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Kinetics and mass transfer models for sorption of titanium industry effluent in activated carbon

Nisha Subash, R. Krishna Prasad*

Department of Chemical Engineering & Materials Science, Center of Excellence in Advanced Materials & Green Technologies, Amrita Vishwa Vidyapeetham University, Ettimadai, Coimbatore 641 112, India, Tel. +91 422 268500; Fax: +91 422 2656274; emails: nishasubash92@gmail.com (N. Subash), rkprasad_cbe@rediffmail.com (R. Krishna Prasad)

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ABSTRACT

The batch adsorber data obtained for removal of dissolved solids in titanium industry effluent by sorption in activated carbon was found to fit Freundlich, Langmuir, and Dubinin–Radushkevich isotherm models and the various non-linear error functions evaluated have low error values for these adsorption models. The applicability of pseudo-second-order models in adsorption kinetics has been explained and the predictive models at various dilutions were obtained. The external mass transfer coefficient obtained from various models, such as Mathews–Weber and Furusawa–Smith, was used to calculate the Biot number. The Biot number values were less than 100, which suggest that the external film coefficients control the adsorption process. The change in enthalpy of the adsorption process was $-48\ \mathrm{kJ\,mol^{-1}}$, suggesting the release of exothermic heat during the sorption process. The analysis of various functional groups in the effluent was done using Fourier transform infrared spectroscopy.

Keywords: Adsorption; Titanium effluent; Mass transfer models; Adsorption kinetics; Thermodynamic analysis; Activated carbon

1. Introduction

Titanium dioxide is manufactured by either the sulfate process or chloride process. The sulfate process was the first commercial-scale technology used to convert ilmenite (mixture of titanium, ferrous iron, and ferric iron) to titanium dioxide [1]. The sulfate effluent is extremely acidic and toxic, which can be treated by various techniques such as neutralizing with alkaline medium, acid recovery process, and conversion of effluent to non-toxic forms [2]. The treatment of sulfate effluents by neutralizing with alkaline medium produces low-quality products like gypsum having low sales value when compared with effluent treatment cost and the acid recovery is a highly energy-intensive process [2].

The application of the adsorption technique is widely used to remove the volatile organic compounds and dyes due to its low cost, simple operation, and possibility of recovery of valuable solutes adsorbed [3]. The various forms of adsorbents used in effluent treatment are activated carbon from coal, coke, and peat [4], coal fly ash [5], biomass-activated carbon [6], fly ashes [7], rice husk ash [8], and sawdust [9]. The activated carbon is used to adsorb inorganic pollutants from wastewater, due to their high surface

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*Corresponding author.

area, microporous character, and chemical nature of their surface [10,11]. This study is performed to analyze the usefulness of activated carbon as adsorbent in removing the pollutants present in titanium industry effluent.

2. Materials and methods

The effluent used in this study was collected from titanium dioxide manufacturing plant. The physico-chemical characteristics of the effluent studied are provided in Table 1. The batch adsorption studies were done with 100 ml samples at different dilutions (10, 20, 30, and 40% of original sample) treated with a powdered activated carbon dosage of 2 g. The samples were stirred in an ultrasonicator at different temperatures (303, 313, and 323 K) for 2 h. The total dissolved solids in the effluent samples were measured after filtration with Whatman 42 filter paper for every 30 min using total dissolved solids meter. The initial total dissolved solids in the titanium effluent at different dilutions, such as 10, 20, 30, and 40% of the original solution are 15,200, 28,000, 47,200, and 53,000 mg l^{-1}, respectively. The chemical oxygen demand of the titanium effluent at different dilutions such as 10, 20, 30, and 40% of the original solution are 192, 260, 400, and 3,000 mg l^{-1}, respectively. The Fourier transform infrared spectroscopy (FT-IR) recorded using Thermo Nicolet is 10. FT-IR spectrometer using KBr pellets was in the range of 500–4,000 cm^{-1}.

