Research Article

Equilibrium and Kinetic Studies on Removal of Zn(II) from Aqueous Solution Using Modified Duolite XAD-761 Polymeric Resin

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Abstract

The removal of Zn(II) from aqueous solution by using surfactant-EDTA modified Duolite XAD-761 polymeric resin was investigated. The effect of contact time, pH, modified resin dosage and initial metal ion concentration on the removal of Zn(II) were studied in a batch process mode. The optimum pH required for maximum removal of Zn(II) was found to be 5.0. The data were fitted with the Langmuir and Freundlich equations to describe the equilibrium isotherms. The maximum adsorption capacity of Zn(II) on modified resin was found to be 39.72 mg/g. Adsorption kinetics data were modelled using the pseudo-first and pseudo-second-order models. The results indicate that the pseudo-second-order model best describes adsorption kinetic data. The modified resin was regenerated by using 5% NaCl and used again to remove Zn(II) ions.

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Introduction

Pollution of environment and its detrimental effects on ecology have been studied intensively during last decade years. Problems of the contaminants removal from wastewater were increased with fast industrialization.It is well established that heavy metals obstruct with functional groups of enzymes even at very lesser concentration [1].

Zinc is the earth crust metal. The natural source of zinc present in the rocks and soil. The anthropogenic sources of zinc are emission from wood combustions, morphemic emission and municipal waste waters, galvanic industries and battery production. The toxicity of zinc participates in proteins and carbonates metabolism of animals. The toxicity of zinc levels may cause retarded growth, immunity, anaemia, puberty in humans. The toxicity depends on a number of biological factors like species of test organisms, age and weight stage of life cycle. According to U.S. Environmental Protection Agency (EPA) standards, the permissible limit of zinc discharge in industrial effluents into water bodies is limited to 2.0 mg/L [2]. Hence, the elimination of heavy metals from water and wastewater is very important in terms of public health and also environment. The most widely used methods for removing heavy metals from wastewater include ion exchange, chemical precipitation, reverse osmosis, electro dialysis, evaporation and membrane filtration [3]. Most of these methods suffer from some drawbacks such as high capital, operation cost and the disposal of the residual metal sludge which are not suitable for small-scale industries.

The development of chelating resins as adsorbents for heavy metal ions removal has been increased significantly. Their advantages include good selectivity, preconcentration factor, binding energy and mechanical stability, easy regeneration for multiple sorption-desorption cycles and good reproducibility in sorption characteristics [4-6]. Polymeric XAD resins as the backbone for the immobilization of chelating ligands have physical superiorities such as porosity, uniform pore size distribution, high surface area, durability, chemically homogeneous non-ionic structure and chemical stability towards acids, bases and oxidizing agents [7,8]. Surface modification method using impregnation of surfactants can significantly enhance the capacities of adsorbents to adsorb heavy metals from aqueous medium [9-11]. Surfactant modified adsorbents are not only superior in terms of removal efficiency than the conventional adsorbents, but also encourage the selective separation and recovery of precious and noble metals as

well [12-13]. The aim of this article is to assess the potential of modified Duolite XAD-761 resin for the removal of Zn(II) ion from aqueous solutions. The adsorption capacity of modified Duolite XAD-761 resin was investigated using batch experiments. The influence of contact time, pH, modified resin dose and initial Zn(II) concentration were investigated and the experimental data obtained were evaluated and fitted using adsorbent equilibrium isotherms and kinetic models.

Experimental

Apparatus and instrumentation

The zinc(II) concentrations in the sample were determined using atomic adsorption spectrophotometer (Elico SL 163). The pH measurements were made using a pH meter (Elico LI 120). All experimental treatments in this study were conducted in acid washed (2% HNO_3) polyethylene bottles.

Reagents and solutions

The synthetic solutions were all prepared by diluting Zn(II) standard stock solutions (concentration 1000±2 mg/L) obtained by dissolving 2.144 g of anhydrous $ZnCl_2$ (S.D. Fine, Mumbai) in distilled water. Fresh dilutions were used in each experiment. The Duolite XAD-761 resin (phenol-formaldehyde) was supplied by Rohm Hass (Philadelphia, PA, USA). The SDOSS (LOBA chemi, India) and EDTA- disodium salt (S.D. fine chem, India) were used as such for the preparation modified resin. The pH of the solution was adjusted with 0.1 M HCl or 0.1 M NaOH.

