Removal of Cadmium Ions from Synthetic Aqueous Solutions with a Novel Nanosulfonated Poly(glycidyl methacrylate) Cation Exchanger: Kinetic and Equilibrium Studies

M. S. Mohy-Eldin,[1] **M. F. Elkady,**[2] **M. A. Abu-Saied,**[1] **A. M. Abdel Rahman,**[3] **E. A. Soliman,**[1] **A. A. Elzatahry,**[1] **M. E. Youssef**[4]

[1]Polymer Materials Research Department, Advanced Technology and New Materials Research Institute, Mubarak City for Scientific Research and Technology Applications, New Boarg El-Arab City 21934, Alexandria, Egypt
[2]Fabrication Technology Department, Advanced Technology and New Materials Research Institute, Mubarak City for Scientific Research and Technology Applications, New Boarg El-Arab City 21934, Alexandria, Egypt
[3]Nano and Composite Materials Research Department, Advanced Technology and New Materials Research Institute, Mubarak City for Scientific Research and Technology Applications, New Boarg El-Arab City 21934, Alexandria, Egypt
[4]Computer Based Engineering Applications, Informatics Research Insitute, Mubarak City for Scientific Research and Technology Applications, New Boarg El-Arab City 21934, Alexandria, Egypt

ABSTRACT: A fundamental investigation of the removal of cadmium ions from aqueous solutions by synthesized sulfonated poly(glycidyl methacrylate) (SPGMA) was conducted under batch conditions. The kinetic and equilibrium results obtained for cadmium sorption with different initial cadmium concentrations onto synthesized SPGMA were analyzed. Kinetic modeling analysis with four different types of kinetic sorption models (pseudo-first-order, pseudo-second-order, simple Elovich, and intraparticle diffusion rate models) was applied to simulate the cadmium-sorption data. The analysis of the kinetic data indicated that the sorption was a second-order process and was pore-diffusion-controlled. An ion-exchange mechanism may have existed in the cadmium-sorption process with the synthesized SPGMA. The cadmium uptake by SPGMA was quantitatively evaluated with equilibrium sorption isotherms. To describe the isotherms mathematically, the experimental data of the removal equilibrium were correlated with the Langmuir, Freundlich, Temkin, and Dubi-nin–Radushkevich (D–R) isotherm models, and the applicability of these isotherm equations to the sorption systems was compared on the basis of the correlation coefficients. The applicability of the equilibrium isotherm models followed this order: Freundlich > Langmuir > Temkin > D–R. The maximum sorption capacity, determined from the Langmuir isotherm, was 555.55 mg/g at 25°C. Thermodynamic parameters, including changes in the enthalpy, Gibbs free energy, and entropy, were calculated. Positive values for the change in enthalpy and negative values for the change in the Gibbs free energy showed the endothermic and spontaneous nature of sorption, respectively. The relatively small value of the activation energy (32.12 kJ/mol) confirmed that the cadmium-sorption process was diffusion-controlled. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 118: 3111–3122, 2010

Key words: adsorption; functionalization of polymers; ion exchangers; nanotechnology; separation techniques

INTRODUCTION

The discharge of heavy metals into watercourses is a serious environmental problem that significantly affects the quality of the water supply. Increasing concentrations of these metals in the water constitute a severe health hazard because of their toxicity, persistence in nature, and nonbiodegradability, particularly when they exceed the permissible limits.[1,2]

Heavy metals do not degrade into harmless end products by metabolism; they accumulate in the food chain (water to plants to animals to humans)[3] and therefore pose the greatest threat to living organisms.

Cadmium is introduced into the water from smelting, metal plating, cadmium–nickel batteries, phosphate fertilizers, mining, pigments, stabilizers, alloy industries, and sewage sludge.[4] The harmful effects of Cd(II) include acute and chronic metabolic disorders, such as itai–itai disease, renal damage, emphysema, hypertension, and testicular atrophy.[5]

Generally, the techniques employed for the effective removal of heavy metals from aqueous solutions

are reduction and precipitation, coagulation, flotation, adsorption, ion exchange and reverse osmosis, electrodialysis, and so forth.[6–9] However, the broad applicability of ion exchange to the separation of heavy metals has made it a powerful and versatile tool for chemical separation. The technique originally used nonsynthetic or natural compositions as ion-exchange media, such as cellulose, clay, and other minerals, which contained mobile ions that could be exchanged with ionic materials in the surrounding solute phase. Because of the low ion-exchange capacity of such natural compositions, which limited their use, synthetic organic ion-exchange polymers were developed. Ion-exchange resins were among the first generation of synthetic ion-exchange materials. The fundamental structure of ion-exchange resins is an elastic three-dimensional hydrocarbon network comprising ionizable groups, either cationic or anionic, chemically bonded to the backbone of a hydrocarbon framework. The network is normally fixed, insoluble in common solvents, and chemically inert. The ionizable functional groups attached to the matrix carry active ions that can react with or can be replaced by ions in the solute phase. Therefore, the ions in the solute phase can be easily exchanged for the ions initially bound to the polymeric resins. Cation-ion exchangers have fixed anionic functional groups, such as $-CO_2-M^+$, $-SO_3-M^+$, and $-P0_3=H_2^+$. Anion-ion exchangers have fixed cationic functional groups, such as $-NH$, $-NRH$, and $-N_2-N+R_3X-$. Many researchers have concentrated on metal-ion recovery with chelating polymers because they are reusable, are easy to handle, and have higher adsorption capacity and efficiency as well as high selectivity to some metal ions.[10–13] Hence, numerous chelating resins have been prepared through the polymerization of conventional chelating monomers such as acrylic acid,[14] allylthiourea,[15] vinyl pyrrolidone,[16] and vinyl imidazole.[17] Additionally, the modification of a synthetic polymer[10,18–24] or a natural polymer matrix[11,25–28] by functionalization reactions has also been used to form a chelating polymer. Among the vinyl monomers, glycidyl methacrylate (GMA) is a commercial industrial material that is cheaper than any other vinyl monomer possessing an epoxy ring in the side chain. Thus, nowadays the use of chelating resins that have suitable functional groups capable of interacting with metal ions is one of the promising methods for the removal of metal ions. In our laboratory, a nanoscale chelating resin derived from GMA was synthesized and then functionalized with sulfo groups, and it was investigated for the removal of cadmium metal ions from aqueous solutions. Kinetic, equilibrium, and thermodynamic aspects of cadmium sorption with synthesized sulfonated poly(glycidyl methacrylate) (SPGMA) were examined.

Theoretical models for describing both the kinetic and equilibrium data were investigated.

EXPERIMENTAL

Reagents and equipment

All the necessary chemicals used in this study, such as cadmium chloride (Pangalore, India), were analytical-reagent-grade and were used without further purification. Distilled water was used during the preparation of the polymer and the synthetic aqueous solution.

A selective ion electrode (Denver Instrument Co., United States) was used for the determination of the Cd(II) content in standard and treated solutions. The batch experiments were carried out with a digital heating-controlled magnetic stirrer (J.P. Selecta, Spain). The pH of the solution was measured with a pH meter (Denver Instrument).

Preparation of the SPGMA nanocation exchanger

Two steps were followed to prepare the SPGMA nanocation exchanger. The first step was the polymerization process of GMA, which was followed by the second step of sulfonation of poly(glycidyl methacrylate) (PGMA). The details of the two steps were determined from previous results and are discussed in the following sections.[29]

Polymerization process

Polymerization was carried out with a monomer concentration of 10% (v/v) through the dissolution of GMA in an alcohol solution (1 : 1 ethanol/water) of potassium persulfate (0.010M). Polymerization was carried out at 55°C in a water bath for 4 h.

