribute to the adsorption of CR on the activated carbons.

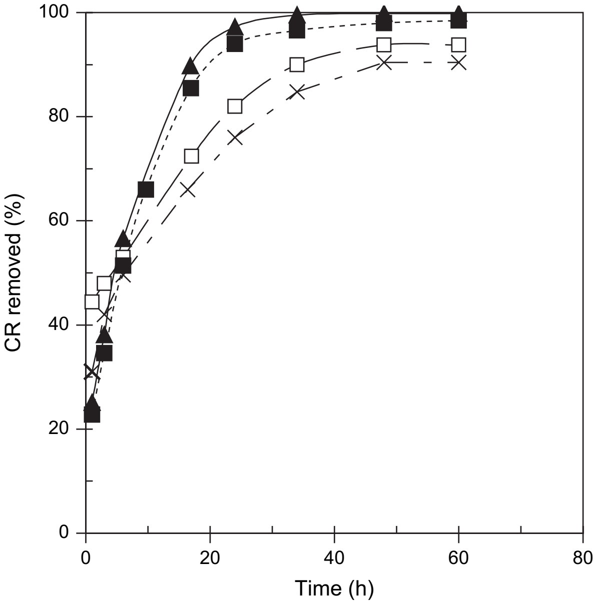

Fig. 2. Effect of agitation time on removal of Congo Red on activated carbons: ▲, SA/N/CaFe; ■, KJA/N/CaFe; □, KJA/S/CaFe; ×, KJA/Ti.

Table 2
Characteristics of activated carbons used

Parameter	KJA/Ti	KJA/S/CaFe	KJA/N/CaFe	SA/N/CaFe
S_{BET} (m^2/g)	679	475	331	370
V_{mic} (cm^3/g)	0.234	0.122	0.093	0.111
V_{mes} (cm^3/g):	0.271	0.403	0.427	0.471
2–3 nm	0.080	0.113	0.063	0.062
3–5 nm	0.072	0.069	0.022	0.022
5–10 nm	0.072	0.135	0.087	0.074
10–50 nm	0.047	0.086	0.255	0.313
V_{tot} (cm^3/g)	0.505	0.525	0.520	0.582
V_{mes}/V_{tot} (%)	53.4	76.8	82.1	80.9
pH_{PZC}	10.20	11.35	11.96	12.20

3.2.2. Kinetics of adsorption

Several kinetic models have been applied to examine the controlling mechanism of dyes adsorption from aqueous solutions and interpret the experimental data obtained [5,8,12,15,31,32]. The kinetics of adsorption can be described by the first-order Lagergren equation that is given by Eq. (1) [6,8,14]:

$$\log(q_{e\,exp} - q_t) = \log q_e - (k_1 t)/2.303 \tag{1}$$

In some cases a pseudo-second-order model given by Eq. (2) provides a better fit [5,10,14]:

$$t/q_t = 1/(k_2 q_e^2) + t/q_e \tag{2}$$

where t and q_t are, respectively, time (min) and the amount of dye adsorbed by carbon at time t (mg/g). $q_{e\,exp}$ and q_e are the amount of dye adsorbed at equilibrium-experimental data and equilibrium-calculated data, respectively, expressed as mg/g sample. k_1 and k_2 are the first (1/min) and second (g/mg min) order rate constant of adsorption.

It was reported that the adsorption of CR fits the Lagergren kinetic model for orange peel [10] and waste red mud [6] and the pseudo-second-order kinetic model when activated carbon was used as adsorbent [13]. Both models have been applied to describe the adsorption of CR on mesoporous activated carbons in our work. The calculated results are given in Table 3. The correlation coefficients (R^2) for the Lagergren equation are not too high, between 0.915 and 0.982. For some carbons, the experimental $q_{\mathrm{e\,exp}}$ values do not agree well with the calculated ones. The plots of the linearized form of the pseudo-second-order kinetic model for the adsorption of CR on different mesoporous activated carbons are shown in Fig. 3. The correlation coefficients are much greater in this case, in the range of 0.980–0.991, confirming a very good agreement with experimental data.

