Full Articles

Kinetics and adsorption equilibrium in the system aqueous solution of copper ions—granulated activated carbon

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The feasibility of using granulated activated carbon for adsorption removal of copper from aqueous solution was studied. The influence of pH, amount of the adsorbent, contact time, and copper concentration on adsorption of copper was investigated. The single-component equilibrium data on copper adsorption were analyzed using the Langmuir, Freundlich, Redlich—Peterson, Temkin, and Toth adsorption isotherms. The adsorption process was followed by two simplified kinetic models including pseudo-first- and pseudo-second-order equations. Kinetic parameters, rate constants, equilibrium sorption capacities, and the corresponding correlation coefficients were calculated and examined for each kinetic model. It was shown that copper adsorption can be described by the pseudo-second-order equation.

Key words: copper, adsorption, isotherms, kinetics, removal from solution.

Numerous recent data on the negative environmental impact of heavy metals have prompted a demand for the purification of industrial wastewaters. Unlike organic contaminants, the most part of which undergo biological degradation, heavy metals are non-degradable into nontoxic products. Since heavy metals, especially chromium, copper, zinc, iron, mercury, and lead, are toxic,[1] their concentration in wastewaters should be reduced to environmentally acceptable levels before being discharged into environment. Principal sources of copper contaminates in industrial wastewaters are electrolysis and metal cleaning, washing of brass units, boiler pipes, and cooking utensils, and fertilizer production. Another pollutant source is copper metal working, which requires periodic oxide removal by immersing the metal in strong acid baths. Therefore, the elimination of heavy metals from industrial wastewaters is important to protect public health. For humans, copper is an essential element and the body can regulate its level haemostatically, although large acute doses can have harmful and even fatal effect. In particular, copper is highly toxic because of its carcinogenic and mutagenic properties.[2—4] Some of the conventional techniques for

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removal of metals from industrial wastewaters include chemical precipitation, adsorption, solvent extraction, membrane separation, ion exchange, and electrolysis.[5—11] The increasing stringent environmental regulation and enforcement of discharge limits require efficient wastewaters decontamination and purification methods. It is known that solid phase adsorption is one of the most reliable techniques. The adsorption process proved its advantage over other processes because of its cost effectiveness and the high-quality of the treated effluents it produces. Activated carbon found wide use as adsorbent due to its high adsorption capacity.[12—14]

In this study, commercial granulated activated carbon (GAC) was used as an adsorbent for the removal of Cu^{2+} ions from aqueous solutions at 30 °C. The influence of such parameters as pH, adsorbent dose, contact time, and the initial concentration of Cu^{2+} ions on adsorption was studied. Adsorption processes were studied from isotherm and kinetic standpoints.

Experimental

Commercial granulated activated carbon (GAC) procured from Loba Chemia Private Limited (India) was used as an adsorbent material. The fraction with the particle size 0.25—0.35 mm was used for adsorption measurements. The specific surface and parameters of the GAC porous structure were determined on a sorption meter (Quantachrome, Autosorb-I) from nitrogen adsorption at 77 K. The specific surface was calculated by the BET equation.[15] The used GAC had the following BET characteristics: specific surface 1119 $m^2 g^{-1}$, pore volume 0.48 $cm^3 g^{-1}$, average particle size 0.335 mm, and packed density 0.45 $g cm^{-3}$.

A stock solution of Cu^{2+} (1000 mg L^{-1}) was prepared by dissolving $CuSO_4 \cdot 5H_2O$ (analytical reagent grade) in distilled water. The working solutions with the concentration ranging from 100 to 1000 mg L^{-1} were prepared by dilution of the stock solution with distilled water.

The copper concentrations in the solutions before and after equilibrium were determined with a Perkin—Elmer 3100 atomic absorption spectrometer. The pH value of solutions was measured with a Hanna pH-meter using a combined glass electrode.

