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Removal of Ni(II) from Aqueous Solution by Using Surfactant-EDTA Modified Amberlite XAD-7HP and Duolite XAD-761 Resins

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The aim of this work is to evaluate the removal of Ni(II) from aqueous solutions by modified Amberlite XAD-7HP and Duolite XAD-761 resins. These modified resins have been individually prepared by complete mixing of parent resins with anionic surfactant-sodium dioctyl sulphosuccinate (SDOSS) and EDTA-disodium salt (chelating agent) in an aqueous solutions. The equilibrium adsorption level was determined as a function of contact time, pH and adsorbent doses. Adsorption isotherms of Ni(II) on adsorbents were determined and correlated with common isotherm equations such Langmuir and Freundlich models. The results showed that the adsorption kinetics of Ni(II) on modified XAD-7HP and XAD-761 resins could be best described by the pseudo-second-order model. The nickel(II) ions could be successfully recovered from the modified resin by treatment with 3-5 % NaCl. The modified resins thus regenerated could be used again to remove the heavy metal ions.

Key Words: Nickel(II) removal, Surfactant-EDTA, Modified XAD, Isotherms, Kinetics, Desorption.

INTRODUCTION

The increased use of heavy metals has resulted in an increased flux of metallic substances in different environmental segments. Once metal ions enter the environment, their chemical form largely determines their potential toxicity. It is well established that heavy metals interfere with functional groups of essential enzymes even at very less concentration[1,2]. Nickel beyond permissible quantities causes various chronic disorders in human beings and it can damage nerves, lungs, liver, bones, renal edema and skin dermatitis[3]. Due to the extreme toxicity of Ni(II) its selective determination and removal from the polluted sites is of particular important.

The development of chelating resins for heavy metals removal have been increased significantly[4-6]. Their advantages include good selectivity, preconcentration factor, binding energy and mechanical stability, easy regeneration for multiple sorption-desorption cycles and good reproducibility in the sorption characteristics[7]. XAD resins exhibit good physical properties such as porosity, uniform pore size distribution, high surface area and chemically homogeneous non-ionic structure[8]. Therefore, they have been used as supports for immobilization of chelating agents for metal removal[9].

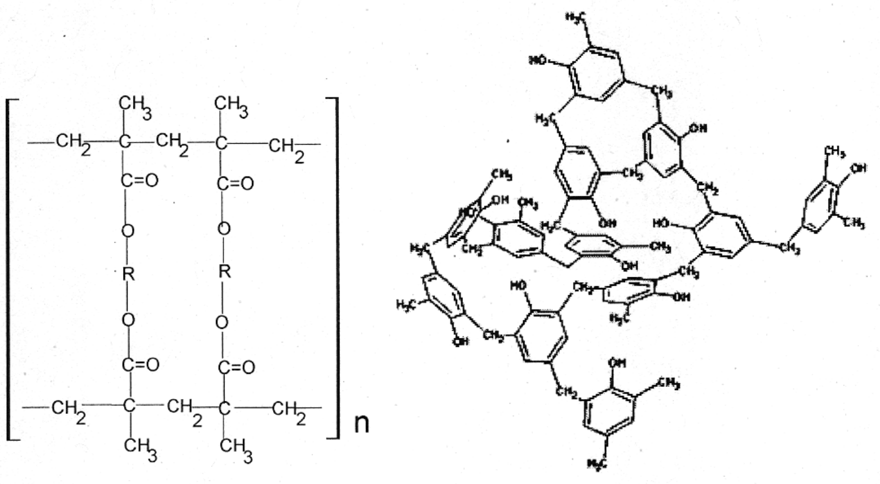
Separation methods using surfactant micelles as separation media to remove heavy metals from water and wastewater have been extensively studied[10-13]. The sorption of a surfactant on the external surface of a natural zeolite for heavy metal removal has been studied[14]. The most successful applications of surfactant loaded on Amberlite XAD-4 for the collection of precious metals from water[15,16]. Several studies discovered that surfactants in combination with a complexing agent had an even greater capability of extracting heavy metals from contaminated soil[17,18]. The joint application of surfactants and EDTA improved the metal removal from municipal sludge[19] and purple soil[20]. EDTA can form complexes with heavy metals and thus substantially increase heavy metal removal from contaminated soil[21]. Based on the risk assessment report on EDTA approved by the Technical Meetings of European Union Member state representatives[22], EDTA was reported to have low aquatic toxicity and no bioaccumulation in living organisms through the food chain.