Sulfonation process

The epoxy group of the PGMA chains reacted with different concentrations of sodium sulfite (Na_2SO_3) dissolved in an alcohol solution (30% v/v ethyl alcohol) in a water bath at 80°C for 2 h.

Preparation of the Cd(II) standard

A stock solution of cadmium (Pangalore, India; 1000–5000 mg/L) was prepared through the dissolution of 0.179–0.895 g of CdCl$_3$·H$_2$O in 200 mL of distilled water. After dissolution, the solution was diluted to 1000–5000 mL with double-distilled water in a 1000-mL volumetric flask. The concentration range of cadmium prepared from the stock solution varied between 100 and 5000 mg/L. Before the synthesized SPGMA sorbent was mixed, the pH of the last solution was adjusted to the required value with

dilute solutions of 0.1N HCl and 0.1N NaOH. Batch adsorption experiments were performed after the proper dilution of the stock solution.

Batch-mode sorption studies

Batch sorption tests were performed in a stoppered 100-mL glass cone to determine the cadmium sorption with the synthesized SPGMA. Metal solutions of various initial concentrations (100–5000 ppm) with a known volume (50 mL) were shaken for a specified period of contact in a digital heating-controlled magnetic stirrer. All the experiments were carried out in duplicate, and the mean values are presented. Then, kinetic studies of cadmium sorption were carried out: the extent of sorption was investigated as a function of the contact time, which varied from 15 to 300 min. However, the equilibrium studies were performed at 120 min.

Thermogravimetric analysis (TGA)

The thermal degradation behaviors of poly(vinyl chloride) (PVC) were studied with a thermogravimetric analyzer (TGA-50, Shimadzu, Japan) in the temperature range of 20–600°C under nitrogen at a flow rate of 20 mL/min and at a heating rate of 10°C/min.

Morphological characterization [scanning electron microscopy (SEM)]

The surface morphology of PVC and modified PVC was observed with SEM (JSM 6360LA, JEOL, Japan) at an accelerated voltage of 25 kV. The fracture surfaces were vacuum-coated with gold for SEM.

Fourier transform infrared (FTIR) spectroscopic analysis

The structure of the PVC membranes and modified PVC membranes was analyzed on the basis of FTIR spectra. Samples were mixed with KBr to make pellets. FTIR spectra in the absorbance mode were recorded with an FTIR spectrometer (FTIR-8400 S, Shimadzu) connected to a personal computer, and the data were analyzed with IR Solution software (version 1.21).

Particle size analysis

The particle size of the PVC microspheres was analyzed with a submicrometer particle size analyzer (Beckman Coulter, United States). The sample, dispersed in water at 20°C, had a viscosity of 1.002 and a refractive index of 1.33.

PET analysis

The surface area analysis of the polymer particles was performed with a surface area analyzer (SA3100, Beckman Coulter). The samples were outgassed for 15 min at 120°C.

RESULTS AND DISCUSSION

Sorption isotherm models

Sorption isotherms are mathematical models that describe the distribution of adsorbate species among solid and liquid phases, and they are thus important for chemical design. The results obtained for the sorption of Cd^{2+} onto the synthesized SPGMA were analyzed with the well-known Freundlich, Langmuir, and Dubinin–Radushkevich (D–R) models. The sorption data obtained for equilibrium conditions were analyzed with the linear forms of these isotherms.

The Freundlich isotherm is a widely used equilibrium isotherm model but provides no information on the monolayer sorption capacity, in contrast to the Langmuir model.[30,31] The Freundlich isotherm model assumes neither homogeneous site energies nor limited levels of sorption. The Freundlich model is the earliest known empirical equation and has been shown to be consistent with the exponential distribution of active centers, which is characteristic of heterogeneous surfaces:[32]

$$\ln q_e = \ln K_F + \frac{1}{n_f} \ln C_e \qquad (1)$$

where q_e is the amount of ions sorbed at equilibrium (mg/g); C_e is the equilibrium concentration of the adsorbate ions (mg/L); and K_F and n_f are Freundlich constants related to the adsorption capacity and adsorption intensity, respectively. When $\ln q_e$ is plotted against $\ln C_e$, a straight line with slope $1/n_f$ and intercept $\ln K_F$ is obtained. The intercept of the line, K_F, is roughly an indicator of the adsorption capacity, and the slope, n, is an indication of adsorption effectiveness. For the sorption isotherms, the initial cadmium-ion concentration was varied, whereas the pH and temperature of the solution, the agitation speed, and the sorbent weight in each sample were held constant. Linear fits of the sorption data of Cd^{2+} are provided in Figure 1. According to this figure, the Freundlich equation predicts that the metal-ion concentration on the sorbent will increase as long as there is an increase in the metal-ion concentration; this is compatible with the experimental results. Furthermore, on the basis of the correlation coefficient (R^2) value (0.95), it was demonstrated that the removal of cadmium with SPGMA obeyed the
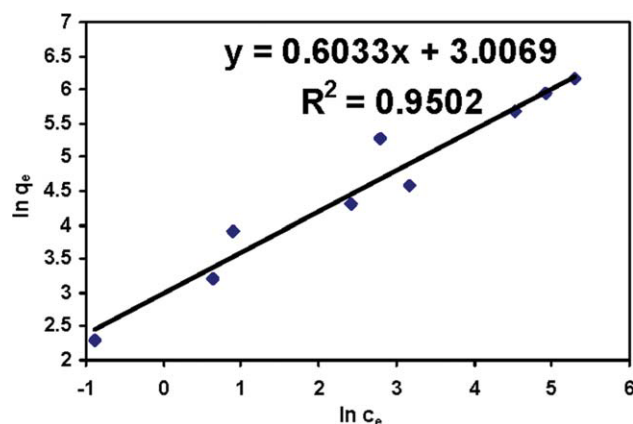
Figure 1 Freundlich isotherm for cadmium-ion removal with various initial solution concentrations (polymer dosage = 10 g/L, pH = 7, cadmium volume = 50 mL, agitation speed = 500 rpm, temperature = 25°C). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Freundlich isotherm. The values of Freundlich constants n_f and K_F, estimated from the slope and intercept of the linear plot, were 1.658 and 20.23, respectively. From the estimated value of n_f, it was found that $n_f > 1$ dictated favorable sorption for cadmium ions with the synthesized SPGMA.[33]

The Langmuir equation, which is valid for monolayer sorption onto a completely homogeneous surface with a finite number of identical sites and with negligible interaction between adsorbed molecules, is as follows:[34]

$$\frac{C_e}{q_e} = \frac{1}{q_m K} + \frac{C_e}{q_m} \quad (2)$$

where q_m and K are Langmuir constants related to the maximum adsorption capacity (monolayer capacity; mg/g) and energy of adsorption (L/mg), respectively.