Preparation of modified Duolite XAD-761 resin

The Duolite XAD-761 resin was purified with a 50% ethanol-water solution containing 4 M HCl to remove inorganic impurities and monomeric materials. After that, the resins were rinsed thoroughly with distilled water to eliminate chloride ions. 1 g of fresh Duolite XAD-761 resin was well mixed with an equal ratio (1:1) mixture of 20 mL of 66.6 % (v/v) water-ethanol mixture containing 2 g of SDOSS and 20 mL of water containing 2 g of EDTA-disodium salt for 24 h [6]. The polymeric beads were separated from the impregnated solutions by filtration using Whatman filter paper (No.1) and then beads were thoroughly washed with water and dried at 50^0 C. The dried resins were used for further experiments. The amount of ligand (micellar solubilized chelating agent complex) loaded on Duolite XAD-761 resin was calculated from the material balance. The amount of ligand impregnated onto dry resin was found to be 0.253 g/g.

Batch experiments

Batch adsorption tests were conducted by mixing known weight of modified resin and 100 mL of Zn(II) ion solution of known concentration adjusted to a known pH. The mixture was taken in a polythene bottle of 300 mL capacity and shaken in a mechanical shaker (200 rpm) for a predetermined period at 30 ± 1 ^{0}C. Then the equilibrated solutions were centrifuged and the concentration of Zn(II) ions in the supernatant solution was measured by Atomic Absorption Spectrophotometer. Adsorption isotherm and kinetic studies were carried out with different initial concentrations of Zn(II) ions by maintaining the modified resin dosage at constant level. Metal ion removal (%) was calculated using the following equation

$$\text{Removal (\%)} = \frac{C_i - C_f}{C_i} \times 100 \qquad (1)$$

where C_i and C_f are the initial and final Zn(II) concentrations respectively.

Results and Discussion

Effects of modification on the removal of Zn(II)

Both surfactant and EDTA-disodium salt were individually loaded on Duolite XAD-761 resin and then tested for the removal of Zn(II) ions. However, individually loaded resins could not remove the Zn(II) ions from the solution effectively. The primary studies indicated that percentage removals were found to be 78.4% for surfactant modified resin and 34.2% for EDTA modified resin for an initial Zn(II) concentration of 10 mg/L and for a modified resin dosage of 0.2 g/100 mL respectively. When the surfactant-EDTA complex loaded on Duolite XAD-761 resin, the results showed that both surfactant-EDTA complex could stimulate the adsorption Zn(II) ions from the solution. Hence the complex effect of surfactant and EDTA on the polymeric resin has been considered for the present study.

Effect of contact time

Contact time is an important parameter for successful use of adsorbents for practical applications [13]. **Figure 1** shows the effect of contact time on the removal of Zn(II) by modified resin. It could be seen that the removal of Zn(II) increases with increase in time and attains equilibrium at 120 min. The removal efficiency was found to be 99 ± 0.1% for an initial concentration of 10 mg/L of Zn(II). Therefore, optimum contact time was selected as 120 min for further experiments.

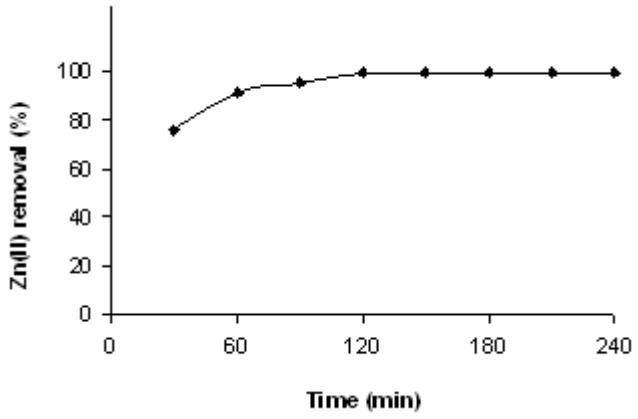

Figure 1 Effect of equilibration time on removal of Zn(II) by modified Duolite XAD-761 resin

Effect of pH

The initial pH of adsorption medium is related to the adsorption mechanisms onto the adsorbent surface from water and reflects the nature of the physiochemical interaction of the species in solution and the adsorptive sites of adsorbents [14]. Moreover, due to the different functional groups on the adsorbent surface, this became active sites for the metal binding at a specific pH. The effect of pH on percentage removal of Zn(II) for pH ranging between 1 to 10 is shown in **Figure 2**. It could be seen that 99 ± 0.1% removal of Zn(II) was achieved by the modified resin over the pH range of 5.0 – 8.0. It is evident from **Figure 2**, the adsorption of efficiency of Zn(II) increased with increasing the pH of the medium until reaching to the optimum pH range.

