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Adsorption characteristics of Cu(II) onto ion exchange resins 252H and 1500H: Kinetics, isotherms and error analysis

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Abstract

The adsorption of Copper(II) onto Amberjet 1500H and Ambersep 252H synthetic ion exchange resins have been studied. All the studies were conducted by a batch method to determine equilibrium and kinetic studies at the solution pH of 5.8 in the concentration ranges from 10 to 20 mg/L. The experimental isotherm data were analyzed using the Freundlich, Langmuir, Redlich Perterson, Temkin, Dubinin-Radushkevich equations. Correlation co-efficient was determined for each isotherm analysis. Error functions have been used to determine the alternative single component parameters by non-linear regression due to the bias in using the correlation coefficient resulting from linearisation. From the error analysis the EABS error function provides the best parameters for the isotherm equation in this system. Adsorption kinetics data were tested using pseudo-first-order, pseudo-second-order and intraparticle diffusion models. Kinetic studies showed that the adsorption followed a pseudo-second-order reaction. The initial sorption rate, pseudo-first-order, pseudo-second-order and intraparticle diffusion rate constants for different initial concentrations were evaluated and discussed.
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Keywords: Adsorption; Ion exchange resins; Copper(II); Isotherms; Error analysis; Diffusion and kinetics

1. Introduction

The problem of removing pollutants from water and wastewater is an important process and is becoming more important with the increasing of industrial activities. In order to solve heavy metal pollution in ecosystem, it is important to bring applicable solutions to the subject. It is possible to clean polluted environment only with long study requiring expensive and complex plants. Therefore, it is important to take effective precautions to prevent water, soil and air pollutions. Copper is present in the wastewater of several industries, such as metal cleaning and plating baths, refineries, paper and pulp, fertilizer, and wood preservatives and it is highly toxic [1]. The excessive intake of copper by man leads to severe mucosal irritation, widespread capillary damage, hepatic and renal damage, central nervous problems followed by depression, gastrointestinal irritation, and possible necrotic changes in the liver and kidney [1]. The World Health Organization (WHO) recommended a maximum acceptable concentration of Cu(II) in drinking water of 1.5 mg/L [2]. Table 1 summarizes copper standards in current EPA regulations [3]. Therefore it is essential that potable waters be given some treatment to remove copper before domestic supply. There are many different methods for treating wastewaters. Current methods for wastewater treatment include precipitation, coagulation/flotation, sedimentation, flotation, filtration, membrane processes, electrochemical techniques, biological process, chemical reactions, adsorption and ion exchange. But the selection of the wastewater treatment method is based on the concentration of waste and the cost of treatment. Adsorption with ion exchange resin is one of the popular methods for the removal of heavy metals from the water and wastewater [4,5].

Ion exchange resins have been developed as a major option for treating wastewaters over the past few decades [6–8]. Selective resins reduce the residual concentration of heavy metal to below the maximum limits [9–12]. The influence of complex

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Nomenclature

a_R	constant of Redlich–Peterson isotherm (L/mg)
A	Temkin isotherm constant related to adsorbate/adsorbate interaction (L/g)
b	Langmuir constant (L/mg)
B	Temkin isotherm constant
C_e	equilibrium adsorbate concentration (mg/L)
C_t	solution phase adsorbate concentration at time t (mg/L)
C_0	initial concentration of adsorbate (mg/L)
E	Dubinin–Radushkevich isotherm constant
k_1	rate constant of pseudo-first-order adsorption model (h^{-1})
k_2	rate constant of pseudo-second-order adsorption model (g/mg h)
K_F	Freundlich constant (mg/g)
k_{id}	intraparticle diffusion rate constant (mg/g $h^{1/2}$)
K_R	constant in Redlich–Peterson isotherm (L/g)
M	mass of the adsorbent (g)
n	Freundlich isotherm constant related to adsorption intensity
N	number of data points
q_e	equilibrium adsorption uptake concentration (mg/g)
$q_{e,cal}$	calculated value of adsorbate concentration at equilibrium (mg/g)
$q_{e,exp}$	experimental value of adsorbate concentration at equilibrium (mg/g)
q_{max}	maximum adsorption capacity of adsorbent (mg/g)
q_s	Dubinin–Radushkevich isotherm constant related to adsorption capacity (mg/g)
q_t	amount of adsorbate adsorbed by adsorbent at time t (mg/g)
Q^0	Langmuir constant (mg/g)
R	universal gas constant (8.314 J/mol K)
R^2	correlation coefficient
T	absolute temperature (K)
t	time (h)
V	volume of the solution (L)

Greek letter

β	constant of Redlich–Peterson isotherm ($0 < \beta < 1$)

formation on ion exchange sorption equilibrium and on the distribution of metal ions between the liquid and resin phase has been extensively studied [13–16]. Many studies on the adsorption of metal ions on ion exchange resins such as IR-120, Dowex A-1, Duolite GT-73 [17], IRN77 [18], and NKA-9 [5] have been reported.

The present work is aimed at evaluating the kinetics, isotherm, error analysis and diffusion parameters for the adsorption of Cu(II) onto 252H and 1500H ion exchange resins for the adsorption process. The effect of various system parameters such as initial concentration, time, pH and resin dosage are studied and the results obtained are discussed.

Table 1
EPA copper discharge limits

EPA regulation	Limit
Toxic Release Inventory (TRI)	1 mg/L
Clean Water Act (CWA) (daily)	3.39 mg/L
Clean Water Act (CWA) (30-day average)	2.07 mg/L
Safe Drinking Water Act (SDWA)	1.3 mg/L
Superfund Amendments and Reauthorization Act (SARA)	4.5 kg/year

2. Experimental

2.1. Adsorbate

All the reagents used were analytical grade chemicals. A stock solution of copper ions (1000 mg/L) was prepared by dissolving appropriate amount of $CuCl_2 \cdot 2H_2O$ (Aldrich Chemical Company, USA) in double distilled water.