A plot of C_e/q_e versus C_e should present a straight line of slope $1/q_m$ and intercept $1/q_m K$. Figure 2 illustrates a linear plot of the Langmuir equation for cadmium-ion removal with the synthesized polymer at various initial ion concentrations. According to the R^2 value, which is regarded as a measure of the goodness of fit of experimental data for the isotherm model, the Langmuir equation represents the sorption process of cadmium ions very well; the R^2 value is higher than 0.85 and thus indicates a good mathematical fit. The Langmuir parameters for cadmium-ion removal, q_m and K, were calculated from the slope and intercept of this figure; it was found from the calculated value of q_m (555.55 mg of cadmium metal/g of synthesized polymer) that the polymer was highly efficient for cadmium removal and had a low energy of sorption (0.019 L/mg).

The essential characteristics of the Langmuir isotherm are defined by a dimensionless separation factor (R_L) that is indicative of the isotherm shape, which predicts whether an adsorption system is favorable or unfavorable. R_L is defined as follows:[35]

$$R_L = \frac{1}{1 + KC_0} \quad (3)$$

where C_0 is the initial concentration of the metal ions in solution (mg/L). The calculated values of R_L for cadmium removal (Table I) show favorable adsorption because the R_L values fall between 0 and 1.[36] This again confirms that the Langmuir isotherm was favorable for the sorption of Cd^{+2} ions onto the synthesized polymer under the conditions used in this study.

Langmuir and Freundlich isotherms are insufficient to explain the physical and chemical characteristics of adsorption. The D–R isotherm is commonly used to describe the sorption isotherms of single solute systems. The D–R isotherm, apart from being an analogue of the Langmuir isotherm, is more general than the Langmuir isotherm because it rejects the homogeneous surface or constant adsorption potential.[37] The D–R isotherm is expressed as follows:

$$\ln q_e = \ln V'_m - K' \varepsilon^2 \quad (4)$$

where q_e is the amount of heavy metal removed per unit of ion-exchanger mass (mg/g), V'_m is the D–R sorption capacity (mg/g), K' is a constant related to the adsorption energy (mol²/kJ²), and ε is the Polanyi potential. ε is calculated with the following equation:
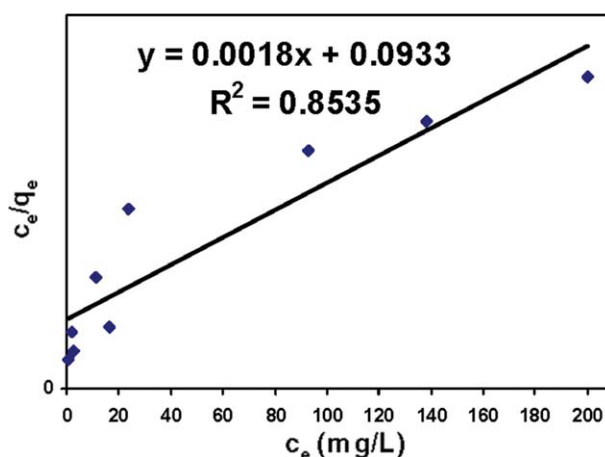

Figure 2 Langmuir isotherm for cadmium-ion removal with various initial solution concentrations (polymer dosage = 10 g/L, pH = 7, cadmium volume = 50 mL, agitation speed = 500 rpm, temperature = 25°C). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Initial cadmium concentration (ppm)	R_L
100	0.341
250	0.172
500	0.094
750	0.065
1000	0.049
2000	0.025
3000	0.0169
4000	0.0127
5000	0.011

$$\varepsilon = RT \ln(1 + 1/C_e) \qquad (5)$$

where R is the gas constant (8.314×10^{-3} kJ/mol K) and T is the temperature (K).

The constant K' gives the mean free energy of sorption per molecule of the sorbate (E) when it is transferred to the surface of the solid from infinity in the solution. This energy gives information about the physical and chemical features of the sorption process[38] and can be computed with the following relationship:[39]

$$E = (2K')^{-0.5} \qquad (6)$$

This energy gives information about the sorption mechanism; it is perceived as the amount of energy required to transfer 1 mol of the adsorbate ion from infinity in the bulk of the solution to the site of sorption. If E is between 8 and 20 kJ/mol, the sorption process follows chemical-ion exchange, and if E is less than 8 kJ/mol, the sorption process has a physical nature.[40,41]

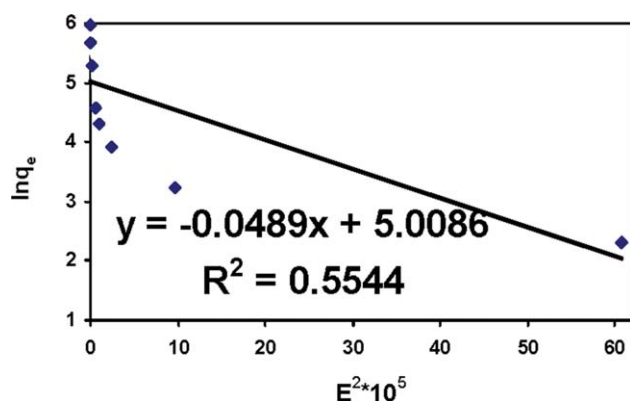The D–R isotherm model was applied to the equilibrium data obtained from the empirical studies for cadmium-ion removal with the prepared SPGMA to determine the nature of the sorption processes (physical or chemical). A plot of ln q_e against ε^2 is given in Figure 3. The D–R plot yields a straight line with the R^2 value equal to 0.55, and this indicates that the D–R model less fits the experimental data in comparison with the Langmuir and Freundlich isotherm models. According to the plotted D–R isotherm, the model parameters V'_m, K', and E are equal to 149.69 mg/g, 0.048 mol²/kJ², and 3.197 kJ/mol, respectively. The calculated adsorption energy ($E < 8$ kJ/mol) indicates that the cadmium-ion sorption processes could be considered physisorptional in nature.[42] Therefore, it is possible that physical means such as electrostatic forces played a significant role as sorption mechanisms for the sorption of cadmium metal ions in this work.

Finally, the Temkin isotherm considers the effects of indirect adsorbent/adsorbate interactions on the adsorption process. The heat of adsorption of all molecules in a layer decreases linearly with coverage because of adsorbent/adsorbate interactions.[43] This can be expressed in a linear form as follows:[44]

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

where K_T is the Temkin equilibrium binding constant corresponding to the maximum binding energy and B is the Temkin constant related to the heat of sorption. A plot of q_e versus ln C_e (Fig. 4) enables the determination of isotherm constants B and K_T from the slope and the intercept, respectively. According to Figure 4, the calculated value of K_T is 0.8344 L/g, and this represents the equilibrium binding constant corresponding to the maximum binding energy; however, constant B, which is 72.742 J/mol, is related to the heat of sorption.