At lower pH values, H_3O^+ ions compete with Zn^{2+} ions for exchange sites in the adsorbent. Zn^{2+} uptake decreased because the surface area of the adsorbent was more protonated. Competitive adsorption occurred between H^+ protons and free Zn^{2+} ions and their hydroxide fixation sites[15]. Moreover, the stability of the SDOSS-EDTA complex which was loaded on the polymer matrix surface might be reduced with the result the adsorption of Zn(II) decreases at lower

pH. When the pH value increased, adsorbent surfaces were more negatively charged and functional groups of the modified resins more deprotonated which results higher attraction of Zn(II) ions. The reduction in Zn(II) removal beyond pH 8.0 and more basic pH conditions, may suggest the possibility of $Zn(OH)_2$ precipitates occupying the adsorption sites and preventing further removal of Zn(II) [14]. Hence, all experiments were carried out at pH 5.0.

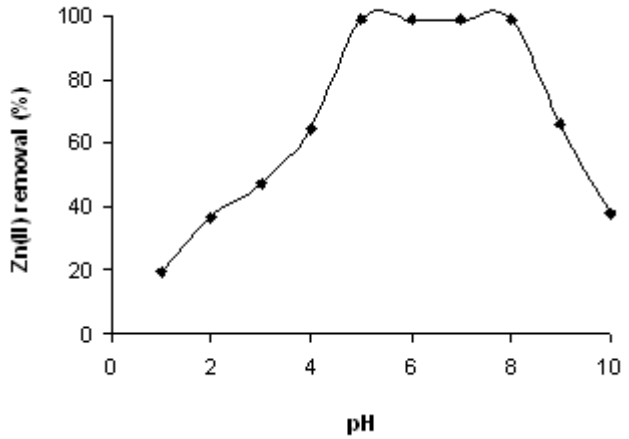

Figure 2 Effectof pH on removal of Zn(II) by modified Duolite XAD-761 resin

Effect of modified resin dosage

Adsorbent dosage is an important parameter because it determines the capacity of an adsorbent for a given concentration of the adsorbate. The influence of modified resin dosage on the removal of Zn(II) ion is shown in **Figure 3**. Zn(II) removal increases with increasing the modified resin dosage. The removal efficiency was found to be 99 ± 0.1% at a modified resin dose of 0.2 g/100 ml for an initial concentration of 10 mg/L. The results showed that the adsorption increases with the increase in the dose of modified resin. This is because of the availability of more binding sites on the surface at higher concentration of the adsorbent for complexation of metal ions.

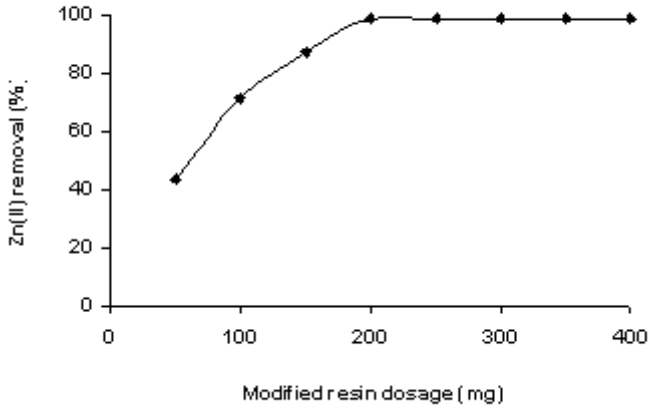

Figure 3 Effect of modified resin dosage on removal of Zn(II) by modified Duolite XAD-761 resin

Effect of initial Zn^{2+} concentration

The removal of Zn^{2+} ions was carried out at different initial Zn^{2+}ion concentrations ranging from 10 to 60 mg/L at pH 5.0. The results are presented in **Figure 4**. Zn(II) removal percentage increases when the initial Zn(II) ion concentration decreases. At low Zn(II) concentration the surface active sites to the total metal ions in the solution is

high and hence all the Zn(II) ions may interact with the binding sites of the modified resin and may be removed from the solution. However, the amount of Zn(II) adsorbed per unit weight of modified resin (x/m) is higher at high concentration.

