Cent. Eur. J. Chem. • 8(4) • 2010 • 906–912
DOI: 10.2478/s11532-010-0055-6

Central European Journal of **Chemistry**

Kinetics and thermodynamics of adsorption of congo red on cellulose

Research Article

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Received 20 January 2010; Accepted 26 March 2010

Abstract: Thermodynamics and kinetics of adsorption of congo red (CR) on cellulose are studied at 308-328 K. In the used concentration range of CR, interaction of CR with cellulose is exothermic and CR molecules adsorb chemically on cellulose surface. The effects of contact time, temperature and initial concentration of CR on kinetics of its adsorption on cellulose were investigated. The process proceeds according to the pseudo-second-order equation. Initial adsorption rate of adsorption is first-order in CR and the intraparticle diffusion of CR molecules within cellulose is identified as the main rate-limiting step.

Keywords: *Adsorption kinetics • Congo red • Cellulose • Avrami equation • Langmuir isotherm*

1. Introduction

The removal of color from aquatic systems caused by presence of synthetic dyes that usually contains azo-aromatic groups is extremely important from the environmental viewpoint because most of these dyes are toxic, mutagenic, and carcinogenic [1]. Dye producers and users are interested in stability and fastness, and consequently, are producing dye compounds, which are more difficult to degrade after use [2]. Congo red (CR) is an anionic dye widely used in textile, rubber, paper, and plastic industries, and as a pH indicator [2,3]. However, its use in the cellulose industries (cotton textile, wood pulp, and paper) has long been abandoned, because of its tendency to change color when touched by sweaty finger and because of its toxicity. This dye is a benzidine-based dye, Figs. 1a and b, and has been known to cause an allergic reaction and metabolize to benzidine, a human carcinogen [3,4]. Synthetic dyes such as CR are difficult to biodegrade. Adsorption has been shown to be the most promising option for nondegradable dyes for the removal from aqueous streams. A number of adsorbents such as Anilinpropylsilica xerogel [2], cattail root [5], and palm kernel coat [6] were investigated as adsorbents for adsorption of CR.

Cellulose is a polysaccharide consisting of a linear chain of several hundred to over ten thousand β(1→4) linked D-glucose units, Fig 1c. Cellulose is the major constituent of paper, paperboard, card stock and of textiles made from cotton, linen, and other plant fibers. Using kinetic models, we can investigate the mechanism

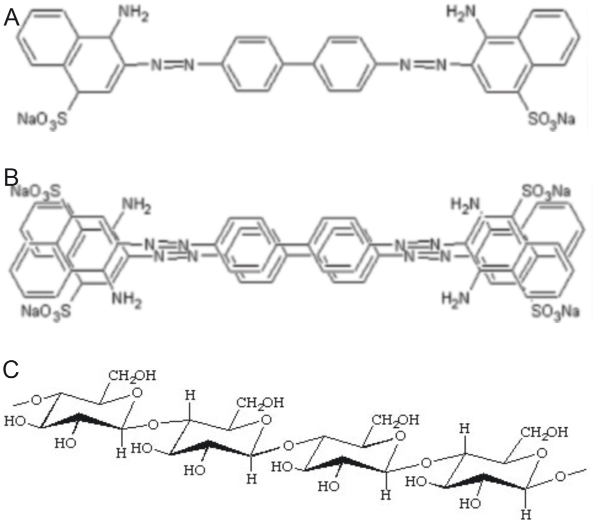

Figure 1. Molecular structures of (a) congo red, (b) congo red dimer, and (c) cellulose.

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of adsorption. The study of adsorption kinetics describes the adsorbate uptake rate and evidently this rate controls the residence time of adsorbate at the solid-liquid interface.

In this work, adsorption of CR on cellulose was investigated using the Freundlich, Langmuir and Dubinin-Radushkevich equations. The effects of CR concentration, contact time and temperature on the adsorption rate of CR on cellulose were studied. Kinetics of adsorption process was evaluated by the Lagergern, pseudo-second-order, Avrami, Tobin, Elovich and pore-diffusion equations.

2. Experimental Procedure

2.1. Materials

CR was purchased from BDH and chromatography paper (grade 1 Chr) was prepared from Whatman.