Figure 3 D–R isotherm for cadmium-ion removal with various initial solution concentrations (polymer dosage = 10 g/L, pH = 7, cadmium volume = 50 mL, agitation speed = 500 rpm, temperature = 25°C). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
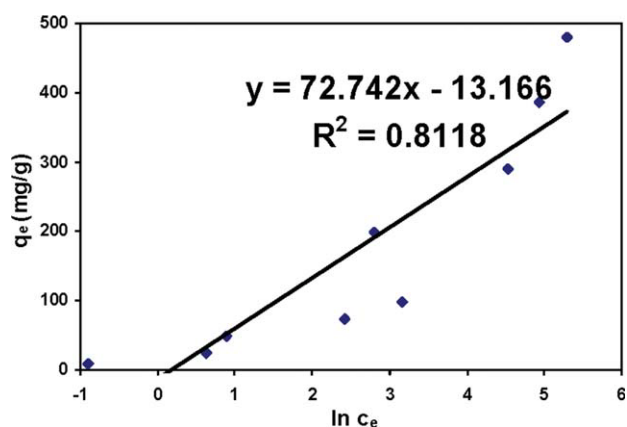

Figure 4 Temkin isotherm for cadmium-ion removal with various initial solution concentrations (polymer dosage = 10 g/L, pH = 7, cadmium volume = 50 mL, agitation speed = 500 rpm, temperature = 25°C). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE II
R^2 Values for Cd^{2+}-Ion Removal with the Different Studied Equilibrium Isotherms

Equilibrium isotherm	Langmuir	Freundlich	D–R	Temkin
R^2	0.8535	0.9502	0.5544	0.818

Finally, all the R^2 values obtained from the four equilibrium isotherm models applied to cadmium sorption on the synthesized polymer are summarized in Table II. The Freundlich model yielded the highest R^2 value (>0.95), and this showed that cadmium sorption on the synthesized polymer was best described by this model. This suggested that some heterogeneity on the surfaces or pores of the synthesized polymer played a role in cadmium sorption.[45]

Sorption kinetic models

Kinetic study is important for an adsorption process because it depicts the uptake rate of the adsorbate and controls the residual time of the whole adsorption process. Four kinetic models (pseudo-first-order, pseudo-second-order, Elovich, and diffusion kinetic models) were selected in this study to describe the sorption process.

The pseudo-first-order kinetic model has been widely used to predict sorption kinetics. The model given by Langergren and Svenska[46] is defined as follows:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (8)$$

where q_t is the amount of ions sorbed at time t (mg/g) and t is measured in minutes. k_1 (min^{-1}) is the first-order reaction rate constant. The values of k_1 and R^2, obtained from the slope of the plot of $\ln(q_e$

TABLE III
Estimated Kinetic Parameters of the First-Order Rate Model and Comparison of the Experimental and Calculated q_e Values for Different Cadmium Concentrations

Cadmium concentration (ppm)	R^2	k_1 (min^{-1})	q_e (mg/g) Calculated	Experimental
100	0.9241	0.0339	0.0887	9.95
250	0.6778	0.0363	1.093	24.8
500	0.8451	0.0893	11.1864	49.75
750	0.8911	0.1477	20.74	73.88
1000	0.8947	0.1271	20.822	97.65

$- q_t$) versus time (Fig. 5), are reported in Table III. The R^2 values were not high for the different cadmium concentrations. Also, the estimated values of q_e, calculated with the equation, differed from the experimental values, and this showed that the model was not appropriate to describe the sorption process.

In addition, a pseudo-second-order rate model based on the sorption equilibrium capacity may be expressed in the following form:[47]

$$t/q_t = (1/k_2 q_e^2) + t/q_e \quad (9)$$

where k_2 is the second-order reaction rate equilibrium constant (g/mg min). If the pseudo-second-order kinetics is applicable to the experimental data, a plot of t/q_t versus t should present a linear relationship, as illustrated in Figure 6; the calculated values of q_e and k can be determined from the slope and intercept of the plot, respectively. The values of R^2 for the sorption of different initial concentrations of cadmium ions on SPGMA are tabulated in Table IV. On the basis of linear regression values from this table ($R^2 = 1$), the kinetics of cadmium sorption onto SPGMA can be described well by a second-order
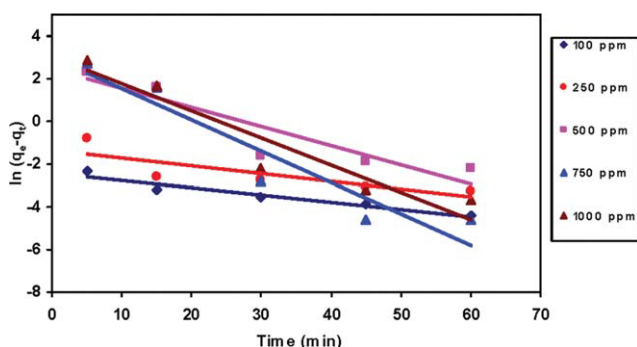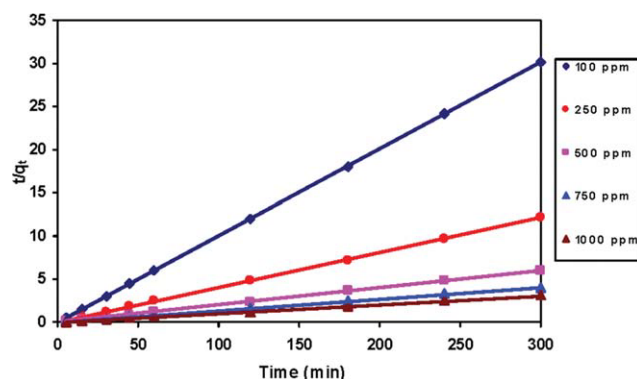

Figure 5 First-order plots for the removal of different cadmium concentrations with SPGMA (polymer dosage = 10 g/L, pH = 7, cadmium volume = 50 mL, agitation speed = 500 rpm, temperature = 25°C). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figure 6 Second-order plots for the removal of different cadmium concentrations with SPGMA (polymer dosage = 10 g/L, pH = 7, cadmium volume = 50 mL, agitation speed = 500 rpm, temperature = 25°C). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE IV
Estimated Kinetic Parameters of the Second-Order Rate Model and Comparison of the Experimental and Calculated q_e Values for Different Cadmium Concentrations

Cadmium concentration (ppm)	R^2	k_2 (g/mg min)	q_e (mg/g) Calculated	q_e (mg/g) Experimental
100	1	0.845	9.97	9.95
250	1	0.541	24.82	24.8
500	1	0.017	50	49.75
750	1	0.0331	74.07	73.88
1000	1	0.096	97.09	97.65

Figure 7 Simple Elovich plots for the removal of different cadmium concentrations with SPGMA (polymer dosage = 10 g/L, pH = 7, cadmium volume = 50 mL, agitation speed = 500 rpm, temperature = 25°C). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

equation; this suggests that the rate-limiting step in these sorption processes may be chemisorption involving valent forces through the sharing or exchange of electrons between the sorbent and sorbate.[48] Additionally, we compared the calculated values of q_e that resulted from the intersection points of the second-degree reaction kinetic curves (Table IV) with those obtained from the experimental data for the different studied cadmium concentrations. Thus, the second-order rate expression fit the data most satisfactorily.

