KINETICS OF ZINC IONS ADSORSOPTION FROM WATER AND WASTEWATER BY ION EXCHANGE RESINS

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Abstract:*Innovative processes for treating industrial wastewater containing heavy metals often involve technologies for reduction of toxicity in order to meet technology-based treatment standards.*
The capacity of ion exchange resins, Purolite MN 500 and Purolite C 100 H, for removal of Zn^{2+} from aqueous solution has been investigated under different conditions namely initial solution pH, initial metal-ion concentration, and contact time. The equilibrium data obtained in this study have been found to fit both the Langmuir and Freundlich adsorption isotherms. The adsorption of Zn^{2+} on these resins follows first-order reversible kinetics.
Keywords: *ion exchange, zinc ions, wastewater, adsorbtion*

1. INTRODUCTION

Heavy metal pollution has become one of the most serious environmental problems today. The treatment of heavy metals is of special concern due to their recalcitrance and persistence in the environment. In recent years, various methods for heavy metal removal from wastewater have been extensively studied [1].

Pollutant load of industrial waste waters is the most massive and harmful type of pollution. After the Romanian adjuration to the European Union, heavy metal retention from mine waters will become a mandatory operation from at least two points of view. First, because heavy metals ions are toxic and are presently being dumped in water sources, polluting surface water as well, rendering it not healthy for drinking. Secondly, aquatic flora and fauna are affected by this pollution. Using those waters as irrigation sources is not recommended because the heavy metals accumulate in the soil and in some plants. Animals that consume these plants carry the accumulated heavy metals further in milk and meat products that we humans consume. Retaining the heavy metals is also useful from an economic point of view. Retaining those rare and expensive to produce metals could lead to a decrease in purification costs.

Various processes (i.e. adsorption, chemical precipitation/ coagulation, ultrafiltration, electrodialysis, etc.) have been practiced to remove the dissolved metal ions from aqueous solution [2]. Among these processes, adsorption is known as one of the most applicable treatment techniques, and it offers flexibility in operation accompanied with a satisfaction of lower levels of metal ion concentration in effluent [3,4]. Mostly, surface characteristics that provide the higher adsorption capacity including ion exchange ability are important to select materials as adsorbents [5–10].

Industrial effluents from electroplating industries contain high amounts of heavy metal ions, such as chromium, nickel, copper, cadmium and zinc. These heavy metal bearing wastewaters are of considerable concern because they are non-biodegradable, highly toxic and probably carcinogen. Only 30-40% of all metals used in plating processes are effectively utilized i.e. plated on the articles. The rest contaminates the rinse waters during the plating process when the plated objects are rinsed upon removal from the plating bath. Electroplating rinse waters may contain up to 1000 mg/L toxic heavy metals which, according to environmental regulations worldwide must be controlled to an acceptable level before being discharged to the environment. Several treatment processes have been suggested for the removal of heavy metals from aqueous waste streams: adsorption, biosorption, ion exchange, chemical precipitation and electrochemical methods: electro winning, electro deionization, membrane-less electrostatic shielding electro dialysis/electro deionization and electro coagulation [6]. Chemical hydroxide precipitation is the most economic and the most commonly utilized procedure for the treatment of heavy metal-bearing industrial effluents but after this treatment the wastewater

stream can still contain up to 5ppm heavy metals, which is an unacceptable concentration for discharge to the environment. In order to remove heavy metals down to the ppb concentration level, the wastewater stream must be further treated using a second sulfide precipitation as a polishing step or a series of ion exchange columns.

The large amounts of precipitated sludge which contains concentrated heavy metal hydroxides or sulfides are an extremely hazardous waste and must be disposed of using special facilities at great expense to industry. From the environmental protection and resource saving point of view, effective recycling and reusing of the heavy metal wastewater is strongly expected. Closed-recycle system or so-called effluent-free technology should be developed [7].

Chemical coagulation is a quite effective method for treating heavy metal bearing wastewaters but may induce secondary pollution by adding coagulants, such as aluminum or iron salts or organic poly-electrolytes to remove colloidal matter as gelatinous hydroxides. Also this wastewater treatment process produces large amounts of sludge.

The use of physicochemical treatment generally enables the legislation concerning liquid industrial effluent to be respected but this conventional treatment does not completely remove pollution. However, as it has to cope with an increasingly strict framework, the industrial sector continues to look into new treatment methods to decrease the levels of pollution still present in the effluent, the aim being to tend towards zero pollution out flow. [8]

Zinc is one of the most important pollutants for surface and ground water. Because of its acute toxicity and non-biodegradability, zinc-containing liquid and solid wastes are considered as hazardous wastes [3,4]. Among the materials used in ion exchange processes, synthetic resins are commonly preferred as they are effective and inexpensive [9]. Cation exchange resins generally contain sulphonic acid groups.