Batch adsorption experiments were performed by contacting 2 g of GAC with 100 mL of an aqueous copper solution with different initial concentrations (from 100 to 1000 mg L^{-1}) at different solution pH. Experiments were carried out for 1 h at room temperature (30 °C) in 250-mL Erlenmeyer flasks, which were placed in a writst action shaker working with a constant agitation speed of 120 rpm. Continuous stirring was provided for better mass transfer with high interfacial surface area. After adsorption at different time intervals, the solution with the adsorbent was filtered through Whatman GF/A filter paper and the residual concentration of Cu^{2+} ions in the filtrate was determined by atomic absorption spectroscopy. The concentration of Cu^{2+} adsorbed by the adsorbent was calculated by the formula

$$q_e = \frac{(C_i - C_e)V}{W}, \qquad (1)$$

where q_e is the amount of copper adsorbed after equilibration (mg g^{-1}); C_i and C_e are the initial and equilibrium concentrations of Cu^{2+} in the solution (mg L^{-1}), respectively; V is volume (L); W is the adsorbent weight (g).

The effect of the adsorbent dosages (5—30 g L^{-1}) on the equilibrium adsorption of Cu^{2+} on the carbon was studied at room temperature (30 °C) in solutions with different initial copper concentrations (100, 300, and 500 mg L^{-1}). The flask was shaken at a constant stirring speed (120 rpm) and constant pH of the solution (pH 5) until equilibrium was attained. To obtain data necessary for plotting adsorption isotherms, solutions with different initial concentrations of Cu^{2+} ions were stirred with a carbon weighed sample until equilibrium was attained. The adsorption kinetics was studied by analyzing the adsorptive uptake of Cu^{2+} from aqueous solutions at different time intervals.

Results and Discussion

Effect of pH. Acidity of solution, pH, is one of the most important parameters controlling the uptake of heavy metals from aqueous solutions. The percentage of removal of copper from the aqueous solution with an initial copper concentration of 100 mg L^{-1} is strongly affected by the pH of the solution (Fig. 1). The minimum adsorption observed at low pH (pH 2) may be due to the fact that the higher concentration and higher mobility of H^+ ions present favored the preferential adsorption of hydrogen ions compared to Cu^{2+} ions.[16] It would be plausible to suggest that at low pH the adsorbent surface is surrounded by hydroxonium ions (H^+) thereby preventing the metal ions from approaching the binding sites of the sorbent.[17] Correspondingly, at higher concentration of H^+ the GAC surface becomes more positively charged so that the attraction between the adsorbent and metal cations is reduced.[18] In contrast as the pH increases, more negatively charged surface becomes available, thus facilitating the predominant removal of Cu^{2+} ions from the solution. The sorption of metal cations is enhanced with increasing pH, because the stability of metal ions decreases in such solutions. However, at higher pH values (pH 6—9) the percentage removal of Cu^{2+} ions again decreases, which is evidently due to copper precipitation. At pH 6, copper exists in solution in three forms,[19] mainly as $Cu(OH)^+$ and $Cu(OH)_2$, whereas Cu^{2+} ions are present in insignificant concentrations. All these species are adsorbed on the

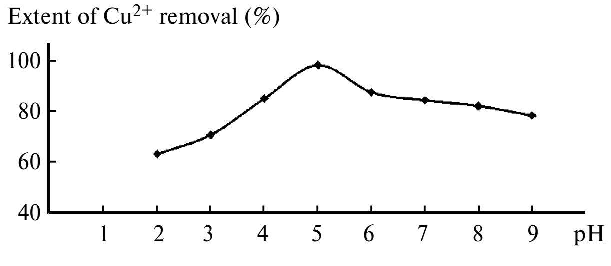

Fig. 1. Effect of pH of the solution on the adsorption of copper ions.

adsorbent surface following the mechanism of ion exchange with functional groups of the adsorbent or by hydrogen bonding.