Furthermore, the simple Elovich model is one of the most useful models for describing the kinetics of chemisorption:[49]

$$q_t = \alpha + \beta \ln t \qquad (10)$$

where α represents the initial sorption rate (mg/g min) and β is the extent of surface coverage and activation energy for chemisorption (g/mg). A plot of q_t versus $\ln t$ should present a linear relationship for the applicability of simple Elovich kinetics. Figure 7 illustrates a plot of q_t against $\ln t$ for the sorption of different initial concentrations of cadmium ions onto SPGMA. From the slope and intercept of the linearization of the simple Elovich equation, the estimated Elovich equation parameters are tabulated in Table V. The value of β is indicative of the number of sites available for adsorption, whereas α is the adsorption quantity when $\ln t$ is equal to 0, that is, the adsorption quantity when t is 1 h. This value is helpful in understanding the adsorption behavior of the first step.[50] Also, on the basis of this table, it was declared that the Elovich equation fit the experimental data well with high R^2 values. This suggests that the studied sorption systems may include chemisorption involving valence forces through the sharing or exchange of electrons between the sorbent and sorbate.[51] From the results collected for the three studied kinetic models, we confirmed that the ion-exchange mechanism played a significant role in all the studied cadmium-sorption systems.
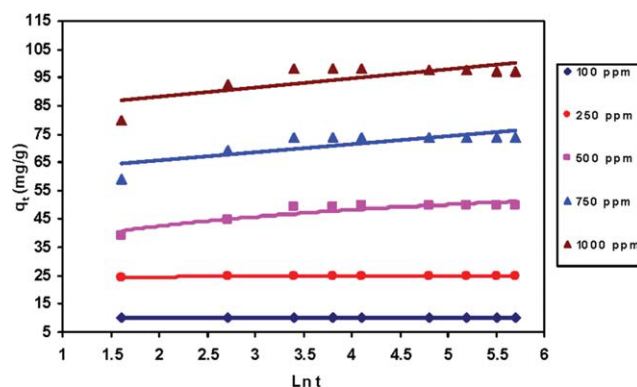
Finally, we consider the intraparticle diffusion model. The sorption of any metal ions from an aqueous phase to a solid phase is a multistep process involving the transport of metal ions from the aqueous phase to the surface of the solid particles (bulk diffusion) and then the diffusion of metal ions via the boundary layer to the surface of the solid particles (film diffusion) followed by the transport of metal ions from the solid particle surface to the interior pores (pore diffusion or intraparticle diffusion). This is likely to be a slow process; therefore, it may be the rate-determining step. In addition, the sorption of metal ions at an active site on the solid phase surface could also occur, and this is a chemical reaction such as ion exchange, complexation, or chelation. The metal-ion sorption is controlled usually by either the intraparticle (pore diffusion) or liquid-phase mass transport rates (film diffusion).[52] If the experiment is a batch system with rapid stirring, there is a possibility that intraparticle diffusion is the rate-determining step.[53] The possibility of intraparticle diffusion resistance affecting sorption was explored by Weber and Morris[54] with the intraparticle diffusion model:

TABLE V
Parameters Obtained with the Simple Elovich Model for Different Cadmium Concentrations

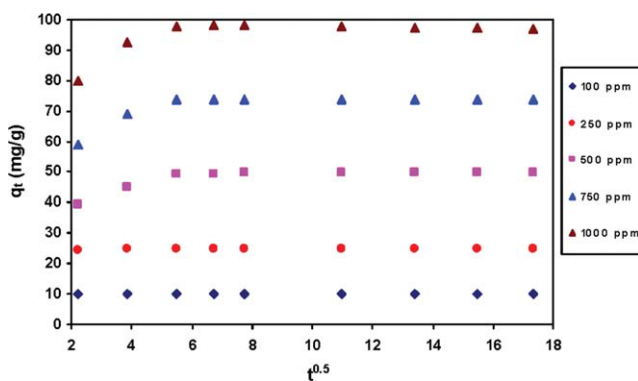| Cadmium concentration (ppm)	R^2	α (mg/g min)	β (g/mg)
100	0.842	9.8407	0.0249
250	0.8996	24.48	0.0728
500	0.678	38.87	2.217
750	0.619	59.83	2.8812
1000	0.5664	81.8	3.262

Figure 8 Intraparticle diffusion plots for the removal of different cadmium concentrations with SPGMA (polymer dosage = 10 g/L, pH = 7, cadmium volume = 50 mL, agitation speed = 500 rpm, temperature = 25°C). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

$$q_t = k_{id}t^{1/2} + I \tag{11}$$

where k_{id} is the intraparticle diffusion rate constant and I provides an idea about the thickness of the boundary layer[54] (i.e., the larger the intercept, the greater the boundary layer effect).[55] A plot of q_t versus $t^{1/2}$ is presented in Figure 8 for the different cadmium concentrations with SPGMA. If intraparticle diffusion were involved in the sorption process, then the plot of q_t versus $t^{1/2}$ would result in a linear relationship, and intraparticle diffusion would be the controlling step if this line passed through the origin.[52] The shape of Figure 8 confirms that straight lines did not pass through the origin for all the studied cadmium-sorption processes. The deviation of the straight lines from the origin, as shown in the figure, may be due to the difference between the rates of mass transfer in the initial and final steps of the sorption process. Furthermore, such a deviation from a straight line from the origin indicates that pore diffusion is not the sole rate-controlling step.[56] Figure 8 shows that there are two separate regions: the first portion is attributed to film diffusion, and the second portion is attributed to intraparticle diffu-

sion.[57] The values of $k_{id,1}$ and $k_{id,2}$, obtained from the slopes of the two straight lines, are listed in Table VI. Also, the values of I_1 and I_2, obtained from the intercepts of the two straight lines, give an idea about the thickness of the boundary layers due to both film diffusion and intraparticle diffusion, respectively, and they are listed in the same table. It is clear from this table that the thickness of the boundary layer in the second portion, which corresponds to intraparticle diffusion (I_2), is larger than that of the first portion, which concerns film diffusion (I_1). Consequently, the values of the intraparticle diffusion rate ($k_{id,2}$) are lower than those of the film diffusion rate ($k_{id,1}$). This leads to the prediction that the sorption systems will be governed mainly by intraparticle diffusion.

Sorption thermodynamics

Experimental data obtained at different temperatures (298–353 K) were used in calculating the thermodynamic parameters of cadmium sorption with the synthesized SPGMA. The changes in enthalpy ($\Delta H°$), entropy ($\Delta S°$), and Gibbs free energy ($\Delta G°$) were determined with the following well-known equations:[58]

$$\Delta G° = -RT \ln R_d \tag{12}$$

$$\Delta H° = R \ln \frac{R_d(T_2)}{R_d(T_1)} \left[\frac{T_1 T_2}{T_2 - T_1} \right] \tag{13}$$

$$\Delta S° = \frac{\Delta H° - \Delta G°}{T} \tag{14}$$

where R_d, defined as q_e/C_e, is the distribution ratio (mL/g) and reflects the extent of the distribution of the adsorbate ions between the solid and liquid phases at equilibrium. R_d is valid at a particular initial concentration and under particular reaction conditions. The apparent values of $\Delta G°$ obtained for the studied solution temperature range and the values of $\Delta H°$ and $\Delta S°$ calculated for cadmium-ion uptake on the synthesized SPGMA over the same

TABLE VI
Parameters Obtained with the Interparticle Diffusion Model for Different Cadmium Concentrations

Cadmium concentration (ppm)	$k_{id,1}$	I_1	R_1^2	$k_{id,2}$	I_2	R_2^2
100	0.0173	9.8336	0.8655	0.0033	9.9184	0.5036
250	0.0646	24.405	0.6202	−0.0003	24.839	0.752
500	1.9378	36.444	0.8467	−0.0151	49.912	0.9488
750	2.6253	56.24	0.7977	−0.0464	74.411	0.9198
1000	3.1365	77.029	0.7799	−0.088	98.64	0.968

<div style="display:flex">
<div>

TABLE VII
$\Delta G°$ Values for the Different Solution Temperatures Used for Cadmium Removal with SPGMA

Solution temperature (°C)	$\Delta G°$ (kJ/mol)
25	−3.85
40	−4.26
60	−5.56
80	−11.79

temperature range are summarized in Tables VII and VIII, respectively.

