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Removal of Zn(II) from aqueous solutions using Lewatit S1468

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ABSTRACT

Adsorption of Zn(II) ions from aqueous solution onto Lewatit S1468 has been investigated to evaluate the effect of ground resin. Experimental data obtained from batch equilibrium tests have been analyzed by three two-parameter models (Freundlich, Langmuir and Temkin) and kinetic models including the Lagergren pseudo-first order and pseudo-second order. The equilibrium adsorption results are fitted better with Langmuir and Temkin isotherm compared to Freundlich models. It was determined that removal Zn(II) was well-fitted by first-order reaction kinetic. The adsorption process was relatively fast due to 90% of Zn(II) sorption was occurred within 1 min and equilibrium was reached at about 5 min for ground form of resin.

Keywords: Adsorption; Kinetic; Isotherms; Zinc; Resin; Lewatit S1468

1. Introduction

The problem of removing pollutants and heavy metals from water and wastewater has grown with rapid industrialization [1]. Many industries containing oil refining, textile industry, metal plating facilities, electroplating, mining operations, pigments and dyes manufacturing, fertilizer, and batteries produce heavy metals [2]. Heavy metals such as zinc, lead and copper are prior toxic pollutants in industrial wastewater, and they also become common groundwater contaminants [3]. Zinc is one of the most important pollutants and in due to its acute toxicity and non-biodegradability, zinc-containing liquid and solid wastes are considered as hazardous wastes [4,5].

The most important technologies for removal or reduction of metal ions in water are chemical precipitation, ion-exchange, phytoextraction, ultra filtration, reverse osmosis, and electro dialysis and sorption [6–8]. Sorption operations such as adsorption and ion exchange are suitable for aqueous solutions [9,10]. The main advantages of ion exchange are the recovery of metal, selectivity, less sludge produced and the meeting of strict discharge specifications. The use of synthetic resins with high adsorption capacity and low cost could be suitable method for removing toxic metal contaminants in water and wastewater [11,12].

In the presented work Zn(II) ions removal from aqueous solutions using ion-exchange resin Lewatit S1468 was investigated. The experiments in this study were performed for two different forms of Lewatit S1468 – bead form and ground form.

2. Materials and methods

2.1. Resin and reagents

The resin Lewatit S1468 (Bayer AG, Chemicals) used in the experiments is a strongly acid gelular cation exchange resin with beads of uniform size based

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Table 1
Characteristics of tested Lewatit S1468

Ionic form as shipped	Na^+
Functional group	sulfonic acid
Matrix	cross-linked polystyrene
Structure	gel type beads
Mean bead size	0.6 (± 0.05) mm
Bulk density	820 (± 5%) g/l
Density	1.28 g/ml
Total capacity	2 eq/l

on a styrene-divinylbenzene copolymer. The main physical and chemical properties are given in Table 1. The ground form of Lewatit S1468 used in the experiments was resin powder. The monodisperse beads were ground in an iron mill and treat by means of a magnetic separator. The size distribution of ground resin particles is presented in Fig. 1. The zeta potential of ground resin was −49.99 mV at pH 8.28.

Both the forms of resin were washed using distilled water to remove all impurities and dried in an oven at 70°C for 2 h.

The stock solutions of particular concentrations were prepared by dissolving analytical grade $ZnSO_4 \cdot 7H_2O$ in deionised water.

2.2. Apparatus

Thermo SCIENTIFIC model iCE 3000 SERIES atomic absorption spectrometer (AAS) operating with air-acetylene flame was used to analyze the concentration of Zn(II) in solutions. The size distribution of the ground particles was measured by the MasterSizer (Malvern Instruments, UK) and the pH and zeta potential was analysed using ZetaSizer instrument (Malvern Instrument Ltd., UK).