2.2. Adsorbent

The cation exchange resins 1500H and 252H (Rohm and Hass Korea Co., Ltd) used in this study are generally used for the removal of heavy metals from water and wastewater. The Physico-chemical properties and specifications of ion exchange resins are presented in Table 2.

Table 2
Characteristic properties of the ion exchange resins used[a]

AMBERJET 1500H	
Matrix	Styrene divinylbenzene copolymer
Functional groups	Sulphonates
Physical form	Dark amber beads
Ionic form as shipped	H^+
Total exchange capacity	≥2.0 equiv./L (H^+ form)
Moisture holding capacity	45–51% (H^+ form)
Specific gravity	1.28–1.32 (Na^+ form)
Shipping weight	820 g/L
Particle size Uniformity coefficient	≤1.20
Harmonic mean size	650 ± 50 μm
Fine contents	<0.425 mm: 0.5% max
Maximum reversible swelling	$Na^+ \rightarrow H^+$: 10%
AMBERSEP 252H	
Matrix	Styrene divinylbenzene copolymer
Functional groups	$-SO_3-$
Physical form	Light grey beads
Ionic form as shipped	H^+
Total exchange capacity	≥1.65 equiv./L (H^+ form)
Moisture holding capacity	52–58% (H^+ form)
Specific gravity	1.18–1.22 (H^+ form)
Shipping weight	755 g/L
Particle size harmonic mean size	0.90–1.10 mm
Uniformity coefficient	≤1.4
Fine contents	<0.600 mm: 1.0% max
Maximum reversible swelling	$Na^+ \rightarrow H^+$: 7%

[a] Manufacturer supplied.

2.3. Batch mode studies

The stock solution was diluted as required to obtain standard solutions containing 5–30 mg/L of Cu(II). A 100 mL of Cu(II) solution of a desired concentration, adjusted to a desired pH, was taken in reaction bottles of 300 mL capacity and known amounts of ion exchange resins were added. The solution pH was adjusted by using hydrochloric acid or sodium hydroxide solutions. The solutions were agitated for a predetermined period at 25 ± 1 °C in a shaking incubator (JEIO TECH SI-900R). The agitation speed of the shaker was fixed at 150 rpm for all the batch experiments. The resins were separated and the filtrate was analyzed by an inductively coupled plasma spectrophotometer (ICP) (ULTIMA 2, Jobin Yvon Horiba) for copper content.

2.4. Isotherm experiments

Adsorption isotherm studies were carried out in a series of 300 mL reaction bottles. Each bottles was filled with 100 mL of different initial Cu(II) concentrations while maintaining the resin dosage at constant level. After equilibration, the solution was separated and analyzed. The initial concentrations of solutions taken for the studies were 10, 15 and 20 mg/L. The equilibrium adsorption capacity was calculated using

$$q_e = \frac{(C_0 - C_e)V}{M} \quad (1)$$

where q_e (mg/g) is the equilibrium adsorption capacity, C_0 and C_e the initial and equilibrium concentration (mg/L) of copper ions in solution, V (L) the volume, and M (g) is the weight of the adsorbent.

2.5. Kinetic studies

Kinetic experiments were conducted by using a known weight of resin dosage and employing Cu(II) concentration in the range of 10–20 mg/L. The samples at different time intervals (0–360 min) were taken and centrifuged. Suitable aliquots were analyzed for copper concentration and recorded. The rate constants were calculated by using the conventional rate expression. The amount of metal ion sorbed, q_t, was calculated from

$$q_t = \frac{(C_0 - C_t)V}{M} \quad (2)$$

where q_t (mg/g) is the equilibrium adsorption capacity, C_0 and C_t the initial and equilibrium concentration (mg/L) of copper ions in solution, V (L) the volume, and M (g) is the weight of the adsorbent.

3. Results and discussion

3.1. Adsorption isotherm studies

The quantity of metal that could be taken up by a resin is a function of both the concentration of the metal and the temperature. The amount of material adsorbed is determined as a function of the concentration at a constant temperature that could be explained in adsorption isotherms. Equations that are often used to describe the experimental isotherm data were developed by namely, Freundlich, Langmuir, Redlich–Peterson, The Temkin Isotherm, and The Dubinin–Redushkevich isotherm.

The Freundlich isotherm model was also used to explain the observed phenomena.

$$\log q_e = \log K_F + n \log C_e \quad (3)$$

where K_F (mg/g) is the Freundlich constant and 'n' the Freundlich exponent. Where, C_e is the equilibrium concentration (mg/L), q_e the amount of Cu(II) adsorbed by per gram of the ion exchange resins and K_F and n are constants incorporating all factors affecting the adsorption process such as adsorption capacity and intensity. Linear plots of $\log q_e$ versus $\log C_e$ shows that the adsorption follows Freundlich isotherm model. K_F and n were calculated from the intercept and slope of the plot. The constants K_F and n for Cu(II) and ion exchange resin systems are presented in Table 3. The values of n lie between 1 and 10 indicating favorable adsorption [19].

The Langmuir isotherm was applied for adsorption equilibrium for both Amberjet 1500H and Ambersep 252H ion exchange resins [20]. The Langmuir sorption isotherm is often used to describe sorption of a solute from a liquid solution as

$$\frac{1}{q_e} = \frac{1}{Q^0} + \frac{1}{bQ^0}\frac{1}{C_e} \quad (4)$$

where C_e is the equilibrium concentration (mg/L), q_e the amount adsorbed at equilibrium (mg/g) and Q_0 and b are Langmuir constants related to adsorption capacity and energy of adsorption, respectively. The linear plots of $1/q_e$ versus $1/C_e$ show that the

Table 3
Freundlich, Langmuir, Redlich–Peterson, Temkin and Dubinin–Radushkevich isotherm constants for copper ion sorption in ion exchange resins 1500H and 252H