Specific uptake is calculated using the following expression [12]:

$$q_t = \frac{(C_0 - C_t)}{M} \tag{1}$$

Table 1
Physico-Chemical characteristics of titanium dioxide effluent

Properties	Value
Color	350 Hazen
Odor	Acidic
pH	0.7
Total dissolved solids (TDS)	70,900 mg l^{-1}
Total suspended solids (TSS)	14 mg l^{-1}
Turbidity	0.4 NTU
H_2SO_4	50,156 mg l^{-1}
Sulphates as SO_4	49,173 mg l^{-1}
Biochemical oxygen demand (BOD)	1,321 mg l^{-1}
Chemical oxygen demand (COD)	6,000 mg l^{-1}
Electrical conductivity	118,166 μmhos cm^{-1}

3. Results and discussion

3.1. Studies on various adsorption isotherms

Different adsorption isotherms were studied to determine the best isotherm, which can be used to design the single-stage batch adsorber for adsorption of titanium effluent onto activated carbon. The Freundlich sorption isotherm is represented by the empirical model represented below [13]:

$$q_e = K_f C_e^{1/n_f} \tag{2}$$

The linearized form of Freundlich isotherm is expressed as follows.

$$\ln q_e = \ln K_f + 1/n_f \ln C_e \tag{3}$$

The plot of ln q_e vs. ln C_e yields a straight line with slope $1/n_f$ and intercept ln K_f. Different values of n_f (2.1, 1.75, and 1.62) and K_f (4.33, 1.9, and 1.33) were obtained for batch adsorption studies at 303, 313, and 323 K, respectively. The values of n_f lie in the favorable range of 1–10 for the adsorption process.

The Langmuir adsorption isotherm is based on the characteristic assumptions that only monomolecular adsorption takes place, adsorption is localized, and the heat of adsorption does not depend on surface coverage. The Langmuir isotherm is expressed as follows [14,15]:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{4}$$

The separation factor, R_L of the Langmuir isotherm indicates that the adsorption is spontaneous or non-spontaneous:

$$R_L = \frac{1}{1 + K_L C_0} \tag{5}$$

The parameter R_L indicates the shape of the isotherm and the possibilities of the adsorption process (if $R_L > 1$ the isotherm is unfavorable, if $R_L = 1$ the isotherm is linear, if $0 < R_L < 1$ the adsorption process is favorable, and if $R_L = 0$ the adsorption process is irreversible). The linear forms of the four Langmuir isotherm models are given in Table 2 [14,15]. The Langmuir isotherm parameters and correlation coefficients evaluated for different temperatures studied are provided in Table 2. The separation factor, R_L, for the different temperatures studied was in the range of 0.0012–0.6313 indicating a favorable adsorption

Table 2
Various linear forms of Langmuir isotherm kinetic model, isotherm constants and correlation coefficients

Type	Linear form	Plot	Parameters	303 K	313 K	323 K
1	$\frac{C_e}{q_e} = \frac{1}{q_m}C_e + \frac{1}{K_L q_m}$	$\frac{C_e}{q_e}$ *vs* C_e	K_L (l mg^{-1})	0.020	0.015	0.012
			q_m (mg g^{-1})	939.29	1,217.02	1,454.76
			r^2	0.995	0.986	0.968
2	$\frac{1}{q_e} = \left(\frac{1}{K_L q_m}\right)\cdot\frac{1}{C_e} + \frac{1}{q_m}$	$\frac{1}{q_e}$ *vs* $\frac{1}{C_e}$	K_L (l mg^{-1})	6.22×10^{-5}	3.8×10^{-5}	2.93×10^{-5}
			q_m (mg g^{-1})	898.80	1,308.33	1,696.88
			r^2	0.996	0.995	0.985
3	$q_e = q_m - \left(\frac{1}{K_L}\right)\cdot\frac{q_e}{C_e}$	q_e *vs* $\frac{q_e}{C_e}$	K_L (l mg^{-1})	6×10^{-5}	4.17×10^{-5}	3.84×10^{-5}
			q_m (mg g^{-1})	913.91	1,243.43	1,444.36
			r^2	0.980	0.957	0.863
4	$\frac{q_e}{C_e} = K_L q_m - K_L q_e$	$\frac{q_e}{C_e}$ *vs* q_e	K_L (l mg^{-1})	5.88×10^{-5}	3.99×10^{-5}	3.32×10^{-5}
			q_m (mg g^{-1})	921.91	1,272.69	1,571.48
			r^2	0.980	0.957	0.863

process. The values of non-linear error functions are found to be higher than those of Freundlich, but lower than those of other isotherms.