These groups can also be carboxylic, phosphonic or phosphinic. Certain general rules for cation exchange are: (i) the exchanger prefers ions of high charge, (ii) ions of small hydrated volume are preferred and (iii) ions, which interacts strongly with the functional groups of the exchangers are preferred [10,11].

In literature, there have been various investigations about removal of heavy metals by ion exchange resins. Halle et al. observed that macro porous carboxylic cation exchanger Wofatit CA-20 in the sodium form exhibites high removal efficieny for treatment of Ni(II) ions from washings formed during the nickel plating [12]. Cu (II) ions are effectively removed from sea and river water by Amberlyst A-27 and Diaion PA-318, strongly basic anion exchangers and batocuproinodisulphonate as a chelating agent [13]. Also, Dowex HCR S/S and Dowex Marathon C resins provided adsorption capacities of 26.27mg/g and 46.55 mg/g for copper removal [14]. Macroporous strongly basic anion exchanger-Lewatit MP-500A is characterized by high selectivity for Cr(VI) ions [15].

2. MATERIALS AND METHODS

2.1 Chemicals

All chemicals used during the experiments, were purchased from Merck (Germany). All the experiments were carried out in duplicate sets. All measurements were performed in parallels in each set. The removal efficiency reported are the average of the parallel measurements of the duplicate sets and the parallel measurements.

Analytical grade reagents were used in experimental studies. Nitrate salts of test metals ($Zn(NO_3)_2 \cdot 6H_2O$ were used for preparing certain concentrations of synthetic solutions. pH adjustments were carried out by using 0.1N HCl.

Ion exchange studies were done by contacting synthetic aqueous solutions, containing 100 mg/L Zn^{2+}, with an ion exchange resin, in a batch system. In these studies, a weakly basic anion exchanger, Purolite MN 500 and Purolite C 100 H type was used.

MN 500 is a hyper crosslinked strong acid resin and C 100 H is a premium gel, polystyrenic, strong acid cation exchange resins.

2.2. Apparatus

Cintra 5 spectrophotometer was used for the determination of remaining metal concentrations in solutions. Used Zincon Method (Method no: 8009) for zinc analyses. Batch experiments were carried out in *NUVE* shaker. Testo pH-meter was used for pH measurements.

3. RESULTS AND DISSCUDION

3.1. Equilibrium studies

In order to study the ion exchange equilibrium, the ion exchange isotherms were determined. For this purpose the $Zn(NO_3)_2$ solutions (7 samples) of different concentrations (between 5 and 100 mg/L) were prepared.

Each experiment consists of the contact between the 50 mL $Zn(NO_3)_2$ solution of known concentration and 1 g resin.

The resin-solution system was stirred in the thermostated vessel during 24 hours, enough to reach the equilibrium. Each sample was spectrofotometrically analyzed, and the resin loading was calculated using equation (2).

3.2. Kinetic study

1g ion exchanger was put in contact with 50 mL $Zn(NO_3)_2$ (concentration 100 mg/L) in an Erlenmayer jar. The samples were stirred at 300 rpm for 5 minutes, 10 minutes, 20 minutes, 30 minutes, 60 minutes and 90 minutes using a Heidolph Unimax shaker. The experiments were carried out at 20˚C. After mixing, samples were filtrated using blue ribbon filter paper and brought to a 50 mL flask. 10 mL samples from the filtrate were taken and spectrofotometrically analysed. The coloured samples were blue. The calibration curve was achieved first.

Equilibrium studies

The equilibrium adsorption isotherm is important in the adsorption system design. The distribution of Zn^{2+} between the liquid and the solid phase in equilibrium is expressed by the Freundlich and Langmuir models. These equations are widely used, the former being empirical while the second assumes that the maximum adsorption occurs when the surface is covered by the functional groups.
Langmuir developed a theoretical equation, considering that a monomolecular adsorption layer occurs on an energetically homogeneous surface, and that there is no interaction between the adsorbed molecules. The Langmuir adsorption isotherm plot (q_e vs. C_e). C_e (Figures 1 and 2) indicates the applicability of Langmuir adsorption isotherm. The values of q_m and b were calculated from the slope and the intercept of the linear plots C_e/q_e vs. C_e (Table 1). To predict the adsorption efficiency of the adsorption process, the dimensionless equilibrium parameter was determined by using the following equation:

$$q_e = \frac{q_m \cdot b \cdot C_e}{1 + b \cdot C_e} \tag{3}$$

where: q_e - the adsorbent equilibrium concentration (mg/g); q_m – the adsorbent capacity for a monolayer adsorption (mg/g); b – equilibrium constant; C_e – the equilibrium concentration in liquid phase (mg/L).
The Langmuir adsorption isotherm model may be rearranged as follows:

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

Table 1 shows the thermodynamic parameters calculated using the Langmuir isotherm at 20°C.
The Freundlich model is an indicative of the sorbent surface behaviour. The Freundlich equation, which is an empirical one, is as follows:

$$q_e = K_f \cdot C_e^{(1/n)} \tag{5}$$

where: K and n are constants which were experimentally determined.

$$\log q_e = \log K_f + \frac{1}{n} \cdot \log C_e \tag{6}$$

where: K_f and 1/n are Freundlich constants in respect of the adsorption capacity and adsorption intensity, respectively.
The K_f and 1/n are Freundlich constants related to the adsorption capacity and adsorption intensity, respectively.
The resin behavior showed a better fit to the Langmuir isotherm than the Freundlich one.
Table 1 shows the empirical Freundlich equation coefficients (4) as obtained by logarithmic transformation.

Table 1. Langmuir equilibrium parameters at 20˚C

Ion exchanger	Langmuir, 20°C			Freundlich, 20°C		
	q_m	b	R^2	R^2	k	n
MN 500	38.5	0.046	0.90	0.91	0.046	0.98
C 100 H	40.5	0.049	0.84	0.80	0.049	0.97

The isotherms obained by fitting the experimental data using the two isotherms reveal that Langmuir isotherm are more in line with the experimental results.
Comparing isotherms 1-2 the high exchange capacity of the Purolite MN 500 for Zn^{2+} ions versus the Purolite C 100 H could be observed.
The experimental data are presented in Fig. 1-2 in q_e –C_e coordinates, where q_e is the ion exchange loading at equilibrium, mg/g, and C_e – $Zn(NO_3)_2$ concentration at equilibrium, mg/L.
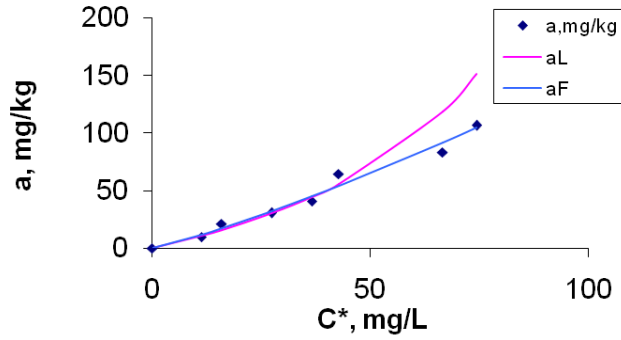
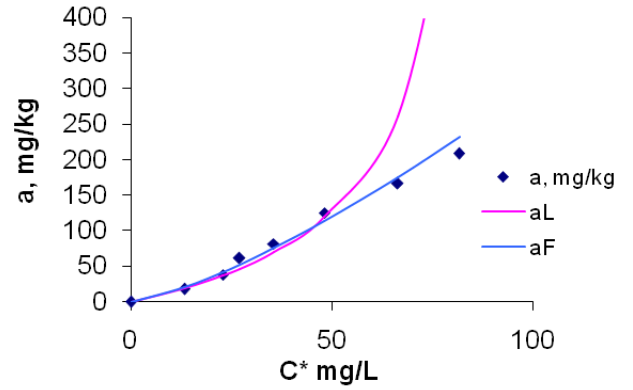**Figure 1.** Equilibrium isotherm for loading Zn^{2+} onto Purolite MN 500 at 20˚C

Figure 2. Equilibrium isotherm for loading Zn^{2+} onto Purolite C 100 H at 20˚C

As expected, the adsorption capacity, q_m, in monomolecular layer, is higher for C 100 H cationite. This fact was verified using the linearized Langmuir equation. The resin showed a better fit for the Langmuir isotherm than the Freundlich isotherm. The results are virtually identical to those obtained by fitting the experimental results presented in Figure 1 and 2.

The aspect of the ion exchange isotherms shown in Figure 1 and 2 indicates that both cation exchangers in H^+ form have a good capacity of Zn^{2+} retention by ion exchange, but the values are strongly influenced by the exchanger type. The cation exchanger C 100H retains a larger amount of Zn^{2+} than the cation exchanger MN 500. The removal efficiency increases to an optimum dosage beyond which the removal efficiency is negligible. The Zn^{2+} concentration at equilibrium in solution increases with the increasing initial concentration of Zn^{2+} in initial solution.