2.3. Adsorption experiments

A desired amount of treated S1468 resin (0.1 g) was weighed and added into an Erlenmeyer flask (100 ml) into which a desired volume of distilled water was added. After 24 h a required amount of standard solution of Zn(II) was added to the flask. The experiments were carried out by varying concentrations of initial Zn(II) solution (1–1500 mg/l). In all the experiments the flasks were shaken on an orbital shaker at 200 rpm and 25°C for 4 h to ensure ion-exchange equilibrium. The suspensions were then filtered with a micro filter of 0.8 μm pore size and the filtrates were analysed using AAS in order to determine the final Zn(II) concentration in solutions.

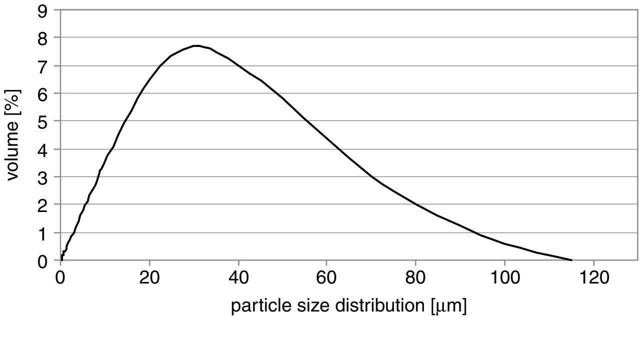

Fig. 1. Ground resin particle size distribution.

The Zn(II) concentration retained in the adsorbent phase q_e, was calculated according to the following equation:

$$q_e = \frac{(C_e - C_0) \cdot V}{m} \tag{1}$$

where q_e (mg/g) is the equilibrium adsorption capacity, C_0 and C_e (mg/l) are the initial and equilibrium concentrations of Zn(II) ions in the solution, respectively, V (l) is the total volume of the solution, and m(g) is the amount of the resin. Using this formula q_e values for different initial metal concentrations were calculated [13].

Kinetic experiments were realised using 100 ml of solutions with initial concentrations of 300 and 500 mg/l Zn(II). The aqueous samples were taken at different time intervals (0–120 min) and immediately filtered with a micro filter of 0.8 μm pore size.

The initial concentration of resin was (1 g/l). The following equation was used to determinate adsorbed metal concentration q_t:

$$q_t = \frac{(C_0 - C_t) \cdot V}{m} \tag{2}$$

where q_t (mg/g) is the adsorption capacity at time t, C_0 (mg/l) is the initial metal ions concentration, C_t (mg/l) is the concentration of metal ions in solution at time t, V (l) is the total volume, and m(g) is the amount of the resin [14].

Each experiment was performed twice and the result was taken as the average value of the two experiments.

3. Results and discussion

Results obtained for the adsorption of Zn(II) ions were analysed using Freundlich, Langmuir and Temkin adsorption models [15]. The equilibrium isotherm results were input into the Excel spreadsheet and the parameters of each isotherm were calculated by the modelling equations by minimizing the difference between the experimental data and the theoretically predicted models data. The plots in Fig. 2 (a) and (b) show the isotherms, as well as fitting of the experimental results to the curves of adsorption models approached.

The Freundlich ion-exchange capacities (K_f) and ion-exchange intensities (n) were similar for both forms of the resin. The values of n greater than 1 show favourable ion exchange of metal on ion-exchange resin [16]. The Langmuir constant (q_m) representing the maximum monolayer adsorption capacity was calculated to be 214.171 (mg/g) and 229.398 (mg/g) for ground and bead forms, respectively. Comparing the correlation coefficient (R^2) values the Langmuir isotherm the best fitted the experimental data. Alyüz et al. [6] observed that zinc adsorption provided similar Langmuir isotherm constants for cation exchange resin Dowex XCR S/S.

The Temkin constant K_T represents the adsorbate–adsorbate interactions and b is a constant related to the adsorption heat [17]. Both constants were higher for ground form of the resin. The calculated values of all isotherm constants are listed in Table 2.

The adsorption kinetics results were analysed using Lagergren pseudo-first order and pseudo-second order reactions.