The Sips isotherm is a combination of Freundlich and Langmuir isotherm models and is expressed as follows [16]:

$$q_e = \frac{q_m (a_{\mathrm{LF}} C_e)^n}{1 + (a_{\mathrm{LF}} C_e)^n} \tag{6}$$

The Sips isotherm reduces to the Freundlich model at low concentrations of the adsorbate and to the Langmuir model at high concentrations of the adsorbate. The equation parameters are mainly dependent on the operating conditions, such as pH, temperature, and concentration. The Sips isotherm constants evaluated using Curve Expert 1.4 are given in Table 3. The linear regression coefficients at different temperatures are close to one, but the non-linear errors evaluated (not shown) showed a larger deviation from the experimental data and hence the Sips model is not considered representing the adsorption data obtained.

The Dubinin–Radushkevish (DR) isotherm assumes that sorption has a multilayer character with heterogeneity of surface energies and involves van der Waals forces. The linear form of the DR isotherm is expressed as follows [17]:

$$\ln C_{\mathrm{ads}} = \ln X_m - \beta\varepsilon^2 \tag{7}$$

$$\varepsilon = RT \ln \frac{C_0}{C_e} \tag{8}$$

β can be correlated with the mean free energy, E, of sorption per molecule of adsorbate, when it is transferred to the solid from infinity in the solution:

$$E = \frac{1}{(-2\beta)^{0.5}} \tag{9}$$

The isotherm parameters of DR model are given in Table 3 and the energy of adsorption indicates a physisorption process.

The values of the non-linear error functions for Freundlich, Langmuir, and DR models showed less deviation as shown in Table 4.

3.2. Studies on adsorption kinetics

Different adsorption kinetics, such as first and second order, were studied for analyzing the best

Table 3
Sips isotherm constants and Dubinin–Radushkevich isotherm constants for the sorption of titanium effluent onto activated carbon at different temperatures

	Sips isotherm constants				Dubinin–Radushkevich isotherm constants			
Temperature (K)	q_m (mg g^{-1})	a_{LF} (l mg^{-1})	n	r^2	X_m (mg g^{-1})	β ($\times10^{-7}$ g/mg)	E (kJ g^{-1})	r^2
303	94.73	9.96	0.391	0.999	837.61	5.12	−987.54	0.994
313	60.90	6.69	0.484	0.986	1,245.82	6.08	−906.35	0.935
323	84.33	7.28	0.235	0.990	1,503.92	5.37	−964.36	0.789

Table 4
The values of error functions for different isotherms for sorption of titanium effluent in activated carbon at 303 K

Isotherm	χ^2	SSE	HYBRD	MPSD	ARE	EABS
Freundlich	0.246	120.94	0.244	0.0005	0.037	18.084
Langmuir Type-1	0.869	421.33	0.868	0.0019	0.084	40.780
Langmuir Type-2	1.032	592.81	1.025	0.0018	0.069	37.874
Langmuir Type-3	0.001	485.82	0.886	0.0017	0.075	39.137
Langmuir Type-4	0.001	452.30	0.852	0.0017	0.078	39.722
Dubinin–Radushkevich	0.957	566.55	0.949	0.0016	0.076	42.20
HO Type-1	2,479	5,373,430	16,049	48.793	9.141	3,445
HO Type-2	1,027	1,202,979	3457.8	10.217	4.517	1,751
HO Type-3	189	146,884	282.45	0.555	1.256	649
HO Type-4	5,949	3,026,692	93,343	289	19.894	7,025
Lagergren	1,476	1,866,473	3481.04	7	5.178	2,610

Table 5
Elovich isotherm constants for the sorption of titanium effluent onto activated carbon at different temperatures

	303 K			313 K			323 K		
Dilution (%)	α	β	r^2	α	β	r^2	α	β	r^2
10	7.92	0.006	0.874	9.45	0.006	0.964	65.30	0.014	0.949
20	13.65	0.005	0.879	20.54	0.005	0.859	34.77	0.005	0.996
30	39.74	0.005	0.981	40.24	0.004	0.985	69.44	0.004	0.975
40	22.57	0.004	0.791	29.95	0.003	0.904	41.67	0.003	0.975

Table 6
Pseudo first order constants and predicative correlations for the sorption of titanium effluent in activated carbon at different dilutions