The positive value of $\Delta H°$ demonstrates that the sorption process is endothermic in nature. This behavior indicates that higher temperatures are preferred for higher cadmium sorption. This finding is consistent with the results obtained experimentally, which showed that the SPGMA uptake increased with increasing solution temperature. The adsorption reaction for the endothermic processes could be due to the fact that the increase in temperature increased the rate of diffusion of the adsorbate molecules across the external boundary layer and in the internal pores of the adsorbent particle because of the decrease in the viscosity of the solution.[59] Senthilkumaar et al.,[60] on the other hand, suggested that an increase in adsorption uptake with an increase in temperature is due to the possibility of an increase in the mobility of the adsorbate molecules.

The calculated negative values of $\Delta G°$ show that the sorption reactions are largely driven toward the products (i.e., the spontaneous behavior of the cadmium-sorption processes).[61] The decrease in the value of $\Delta G°$ with an increase in temperature shows that the reaction is more spontaneous at high temperatures, and this indicates that the sorption processes are favored by an increase in temperature.[62] The calculated value of $\Delta S°$ refers to the entropy change of the adsorption system (not the total entropy change), and this can have positive or negative values. As shown in Table VIII, a positive value theoretically means that more disorder is associated with the adsorption process. This might be intuitively explained by the increase in the dehydration steps of the adsorbate ions, which are known to possess relatively high energies of solvation and thus are stabilized by water sheaths in the absence of the adsorbent.[63]

Finally, the Arrhenius equation has been applied to evaluate the activation energy of cadmium sorption, which represents the minimum energy that reactants must have for the reaction to proceed:[64]

$$\ln k_2 = \ln A - E_a/RT \qquad (15)$$

</div>
<div>

TABLE VIII
$\Delta H°$ and $\Delta S°$ for the Solution Temperatures Used for Cadmium Removal with SPGMA

$\Delta H°$ (kJ/mol)	$\Delta S°$ (J/mol K)
84.184	295.4

where A is a temperature-independent factor (i.e., frequency factor; g/mg min), k_2 is the second-order rate constant value for ion sorption, and E_a is the activation energy (kJ/mol). As shown in Figure 9, a plot of $\ln k_2$ versus $1/T$ is linear with acceptable R^2 values for cadmium-ion removal for all studied temperatures. The activation energy for the studied sorption system was derived from the slope of this plot and was found to be 32.12 kJ/mol. The magnitude of the activation energy may give us an idea about the type of sorption. The relatively small value of the activation energy below 42 kJ/mol confirms the fact that the process of cadmium-ion removal using the synthesized SPGMA is diffusion-controlled; that is, the chemical step is much faster than the mass transfer of ions inside the ion-exchanger pores.[65]

Characterization of the synthesized SPGMA

The occurrence of sulfonation was verified with FTIR analysis and TGA of the prepared SPGMA with various concentrations of the sulfating agent. For the five different samples prepared, the absorption band at 1725 cm^{-1} was caused by the stretching vibration of the ester carbonyl groups. Two strong peaks were observed at 1650 and 3465 cm^{-1}, which were ascribed to the stretching vibrations of the
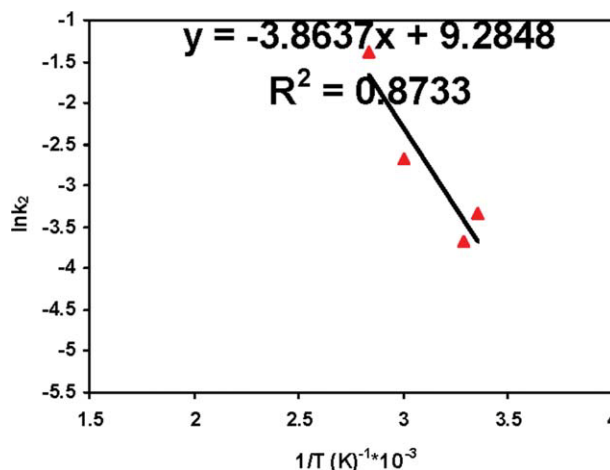

Figure 9 Arrhenius plot for different solution temperatures for cadmium removal with SPGMA (polymer dosage = 10 g/L, pH = 7, cadmium volume = 50 mL, agitation speed = 500 rpm, temperature = 25°C). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
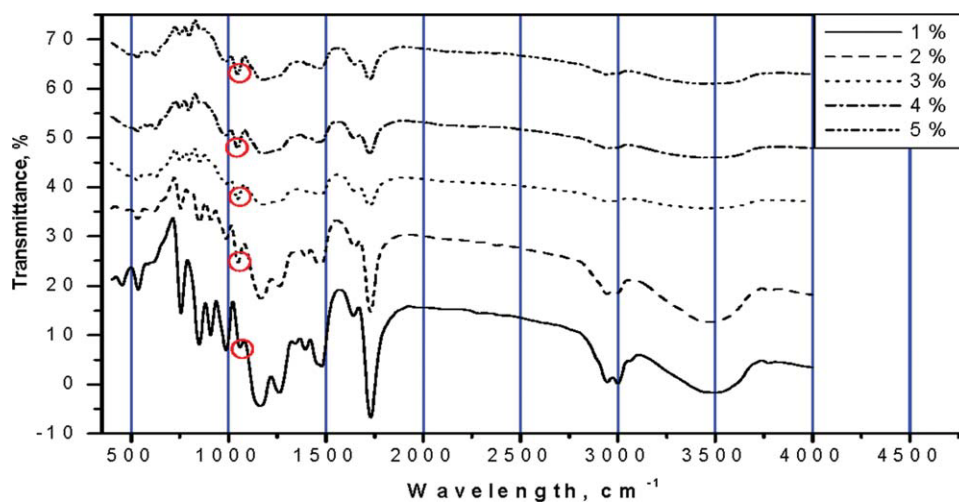
</div>
</div>

3120 MOHY-ELDIN ET AL.

Figure 10 FTIR spectrum of SPGMA. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

C=O group in carboxylate salts (COO—) and OH groups.[66] Finally, the band located at 1048 cm^{-1} was assigned to the symmetric stretching vibration of the sulfonated group.[67] It is evident that the symmetric peak at 1048 cm^{-1} increased with the Na$_2$SO$_3$ concentration increasing from 1 to 3%. Beyond this concentration, the increase in the peak intensity became negligible (Fig. 10). On the other hand, TGA thermograms showed that, because of water evaporation, the samples increasingly lost weight at 120°C with increases in the concentration of Na$_2$SO$_3$ (the sulfonating agent) up to 3%. A further increase in the Na$_2$SO$_3$ concentration did not show a significant increase in the weight loss. Remarkable thermal stability was observed for the sulfonated samples with a positive shift of the characteristic thermogram peak of PGMA from 240°C to the higher temperature range of 260–280°C. At 300°C, the PGMA sample lost 55% of its weight, but the sulfonated samples lost 10–18% only (Fig. 11). In conclusion, the FTIR and TGA data proved the occurrence of the sulfonation process. The adsorption of soluble species onto the surface and/or within the pores of the solid matrix was directly affected by the surface area, pore volume, and pore diameter and indirectly by the particle size of the matrix. The data for the particle size analysis (Fig. 12) showed that the size of the particles was nanoscale, and this reflected the large surface area (0.896 m^2/g). This large surface area explained the quickness of the removal process. On the other hand, the total pore volume was 0.0064 mL/g. The pore diameter ranged from 6 to 80 nm; this represented 85% of the pores. Water in the solvent polymerization system played the rule of a porogen agent because of its immiscibility with the GMA monomer. The presence of a relatively small pore volume explained the interparticle diffusion behavior of the adsorption process. The surface morphologies of SPGMA are illustrated in Figure 13. An obvious heterogeneous morphology was
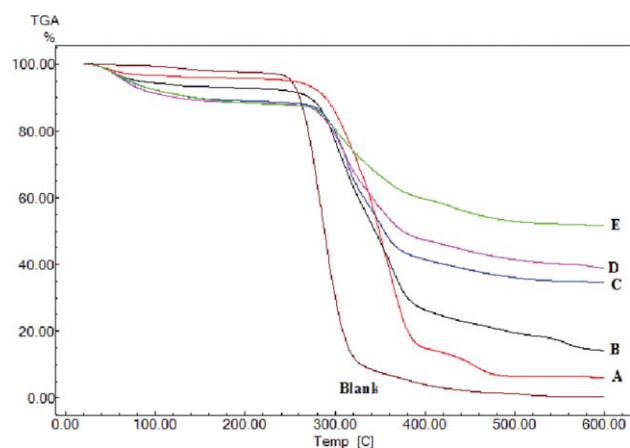