Isotherms	Name of the resins	
	Amberjet 1500H	Ambersep 252H
Freundlich		
K_F (mg g^{-1})	22.3408	24.344
n	0.4226	0.5
R^2	0.9662	0.9819
Langmuir		
Q^0 (mg g^{-1})	24.57	11.7412
b (L mg^{-1})	8.4792	26.28
R^2	0.9921	0.9631
Redlich–Peterson		
K_R (L g^{-1})	294.12	68.4932
a_R (L mg^{-1})	14.32	3.1219
R^2	0.9806	0.9664
Temkin		
B	4.7036	3.2975
A (L g^{-1})	95.031	149.053
R^2	0.9821	0.8694
Dubinin–Radushkevich		
q_s (mg g^{-1})	26.488	14.1866
E	3535.5	5972.94
R^2	0.8831	0.9669

adsorption obeys Langmuir isotherm model for both Amberjet 1500H and Ambersep 252H. The values of Q_0 and b were determined from the slopes and intercepts of the Langmuir plots and represented in Table 3. The Langmuir equation is applicable to homogeneous sorption where the sorption of each sorbate molecule on to the surface has equal sorption activation energy. As shown in Table 3, maximum uptake of Cu(II) on 1500H is about two times larger than that of 252H. This may be due to the intrinsic properties such as ion exchange capacity of resin in Table 2.

Redlich and Peterson [21] incorporated the features of the Langmuir and Freundlich isotherms into a single equation and presented a general isotherm equation as followed:

$$\frac{C_e}{q_e} = \frac{1}{K_R} + \frac{a_R}{K_R} C_e^{\beta} \tag{5}$$

where the exponent, β, lies between 0 (Henry's law equation) and 1 (Langmuir form). Plotting the C_e/q_e of the above equation against C_e^{β} to obtain the isotherm constants is not possible because of the three unknowns, a_R, K_R and β. Therefore a minimization procedure is adopted to solve the above equation by maximizing the correlation coefficient between the theoretical data for q_e predicted from the above equation and the experimental data. Redlich–Peterson values for the adsorption of copper on to Amberjet 1500H and Ambersep 252H and the constants and optimized values are presented in Table 3. The fitted values of β for 1500H and 252H are 0.5 and 0.2, respectively. It means that 1500H resin is well fitted with the Langmuir isotherm, while 252H follows Henry's law.

Temkin isotherm, which considers the effects of the heat of adsorption that decreases linearly with coverage of the adsorbate and asorbent interactions, is given as Choy et al. [22].

The Temkin isotherm has been used in the form as follows:

$$q_e = \frac{RT}{b} \ln A + \frac{RT}{b} \ln(C_e) \tag{6}$$

where $\frac{RT}{b} = B$

The sorption data can be analyzed according to Eq. (6). The liner plots of q_e versus $\log C_e$ enable to determine the constant A and b. From Table 3 an A value of 252H is larger than that of 1500H. This means that the adsorbate/adsorbate interaction of 252H resin is larger than that of 1500H.

Another popular equation for the analysis of isotherm of a high degree of rectangularity is that proposed by Dubinin and Radushkevich [4].

$$\ln q_e = \ln q_S - B\varepsilon^2 \tag{7}$$

where ε can be correlated:

$$\varepsilon = RT \ln\left[1 + \frac{1}{C_e}\right] \tag{8}$$

The constant B gives the mean free energy E of sorption per molecule of the sorbate when it is transferred to the surface of the solid from infinity in the solution and can be computed using the relationship:

$$E = \frac{1}{\sqrt{2B}} \tag{9}$$

where R is the gas constant (8.31 J/mol K) and T is the absolute temperature. Therefore a plot of $\ln q_e$ versus ε^2 enables one to determine the constants q_e and E and represented in Table 3. From Table 3, 252H ion exchange resin is having more sorption energy per sorbate when compared with Amberjet 1500H.

Based on the adsorption isotherm studies the uptake capacity of 1500H is larger than that of 252H due to the intrinsic ion exchange capacity, while the adsorbate/adsorbate interaction of 1500H is smaller than that of 252H.

3.2. Error analysis for isotherm studies

In the single component isotherm studies, the optimization procedure requires an error function to be defined in order to be able to evaluate the fit of the isotherm to the experimental equilibrium data. In this study, five different error functions were examined and in each case the isotherm parameters were determined by minimizing the respective error function across the concentration range studied [23]. The error functions studied were as follows.

3.2.1. The sum of the squares of the errors (ERRSQ)

The sum of the squares of the errors method can be represented by the equation

$$\sum_{i=1}^{p} (q_{e,calc} - q_{e,meas})_i^2 \tag{10}$$

where $q_{e,calc}$ are the theoretical adsorbed solid phase concentration of copper on ion exchange resin, which have been calculated from the isotherm Eqs. (3) and (4), and $q_{e,meas}$ are the experimentally determined adsorbed copper concentrations obtained from Eq. (1) using the experimentally measured equilibrium copper liquid phase concentrations, C_e.

Although this is the most common error function in use, it has one major drawback. Isotherm parameters derived using this error function will provide a better fit as the magnitude of the errors and thus the squares of the errors increases-biasing the fit toward the data obtained at the high end of the concentration range.

3.2.2. The hybrid fractional error function (HYBRID)

This error function was developed by the Ng et al. [23] to improve the fit of the sum of the squares of the errors at low concentrations by dividing it by the measured value. It also includes the number of degrees of freedom of the system – the number of data points, n, minus the number of parameters, p, of the isotherm equation – as a divisor:

$$\frac{100}{n-p} \sum_{i=1}^{n} \left[\frac{(q_{e,meas} - q_{e,calc})^2}{q_{e,meas}}\right]_i \tag{11}$$

3.2.3. Marquardt's percent standard deviation (MPSD)

This error function was used previously by a number of researchers in the field [24]. It is similar in some respects to a geometric mean error distribution modified according to the number of degrees of freedom of the system:

$$100\sqrt{\frac{1}{n-p}\sum_{i=1}^{p}\left(\frac{(q_{\mathrm{e,meas}}-q_{\mathrm{e,calc}})^2}{q_{\mathrm{e,meas}}}\right)_i} \quad (12)$$