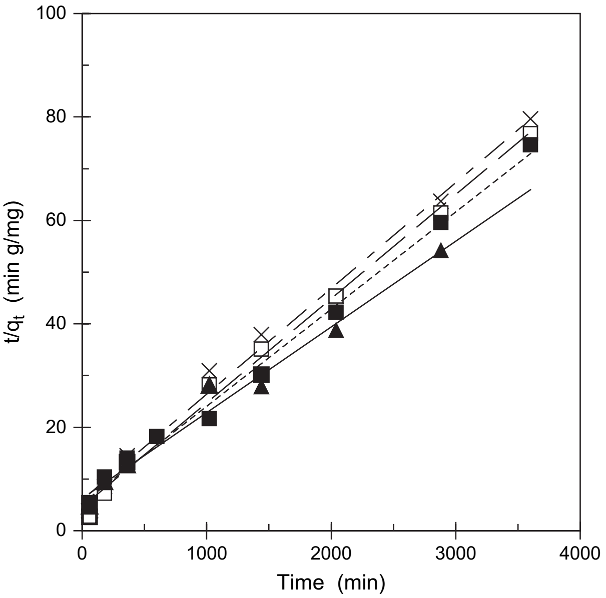

Fig. 3. Pseudo-second-order adsorption kinetics of Congo Red on activated carbons: ▲, SA/N/CaFe; ■, KJA/N/CaFe; □, KJA/S/CaFe; ×, KJA/Ti.

The model proposed by Weber and Morris [33] has been applied to gain a deeper knowledge about the mechanism of dye adsorption onto mesoporous activated carbon. In this model, described by Eq. (3), the intraparticle diffusion is considered as a rate-limiting step

$$k_{\mathrm{p}} = q_{\mathrm{t}}/t^{1/2} \tag{3}$$

where q_{t} and k_{p} are the amount adsorbed at time t (mg/g) and intraparticle rate constant (mg/g min$^{1/2}$), respectively. Such a plot may present a multi-linearity, indicating that a few steps take place. The first, sharper portion is attributed to the diffusion of adsorbate through the solution to the external surface of adsorbent or the boundary layer diffusion of solute molecules. The second portion describes the gradual adsorption stage, where intraparticle diffusion rate is rate-limiting. The third portion refers to the final equilibrium stage for which the intraparticle diffusion starts to slow down due to the extremely low adsorbate concentration left in the solution [13–15,34]. The rate of uptake might be limited by the size of adsorbate molecule, concentration of the adsorbate and its affinity to the adsorbent, diffusion coefficient of the adsorbate in the bulk phase, the pore size distribution of the adsorbent, and degree of mixing. Usually, the intraparticle diffusion is the rate-limiting step for the systems with high concentration of the adsorbate, good mixing, large particle size of adsorbent and low affinity towards adsorbent [34,35]. Fig. 4 shows the plots of fractional uptake for CR versus square root time on different mesoporous ACs. It can be observed that the plots are not linear over the whole time range, implying that more than one process affects the CR adsorption. The multiple nature of these plots can be explained in terms of few processes, i.e., boundary layer diffusion which gives the initial part of the plot and the intraparticle diffusion which gives further the two linear parts. If the intraparticle diffusion is the only rate-controlling step then the plot passes through the origin if not, the boundary layer diffusion affects the adsorption to some extent [12]. As can be seen in Fig. 4, for KJA/Ti and KJA/S/CaFe carbons, the diffusion in bulk phase to the exterior surface affects the rate of adsorption. The intraparticle diffusion is likely to occur in two stages. The adsorbate molecule rapidly enters macropores and wider mesopores and then penetrates more slowly into smaller mesopores. This implies that the intraparticle diffusion of CR molecules into small mesopores is the rate-limiting step in the adsorption process. For KJA/N/CaFe and SA/N/CaFe carbons, the same slope of the initial part passing through the origin and the linear part attributed to the diffusion into macropores and wider mesopores can be observed (Fig. 4). This figure indicates that the intraparticle diffusion into smaller mesopores is the only rate-controlling step. Moreover, for all carbons the last part of plots is almost parallel suggesting that the rate of adsorption in small mesopores is comparable regardless the differences in their porous structure. One can observe the difference in the slope of the part which is designed to the diffusion in macropores and wider mesopores. This slope increases in the order KJA/S/CaFe, ~KJA/Ti < KJA/N/CaFe, SA/N/CaFe indicating an enhanced diffusion of CR molecules for the carbons with bigger volume of mesopores in the size range of 10–50 nm.