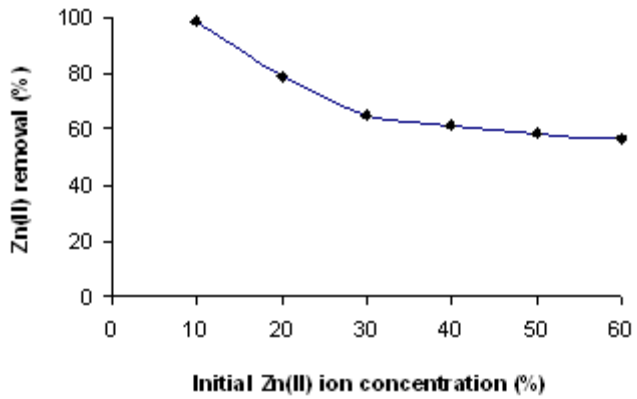

Figure 4 Effect of concentration on removal of Zn(II) by modified Duolite XAD-761 resin

Adsorption isotherm models

The nature of the adsorption could be described by relating the adsorption capacity (mass of solute adsorbed per unit mass of adsorbent) to the equilibrium concentration of the solute remaining in the solution and such a relation is known as an adsorption isotherm. It can also be used to compare the adsorptive capacities of the adsorbent for different pollutants [15,16]. The Langmuir and Freundlich models are the most frequently employed models. In this work, both models were used to describe the relationship between the amount of Zn(II) ions adsorbed and its equilibrium concentration in solution at room temperature for 24 h.

Langmuir isotherm

The main assumption of the Langmuir method is that adsorption occurs uniformly on the active part of the surface, and when a molecule is adsorbed on active sites, the other molecules could not be interacted with this active [17].
The linear form of Langmuir equation may be written as

$$\frac{C_e}{q_e} = \frac{1}{q_0 b} + \frac{C_a}{q_0} \qquad (2)$$

Where q_e is the amount of solute adsorbed per unit weight of adsorbent (mg/g) and C_e is the equilibrium concentration of solute in the bulk solution (mg/L) while q_0 is the monolayer adsorption capacity (mg/g) and b is the constant related to the free energy of adsorption (L/mg). A linear plot of C_e/q_e versus C_e exhibits that the adsorption obeys the Langmuir isotherm and values of Langmuir constants (q_0 and b) calculated from the slope and the intercept (**Figure 5**) are presented in **Table 1**.
The essential characteristics of the Langmuir isotherm can also be expressed in terms of a dimensionless constant of separation factor or equilibrium parameter, R_L, which is defined as [18]

$$R_L = \frac{1}{1 + b\,C_0} \qquad (3)$$

where b is the Langmuir constant and C_0 is the initial concentration of Zn(II) ion. Separation factor shows the nature of adsorption process and its value indicates the sorption process could be favourable, linear and unfavourable when 0

< R_L <1, R_L =1, R_L > 1, respectively. The R_L values at different concentrations were found be in the range of 0 to 1 indicated a highly favourable adsorption of Zn(II) ions onto modified resin.

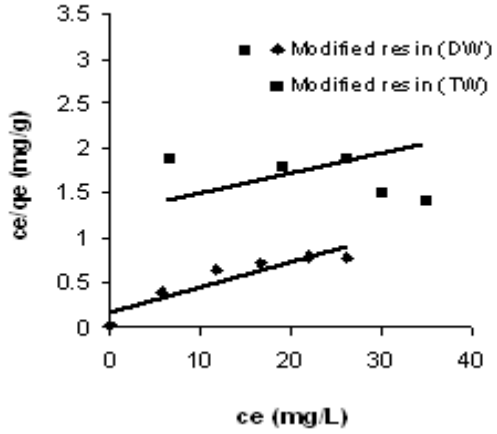

Figure 5 Langmuir isotherm plot for the adsorption of Zn(II) by Duolite XAD-761 resin in distilled water-DW and tap water-TW

Freundlich isotherm

It is an empirical expression that takes into account the heterogeneity of the surface and multilayer adsorption to the binding sites located on the surface of the sorbent [19]. The logarithmic form of Freundlich model is expressed as follows

$$\log \frac{x}{m} = \log K_F + \frac{1}{n} \log C_e \qquad (4)$$

where C_e is the equilibrium concentration (mg/L) and x/m is the amount of metal ion adsorbed per unit weight of adsorbent (mg/g). The K_F is Freundlich constant related to the adsorption capacity (mg/g) and n shows the adsorption intensity (L/mg). The linear plot of log (x/m) versus log C_e (**Figure** 6) exhibits that the adsorption obeys the Freundlich isotherm and value of Freundlich constants (K_F and 1/n) calculated from the intercept and slope of the plot are presented in **Table 1**. The adsorption intensity 1/n value was found to be between zero and one which indicate the favourable adsorption of Zn(II) ions onto surface of modified resin.