2.2. Methods

In adsorption kinetic experiments, 20 mL of CR aqueous solution in the concentration range of 2×10^{-5}–2×10^{-4} M was transferred to a series of glass stoppered bottles, each containing 0.1 g of chromatography paper sample. At predetermined times, the content of CR in the solutions was determined by UV spectrometry (UV-Vis 160, Shimadzu) at λ_{max}= 499 nm. In adsorption experiments, concentrations of CR were in the range of 1×10^{-5}–2×10^{-4} M and the contact time was 20 h to attain equilibrium conditions. These experiments were conducted by batch procedure and constant shaking (148 rpm) at 308, 318 and 328 K within ±0.1 K in a thermostated shaker. In adsorption kinetic experiments, the adsorption capacity of CR on the adsorbent at a predetermined time *t*, q_t (mg g^{-1}), was calculated by a mass balance relation as follows

$$q_t = \frac{(c_0 - c_t)Mv}{1000w} \tag{1}$$

where c_0 and c_t are the initial concentration of adsorbate and its concentration in M at a given time *t*, respectively, *v* is the volume of solution (mL), *w* is the weight of the used adsorbent (g) and *M* is the molecular weight of adsorbate (g). In adsorption experiments, q_t and c_t are replaced by q_e (equilibrium adsorption capacity) and c_e (equilibrium concentration of adsorbent), respectively.

Also, the percentage of CR molecules removed (R%) from the solution is calculated using Eq. 2

$$R\% = \frac{(c_0 - c_t)}{c_0} \times 100 \tag{2}$$

The relationship between q_e (mg g^{-1}) and c_e (M), has been studied using following adsorption isotherm equations. The Freundlich equation [7,8] is given as

$$q_e = K_F c_e^n \tag{3}$$

where *n* and K_F are the constants of equation. The parameter *n* in the Freundlich isotherm is as a measure of the heterogeneity of binding sites. Values of *n* range from 0 to 1 for decreasing heterogeneity.

The Langmuir equation [9] is represented by

$$\frac{c_e}{q_e} = \frac{1}{q_{\max} K} + \frac{c_e}{q_{\max}} \tag{4}$$

where *K* is the Langmuir adsorption constant and q_{max} is the monolayer capacity. The Dubinin-Radushkevich equation [10-12] is given by

$$ln\ q_e = ln\ q_D - B_D \left(RT\ ln\left(1 + \frac{1}{c_e}\right)\right)^2 \tag{5}$$

where B_D is related to the free energy of adsorption per mole of adsorbate (mol^2 J^{-2}) and q_D is the theoretical monolayer saturation capacity. The apparent energy of adsorption from Dubinin-Radushkevich isotherm, *E*, (J mol^{-1}) that gives information about chemical and physical adsorption can be computed using the relationship

$$E = \frac{1}{(2B_D)^{\frac{1}{2}}} \tag{6}$$

The Lagergern pseudo-first-order equation [13] is generally expressed as follows

$$\frac{dq_t}{dt} = k_1 (q_{e,1} - q_t) \tag{7}$$

where k_1 is the pseudo-first-order rate constant (min^{-1}) that relates to the amount of adsorbed CR and $q_{e,1}$ denotes the calculated equilibrium adsorption capacity.

After definite integration and applying the initial conditions $q_t=0$ at $t=0$ and $q_t=q_t$ at $t=t$, Eq. 7 becomes

$$ln(q_{e,1} - q_t) = ln\ q_{e,1} - k_1 t \tag{8}$$

But it is necessary to say that the Lagergern equation may be viewed as equivalent to the classical Vermeulen-Hiester approach of describing sorption rate by a series of resistances due to external mass transfer, intraparticle diffusion and adsorbate-adsorbent interaction. As a result, the Lagergern equation and its rate parameter lack clear cut significance since the parameter may be a rate constant, mass transfer coefficient, or their combinations [14-16].