Table 3
Comparison of the pseudo-first and second-order kinetics models of CR adsorption

Carbons	First-order kinetic model				Second-order kinetic model		
	$q_{\mathrm{e\,exp}}$ (mg/g)	q_{e} (mg/g)	k_1 (1/min)	R^2	q_{e} (mg/g)	k_2 (g/mg min)	R^2
KJA/Ti	45	44	0.002	0.915	49	7.0×10^{-5}	0.985
KJA/S/CaFe	47	27	0.001	0.982	48	9.5×10^{-5}	0.991
KJA/N/CaFe	48	52	0.003	0.969	55	5.8×10^{-5}	0.990
SA/N/CaFe	53	52	0.002	0.954	60	4.4×10^{-5}	0.980

3.2.3. Adsorption isotherms

Adsorptions isotherms are important for the description of how molecules of adsorbate interact with adsorbent surface and also, are critical in optimizing the use of carbon as an adsorbent. Hence, the correlation of equilibrium data using either a theoretical or empirical equation is essential for the adsorption interpretation and prediction of the extent of adsorption.

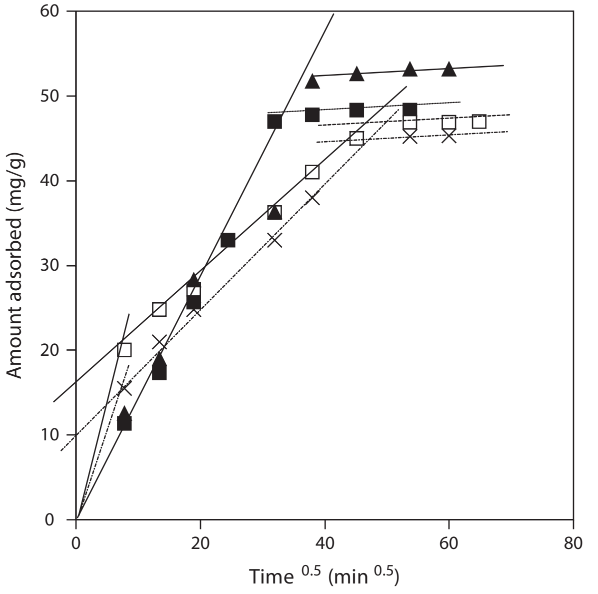

Fig. 4. Intraparticle diffusion for the adsorption of Congo Red on activated carbons: ▲, SA/N/CaFe; ■, KJA/N/CaFe; □, KJA/S/CaFe; ×, KJA/Ti.

Two well known isotherm equations, the Langmuir and Freundlich, have been applied for deeper interpretation of the adsorption data obtained.

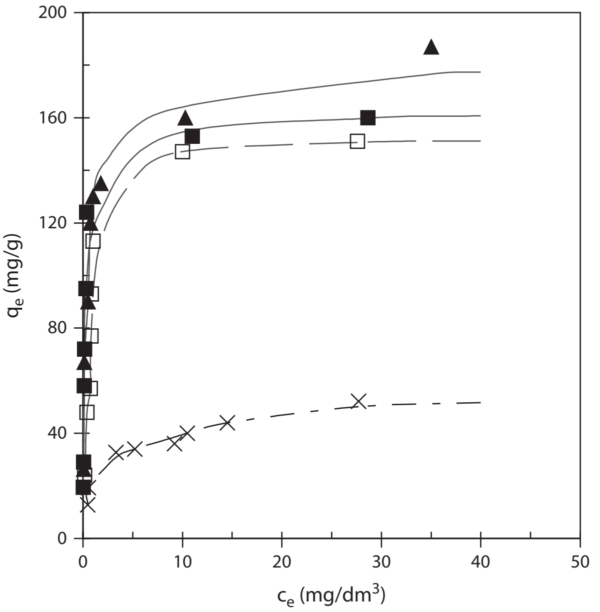

Fig. 5. Adsorption isotherms for Congo Red on activated carbons: ▲, SA/N/CaFe; ■, KJA/N/CaFe; □, KJA/S/CaFe; ×, KJA/Ti.