In the present work, attempts were made to prepare modified XAD resins such as, Amberlite XAD-7HP resin and Duolite XAD-761 resin with the use of non-hazardous sodium dioctyl sulphosuccinate (SDOSS)[23] and EDTA-disodium salt (chelating agent) for the separation of nickel metal[11] from the aqueous solution. Attempts were made to study the effects of process variables such as contact time, pH and adsorbent dose on the adsorption capacity. In order to evaluate the removal process by modified resins, kinetics and equilibrium isotherms were also studied.

EXPERIMENTAL

All chemicals used in this work were of analytical reagent grade and were used without further purification. The two polymeric resins, Amberlite XAD-7HP resin (acrylic ester) (surface area 450 m^2/g, size 0.3-0.9 mm) and Duolite XAD-761 resin (phenol-formaldehyde polycondensate) (surface area 150-250 m^2 g^{-1} and size 0.56-0.76 mm) were 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 of modified resin. A stock solution of 1000 mg/L was prepared by 4.475 g of $NiSO_4 \cdot 6H_2O$ (BDH, India) in distilled water. The working solution of nickel was obtained by the dilution of the stock solution. The pH was adjusted with 0.1 M HCl or NaOH. The structures of Amberlite XAD-7HP and Duolite XAD-761 are given in Fig. 1a and 1b, respectively.

Impregnation procedure: The polymeric resins XAD-7HP and XAD-761 were individually purified with a 50 % ethanol-water solution containing 4 M HCl to remove inorganic impurities and monomeric material. After that, the resin was rinsed thoroughly with distilled water to eliminate chloride ions. For the impregnation method, slightly modified version of the dry method was followed[9]. 1 g of fresh XAD-7HP and XAD-761 resins were individually well mixed with 20 mL of 66.6 % (v/v) water-ethanol mixture containing SDOSS at different concentration (0.01-0.1 g/mL) and 20 mL of water containing EDTA-disodium salt at different concentration (0.01-0.1 g/mL) for 24 h. The polymeric beads were separated from the impregnated solutions by filtration, washed with water and dried at 50 ºC. The amount of impregnated resin was calculated from the material balance.



(a) (b)

Fig. 1. Structures of Amberlite XAD-7HP (a) and Duolite XAD-761 (b)

Adsorption experiments: The adsorption of Ni(II) was carried out with batch experiments at 30 ± 1 °C. 100 mL of Ni(II) solution with desired concentration adjusted to a desired pH were taken in polythene bottles of 300 mL capacity. Required amount of modified XAD-7HP and XAD-761 resins were added to it. The solutions were agitated for a predetermined period and then resin particles were separated by filtration. The concentration of metal ions was determined by atomic absorption spectrophotometer (Elico, Model-SL 163). Adsorption isotherm and kinetic studies were carried out with different initial concentrations of Ni(II) by maintaining the modified resin dosage at constant level. Ni(II) per cent removal (%) was calculated using the following equation:

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

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

RESULTS AND DISCUSSION

Effects on the adsorption capacity of modified XAD-7HP and XAD-761 resins: Both surfactant and EDTA-disodium salt (a chelator) were individually loaded on XAD-7HP and XAD-761 resins, then tested for Ni(II) adsorption. However, individually loaded resins could not remove the Ni(II) from the solution effectively. The initial studies indicated that removals were found to be 75 % for surfactant loaded resin and 40 % for EDTA-disodium salt for both resins, respectively. When the compound of surfactant and EDTA loaded on XAD-7HP and XAD-761 resins, the results showed that both surfactant and EDTA could stimulate the adsorption of nickel metal from aqueous solution. Hence the complex effect of surfactant and

EDTA (disodium salt) loaded on the polymeric resins has been considered for the present study.

Effect of agitation period: Fig. 2 represents the effects of agitation time on the removal of Ni(II) by the modified XAD-7HP and XAD-761 resins. 200 mg/100 mL for both modified resins were used for an initial concentration of 10 mg/L. The results indicated that quantitative removal (99.9 %) of Ni(II) could be achieved by both modified resins at an optimum time of 3 h.