Figure 11 TGA thermograms of SPGMA. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
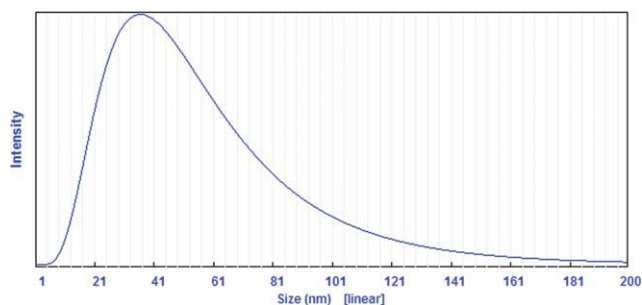

Figure 12 Particle size distribution of SPGMA. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
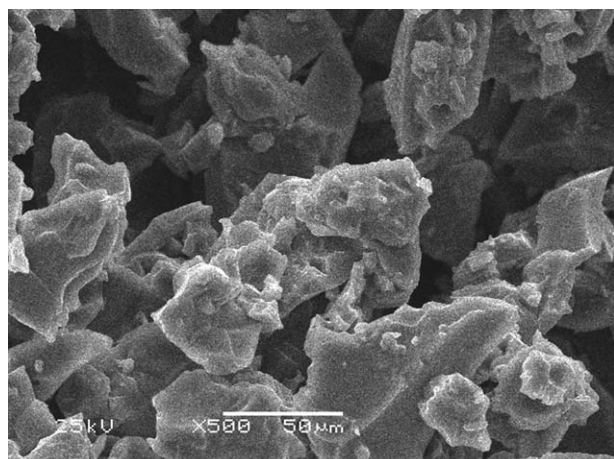
Journal of Applied Polymer Science DOI 10.1002/app

Figure 13 SEM photograph of SPGMA.

noticed, and this explained the heterogeneity of the adsorption center distribution.

CONCLUSIONS

The bench-scale studies carried out for cadmium removal with SPGMA showed a high sorption capacity for the synthesized polymer (555.55 mg/g at 25°C according to the Langmuir isotherm). Among the four adsorption isotherms tested, the Freundlich isotherm showed the best fit, and this suggested that some heterogeneity on the surfaces or pores of the synthesized polymer played a role in cadmium sorption; it was followed by both the Langmuir and Temkin isotherms and finally the D–R isotherm, which did not match the data so satisfactorily. The kinetics of the cadmium-sorption rate was best explained by the pseudo-second-order kinetic equation and the simple Elovich and intraparticle diffusion models because the sorption kinetics could be described by several independent processes that could act in parallel or in series. These kinetic models confirmed that the ion-exchange mechanism played a significant role in all the studied cadmium-sorption systems. Moreover, the sorption systems were governed mainly by intraparticle diffusion. The relatively small value of the activation energy (32.12 kJ/mol) confirmed that the cadmium-sorption process was diffusion-controlled. That is, the chemical step was much faster than the mass transfer of ions inside the ion-exchanger pores. According to the calculated thermodynamic parameters, the sorption of cadmium onto SPGMA was a sorption process that was endothermic in nature (according to the positive value of $\Delta H°$) and was spontaneous (according to the negative values of $\Delta G°$). Finally, the positive value of $\Delta S°$ indicated

that disorder was associated with the cadmium-sorption process.

NOMENCLATURE

α	rate of chemisorption at zero coverage (mg/g min)
β	extent of surface coverage and activation energy for chemisorption (g/mg)
$\Delta G°$	change in Gibbs free energy
$\Delta H°$	change in enthalpy
$\Delta S°$	change in entropy
ε	Polanyi potential
A	temperature-independent factor (g/mg min)
B	Temkin constant related to the heat of sorption
C	final metal-ion concentration in an aqueous solution (mg/L)
C_0	initial concentration of the metal ions in solution (mg/L)
C_e	equilibrium concentration of the adsorbate ions (mg/L)
D–R	Dubinin–Radushkevich
E	mean free energy of sorption per molecule of the sorbate (kJ/mol)
E_a	activation energy (kJ/mol)
FTIR	Fourier transform infrared
GMA	glycidyl methacrylate
I	value providing an idea about the thickness of the boundary layer
K	Langmuir constant related to the energy of adsorption (L/mg)
K'	constant related to the adsorption energy (mol^2/kJ^2)
k_1	first-order reaction rate constant (min^{-1})
k_2	second-order reaction rate equilibrium constant (g/mg min)
K_F	Freundlich constant related to the adsorption capacity
k_{id}	intraparticle diffusion rate constant
K_T	Temkin equilibrium binding constant corresponding to the maximum binding energy
Na_2SO_3	sodium sulfite
n_f	Freundlich constant related to the adsorption intensity
PGMA	poly(glycidyl methacrylate)
PVC	poly(vinyl chloride)
q_e	amount of ions sorbed at equilibrium (mg/g)
q_m	Langmuir constant related to the maximum adsorption capacity (mg/g)
q_t	amount of ions sorbed at time t (mg/g)
R	gas constant
R_d	distribution ratio (mL/g)
R_L	dimensionless separation factor
SEM	scanning electron microscopy

SPGMA   sulfonated poly(glycidyl methacrylate)
t time (min)
T solution temperature (K)
TGA   thermogravimetric analysis
V'_m Dubinin–Radushkevich sorption capacity (mg/g)