Effect of the adsorbent dose on the adsorptive uptake was studied at room temperature (30 °C), the adsorbent content in the solution being varied from 5 to 30 g L^{-1}. For all experiments in this series, different initial concentrations of copper were fixed as 100, 300, and 500 mg L^{-1}. Figure 2 shows that the copper uptake increases rapidly with an increase in the GAC amount. Obviously, the higher the adsorbent concentration, the larger surface involved in adsorption. The copper uptake increased especially noticeably with an increase in the adsorbent concentration from 5 to 20 g L^{-1}. An increase in the adsorbent content larger than 20 g L^{-1} induces no considerable changes in the uptake. Therefore, in a certain region of initial metal concentrations the percentage of copper sorption by carbon is determined by the sorption capacity of the sorbent. The maximum removal of copper was achieved in the adsorbent dose of 20 g L^{-1}.

Effect of the contact time. The plots of the percentage removal of copper *vs* contact time of the carbon with copper solutions containing from 100 to 500 mg copper per liter are shown in Fig. 3. It is seen that copper is removed most rapidly at the initial period. This is probably due to the larger surface area of the GAC being available at the beginning for the adsorption of copper ions. As the adsorption surface sites become exhausted the uptake rate is controlled by the rate of adsorbate migration from the exterior to the interior sites of the adsorbent particles. As the contact time increases, the copper uptake increases and the process attains equilibrium in 30 min, after which the amount of Cu^{2+} ions adsorbed from solutions with different initial copper concentrations remains unchanged. The most part of copper is usually removed from solutions after 60 min.

Effect of the initial concentration of Cu^{2+} ions. The dependence of the uptake of copper on its initial concentration in solution is shown in Fig. 4. It was found that an increase in the copper concentration in the initial solution from 100 to 1000 mg L^{-1} increases the amount of copper adsorbed from 4.90 to 40.89 mg g^{-1}, but the percentage copper removal decreases from 97.98 to 81.78%. It may be due to an increase in the number of copper ions for the fixed amount of adsorbent.

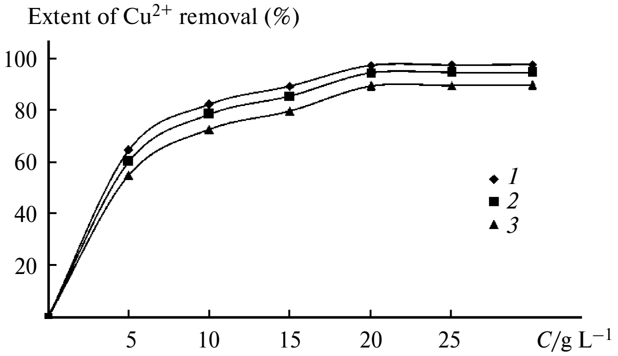

Fig. 2. Extent of removal of Cu^{2+} ions *vs* adsorbent concentration (*C*) at the initial concentrations of Cu^{2+} ions: 100 (*1*), 300 (*2*), and 500 mg L^{-1} (*3*).

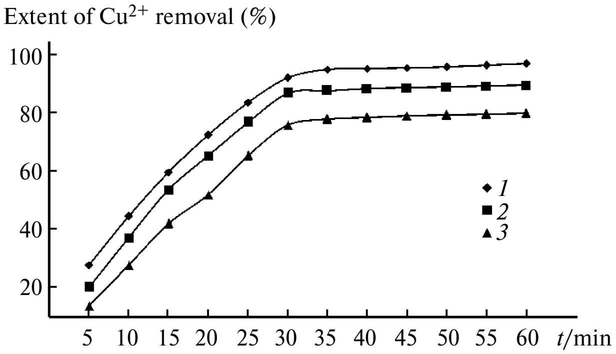

Fig. 3. Extent of removal of Cu^{2+} ions *vs* contact time adsorbent—adsorbate at the initial concentrations of Cu^{2+} ions: 100 (*1*), 300 (*2*), and 500 mg L^{-1} (*3*).