3.2.4. The average relative error (ARE)

This error function [25] attempts to minimize the fractional error distribution across the entire concentration range:

$$\frac{100}{n}\sum_{i=1}^{p}\left|\frac{q_{\mathrm{e,calc}}-q_{\mathrm{e,meas}}}{q_{\mathrm{e,meas}}}\right|_i \quad (13)$$

3.2.5. The sum of the absolute errors (EABS)

This approach is similar to the sum of the squares of the errors. Isotherm parameters determined using this error function would provide a better fit as the magnitude of the error increased biasing the fit towards the high concentration data:

$$\sum_{i=1}^{p}|q_{\mathrm{e,calc}}-q_{\mathrm{e,meas}}|_i \quad (14)$$

Since all the experiments were carried out at m/V ratios of almost exactly g/L, according to the formulation of the problem, both C_e and q_e contribute equally to weighting the error criterion for the model solution procedure. Hence, the difference in the sorbed phase concentration reflects the differences in the predicted concentration for both phases. From Figs. 1–4, the EABS error function method provided the best parameters for the isotherm equations in the copper–ion exchange system, when the errors are being normalized for comparison purposes. The results for the error analyses are shown in Table 4 for Freundlich and Langmuir isotherms. From Table 4 the EABS has the highest R^2 values between different error function methods and more significant. These data are used in the design

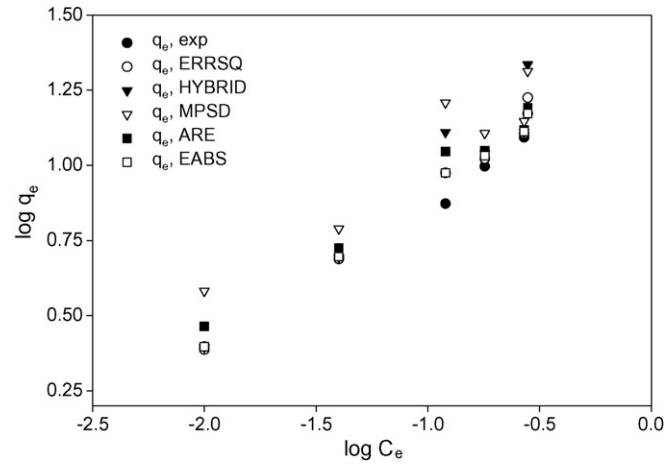

Fig. 2. Freundlich isotherm plots for copper onto Ambersep 252H using various error analysis methods (conditions: resin dosage = 2 g/L; pH = 5.8).

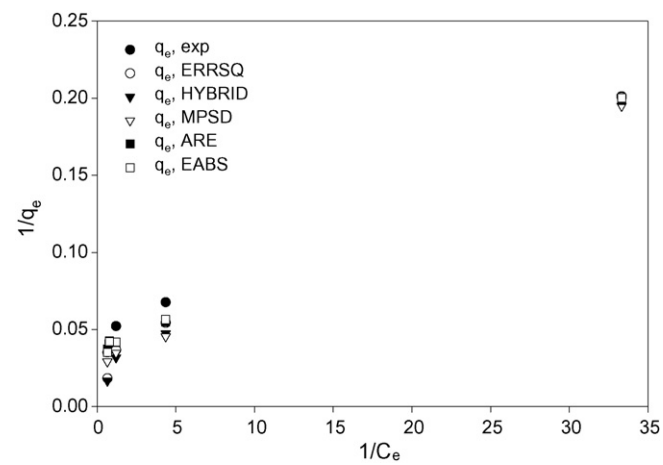

Fig. 3. Langmuir isotherm plots for copper onto Amberjet 1500H using various error analysis methods (conditions: resin dosage = 1 g/L; pH = 5.8).

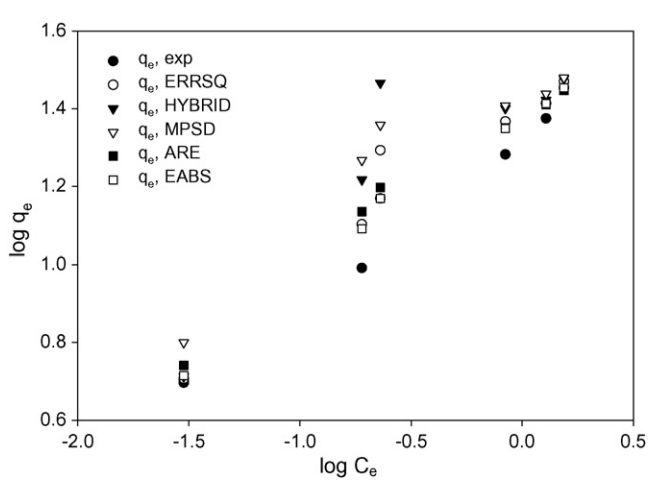

Fig. 1. Freundlich isotherm plots for copper onto Amberjet 1500H using various error analysis methods (conditions: resin dosage = 1 g/L; pH = 5.8).

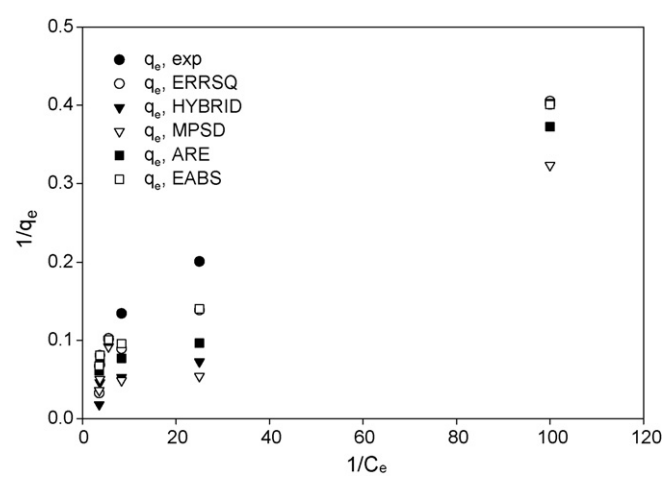

Fig. 4. Langmuir isotherm plots for copper onto Amberjet 252H using various error analysis methods (conditions: resin dosage = 2 g/L; pH = 5.8).