References

1. Calace, N.; Di, A.; Muro, E.; Nardi, M. B.; Petronio, M.; Pietroletti, M. Ind Eng Chem Res 2002, 41, 5491.
2. Larous, S.; Meniai, A. H.; Lehocine, M. B. Desalination 2005, 185, 483.
3. Marina, B. S.; Mile, T. K. Cent Eur J Occup Environ Med 2003, 9, 337.
4. Zhu, C.; Luan, Z.; Wang, Y.; Shan, X. Sep Purif Technol 2007, 57, 161.
5. U.S. Department of Labor. Occupational Exposure to Cadmium.http://www.osha.gov/pls/oshaweb/owadisp.show_document?p_table=preambles&p_id=819 (accessed April 2010).
6. Esalah, J. O.; Weber, M. E.; Vera, J. H. Can J Chem Eng 2000, 78, 948.
7. Zouboulis, A. I.; Matis, K. A.; Lanara, B. G.; Neskovic, C. L. Sep Sci Technol 1997, 32, 1755.
8. Ravindran, V.; Stevens, M. R.; Badriyha, B. N.; Pirbazari, M. AIChE J 1999, 45, 1135.
9. Canet, L.; Llpide, M.; Seta, P. Sep Sci Technol 2002, 37, 1851.
10. Denizli, A.; Ozkan, G.; Arica, M. Y. J Appl Polym Sci 2000, 78, 81.
11. Shukla, S. R.; Pai, R. S.; Shendarkar, A. D. Sep Purif Technol 2006, 47, 141.
12. Chen, C. Y.; Chiang, C. L.; Huang, P. C. Sep Purif Technol 2006, 50, 15.
13. Chen, C. Y.; Chen, S. Y. J Appl Polym Sci 2004, 94, 2123.
14. Li, W.; Zhao, H.; Teasdale, P. R.; John, R.; Zhang, S. React Funct Polym 2002, 52, 31.
15. Kılıç, A. G.; Malcı, S.; Celikbıcak, O.; Sahiner, N.; Salih, B. Anal Chim Acta 2005, 547, 18.
16. Essawy, H. A.; Ibrahim, H. S. React Funct Polym 2004, 61, 421.
17. Pekel, N.; Savas, H.; Guven, O. Colloid Polym Sci 2002, 280, 46.
18. Donia, A. M.; Atia, A. A.; Elwakeel, K. Z. Sep Purif Technol 2005, 42, 111.
19. Zhang, C.; Li, X.; Pang, J. J Appl Polym Sci 2001, 82, 1587.
20. Donia, A. M.; Atia, A. A.; El-Boraey, H. A.; Mabrouk, D. H. Sep Purif Technol 2006, 48, 281.
21. Donia, A. M.; Atia, A. A.; El-Boraey, H. A.; Mabrouk, D. H. Sep Purif Technol 2006, 49, 64.
22. Atia, A. A.; Donia, A. M.; Elwakeel, K. Z. React Funct Polym 2005, 65, 267.
23. Reddy, K. H.; Reddy, A. R. J Appl Polym Sci 2003, 88, 414.
24. Disbudak, A.; Bektas, S.; Patir, S.; Genc, O.; Denizli, A. Sep Purif Technol 2002, 26, 273.
25. Shao, J.; Yang, Y.; Shi, C. J Appl Polym Sci 2003, 88, 2575.
26. Navarro, R. R.; Tatsumi, K.; Sumi, K.; Matsumura, M. Water Res 2001, 35, 2724.
27. Navarro, R. R.; Sumi, K.; Matsumura, M. Water Res 1998, 38, 195.
28. Navarro, R. R.; Sumi, K.; Matsumura, M. Water Res 1999, 33, 2037.
29. Abu-Saied, M. A. Grafted Polymer Applications in Affinity Separation of Proteins; Al-Azhar University: Cairo, 2006.
30. Gode, F.; Pehlivan, E. J Hazard Mater B 2003, 100, 231.
31. Gode, G.; Pehlivan, E. Fuel Process Technol 2005, 86, 875.
32. Ho, Y. S. Bioresour Technol 2005, 96, 1292.
33. Dubinin, M. M.; Zaverina, E. D.; Radushkevich, L. V. Zh Fiz Khim 1947, 21, 1351.
34. Unlu, N.; Ersoz, M. J Hazard Mater 2006, 136, 272.
35. Mohammad, A.; Rifaqat, A. K. R.; Rais, A.; Jameel, A. J Hazard Mater 2000, 79, 117.
36. Ho, Y. S.; Porter, J. F.; McKay, G. Water Air Soil Pollut 2002, 141, 1.
37. Dubinin, M. M.; Zaverina, E. D.; Radushkevich, L. V. Zh Fiz Khim 1947, 21, 1351.
38. Tan, I. A. W.; Ahmad, A. L.; Hameed, B. H. Desalination 2008, 225, 13.
39. Seker, A.; Shahwan, T.; Eroglu, A. E.; Sinan, Y.; Demirel, Z.; Dalay, M. C. J Hazard Mater 2008, 154, 973.
40. Helfferich, F. Ion Exchange; McGraw-Hill: New York, 1962.
41. Malik, U. R.; Hasany, S. M.; Subhani, M. S. Talanta 2005, 66, 166.
42. Smith, J. M. Chemical Engineering Kinetics; McGraw-Hill: New York, 1981.
43. Hameeda, B. H.; China, L. H.; Rengarajb, S. Desalination 2008, 225, 185.
44. Temkin, M. I.; Pyzhev, V. Acta Physicochim 1940, 12, 327.
45. Tan, I. A. W.; Ahmad, A. L.; Hameed, B. H. J Hazard Mater 2009, 164, 473.
46. Langergren, S.; Svenska, B. K. Veternskapsakad Handlingar 1898, 24, 1.
47. Ho, Y. S.; McKay, G. Can J Chem Eng 1998, 76, 822.
48. Ho, Y. S.; McKay, G. Process Biochem 1999, 34, 451.
49. Ozacar, M.; Sengil, I. A. Process Biochem 2005, 40, 565.
50. Tseng, R. L. J Colloid Interface Sci 2006, 303, 494.
51. Namasivayam, C.; Sureshkumar, M. V. Bioresour Technol 2008, 99, 2218.
52. Crini, G.; Peindy, H. N.; Gimbert, F.; Robert, C. Sep Purif Technol 2007, 53, 97.
53. McKay, G. Chem Eng J 1983, 27, 187.
54. Weber, W. J.; Morris, J. C.; Sanity, J. Eng Div Am Soc Civil Eng 1963, 89, 31.
55. Kannan, K.; Sundaram, M. M. Dyes Pigments 2001, 51, 25.
56. Poots, V. J. P.; McKay, G.; Healy, J. J. J Water Pollut Control Fed 1978, 50, 926.
57. Allen, S. J.; McKay, G.; Khader, K. Y. H. Environ Pollut 1989, 56, 39.
58. Gupta, G. S.; Shukla, S. P.; Prasad, G.; Singh, V. N. Environ Technol 1992, 1, 925.
59. Wang, S.; Zhu, Z. H. Dyes Pigments 2007, 75, 306.
60. Senthilkumaar, S.; Kalaamani, P.; Porkodi, K.; Varadarajan, P. R.; Subburaam, C. V. Bioresour Technol 2006, 97, 1618.
61. Zuhra, M. G.; Bhanger, M. I.; Mubeena, A.; Farah, N. T.; Jamil, R. M. Chem Eng J 2008, 38, 616.
62. Syed, M.; Muhammad, I.; Rana, G.; Sadullah, K. Sep Purif Technol 2008, 59, 108.
63. Seker, A.; Shahwan, T.; Eroglu, A.; Yilmaz, S.; Demirel, Z.; Dalay, M. J Hazard Mater 2008, 154, 973.
64. Smith, J. M. Chemical Engineering Kinetics, 3rd ed.; McGraw-Hill: Singapore, 1981.
65. Pickett, D.; Kirk, G. S.; Donald, L. S. Soil Sci Soc Am J 2001, 65, 719.
66. Chen, C. Y.; Chiang, C. L.; Chen, C. R. Sep Purif Technol 2007, 54, 396.
67. Pedicini, R.; Carbone, A.; Sacca, A.; Gatto, I.; Di Marco, G.; Passalacqua, E. Polym Test 2008, 27, 248.