Initial dilution (%)	$q_{e,\mathrm{expt}}$	First order model			Predicted pseudo first order equation
		$q_{e,\ \mathrm{pre}}$	K_1	r_1^2	
10	320	785	0.093	0.649	$q_t = 785–785/\exp^{0.093t}$
20	467	1,127	0.099	0.659	$q_t = 1{,}127–1{,}127/\exp^{0.099t}$
30	613	1,119	0.117	0.913	$q_t = 1{,}119–1{,}119/\exp^{0.117t}$
40	660	1,638	0.103	0.645	$q_t = 1{,}638–1{,}638/\exp^{0.103t}$

Table 7
Pseudo-second-order predicative correlations at different dilutions (10 and 20%) for adsorption of titanium effluent in activated carbon (Temperature = 303 K)

Type	Linear form	10% dilution	20% dilution
Type 1	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$	$\frac{t}{q_t} = \frac{1}{(4.39\times10^{-7})(2{,}503)^2} + \frac{1}{(2{,}503)} t$	$\frac{t}{q_t} = \frac{1}{(5.1\times10^{-6})(1{,}074)^2} + \frac{1}{(1{,}074)} t$
Type 2	$\frac{1}{q_t} = \left(\frac{1}{k_2 q_e^2}\right)\frac{1}{t} + \frac{1}{q_e}$	$\frac{1}{q_t} = \left(\frac{1}{(1.79\times10^{-6})(1{,}287)^2}\right)\frac{1}{t} + \frac{1}{(1{,}287)}$	$\frac{1}{q_t} = \left(\frac{1}{(7.66\times10^{-6})(908)^2}\right)\frac{1}{t} + \frac{1}{(908)}$
Type 3	$q_t = q_e - \left(\frac{1}{k_2 q_e}\right)\frac{q_t}{t}$	$q_t = 362 - \left(\frac{1}{(4.11\times10^{-5})(362)}\right)\frac{q_t}{t}$	$q_t = 750 - \left(\frac{1}{(1.27\times10^{-5})750}\right)\frac{q_t}{t}$
Type 4	$\frac{q_t}{t} = k_2 q_e^2 - k_2 q_e q_t$	$\frac{q_t}{t} = (8 \times 10^{-8})(5,726)^2 - (8 \times 10^{-8})(5,726) q_t$	$\frac{q_t}{t} = (3.35 \times 10^{-6})(1,291)^2 - (3.35 \times 10^{-6})(1,291) q_t$

Table 8
Mass transfer coefficients and Biot number calculations

Dilution (%)	External mass transfer coefficient, k_f Mathews and Weber model ($\times 10^{-5}$) (cm min^{-1})			External mass transfer coefficient, k_f, Furusawa and Smith model ($\times 10^{-5}$) (cm min^{-1})			Internal mass transfer coefficient, D ($\times 10^{-8}$) (cm^2 min^{-1})			Biot number, B_N Using Mathews and Weber			Biot number, B_N Using Furusawa and Smith		
	303 K	313 K	323 K	303 K	313 K	323 K	303 K	313 K	323 K	303 K	313 K	323 K	303 K	313 K	323 K
10	13.98	13.49	6.99	21.5	53.1	7.49	2.94	5.04	24. 1	35.22	19.79	2.148	54.25	77.95	2.300
20	9.06	9.41	9.63	12.1	23.0	10.2	3.12	3.26	31.9	21.47	21.38	2.234	28.77	52.20	2.365
30	4.85	6.31	5.88	9.05	11.2	6.13	16.1	6.90	31.7	2.237	6.767	1.372	4.179	12.04	1.431
40	5.62	6.11	6.55	6.86	9.53	6.78	2.71	3.97	32.8	15.34	11.38	1.476	18.72	17.75	1.528

possible representative kinetics for the sorption of titanium effluent in activated carbon. The Elovich kinetic model is a useful model to describe the reactions that involve chemical adsorption onto a solid surface without desorption of products. In such cases, the rate of adsorption decreases exponentially with time due to increased surface coverage [18].