Table 4
Single component Freundlich and Langmuir isotherm results for copper onto 1500H ion exchange resins using various error functions

Name of the resins	Parameters	ERRSQ	HYBRID	MPSD	ARE	EABS
	K_F	25.86	28.77	28.34	24.53	24.31
1500H (Freundlich isotherm)	n	0.4212	0.3974	0.3619	0.3974	0.4217
	R^2	0.928	0.7688	0.8751	0.9778	0.989
	Q^0	34.96	40.16	34.96	28.08	28.33
1500H (Langmuir isotherm)	b	5.5	4.698	5.72	7.27	7.20
	R^2	0.9871	0.988	0.9962	0.9992	0.9989
	K_F	28.563	35.003	32.063	27.196	27.064
252H (Freundlich isotherm)	n	0.539	0.579	0.468	0.487	0.519
	R^2	0.983	0.931	0.908	0.982	0.995
	Q^0	18.55	38.61	30.96	18.48	14.99
252H (Langmuir isotherm)	b	15.4	7	11.54	17.45	20.21
	R^2	0.978	0.945	0.926	0.970	0.994

of commercial adsorbers and consequently the more accurate the isotherm parameters, the more accurate are the system design.

3.3. Adsorption kinetic model

The kinetics of adsorption describes the rate of copper ions uptake on ion exchange resins and this rate control the equilibrium time. The kinetics of adsorbate uptake is required for selecting optimum operating conditions for the full-scale batch process [26]. The kinetic parameter, which is helpful for the prediction of adsorption rate, gives important information for designing and modeling the processes. Thus, the effects of initial concentration, contact time, and adsorbent dosage were analyzed from the kinetic point of view. Preliminary studies on the adsorption rate show that the amount adsorbed increased with increased Cu(II) concentration. The maximum amount of copper ions was adsorbed within the first 120 min (70–90% of total metal ions adsorbed) and thereafter the adsorption proceeds at a slower rate until equilibrium reached. The equilibrium time was found to be at 360 min for the initial Cu(II) concentration range studied. The rate of uptake increases as the ion exchange resin dosage increases because it leads to more ion exchange sites for adsorption. The kinetics of the adsorption data was analyzed using different kinetic models such as pseudo-first-order and pseudo-second-order models.

3.3.1. Pseudo-first-order kinetic model

For the rate constant for Pseudo-first-order chemical sorption [27,28]

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \quad (15)$$

The term k_1 (h^{-1}) is the first order adsorption rate constant, q_e the amount of metal adsorbed at equilibrium and q_t is the amount adsorbed at time 't'. The first order equation did not apply throughout all the contact times in this work. It was applicable over the initial 15–240 min sorption period. Plot of log ($q_e - q_t$) versus "time" at different adsorbate concentrations (Figs. 5 and 6) deviated considerably from the data after a short period. The calculated slopes and intercepts from the plots were used to determine the rate constant k_1 and equilibrium capacity (q_e). The values of k_1, q_e and regression co-efficient provided in Table 5.

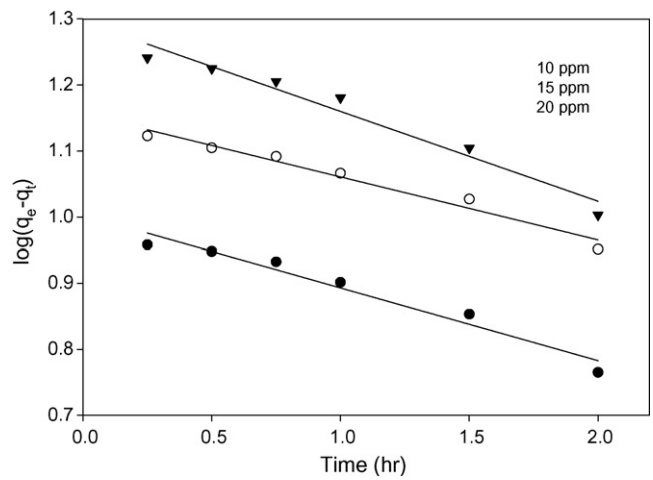

Fig. 5. Pseudo-first-order kinetics for Cu(II) onto Amberjet 1500H (conditions: resin dosage = 1 g/L; pH = 5.8).

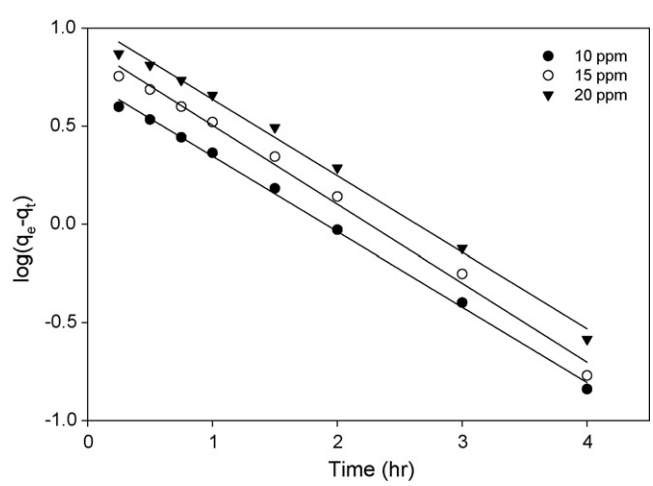

Fig. 6. Pseudo-first-order kinetics for Cu(II) onto Ambersep 252H (conditions: resin dosage = 2 g/L; pH = 5.8).