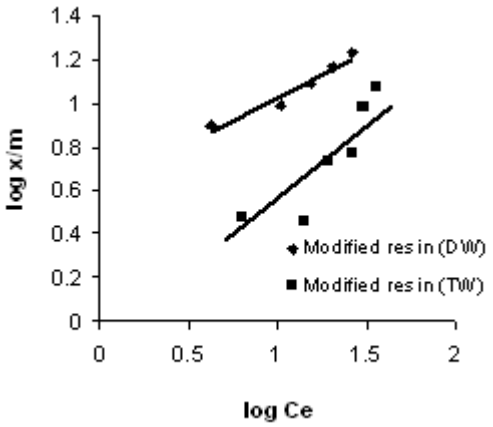

Figure 6 Freundlich isotherm plot for the adsorption of Zn(II) by modified Duolite XAD-761 resin in distilled water-DW and tap water-TW

Table 1 Langmuir and Freundlich constants for Zn(II) adsorption by modifie Duolite XAD-761 resin in distilled water and tap water

Metal ion	Langmuir model			Freundlich model		
	q_o (mg/g)	b (L/mg)	R^2	K_F (mg/g)	1/n (L/mg)	R^2
Zn(II) in DW	39.72	0.2022	0.903	4.05	0.4187	0.944
Zn(II) in TW	9.45	0.0565	0.521	1.38	0.171	0.776

It could be seen from the **Table 1** that the decrease in the adsorption capacity was noticed in the case of modified Duolite XAD-761 resins in tap water. This could be due to the presence of common cations available in tap water competing for the adsorption sites on the modified Duolite XAD-761 resin. The correlation coefficient (R^2) values of Freundlich model are found to be higher than Langmuir model and more closer to unity. These results indicated that the Langmuir model is not able to describe adequately the relationship between the amounts of zinc(II) ions adsorbed and their equilibrium concentration in the solution. Therefore, it could be concluded that the Freundlich isotherm model was found to be a best fit with the equilibrium data since R^2 values were closer to unity.

Kinetic studies

The study of adsorption kinetics is significant as it provides valuable insights into the reaction pathways and the mechanism of the reactions. Several kinetic models are used to explain the mechanism of the adsorption processes. A simple pseudo-first order equation was given by Lagergren equation [20]

$$\log (q_e - q_t) = \log q_e - k_1 t/2.303 \quad (5)$$

where q_e and q_t are the amounts of Zn(II) adsorbed (mg/g) at equilibrium time and any time t, respectively, while k_1 is the rate constant of adsorption (min^{-1}). Plot of log (q_e - q_t) versus t gives a straight line for first order adsorption kinetics (**Figure 7**) which allows computation of the rate constant k_1 and its values are given in **Table 2**.

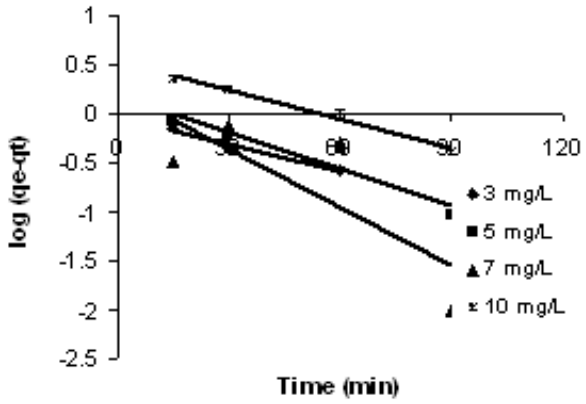

Figure 7 Pseudo-first-order kinetic plots at different concentration for Zn(II) by modified Duolite XAD-761 resin

On the other hand, the pseudo-second order equation based on equilibrium adsorption is expressed as [21,22]

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (6)$$

where k_2 is the pseudo-second order rate constant (mg g^{-1} min^{-1}), q_e and q_t represent the amount of Zn(II) adsorbed (mg/g) at equilibrium and at any time. The plot of (t/q_t) versus t produces straight line with slope of $1/q_e$ and intercept of $1/k_2q^2_e$. It indicated the applicability of pseudo-second-order model (**Figure 8**). The overall rate constants k_2 and other constants of pseudo-first-order kinetics are given in **Table 2**. The correlation coefficients value (R^2) was also calculated and presented in **Table 2**.