The non-linear form of Lagergren pseudo-first order model can be expressed as [18]:

$$q_t = q_e\left(1 - e^{(-k_1 \cdot t)}\right) \tag{3}$$

where k_1 is the rate constant of the first-order adsorption (1/min), q_t is the amount of heavy metal adsorbed at time t (mg/g) and q_e is equilibrium solid phase concentration (mg/g).

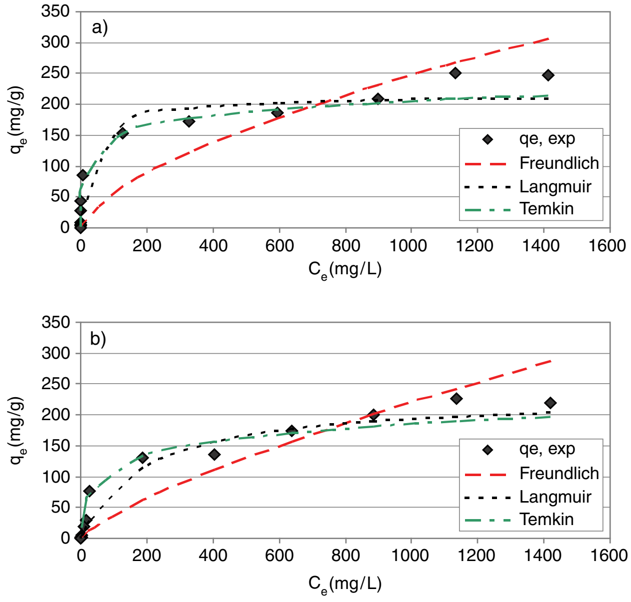

Fig. 2. Sorption isotherms of Zn(II) ions on Lewatit S1468 a) ground resin b) bead resin.

Table 2
Isotherm parameters calculated for Zn(II) using experimental data

Isotherm	Equation	Isotherm constants	
		Ground form	Bead form
Freundlich	$q_e = K_f C_e^{\frac{1}{n}}$	K_f (l/g)	
		3.262	
		n	1.207
		1.155	1.326
		R^2	0.900
		0.883	
Langmuir	$q_e = q_m \dfrac{K_L \cdot C_e}{(1 + K_L \cdot C_e)}$	q_m (mg/g)	
		214.171	
		K_L (l/mg)	229.398
		0.028	0.005
		R^2	0.964
		0.935	
Temkin	$q_e = \dfrac{RT}{b} \ln(K_T \cdot C_e)$	K_T (l/g)	
		3.281	
		b (J/mol)	0.391
		96.034	78.561
		R^2	0.923
		0.976	

The rate constant k_1 was found to lie in the range of 0.353–6.475 (1/min) for ground and bead resin forms for the initial Zn(II) concentration of 300 and 500 mg/l (Table 3). It was observed that the rate constants decreased with the increase of the metal concentration. The calculated equilibrium capacities ($q_{e,cal}$) according to the Lagergren pseudo-first order rate expression were in disagreement with the values of experimental capacities for all the initial concentrations and resin forms. The correlation coefficients (R^2) were in the range 0.937–0.984 for pseudo-first order model (Table 3).

Pseudo-second order model based on adsorption equilibrium capacity can be expressed as [19]:

$$q_t = \frac{q_e{}^2 k_2 \cdot t}{1 + q_e \cdot k_2 \cdot t} \tag{4}$$

where k_2 (g/mg min) is the rate constant of pseudo-second order adsorption.