The pseudo-second-order equation [17] based on adsorption equilibrium capacity may is expressed in the form

$$\frac{dq_t}{dt} = k_2(q_{e,2} - q_t)^2 \quad (9)$$

where k_2 is the pseudo-second-order rate constant (g mg^{-1} min^{-1}) that relates to the amount of CR adsorbed by the solid phase and $q_{e,2}$ denotes the calculated equilibrium adsorption capacity. After integration and applying boundary conditions $t=0$ to $t=t$ and $q_t=0$ to $q_t=q_t$, the integrated form of Eq. 9 becomes

$$\frac{1}{q_{e,2} - q_t} = \frac{1}{q_{e,2}} + k_2 t \quad (10)$$

which in its linear form can be written as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_{e,2}^2} + \frac{t}{q_{e,2}} \quad (11)$$

In order to quantitatively compare the applicability of these two models, Δq_t, normalized standard deviations of q_t, in relation to the experimental and calculated values of q_t, are given as

$$\Delta q_t = 100 \times \sqrt{\frac{\sum\left[\left(q_{t,\exp} - q_{t,cal}\right)/q_{t,\exp}\right]^2}{(n-1)}} \quad (12)$$

where n is the number of data points and $q_{t,exp}$ and $q_{t,cal}$ are experimental and calculated adsorption capacity of cellulose at a given time t, respectively.

To study the kinetics parameters for adsorption process the Avrami equation [18-21] is used to fit experimental results. This equation is as follows:

$$q_t = q_e(1 - \exp(-(k_a t)^{na})) \quad (13)$$

The linearized form of this equation is presented as:

$$ln\left(ln\left(\frac{q_e}{q_e - q_t}\right)\right) = n_a \, ln \, k_a + n_a \, ln \, t \quad (14)$$

where k_a is the Avrami kinetic constant and is a measure of adsorption of adsorbate and n_a is the Avrami exponent of time, which is related to the adsorption mechanism changes.

Aiming at improving the Avrami model, Tobin [22-24] proposed a different expression. The Tobin equation is generally expressed as

$$q_t = \frac{q_e k_t t^{n_t}}{1 + k_t t^{n_t}} \quad (15)$$

The linearized form of this equation is presented as:

$$ln\left(\frac{q_t}{q_e - q_t}\right) = ln \, k_t + n_t \, ln \, t \quad (16)$$

where k_t is the Tobin kinetic constant, and n_t is the Tobin exponent. n_t is governed directly by adsorption mechanism.

To investigate the mechanism of adsorption, the Elovich equation [25,26] was used. The Elovich equation is generally expressed as

$$\frac{dq_t}{dt} = \alpha \exp(-\beta \, q_t) \quad (17)$$

where α is the initial adsorption rate (mg g^{-1} min^{-1}). β is the adsorption constant (g mg^{-1}) related to the surface coverage and is the required mass of adsorbent for adsorption of 1 mg of adsobate. To simplify the Elovich equation, Chien and Clayton assumed αβ t>>1 and by applying the boundary conditions q_t=0 at t=0 and $q_t = q_t$ at $t=t$ Eq. 17 becomes

$$q_t = \frac{1}{\beta} ln(\alpha\beta) + \frac{1}{\beta} ln \, t \quad (18)$$

Mckay and Poots [27,28] proposed a pore-diffusion equation, given by

$$q_t = k_{dif} t^{0.5} + I \quad (19)$$

where k_{dif} (mg g^{-1} $min^{-0.5}$) is the pore-diffusion rate constant and I is proportional to the boundary layer diffusion effects.

3. Results and Discussion

3.1. Adsorption of CR on cellulose

Fig. 2 shows the adsorption of CR on cellulose at 308-328 K. As shown in Table 1, the Langmuir isotherm was fitted better than two other isotherms to the experimental data. Experimental q_e values and those of calculated using the Langmuir isotherm were compared by regression line method and no significant difference was observed.

As obtained from n values of the Freundlich isotherm, the binding sites are heterogeneous, Table 1. The binding constants of CR to cellulose obtained from the Langmuir isotherm, Table 1, were used to calculate enthalpy and entropy of the process. Results show that enthalpy of adsorption process is –25.9 kJ mol^{-1} and its entropy value is –4.6 J mol^{-1} K^{-1}. It is found that adsorption of CR on cattail root [5] and palm kernel coat [6] is exothermic.

Table 1. Coefficients of the Freundlich, Langmuir and Dubinin-Radushkevich isotherms for adsorption of CR on cellulose from aqueous solutions at 308–328 K.