Equilibrium adsorption isotherm. The capacity of the adsorption isotherm is a very important parameter, which allows one to calculate the maximum capacity of the adsorption and also provides a panorama of the course taken by the system in the concise form indicating how efficiently an adsorbent will adsorb and allows an estimate of the economic viability of the adsorbent commercial applications for the specifed solute. In order to adapt for the considered system an adequate model that describes specific features of the studied system and agrees with the obtained experimental results, the Langmuir, Freundlich, Redlich—Peterson, Toth, and Temkin equations were considered. The Langmuir model is the most widely used for isotherm equation

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

where q_m and K_L are the constants in the Langmuir equation designating the maximum sorption capacity for a given adsorbent weighed sample and the energy constant related to the heat of adsorption, respectively.

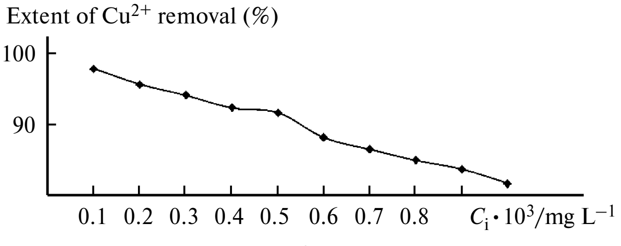

Fig. 4. Extent of removal of Cu^{2+} ions *vs* their initial concentration (C_i).

The Freundlich equation can be written as follows:

$$q_e = K_F C_e^{1/n}, \tag{3}$$

where K_F is the constant of the Freundlich equation $(\text{mg g}^{-1})(\text{L mg}^{-1})^{1/n}$ that reflects the bond energy. The value of $1/n$ is the coefficient of surface nonuniformity and n is the measure of deviation of uptakes from the linear region of the isotherm. The values of this measure can be attributed to deviations from linearity of the uptake—solution concentration plot as follows: if $n = 1$, adsorption is described by a linear dependence; if $n < 1$, adsorption is a chemical process; if $n > 1$, the adsorption process has physical nature.

The Redlich—Peterson isotherm is a combination of the Langmuir—Freundlich model. It approaches the Freundlich model at high concentrations and is in an accord with low concentration limit of the Langmuir equation. The Redlich—Peterson equation takes the form

$$q_e = \frac{K_j C_e}{1 + \alpha_L C_e^{\beta}}, \tag{4}$$

where K_j is the constant in the Redlich—Peterson equation (L g^{-1}), α_L is the constant in the Redlich—Peterson equation (L mg^{-1}), and β is the exponential factor taking values from 0 to 1.

The Toth equation combines the parameters of the Langmuir and Freundlich models and can be presented as

$$q_e = \frac{aC_e}{[b + (C_e)^d]^{1/d}}, \tag{5}$$

where a and b are constants in the Toth equation and d is the exponential factor of this equation $(0 < d \le 1)$. It can be seen that at $d = 1$ the Toth isotherm is transformed into the Langmuir equation.

In addition, the Temkin isotherm equation is used in the this study to fit with the experimental data, and it can be represented as

$$q_e = A\ln C_e + B, \tag{6}$$

where A and B are constants in the Temkin equation.

The experimental data on the effect of the initial copper adsorbed on carbon were fitted to the isotherm models and graphical representation of the these models are given in Fig. 5. The corresponding constants of adsorption equilibrium equations are collected in Table 1.

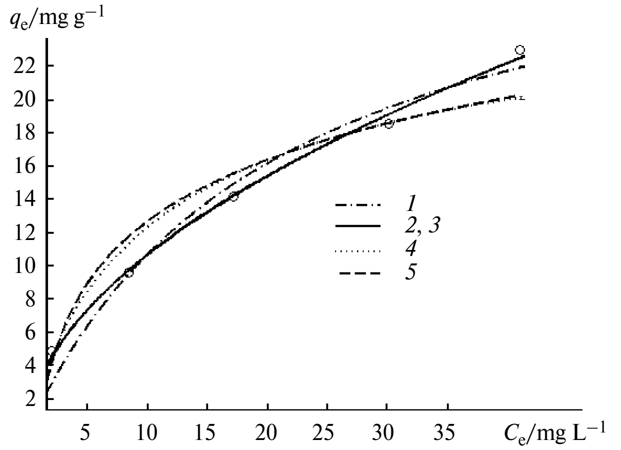

Fig. 5. Adsorption isotherms calculated by the Langmuir (*1*), Freundlich (*2*), Redlich—Peterson (*3*), Toth (*4*), and Temkin (*5*) equations; experimental data are shown by points. The adsorption curves obtained by the Freundlich and Redlich—Peterson equations coincide.