Table 5
The pseudo-first-order rate constant and intraparticle diffusion value at different initial concentrations of copper removal by Amberjet 1500H and Ambersep 252H ion exchange resins

Name of the resin	Concentration of copper (mg/L)	Pseudo-first-order rate constant k_1 (h^{-1})	R^2	Intraparticle diffusion constant, k_{id} (mg/g $h^{1/2}$)
	10	0.2538	0.9601	5.1551
1500H	15	0.2197	0.9712	7.3620
	20	0.3137	0.9609	9.8468
	10	0.8845	0.9977	3.4230
252H	15	0.9255	0.9932	4.8378
	20	0.8965	0.9935	6.1470

The variation in rate should be proportional to the first power of concentration for strict surface ion exchange. However, the relationship between initial solute concentration and rate of adsorption will not be linear when pore diffusion limits the adsorption process. It was observed from Fig. 5 that the Lagergren model fits well for the first 60 min and thereafter the data deviate from the theory. Thus, the model represents the initial stages where rapid adsorption occurs well but cannot be applied for the entire adsorption process. A similar trend was previously observed by Ho and McKay [29] for dyes on peat particles. Ho and McKay [29] reported that the sorption data were represented well by the Lagergren first order kinetic model only for the rapid initial phase that occurs for a contact time of 0–30 min. This confirms that it is not appropriate to use the Lagergren kinetic model to predict the adsorption kinetics for Cu(II) onto ion exchange process for the entire sorption period, which shows that the model can be applied but is not appropriate to describe the entire process.

3.3.2. Pseudo-second order kinetic model

The pseudo-second order reaction is greatly influenced by the amount of metal on the adsorbent's surface and the amount of metal adsorbed at equilibrium [30]. The rate is directly proportional to the number of active surface sites. The pseudo-second order reaction rate expression can be written as

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{16}$$

The product $k_2 q_e^2$ is the initial sorption rate 'h' (Eq. (16))

$$\text{rate} = k_2 q_e^2 \tag{17}$$

where k_2 (g/mg h) is the pseudo-second order rate constant, q_e the amount adsorbed at equilibrium and q_t is the amount of metal adsorbed at time 't'. Plotting t/q_t against "t" at different adsobate concentrations (Figs. 7 and 8) provided second order sorption rate constant (k_2) and q_e values from the slopes and intercepts (see Table 6). The correlation co-efficient (R^2) for these plots are superior. From Table 6, it was observed that the pseudo-second order rate constant (k_2) decreased with increased initial concentration and the initial sorption rate (h) was found to increase with increased initial Cu(II) concentration. The calculated q_e values agree very well with the experimental values, and a regression co-efficient shows that the model can be applied for the entire adsorption process and confirms the chemisorptions of Cu(II) onto ion exchange resins.

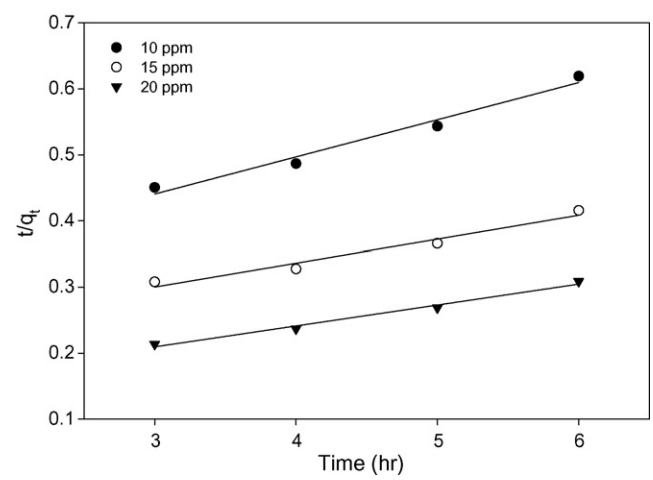

Fig. 7. Pseudo-second-order kinetics for Cu(II) onto Amberjet 1500H (conditions: resin dosage = 1 g/L; pH = 5.8).

3.3.3. Adsorption mechanism

The prediction of the rate-limiting step is an important factor to be considered in the adsorption process [31]. It is governed by the adsorption mechanism, which is generally required

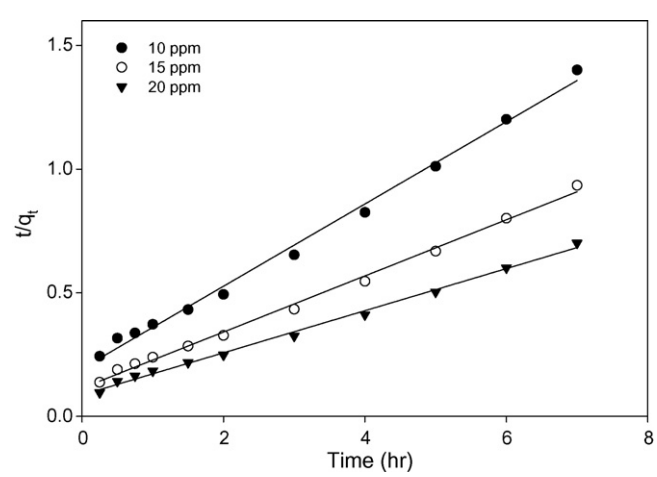

Fig. 8. Pseudo-second-order kinetics for Cu(II) onto Ambersep 252H (conditions: resin dosage = 1 g/L; pH = 5.8).

Table 6
The pseudo-second-order rate constant value at different initial concentrations of copper removal by Amberjet 1500H and Ambersep 252H ion exchange resins

Sorbent name	Concentration of copper (mg/L)	Pseudo-second-order rate constant k_2 (g/mg h)	Equilibrium mass of copper sorbed on ion exchange resins, q_e (mg/g)	R^2
	10	0.01167	17.7619	0.9879
1500H	15	0.0068	27.7008	0.9828
	20	0.0052	37.1747	0.9800
	10	0.1432	6.009	0.9947
252H	15	0.1129	8.810	0.9963
	20	0.0834	11.750	0.9958

for design purposes. For a solid–liquid sorption process, the solute transfer is usually characterized by external mass transfer (boundary layer diffusion), or intraparticle diffusion, or both. The adsorption of Cu(II) onto ion exchange resins may be controlled due to film diffusion at earlier stages and later by the particle diffusion. The most commonly used technique for identifying the mechanism involved in the adsorption process is by fitting and intraparticle diffusion plot.