T	Freundlich			Langmuir			Dubinin-Radushkevich		
(K)	K_F	n	R^2	q_{mon}	K	R^2	$\ln q_D$	E	R^2
308	3148	0.640	0.990	14.4	13515	0.991	4.890	10.1	0.996
318	2004	0.595	0.989	15.3	11891	0.998	4.708	10.7	0.993
328	4875	0.711	0.992	16.6	7260	0.997	5.023	10.1	0.996

Dimensions of K_F, K and E are in $M^{-\frac{1}{n}}$, M^{-1}, and kJ mol^{-1}, respectively. Dimension of q_{mon} and q_D is in mg g^{-1} and n is dimensionless.

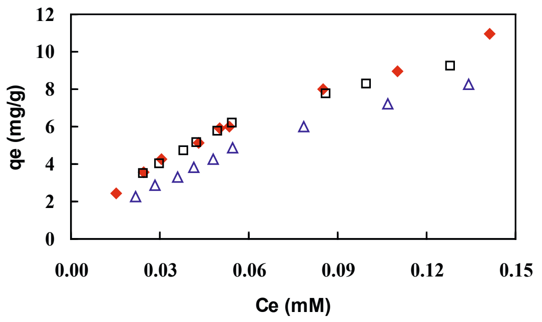

Figure 2. Variation of q_e vs. c_e for adsorption of CR on cellulose at ♦ 308, □ 318 and Δ 328 K.

The mean adsorption energy (E) values, obtained from the Dubinin-Radushkevich equation, are in the range of 10.1-10.7 kJ mol^{-1} at different temperatures which indicates that CR molecules adsorb on cellulose through chemical interaction, Table 1. It is found that CR, like many azo dyes [29-33], has a strong tendency to aggregate. As shown by the UV–Vis spectral changes of CR in its small concentration (3.5×10^{-5} M), CR molecules form face-to-face aggregates with zero or very little offset [34]. Interactions between the aromatic rings of CR molecules result in columnar aggregates of them [34]. CR dimers form from two π-π-stacked CR molecules [35], Fig. 1b. This dye can be adsorbed on the surface of cellulose by electrostatic interaction between -SO_3^- group of CR and OH group of cellulose and hydrogen binding of -NH_2 group of CR and ether oxygen atom of cellulose, Figs. 1b and c.

3.2. Adsorption kinetics

Figs. 3a-c show adsorption amounts of the CR on cellulose. Results show that the that equilibrium CR uptake, q_e, values decrease with increasing temperature, Table 3. Effects of time variations on extent of adsorption can be divided into three different regions, they are: (1) linear increase in adsorption with time, (2) transition region where the rate of adsorption levels off, and (3) a plateau region. The range over which the regions extend varies with the bulk concentration, presence of salt, nature of solid surface and so on [36].