The value of R^2 nearby to 1 indicates that the respective equation better fits the experimental data. The calculation of experimental data by equations derived from different adsorption models gives nonlinear dependences, As can be seen from the data in Table 1, R^2 is not lower than 0.927. Thus, the studied adsorption of copper on carbon is best described by the Langmuir, Freundlich, and Redlich—Peterson equations. Indeed, processing the experimental data, which illustrate the ability of granulated activated carbon to adsorb copper, by the Langmuir, Freundlich, and Redlich—Peterson equations gives good correlations with R^2 equal to 0.966, 0.997, and 0.996, respectively.

Kinetic studies. The model based on a pseudo-first-order equation. The sorption kinetics can be described by the pseudo-first-order equation[20—25]

$$\log(q_e - q_t) = \log q_e - (k_{ad}/2.303)t, \tag{7}$$

where q_t is the amount adsorbed (mg g^{-1}) within time t and k_{ad} is the rate constant of the pseudo-first order adsorption process (min^{-1}).

The linear relationship $\log(q_e - q_t)/t$ was used to determine the rate constants (k_{ad}) and correlation coefficients (R^2) for different copper concentrations (Fig. 6). However, it is seen that the experimental data deviated considerably

Table 1. Parameters of the isotherms calculated by different models and correlation coefficients (R^2)

Isotherm	Parameter	Value	R^2
Langmuir	q_m	20.833	0.967
	K_L	0.149	
Freundlich	K_F	3.112	0.997
	n	1.879	
Redlich—Peterson	k_j	15.512	0.996
	α_L	4.321	
	β	0.4971	
Toth	a	28.362	0.936
	b	5.384	
	d	0.772	
Temkin	A	5.364	0.927
	B	0.274	

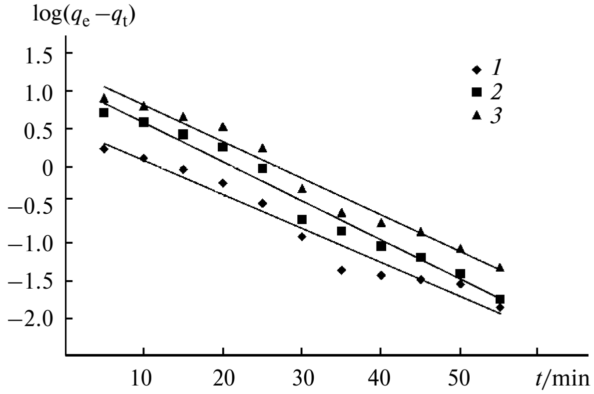

Fig. 6. Kinetic curves of adsorption of Cu^{2+} ions on GAC (solid lines) obtained by experimental data (points) processing using the pseudo-first-order kinetic equations; the initial concentrations of Cu^{2+} ions are 100 (*1*), 300 (*2*), and 500 mg L^{-1} (*3*).