The values of k_2 were found to be in the range of 0.051–0.003 (g/mg min) for ground and bead resin forms (Table 3). The values of the second-order adsorption rate constant (k_2) decreased with the increase of initial Zn(II) concentrations from 300 to 500 mg/l and were higher for the ground form of resin compared to the bead form. The calculated $q_{e,cal}$ values from pseudo-second-order

Table 3
Kinetic parameters for the adsorption of Zn(II)

Initial metal concentration		Pseudo first order				Pseudo second order			
		$q_{e,exp}$ (mg/g)	$q_{e,cal}$ (mg/g)	k_1	R^2	$q_{e,exp}$ (mg/g)	$q_{e,cal}$ (mg/g)	k_2	R^2
300 (mg/l)	ground form	143.709	135.735	6.475	0.984	143.709	143.427	0.051	0.935
	bead form	118.869	121.333	0.518	0.978	118.869	128.513	0.006	0.974
500 (mg/l)	ground form	182.734	168.617	5.038	0.937	182.734	178.529	0.031	0.962
	bead form	160.921	167.739	0.353	0.982	160.921	179.412	0.003	0.958

fitting model are very close to the experimental q_e values. Shek et al. [20] investigated Zn(II) ions removal from effluent with resin D 401 and observed that the rate constants k_1 and k_2 were in the range of 0.0100–0.0132 and 0.0087–0.0116 for different initial concentrations, respectively.

Plots of q_t versus t for initial concentrations of 300–500 mg/l are depicted in Fig. 3 (a), (b), (c) and (d). As shown in Fig. 3 90% of zinc ions were adsorbed within the first minute for the ground resin form and it was much faster than the adsorption with the bead form.

SEM images of the cation-exchange resin before and after Zn(II) sorption for the both resin forms are shown in Fig. 4 (a), (b), (c) and (d). As shown in Fig. 4, a visible change of the surface morphology demonstrates that the sorption of Zn(II) ions took place onto the sorbents.