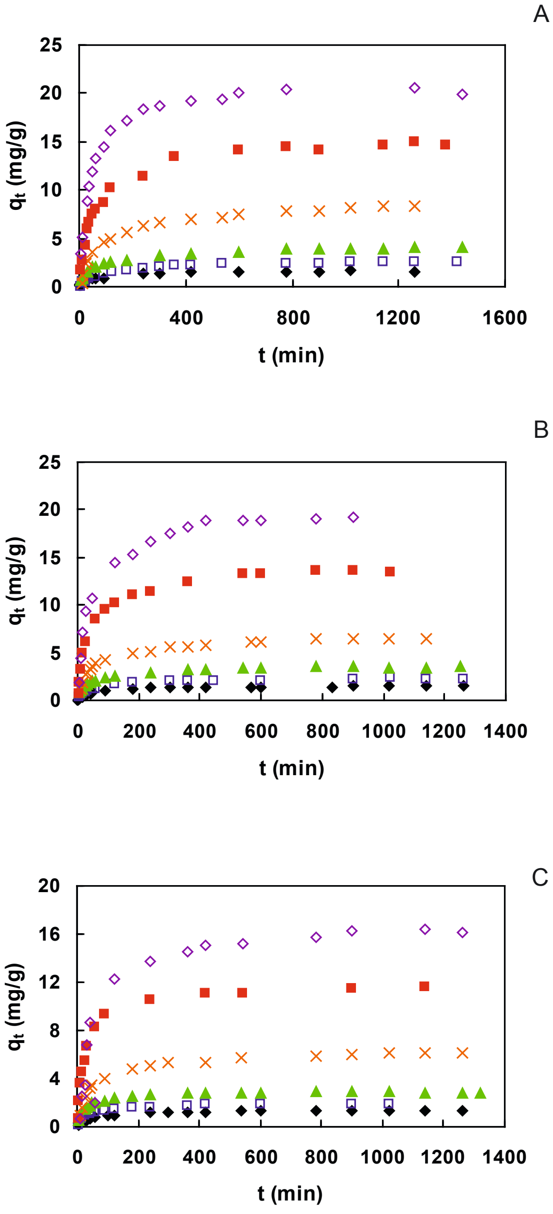

Figure 3. Variation of adsorption capacity, q_t, with time for adsorption of CR on cellulose at different initial concentrations of CR at (a) 308, (b) 318 and (c) 328 K. The initial concentrations of CR are ¨ 0.02, □ 0.045, ▲ 0.07, × 0.2, ■ 0.45 and ◊ 0.7 mM.

Table 2. Coefficients of the Lagergern, pseudo-second-order and Elovich equations for kinetics of CR adsorption on cellulose from aqueous solutions at 308–328 K.

[CR]	Lagergern			Pseudo-second-order			Elovich		
(mM)	$q_{e,1}$	$k_1 \times 10^2$	Δq_t	$q_{e,2}$	$k_2 \times 10^3$	Δq_t	α	β	R^2
					T=308 K				
0.02	1.45	1.60	19.9	1.68	11.0	10.2	0.079	3.186	0.995
0.045	2.35	0.90	16.9	2.76	3.87	7.3	0.063	1.680	0.995
0.07	3.39	1.67	23.0	4.22	3.57	17.2	0.248	1.490	0.997
0.20	7.18	1.13	12.3	8.82	1.25	8.0	0.301	0.626	0.996
0.45	12.88	1.61	10.5	15.34	1.13	5.1	0.643	0.329	0.981
0.70	18.58	1.99	2.6	21.23	1.15	3.9	0.940	0.185	0.988
					T=318 K				
0.02	1.36	1.88	14.2	1.54	15.4	4.4	0.083	3.220	0.995
0.045	1.82	2.04	16.5	2.39	8.01	9.2	0.132	2.294	0.996
0.07	3.06	2.35	18.1	3.62	7.02	10.1	0.304	1.629	0.995
0.20	5.71	2.06	10.1	6.84	2.63	9.9	0.596	0.942	0.996
0.45	11.70	2.58	12.7	14.29	1.58	10.6	1.009	0.374	0.992
0.70	16.98	2.69	4.8	20.00	1.35	9.3	1.547	0.277	0.992
					T=328 K				
0.02	1.19	2.15	21.4	1.43	15.2	13.2	0.095	4.029	0.996
0.045	1.66	2.71	14.4	1.94	15.8	6.8	0.196	2.986	0.996
0.07	2.51	3.28	19.7	2.88	16.3	6.8	0.377	1.954	0.992
0.20	5.28	2.16	7.0	6.33	3.19	6.1	0.355	0.851	0.980
0.45	10.42	3.21	13.6	11.93	2.71	14.0	0.993	0.383	0.988
0.70	14.59	1.80	7.3	17.01	1.02	9.5	1.709	0.425	0.969

Dimension of $q_{e,1}$ and $q_{e,2}$ is in mg g^{-1}. Dimensions of k_1 and k_2 are in min^{-1} and g mg^{-1} min^{-1}, respectively. Dimensions of α and β are in mg g^{-1} min^{-1} and g mg^{-1}, respectively.

Table 3. Coefficients of the Tobin and Avrami equations for kinetics of CR adsorption on cellulose from aqueous solutions at 308–328 K.