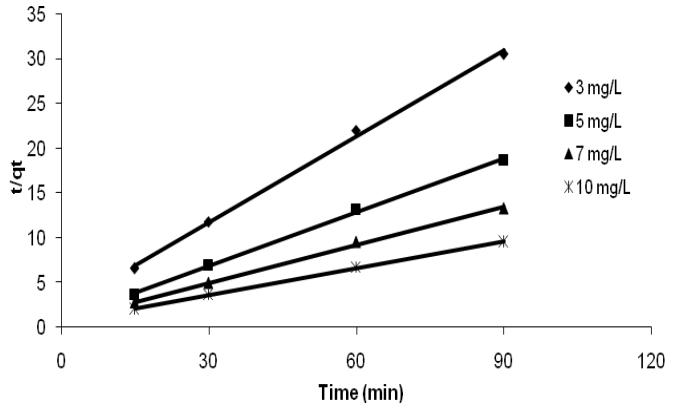

Figure 8 Pseudo-second-order kinetic plots at different concentration for adsorption of Zn(II) by modified Duolite XAD-761 resin

The results are given in the **Table 2** and which indicated that the adsorption of Zn(II) ions onto modified Duolite XAD-761 resin was governed mainly by pseudo-second-order kinetics. Thus, it could be inferred that the loading of Zn(II) onto modified Duolite XAD-761 resin appeared to occur by chemical interactions involving valence forces due to sharing or exchange of electrons between zinc and modified Duolite XAD-761 resin [9].

Table 2 Kinetic parameters obtained from pseudo-first-order and Pseudo-second-order kinetics for Zn(II) adsorption onto modified DuoliteXAD-761 resin

Conc	Expt.q_e	Pseudo-first-order kinetics				Pseudo-second-order kinetics			
(mg/L)	(mg/g)	K_1 (1/min)	$q_{e(theo)}$ (mg/g)	R^2	P	K_2 (g/mg min)	$q_{e(theo)}$ (mg/g)	R^2	P
3	2.95	0.0201	0.928	0.972	68.54	0.0517	3.04	0.997	3.5
5	4.90	0.0164	1.491	0.885	69.57	0.0455	4.99	0.998	1.836
7	6.8	0.0122	2.57	0.862	62.20	0.0274	7.08	0.997	4.11
10	9.9	0.0092	3.46	0.981	65.05	0.0163	10.02	0.998	0.303

Desorption studies

Desorption studies were conducted to recover the Zn(II) ion from the modified Duolite XAD-761 resin. Attempts were made to desorb Zn(II) ions from the spent resins using NaCl (1 % - 10%). The final Zn(II) concentration was determined by AAS. Results showed that 99% of Zn(II) ions could be desorbed from the resin under optimum concentration of 5% NaCl. After the extraction of Zn(II) from modified resin, it was completely washed with distilled water. The adsorption of capacity of modified Duolite XAD-761 resin was again tested for about five cycles of

operation. Results showed that the adsorption capacity of NaCl regenerated modified Duolite XAD-761 resin was maintained over the range of 99%-82% for Zn(II) even upto five cycles of operation.

Conclusion

In the presented study, a simple and modified Duolite XAD-761 resin prepared and found to be useful for separating Zn(II) ions from aqueous solution. Separation media was prepared by mixing the resins in an aqueous solution of anionic surfactant and EDTA, without any chemical synthesis, thereby chelating functionality was easily introduced on the solid support surface. The operating parameters such as, contact time, pH, modified resin dosage and initial metal ion concentration were effective on the adsorption efficiency of Zn(II) ions. Experimental results are good agreement with Freundlich isotherm model and have shown a better fitting to the experimental data. The kinetics of Zn(II) adsorption onto modified resin was found to follow more reliably pseudo second order kinetics. Desorption of Zn(II) was effectively be achieved with 5% NaCl from the modified resin. Moreover, the regenerated modified resins could be used again and again for at least five cycles of operation without major loss in removal capacity and loss of materials. Based on results, it could be concluded that it can be used as an effective and alternative adsorbent to treatment of wastewater containing Zn(II) ions.

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