According to Weber and Morris [32], an intraparticle diffusion coefficient k_{id} is given by the equation

$$q_t = k_{id} t^{0.5} \tag{30}$$

The plot of q_t versus 0.5 as shown in Figs. 9 and 10 represents the different stages of adsorption. An initial steep-sloped portion is followed by a linear portion to the intraparticle diffusion and a plateau to the equilibrium [4]. The initial steep-sloped portion is (from 0 to 1 $h^{1/2}$) is attributed to external surface adsorption or instantaneous adsorption, while the gentle-sloped portion (from 1 to 2 $h^{1/2}$) is attributed to gradual adsorption. This reveals that the intraparticle diffusion is rate-controlled and leads to a plateau to the equilibrium. It should be noted that the intraparticle diffusion starts to slow down due to extremely low solute concentration in solution. The intraparticle diffusion rate was obtained from the slope of the gentle-sloped portion (Table 5). The k_{id} value was higher at the higher concentrations. With the decrease of the copper concentration in the solution,

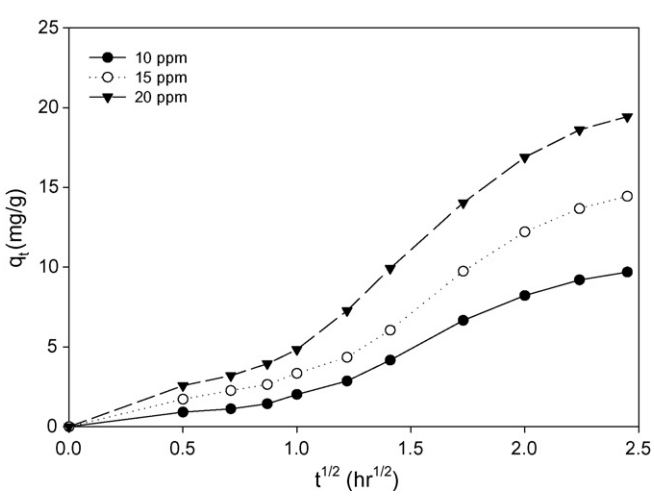

Fig. 9. Intraparticle diffusion plots for adsorption of copper on Amberjet 1500H (conditions: resin dosage = 1 g/L; pH = 5.8).

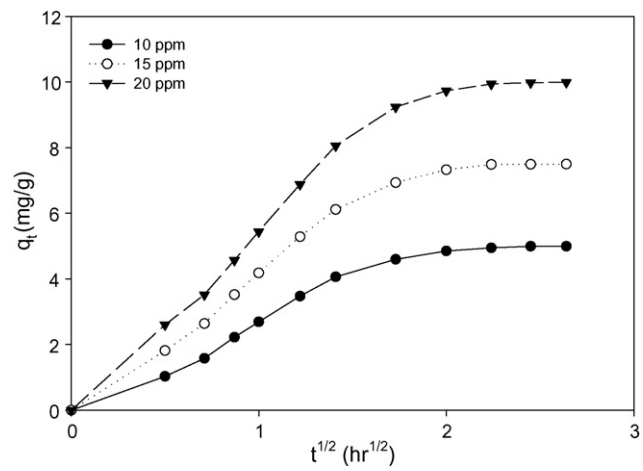

Fig. 10. Intraparticle diffusion plots for adsorption of copper on Ambersep 252H (conditions: resin dosage = 2 g/L; pH = 5.8).

the diffusion rate became lower and lower, and the diffusion process reached the final equilibrium stage. It is seen that the order of adsorption rates was first stage ($k_{id,1}$) > second stage ($k_{id,2}$) > third stage ($k_{id,3}$). Therefore the changes of $k_{id,1}$, $k_{id,2}$, and $k_{id,3}$ could be attributed to the adsorption stages of the exterior surface, interior surface and equilibrium, respectively. This interpretation is consistent with the pseudo-second-order rate.

4. Conclusion

In this study, the effects of parameters such as amount of resin, contact time, isotherm studies, error analysis and kinetic studies have been investigated. The work evaluates the Amberjet 1500H and Ambersep 252H cation exchanger resin containing sulfonated functional groups for removing target pollutant Cu(II) from aqueous solutions and focus on the binding equilibrium and batch studies of metal ions. Amberjet 1500H and Ambersep 252H resins are acidic this makes it highly reactive. The adsorption degrees for the Cu(II) ions were determined at room temperature by using Amberjet 1500H and Ambersep 252H resins. Based on the adsorption isotherm studies the uptake capacity of Cu(II) on 1500H is larger than that of 252H due to the intrinsic ion exchange capacity, while the adsorbate/adsorbate interaction of 1500H is smaller than that of 252H. The EABS error function provides the best parameters for the isotherm equation in this system. The isotherm parameters are different from those values obtained using linearised data analysis and

must be considered more accurate for application in the design of commercial adsorbers. Furthermore, different values of the Freundlich and Langmuir isotherm constants are obtained using the different error analysis methods. This is a significant conclusion even though the constants from the linear and non-linear error analysis are quite close. The kinetic data would be useful for developing an appropriate technology for designing a wastewater treatment plant. For all the system studied, chemical reaction seems significant in the rate-controlling step and the pseudo-second-order chemical reaction kinetics provide the best correlation of the experimental data for both 1500H and 252H. We conclude that ion exchange resins could be exploited for applications in the tertiary level treatment of potablewaters, industrial effluents as well as it can be applied for the treatment of coolant water in the nuclear power plants. Detailed studies will be needed to further evaluate ion exchange resins in the treatment of coolant water in the nuclear power plant.