[CR]	Tobin			Avrami			
(mM)	$k_t \times 10^2$	n_t	R^2	q_e	$k_a \times 10^2$	n_a	R^2
				T=308 K			
0.02	2.39	0.970	0.990	1.60	0.93	0.658	0.991
0.045	1.09	1.048	0.989	2.57	0.65	0.698	0.994
0.07	4.13	0.817	0.987	3.97	0.85	0.549	0.997
0.20	1.37	1.002	0.986	8.26	0.73	0.600	0.996
0.45	1.57	1.056	0.973	14.58	1.12	0.642	0.984
0.70	2.02	1.081	0.995	20.53	1.40	0.712	0.987
				T=318 K			
0.02	2.79	0.959	0.994	1.50	1.24	0.658	0.995
0.045	2.73	0.957	0.994	2.29	1.07	0.598	0.995
0.07	5.05	0.844	0.983	3.53	1.34	0.545	0.993
0.20	3.88	0.864	0.989	6.52	1.14	0.525	0.986
0.45	2.56	1.026	0.986	13.43	1.51	0.593	0.988
0.70	3.98	0.931	0.985	19.20	1.48	0.664	0.984
				T=328 K			
0.02	4.51	0.832	0.997	1.40	1.09	0.573	0.992
0.045	4.27	0.946	0.994	1.86	1.75	0.652	0.989
0.07	6.54	0.894	0.991	2.81	2.26	0.608	0.996
0.20	2.62	0.969	0.987	6.08	1.19	0.564	0.981
0.45	2.94	1.068	0.991	11.65	2.11	0.606	0.981
0.70	1.10	1.158	0.967	16.27	1.44	0.521	0.978

Dimensions of q_e, k_t and k_a are in mg g^{-1}, min^{-nt} and min^{-1}, respectively and n_a and n_t are dimensionless.

To investigate the mechanism of adsorption, a number of kinetic equations were used to test the experimental data. At first, we compared the results obtained from the Lagergern and pseudo-second-order equations.

The best fittings were detected using pseudo-second-order equation, Fig. 4 and Tables 2 and 3, and in all cases $q_{e,2}$ values are more similar to the q_e values compared to $q_{e,1}$ values obtained from the Lagergern equation. As given in Table 2, k_2 values increase with increase in temperature. It is found that in adsorption of CR on anilinpropylsilica xerogel [2], cattail root [5] and palm kernel coat [12], the results were better fitted to pseudo-second-order equation. As reported [37], if the sorption kinetics follows pseudo-first-order, then its rate constant, k_2, should increase with increasing initial concentration of solute in a linear form. But, k_2 is a complex function of the solute initial concentration [37].

It was observed from the Elovich equation that α values increase with increase in concentration of CR and temperature, Table 2. As seen in Fig. 5, the initial adsorption rate of the process is first-order in CR.

According to Table 3, the Avrami rate constant k_a exhibits sensitivity to the change in adsorption temperature and increases with increasing temperature. This is because CR adsorbs faster at higher temperatures. This observation is only true when the temperature is in the range for which adsorption is not the rate-determining factor [38,39]. As seen in Table 3, *n* values are in the range of 0.549-0.712, 0.525-0.664 and 0.521-0.652 at 308, 318 and 328 K, respectively.

Data were fitted properly to the Tobin equation up to $\frac{q_t}{q_e} > 0.9$ and k_t and n_t values of adsorption of CR on the cellulose are shown in Table 3.

For the adsorption of the adsorbates onto the adsorbent in aqueous solution, two diffusion steps are absolutely necessary: (1) mass transfer from water to the adsorbent surface across the boundary layer (film diffusion) and (2) diffusion of adsorbate molecules within the pores of material, binding the pores and capillary spaces (intraparticle diffusion) [21].

When the plots do not pass through the origin, this is indicative of some degree of boundary layer control and this shows further that the intraparticle diffusion is not the only rate-controlling step, but other processes may also control the rate of adsorption, all of which may be operating simultaneously [21].

The values of the intercepts give an idea about the boundary layer thickness: the greater the intercept, the greater the boundary layer effect. The boundary-layer resistance is affected by the rate of adsorption and increase in contact time, which reduces the resistance and increases the mobility of dye during adsorption. However, the negative values of the intercepts of the first region of adsorption kinetics profiles, shown in Table 4, suggest that the boundary-layer effect is close to minimum [21,40] and diffusion of the CR molecules into the filter paper is the main rate-controlling step. As seen in Table 4, in the second region of adsorption kinetics profiles the intraparticle diffusion starts to decrease due to the low concentration of CR in solution as well as fewer available adsorption sites.