The general equation of the Elovich kinetic model is as follows:

$$\frac{dq_t}{dt} = \alpha \exp(-\beta q_t) \tag{10}$$

The above equation is simplified by Chien and Clayton assumption ($\alpha\beta t >> 1$) by applying the boundary condition $q_t = 0$ at $t = 0$ and $q_t = \mathrm{t}$ at $t = t$ as follows [19,20]:

$$q_t = \ln\frac{\alpha\beta}{\beta} + \frac{1}{\beta}\ln t \tag{11}$$

The constants α and β were obtained from the plot q_t vs. ln t, where the slope gives $1/\beta$ and the intercept yields $1/\beta$ ln ($\alpha\beta$). The Elovich kinetic model parameters at different temperatures for adsorption of titanium effluent onto activated carbon are given in Table 5. The Lagergren pseudo-first-order kinetics based on solid capacity gives the pseudo-first-order kinetic model as follows [21].

$$dq_t/dt = K_1(q_e - q_t) \tag{12}$$

Integrating for the boundary conditions $t = 0$ to $t = \mathrm{t}$ and $q_t = 0$ and $q_t = q_e$, the expression reduces as follows:

$$\ln(q_e - q_t) = \ln q_e - (K_1 t)/2.303 \tag{13}$$

The values of q_e and K_1 are obtained from the slope and intercept of the plot ln(q_e—q_t) vs. $t/2.303$. The values of pseudo-first-order constant and predicative correlations for Lagergren pseudo-first-order model at different dilutions for adsorption of titanium effluent onto activated carbon are given in Table 6.

The expression of the pseudo-second-order Ho model based on solid capacity has been presented for the kinetics of sorption of titanium effluent in activated carbon as follows [22,23]:

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \tag{14}$$

Eq. (14) can be rearranged to obtain

$$q_t = \frac{t}{1/k_2 q_e^2 + t/q_e} \tag{15}$$

The pseudo-second-order Ho model can be linearized in four different types as given in Table 7. The predicative correlations for Ho’s four types of isotherm for adsorption of titanium effluent onto activated carbon at different dilutions (10 and 20%) are given in Table 7.

3.3. Mass transfer studies

The different mass transfer models were studied to determine the Biot number and to understand the various diffusion mechanisms. The diffusion-controlled kinetic models based on experimental data predict diffusion mechanisms inside the adsorbent. The external diffusion model assumes that the concentration at the adsorbent surface is zero and the intraparticle diffusion is negligible. The external diffusion is described based on the Mathews and Weber model as follows [24]:

$$\ln\frac{C_t}{C_0} = -k_f \frac{a}{V} t \tag{16}$$

$$\frac{a}{V} = \frac{6M}{\rho D} \tag{17}$$

The plot of $\ln(C_t/C_0)$ vs. t is used to determine the initial external mass transfer coefficient.

The Furusawa and Smith model [25] is used to calculate the external mass transfer coefficient as follows:

$$\begin{aligned}\ln\left(\frac{C_t}{C_0} - \frac{1}{1+m_S K_L}\right) &= \ln\left(\frac{m_S K_L}{1+m_S K_L}\right)\\ &\quad - \left(\frac{m_S K_L}{1+m_S K_L} k_f S_a t\right)\end{aligned} \tag{18}$$

Rearranging Eq. (18)

$$\frac{1}{1+1/m_S K_L}\ln\left(\frac{C_t}{C_0} - \frac{1}{m_S K_L}\left(1-\frac{C_t}{C_0}\right)\right) = -k_f S_a \tag{19}$$

The pore and surface mass diffusion is governed by Fick’s law and intraparticle diffusion. The sum of pore and surface diffusion is calculated from the following equation:

$$-\log\left(1-\left(\frac{q_t}{q_e}\right)^2\right) = \frac{4\pi D t}{2.303 d^2} \tag{20}$$

The Biot number can be calculated using external and internal diffusion coefficients as follows [26]:

$$B_N = k_f \frac{d}{D} \tag{21}$$

The value of the Biot number indicates the predominance of surface diffusion against external diffusion. The adsorption process is mainly controlled by internal diffusion mechanism if the Biot number is greater than 100; and it is controlled by the film transfer if the Biot number is less than 100 [27]. The external mass transfer coefficients calculated using the Mathews–Weber model and the Furusawa–Smith model along with internal mass transfer coefficients and the Biot number are presented in Table 8. The Biot number values calculated using both the models are less than 100, indicating that the adsorption process of titanium effluent onto activated carbon is controlled by film transfer.

3.4. Thermodynamic studies

The thermodynamic parameters ΔG^0, ΔH^0, and ΔS^0 estimated from the experimental data obtained at different temperatures are shown in Table 9.