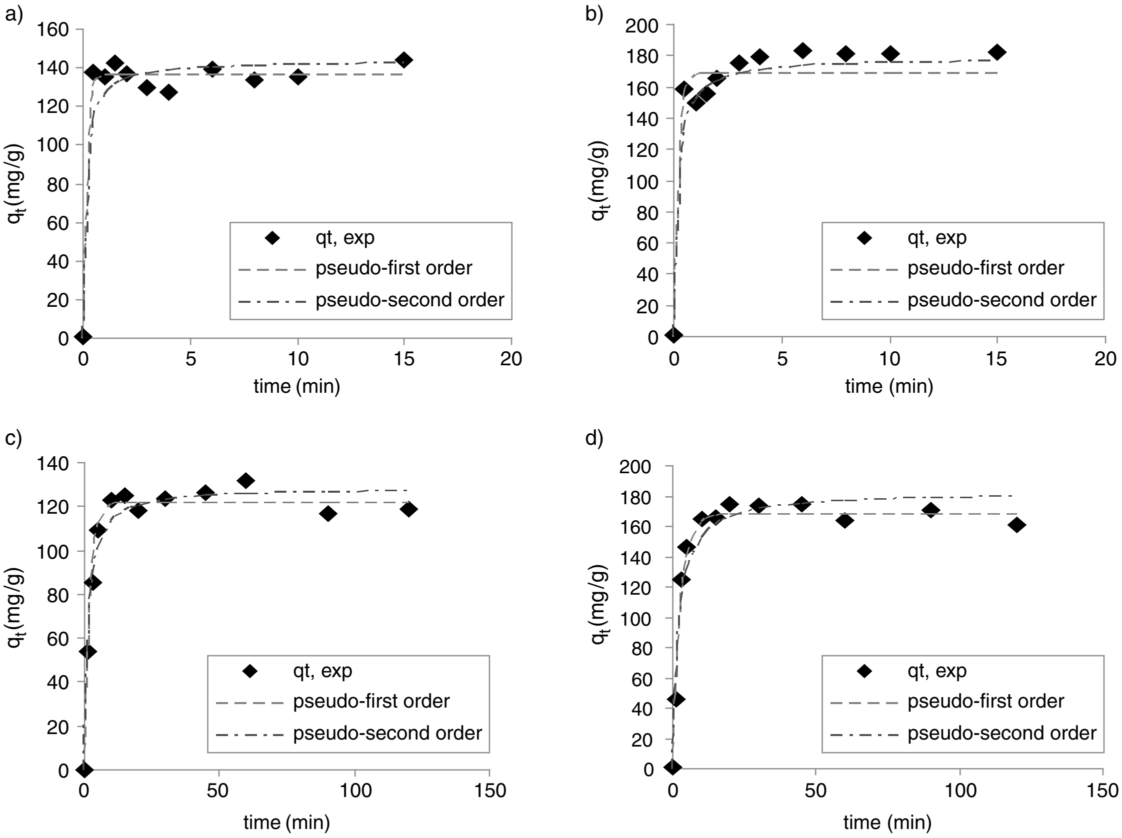

Fig. 3. Plots of q_t vs. t for zinc (II) adsorption a)–b) ground resin form, initial concentrations 300 and 500 mg/l, respectively, c)–d) bead resin form, initial concentrations 300 and 500 mg/l, respectively.

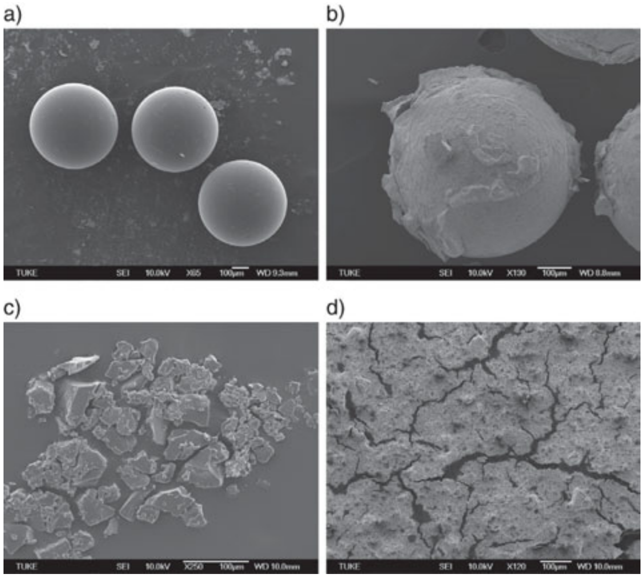

Fig. 4. SEM micrographs of Lewatit S1468 resin bead form a) before and b) after Zn(II) sorption, and the ground form c) before and d) after Zn(II) sorption.

4. Conclusion

In this study, the removal of Zn(II) ions from aqueous solutions using two forms of cation-exchange resin was investigated. Experimental results were evaluated by Langmuir, Freundlich and Temkin isotherms. The batch studies indicated that the adsorption on Lewatit S1468 increased with the increase in initial Zn(II) concentration. The experimental maximum adsorption capacities of Zn(II) were 214.171 and 229.398 mg/g for ground and bead forms of the resin, respectively. Langmuir and Temkin isotherms are more suitable for description of the adsorption of zinc(II) onto the resin compared to Freundlich isotherm. The adsorption process was relatively fast as 90% of Zn(II) was adsorbed within the first minute and the equilibrium was reached after about 5 min for the ground form compared to about 20 min for the bead form to reach the equilibrium. Pseudo-second order kinetic model better described the kinetic data than pseudo-first order. Experimental results of this study demonstrate that Lewatit S1468 cation-exchange resin is suitable for adsorption of zinc from aqueous solutions.

Symbols

b — constant related to the adsorption heat
C_0 — initial metal ions concentration
C_t — concentration of metal ions at time t
k_1 — rate constant of the first-order adsorption
k_2 — rate constant of pseudo-second order adsorption
K_L — equilibrium constant of Langmuir isotherm
K_f — Freundlich ion-exchange capacity
K_T — Temkin isotherm constant
m — amount of the resin
n — ion-exchange intensity
R^2 — correlation coefficient
q_m — monolayer adsorption capacity
V — total volume of the solution
q_e — equilibrium adsorption capacity
$q_{e,cal}$ — calculated equilibrium capacities
q_t — adsorption capacity at time t

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