The effect of contact time on the adsorption of CR onto cellulose was studied. The removal percentage value in the beginning of plateau decreases with increase in both temperature and CR concentration. In this series of experiments, the time required for adsorption to be completed, is at most 1260 min of contact.

4. Conclusion

According to the results obtained from adsorption isotherms, we can conclude that in the used concentration range of CR, interaction of CR with cellulose is exothermic and CR molecules adsorb on cellulose surface through chemical interactions. Kinetic data were modeled using the pseudo-second-order equation. It is obtained from the Elovich equation that initial adsorption rate of adsorption is first-order in CR and diffusion of the CR molecules into the filter paper is the main rate-limiting step of the process.

Table 4. Coefficients of the pore-diffusion equation for the first and second regions for kinetics of CR adsorption on cellulose from aqueous solutions at 308–328 K.

[CR]	Pore-diffusion (1st)			Pore-diffusion (2nd)		
(mM)	k_{dif}	I	R^2	k_{dif}	I	R^2
			T=308 K			
0.02	0.127	–0.103	0.989	0.053	0.429	0.983
0.045	0.149	–0.106	0.973	0.081	0.644	0.986
0.07	0.308	–0.101	0.995	0.098	1.462	0.999
0.20	1.080	–3.078	0.996	0.276	1.949	0.996
0.45	1.397	–2.257	0.969	0.307	6.920	0.938
0.70	1.989	–2.184	0.997	0.661	8.332	0.976
			T=318 K			
0.02	0.123	–0.072	0.995	0.046	0.575	0.994
0.045	0.206	–0.150	0.989	0.025	1.528	0.946
0.07	0.303	–0.005	0.990	0.103	1.306	0.957
0.20	0.774	–1.198	0.993	0.137	2.988	0.978
0.45	1.725	–2.272	0.974	0.294	6.920	0.990
0.70	2.363	–2.411	0.982	0.476	9.175	0.991
			T=328 K			
0.02	0.115	–0.041	0.995	0.024	0.752	0.985
0.045	0.185	–0.076	0.982	0.049	0.878	0.984
0.07	0.301	–0.031	0.997	0.089	1.335	0.983
0.20	0.652	–0.985	0.981	0.116	3.161	0.927
0.45	1.519	–1.711	0.974	0.160	7.853	0.953
0.70	2.521	–7.142	0.999	0.316	8.671	0.994

Dimensions of k_{dif} and *I* are in mg g^{-1} min$^{-0.5}$ and mg g^{-1}, respectively.

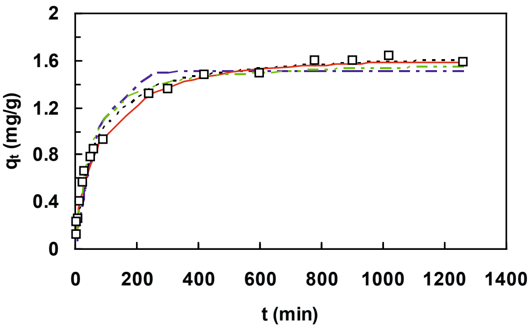

Figure 4. Typical profiles of adsorption capacity, q_t, with time for adsorption of CR on cellulose in 0.02 mM CR obtained from the — Avrami, – . – Lagergern, --- pseudo-second-order, – . . – Tobin equations and □ experimental work at 308 K.

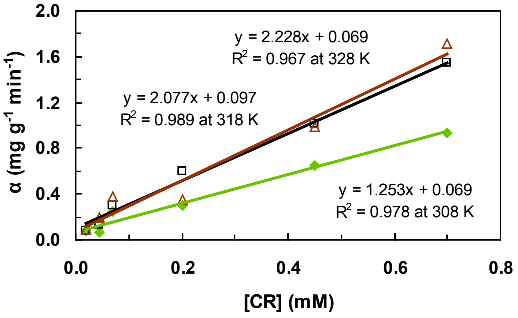

Figure 5. Variation of initial rate constants, α, with initial concentrations of CR for adsorption of CR on cellulose at ♦ 308, □ 318 and Δ 328 K.

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