Gibbs free energy can be related to the enthalpy change and entropy change at constant temperature by the Van’t Hoff equation [28]:

$$\ln K_T = -\frac{\Delta G^0}{RT} = \frac{\Delta S^0}{R} = -\frac{\Delta H^0}{RT} \tag{22}$$

The values of Gibbs free energy obtained at different temperatures are negative, which implies that the

Table 9
Thermodynamic constants calculated for sorption of titanium effluent onto activated carbon using Freundlich isotherm

Temperature (K)	ΔG^0 (kJ mol^{-1})	ΔH^0 (kJ mol^{-1})	ΔS^0 (J mol^{-1} K^{-1})	r^2
303	−3.694	−48.105	147.15	0.957
313	−1.673			
323	−7.746			

adsorption reaction is feasible and spontaneous. The change in enthalpy in the adsorption process is −48 kJ mol^{-1}, which implies that the adsorption process is exothermic and heat is released during the sorption process. The change in entropy of the system is positive, which implies that the randomness of adsorption process increases and the observed entropy change is 147 J mol^{-1} K^{-1}.

4. Conclusion

The data obtained for the adsorption of titanium compounds from the aqueous effluent onto activated carbon were found to fit the Langmuir isotherm model $C_e/q_e = 0.001C_e + 0.054$ at 303 K. The pseudo-second-order model was used to describe the adsorption kinetics of the process at different dilutions. The process of adsorption of titanium effluent onto activated carbon was found to be controlled by external film because the Biot number was less than 100. Gibbs free energy at different temperatures is negative, suggesting that the adsorption reaction is feasible and spontaneous. The change in entropy of the system is 147 J mol^{-1} K^{-1}, which indicates that the randomness of the adsorption process increases. The feasibility of adsorption of titanium industry effluent using activated carbon is proved based on the adsorption capacity of the process in the single-stage adsorber unit.

Nomenclature

q_t	—	amount of spent wash solution adsorbed per unit mass of adsorbent at time t (mg g^{-1})
C_t	—	concentration of spent wash solution at time t (mg L^{-1})
C_0	—	initial concentration of spent wash solution (mg L^{-1})
M	—	dosage of adsorbent (g)
q_e	—	equilibrium concentration in solid phase (mg g^{-1})
C_e	—	equilibrium concentration in liquid phase (mg L^{-1})
n_f, K_f	—	Freundlich parameters
q_m	—	Langmuir isotherm parameter, maximum effluent adsorbed/unit mass of adsorbent (mg g^{-1})
K_L	—	Langmuir adsorption constant (L mg^{-1})
R_L	—	Langmuir separation or equilibrium parameter
n, a_{LF}	—	Sips isotherm constant
C_{ads}	—	amount of sorbate sorbed onto sorbent surface (mg g^{-1})
X_m	—	maximum sorption capacity of sorbent (mg g^{-1})
R	—	universal gas constant (8.314 J mol^{-1} K^{-1})
T	—	temperature (K)
E	—	sorption energy (kJ g^{-1})
K_1	—	pseudo-first-order rate constant (min^{-1})
k_2	—	pseudo-second-order rate constant (g mg^{-1} min^{-1})
a	—	total interfacial area of the particles (cm^2)
V	—	total solution volume (L)
k_f	—	initial external mass transfer coefficient (cm min^{-1})
M	—	amount of adsorbent (g)
d	—	mean particle diameter (cm)
D	—	intraparticle diffusion (cm^2 min^{-1})
B_N	—	Biot number
m_s	—	concentration of sorbent in liquid phase (mg L^{-1})
S_a	—	outer surface area of adsorbent particles per unit volume of particle free slurry (cm^{-1})
ΔG^0	—	Gibbs free energy change (J/mol)
ΔH^0	—	change in enthalpy (J/mol)
ΔS^0	—	change in entropy (J mol^{-1} K^{-1})
K_T	—	sorption equilibrium constant
SSE	—	sum of square errors
HYBRD	—	composite fractional error function
MPSD	—	derivative of Marquardt's percent standard deviation
ARE	—	average relative error
EABS	—	sum of absolute errors
r^2	—	linear regression correlation coefficient

Greek letters

α	—	initial adsorption rate (mg g^{-1} min^{-1})
β	—	desorption constant (g mg^{-1})
ε	—	Polanyi sorption potential
χ^2	—	chi-square
ρ	—	apparent density of the adsorbent (g ml^{-1})

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