The ion exchange isotherms shown in figures 1 and 2 have the same form up to 30 mg Zn^{2+}/L concentration and show similar values for the capacity of Zn^{2+} retention from water under static conditions, although total capacities and morphologies are different. On the other hand the amount of Zn^{2+} removed from water is almost identical in the case of both ion exchangers.

3.3. The kinetic study of ion exchange process

In order to characterize the process from the kinetical point of view, curves were obtained using the experimental apparatus described above.

The process efficiency is controlled by the kinetics of adsorption and hence the several kinetic models are available to predict the mechanism involved in the sorption process. Among these models, there are pseudo first order, pseudo second order and interparticle diffusion, rate equation. [15]

Pseudo-first-order:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2,303} t \qquad (7)$$

Pseudo-second-order:

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 q_e^2} \qquad (8)$$

The interparticle diffusion model was applied to different adsorption systems and was adequate to the adsorption systems [15]

$$q_t = k_p t^{0,5} \qquad (9)$$

Samples were taken after 5, 10, 20, 30, 60 and 90 minutes, the results of the experiments being presented in Fig. 3 and 4.
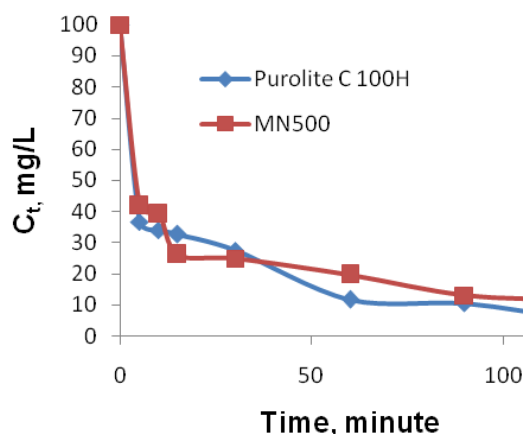
Figure 3. Variation of the nitrate concentration in the solution

The curves from figures 3 reveal that the ion exchange rate is higher in the case of C 100 H, having a higher exchange capacity. The experimental data on ion exchange kinetics for cation exchanger samples with Purolite MN 500 and C 100H are shown in figures 3, as a function of Zn^{2+} concentration in solution versus time. The kinetic curves have a similar shape and reveal a high ion exchange rate at the beginning of the process. The decrease of the ion exchange rate is correlated to the decrease of Zn^{2+} concentration in solution and with the progress of the system towards the equilibrium state.

Several kinetic models including pseudo first order, pseudo second order and pore diffusion were used for the simulation of the experimental data. The kinetic parameters calculated from equations 7-9 for the adsorption of Zn^{2+} at concentrations on Purolite MN 500 and C 100 H are given in Table 2. The pseudo second order successfully fit the adsorption kinetic.

Table 2. The Kinetic model parameters for the adsorption of nitrates

on MN 500 and C100 H

Kinetic model parameters	Temperature, 20°C		Kinetic model parameters	Temperature, 20°C	
MN 500			C 100 H		
Pseudo first order	k_1	0,238	Pseudo first order	k_1	0,023
	r^2	0,876		r^2	0,913
Pseudo second order	k_2	0,033	Pseudo second order	k_2	0,041
	r^2	0,989		r^2	0,998
Pore diffusion	k_p	5,849	Pore diffusion	k_p	6,136
	r^2	0,891		r^2	0,889

4. CONCLUSIONS

The results showed that the MN 500 and C 100 H cation-exchange resins can be used as an adsorbent for the effective removal of Zn^{2+} from aqueous solution. Quantitative removal of these metals from synthetic water confirmed the validity of the results obtained in these batch mode studies. Equilibrium data of Zn^{2+} was well fitted by both the Langmuir and Freundlich models, and the order of affinity was followed as C 100 H > MN 500. The kinetic data would be useful for the fabrication and designing of wastewater treatment plants. Application of this ion-exchanges resin to wastewater treatment is expected to be economical and efficient. Further studies on equilibrium and kinetics of multi-metal systems at low concentrations are under progress.

Kinetically, adsorption of Zn^{2+} was predicted by using the pseudo-second order model with higher correlation coefficients ($r^2 > 0.98$ from C 100 H and > 0.95 from MN 500 respectively). Moreover, initial adsorption rate, h (mg/g min), linearly increased. As a result obtained from large-scale reactor in series, the removal efficiency of Zn^{2+} was approximately 78–98% from C 100 H and 70-95 % from MN 500, respectively, and the proposed process containing C 100 H was applicable to treat a real plating wastewater.

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