Table 4
Langmuir and Freundlich parameters for Congo Red adsorption on mesoporous activated carbons

Carbons	Langmuir			Freundlich		
	$q_{\max}$ (mg/g)	b (dm^3/g)	R^2	K_f (mg^{1-n} dm^{3n}/g)	$1/n$	R^2
KJA/Ti	52	2.08	0.958	73	0.255	0.955
KJA/S/CaFe	159	0.84	0.998	94	0.769	0.914
KJA/N/CaFe	161	0.27	0.999	150	0.738	0.993
SA/N/CaFe	189	0.58	0.996	111	0.182	0.880

Fig. 5 shows the adsorption isotherms for CR on mesoporous activated carbons. All adsorption isotherms show the trend of levelling out at higher adsorbate concentrations and thus are of the Langmuir-type. According to Giles [36] the L type of isotherm is connected with flat position of the adsorbate molecule toward the adsorbent surface and refers to the monolayer coverage. The Langmuir equation is based on the assumption of a structurally homogeneous adsorbent where all sorption sites are identical and energetically equivalent. The Langmuir model is represented by Eq. (4):

$$q_e = (bq_{\max}c_e)/(1 + bc_e) \tag{4}$$

where q_e is the equilibrium dye concentration on the adsorbent (mg/g), c_e is the equilibrium dye concentration in solution (mg/dm^3), $q_{\max}$ is the monolayer capacity of the adsorbent (mg/g), and b is the Langmuir adsorption constant (dm^3/g).

The Freundlich model is applied to describe heterogeneous system characterized by a heterogeneity factor of $1/n$. This model describes reversible adsorption and is not restricted to the formation of the monolayer. The Freundlich model is expressed by Eq. (5):

$$q_e = K_f c_e^{1/n} \tag{5}$$

where q_e and c_e are, respectively, the dye concentrations on adsorbent (mg/g) and in solution (mg/dm^3) and K_f is the Freundlich constant (mg^{1-n} dm^{3n}/g).

The calculated values of the Langmuir and Freundlich equation's parameters are given in Table 4. The comparison of correlation coefficients (R^2) of the linearized form of both equations indicates that the Langmuir model yields a better fit for the experimental equilibrium adsorption data than the Freundlich model. This suggests the monolayer coverage of the surface of mesoporous carbon by CR molecules. The monolayer adsorption was also reported for the CR adsorption onto activated coir pith [13] and red mud [6]. A Langmuir adsorption capacity ($q_{\max}$) of 6.72 and 4.05 mg/g was found for coir pith and red mud, respectively. A higher $q_{\max}$ (22.44 mg/g) was achieved using orange peel [10]. However, these values are considerably lower compared to the $q_{\max}$ determined for the CR adsorption onto mesoporous activated carbons. For the ACs studied, the adsorption capacity was in the range of 52–189 mg/g. The KJA/Ti carbon shows the lowest $q_{\max}$ value among all carbons due to the lowest both the mesopore volume and the mesopore contribution to the porous texture (Table 2). However, the adsorption capacity of KJA/Ti was two and half fold higher than that reported for orange peel [10]. For the activated carbons from ion-exchanged coals (KJA/N/CaFe, KJA/S/CaFe, SA/N/CaFe) a Langmuir adsorption capacity was 7–8 fold higher.

There is a correlation between the monolayer adsorption capacity and the mesoporosity of the ACs. The higher the mesopore volume followed by the contribution of mesopores to the porous texture ($V_{\text{mes}}/V_{\text{tot}}$), the greater the monolayer capacity of the carbon toward CR. This indicates that the ACs with better developed mesoporosity have an enhanced ability to remove Congo Red dye from aqueous solutions.

3.2.4. Effect of ionic strength

The ionic strength of the solution is one of the factors that controls both electrostatic and non-electrostatic interactions between the adsorbate and the adsorbent surface [16]. Figs. 6 and 7 show the equilibrium isotherms for the adsorption of CR on SA/N/CaFe and KJA/Ti carbons, respectively, at two NaCl concentrations (0.01 and 0.1 M) at pH 10. Under these conditions both carbons will be charged positively inducing the attractive forces between the CR molecule and the carbon surface. For SA/N/CaFe the pH_{PZC} is much higher than the pH at which the adsorption process is carried out (12.2 versus 10.0). When salt is not added, strong attractive forces arise between the CR molecule and the carbon surface. With increasing the ionic strength of the solution a marked decrease in the extent of the adsorption is observed (Fig. 6). This might be explained by the screening effect of added salt resulting in the reduction of the electrostatic attractive interactions. For KJA/Ti the attractive forces are very weak because the pH_{PZC} for this carbon is very close to solution pH (10.2 versus 10). It can be observed that using salt concentration of 0.1 M the amount of adsorption is nearly on the same level when no salt is added. This suggests that at pH 10 the adsorption of CR on KJA/Ti is mainly governed by non-electrostatic forces. The extent of the adsorption is determined in this case by the volume of pores accessible to CR molecule.