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References

[1] R. Gundogan, B. Acemioglu, M.H. Alma, Copper (II) adsorption from aqueous solution by herbaceous peat, J. Colloid Interf. Sci. 269 (2004) 303.
[2] C.S. Rao, Environmental Pollution Control Engineering, Wiley Eastern, New Delhi, 1992.
[3] P.D. Johnson, M.A. Watson, J. Brown, I.A. Jefcoat, Peanut hull pellets as a single use sorbent for the capture of Cu(II) from wastewater, Waste Manage. 22 (2002) 471.
[4] S. Rengaraj, Y. Kim, C.K. Joo, K. Choi, J. Yi, Batch adsorptive removal of copper ions in aqueous solutions by ion exchange resins: 1200H and IRN97H, Korean J. Chem. Eng. 21 (2004) 187.
[5] Y. Omer, A. Yalcin, G. Fuat, Removal of copper, nickel, cobalt and manganese from aqueous solution by kaolinite, Water Res. 37 (2003) 948.
[6] D. Muraview, V. Gorshkov, A. Warshawsky, Ion Exchange, Decker, New York, 2000.
[7] G.M. Tillman, Water Treatment Troubleshoot and problem solving, Lewis Publishers, New York, 1996.
[8] J.P. Rawat, A. Ahmad, A. Agrawal, Equilibrium studies for the sorption of Cu^{2+} on lanthanum diethanolamine—a chelating material, Colloid Surf. 46 (1990) 239.
[9] A. Tunceli, A.R. Turker, Flame atomic absorption spectrometric determination of silver after preconcentration on Amberlite XAD-16 resin from thiocyanate solution, Talanta 51 (2000) 889.
[10] N. Rauf, S.S. Tahir, Thermodynamics of Fe(II) and Mn(II) adsorption onto bentonite from aqueous solutions, J. Chem. Thermodyn. 32 (2000) 651.
[11] D.B. Singh, D.C. Rupainwar, G. Prasad, K.C. Jayaprakash, Studies on the Cd(II) removal from water by adsorption, J. Hazard. Mater. 60 (1998) 29.
[12] S.L.C. Ferreira, J.R. Ferreira, A.F. Dantas, V.A. Lemos, N.M.L. Araujo, A.C.S. Costa, Copper determination in natural water samples by using FAAS after preconcentration onto amberlite XAD-2 loaded with calmagite, Talanta 50 (2000) 1253.
[13] A.A. Khan, R.P. Singh, Adsorption thermodynamics of carbofuran on Sn (IV) arsenosilicate in H^+, Na^+ and Ca^{2+} forms, Colloid Surf. 24 (1987) 33.
[14] A. Masaaki, A. Takaak, K. Iliryuki, Fugimta Satsui Nippon Kagaku Kaishi 8 (1984) 1310.
[15] C.H. Lee, J.S. Kim, M.Y. Suh, W. Lee, A chelating resin containing 4-(2-thiazolylazo) resorcinol as the functional group synthesis and sorption behavious for trace metal ions, Anal. Chim. Acta 339 (1997) 303.
[16] J.P. Rawat, K.P. Singh Muktawat, Thermodynamics of ion-exchange on ferric antimonite, J. Inorg. Nucl. Chem. 43 (1981) 2121.
[17] A. Demirbas, E. Pehlivan, F. Gode, T. Altun, G. Arslan, Adsorption of Cu(II), Zn(II), Ni(II), Pb(II), and Cd(II) from aqueous solution on Amberlite IR-120 synthetic resin, J. Colloid Interf. Sci. 282 (2005) 20.
[18] S. Rengaraj, S.H. Moon, Kinetics of adsorption of Co(II) removal from water and wastewater by ion exchange resins, Water Res. 36 (2002) 1783.
[19] F. Slejko, Adsorption Technology A Step by Step Approach to Process Evaluation and Application, Marcel Decker, New York, 1985.
[20] S. Rengaraj, C. Joo, Y. Kim, J. Yi, Kinetics of removal of Chromium from water and electronic process wastewater by ion exchange resins: 1200H, 1500H and IRN97H, J. Hazard. Mater. B 102 (2003) 257.
[21] O. Redlich, D.L. Peterson, A useful adsorption Isotherm, J. Phys. Chem. 63 (1954).
[22] K.K.H. Choy, G. McKay, J.F. Porter, Sorption of acid dyes from effluents using activated carbon, Resour. Conserv. Recycl. 27 (1999) 57.
[23] J.C.Y. Ng, W.H. Cheung, G. McKay, Equilibrium studies of the sorption of Cu(II) ions onto chitosan, J. Colloid Interf. Sci. 255 (2002) 64.
[24] A. Seidel, D. Gelbin, On applying the ideal adsorbed solution theory to multicomponent adsorption equilibria of dissolved organic components on activated carbon, Chem. Eng. Sci. 43 (1988) 79.
[25] A. Kapoor, R.T. Yang, Correlation of equilibrium adsorption data of condensible vapours on porous adsorbents, Gas Sep. Purif. 3 (1989) 187.
[26] V.K. Gupta, S. Sharma, Removal of zinc from aqueous solutions using bagasse fly ash—a low cost adsorbent, Ind. Eng. Chem. Res. 42 (2003) 6619.
[27] S. Lagergren, B.K. Venska, Zur theorie der sogenannten adsorption geloester stoffe, Vaternskapsakad Handlingar 24 (1898) 1.
[28] Y.S. Ho, G. McKay, The sorption of lead(II) ions on peat, Water Res. 33 (1999) 578.
[29] Y.S. Ho, G. McKay, Sorption of dyes from aqueous solution by peat, Chem. Eng. J. 70 (1998) 115.
[30] Y.S. Ho, G. McKay, Pseudo-second order model for sorption processes, Process Biochem. 34 (1999) 451.
[31] M. Sarkar, P.K. Acharya, B. Battacharya, Modeling the adsorption kinetics of some priority organic pollutants in water from diffusion and activation energy parameters, J. Colloid Interf. Sci. 266 (2003) 28.
[32] W.J. Weber, J.C. Morris, Kinetics of adsorption on carbon from solution, J. Sanit. Eng. Div. Am. Soc. Civ. Eng. 89 (1963) 31.