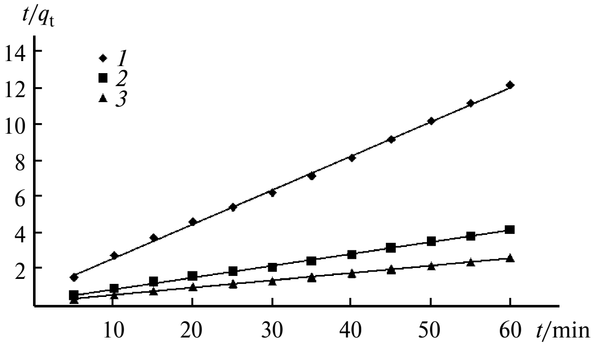

Fig. 7. Kinetic curves of adsorption of Cu^{2+} ions on GAC (solid lines) obtained by experimental data (points) processing using the pseudo-second-order kinetic equations; the initial concentrations of Cu^{2+} ions are 100 (*1*), 300 (*2*), and 500 mg L^{-1} (*3*).

from the theoretical data. The correlation coefficients obtained by experimental result processing are presented in Table 2. It is seen that the correlation coefficients for a first-order kinetic equation obtained for all concentrations studied were considerably lower than 1. In addition, the q_e values found from the first-order kinetic model did not give reasonable values. Therefore, the kinetics of the adsorption process under study cannot be described by a pseudo-first-order equation.

The model based on a pseudo-second-order equation. The adsorption kinetics can be described by the pseudo-second-order equation[22—24,26—28]

$$t/q_t = 1/h + (1/q_e)t, \tag{8}$$

where $h = kq_e^2$ (mg g^{-1} min^{-1}) can be regarded as the initial adsorption rate at $t \to 0$ and k (g mg^{-1} min^{-1}) is the rate constant of the pseudo-second-order adsorption. In the case where experimental data are described by a pseudo-second-order kinetic equation, the dependence of parameter t/q_t on t is linear and the values of q_e, k, and h can be determined from the slope and intercept of this plot, respectively. The plots of the linearized form of the pseudo-second-order of reaction at different Cu^{2+} concentration by GAC are shown in Fig. 7. The pseudo-first-oder and pseudo-second-order rate constants, which were calculated from the data in Figs 6 and 7, are listed in Table 2 along with the corresponding correlation coefficients.

The correlation coefficients for the second-order kinetic model obtained exceeded 0.997 at all copper concentrations in the initial solution. The calculated values of q_e also agree well with the experimental data (see Table 2). These indicate that the studied adsorption process is described in terms of the pseudo-second-order kinetic model. The similar phenomena are also observed for adsorption of dye RR189 on cross-linked chitosan balls,[26] in adsorption of dyes BB69 and DR227 on activated clay,[23] and in adsorption of dye AB9 on the mixed sorbents (activated clay with activated carbon).[25]

Thus, in the present work we studied the equilibrium adsorption and kinetics of copper adsorption from aqueous solutions on granulated activated carbon in the range of copper concentrations from 100 to 500 mg L^{-1} at pH 5.0 and 30 °C. The equilibrium data on adsorption were analyzed using the Langmuir, Freundlich, Redlich—Peterson, Temkin, and Toth equations. The characteristic parameters and the corresponding correlation coefficients were determined for all isotherms plotted according to these equations. The Langmuir, Freundlich, Redlich—Peterson equations were demonstrated to provide the best correlation for the sorption of copper on the activated carbon. The suitability of the pseudo-first- and pseudo-second-order kinetic models for the sorption of

Table 2. Experimental values of q_e and the kinetic parameters of adsorption of ions Cu^{2+} on GAC at different initial concentrations (C_i) calculated by the pseudo-first- and pseudo-second-order equations (I and II, respectively)

C_i /mg L^{-1}	q_e^{exp} /mg g^{-1}	I			II			
		k_{ad} /min^{-1}	q_e /mg g^{-1}	R^2	k /g mg^{-1} min^{-1}	q_e /mg g^{-1}	h /mg g^{-1} min^{-1}	R^2
100	4.93	0.1036	3.451	0.960	0.0473	5.319	1.340	0.998
300	14.23	0.1197	12.942	0.975	0.0157	15.385	3.731	0.998
500	22.52	0.1105	20.464	0.973	0.0085	25.0	5.291	0.997

copper on the activated carbon is also discussed. The pseudo-second-order kinetic model agrees well with the dynamics of copper adsorption on the carbon for different initial copper concentrations over the whole range studied.

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