4. Conclusions

Taking into account the molecular structure size of Congo Red dye, coal-based mesoporous activated carbons were selected to study its removal from aqueous solutions. The ACs were characterized by mesopore volume between 0.271 and 0.471 cm^3/g and high mesopore contribution to the porous texture, ranging from 53.4 to 82.1%.

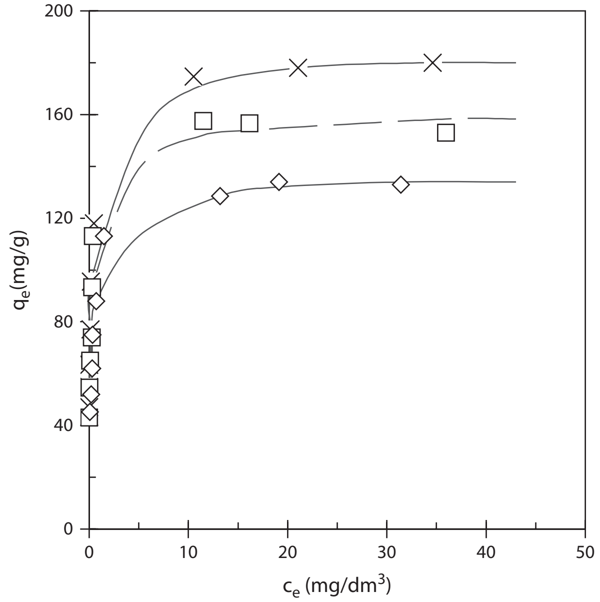

Fig. 6. Congo Red adsorption on SA/N/CaFe at pH 10 at salt concentration: ×, no salt; □, 0.01 M NaCl; ◇, 0.1 M NaCl.

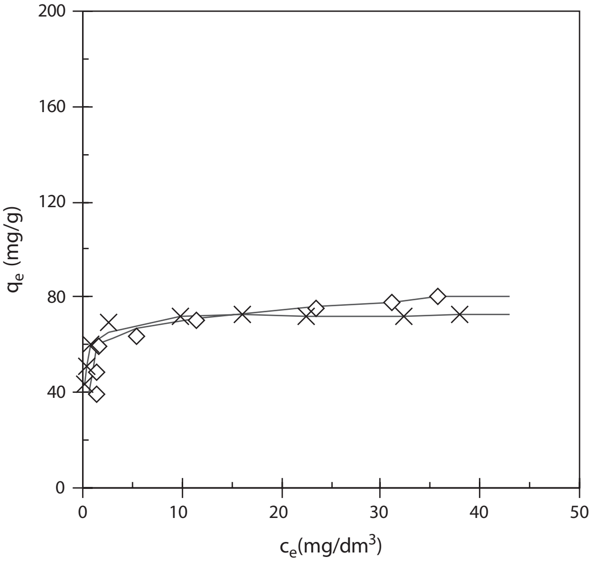

Fig. 7. Congo Red adsorption on KJA/Ti at pH 10 at salt concentration: ×, no salt; ◇, 0.1 M NaCl.

A very good agreement with experimental data obtained indicates that a pseudo-second-order kinetic model is favorable for the CR adsorption on mesoporous activated carbons. The correlation coefficients were between 0.980 and 0.991. The diffusion into small mesopores was found to be the rate-limiting step in the adsorption process.

The adsorption of CR from aqueous solutions onto mesoporous coal-based activated carbons conforms to a Langmuir equation based on the formation of a monomolecular layer. There is a correlation between the Langmuir adsorption capacity and the degree of mesopore development. The higher the both mesopore volume and mesopore contribution to the total pore volume, the higher is the adsorption capacity of the activated carbon with respect to Congo Red dye.

The impact of the ionic strength on the adsorption capacity of ACs at a given pH is related to the pH_{PZC} of the carbon. At pH 10, for a carbon whose pH_{PZC} is close 10, the CR uptake in the presence of salt (0.1 M NaCl) is comparable to that observed when no salt is added. When the pH_{PZC} of the carbon is significantly higher, an increase in the ionic strength results in lowering of adsorption due to the reduction of the attractive forces between the CR molecule and the carbon surface.

Acknowledgements

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