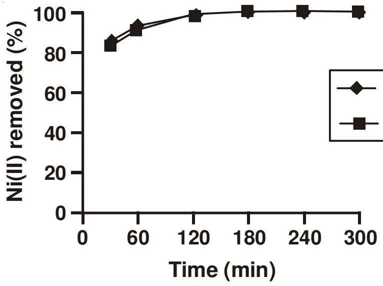


Fig. 2. Effect of contact time on the adsorption of Ni(II)

Effect of pH on adsorption capacity: The most important single parameter influencing the sorption capacity is the pH of adsorption medium[24]. The initial pH of adsorption medium is related to the adsorption mechanisms onto the adsorbent surface from water and reflects the nature of the physicochemical interaction of the species in solution and the adsorptive sites of adsorbents[25]. The effect of pH on nickel(II) removal was conducted with adsorbent dosage 200 mg/100 mL, equilibration time 3 h and initial nickel(II) concentration 10 mg/L for modified XAD-7HP and XAD-761 over the pH ranges 1-10. The results are shown in Fig. 3. It could be seen from the Fig. 3 that nickel(II) removal was found to be maximum in the pH range 4-7 for modified XAD-7HP and 5-7 for modified XAD-761. It is further noticed that XAD-7HP resin has larger pH range than XAD-761 resin. Ni(II) precipitation was observed at higher pH conditions due to OH$^-$ ions in the adsorption medium and consequently the removal processes were decreased for both modified resins. At very low pH values, the surface of resins would be surrounded by the large concentration of hydronium ions which in turn reduce the Ni(II) interaction with binding sites of the modified resins[24,25].

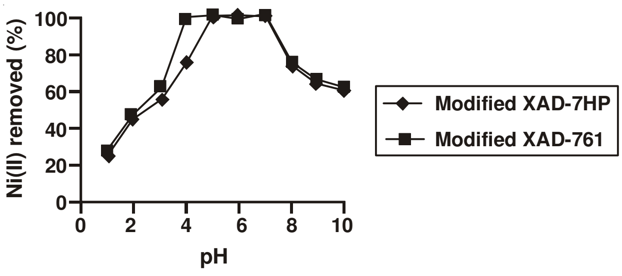


Fig. 3. Effect of pH on the adsorption of Ni(II)

Effect of resin dosage: Experiments were conducted to evaluate the minimum amount of resin required for the removal of nickel(II) by modified resins, by varying the modified resin dosages at pH 5.0 and the results are shown in the Fig. 4. It could be seen that a minimum of 200 mg/100mL is required for both modified XAD-7HP and XAD-761 resins to get quantitative removal of Ni(II) ions from solutions (10 mg/L).

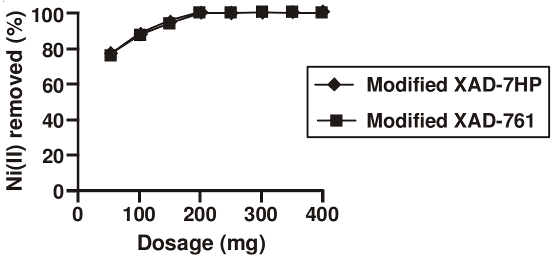


Fig. 4. Effect of dosage on the adsorption of Ni(II)

Adsorption isotherms: The equilibrium adsorption isotherm is fundamental in describing the interactive behaviour between adsorbates and adsorbent and is important in the design of adsorption systems. Two well-known equilibrium models *viz.*, Langmuir and Freundlich models were applied for this study.

The Langmuir equation is given as[26]:

$$\frac{C_e}{q_e} = \frac{1}{q_0 b} + \frac{C_e}{q_0} \tag{2}$$

where the constants q_0 is the adsorption capacity (mg g^{-1}) and b is related to the surface energy of adsorption (L mg^{-1}). A plot of C_e/q_e *versus* C_e as showed linear plot and values of Langmuir constant (q_0 and b) calculated from the slope and the intercept of the plot (Fig. 5) are presented in Table-1. The essential characteristics of Langmuir isotherm model can be explained in terms of dimensionless constant separation factor or equilibrium parameter R_L which is defined as:

$$R_L = \frac{1}{1 + bC_0} \tag{3}$$

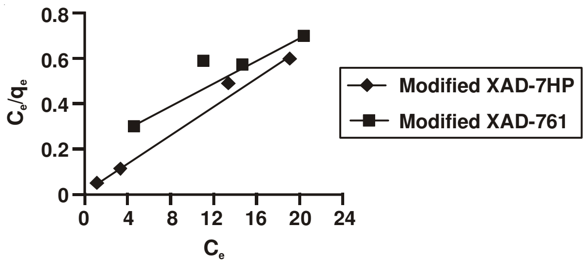


Fig. 5. Application of Langmuir model to the experimental data

TABLE-1
LANGMUIR AND FREUNDLICH CONSTANTS FOR Ni(II)
ADSORPTION ON MODIFIED XAD-7HP AND XAD-761 RESINS

Adsorbent	Langmuir model			Freundlich model		
	q_0 (mg g^{-1})	b (L mg^{-1})	R^2	K_F (mg g^{-1})	n (L mg^{-1})	R^2
Modified XAD-7HP	32	1.5625	0.993	9.49	6.0	0.952
Modified XAD-761	40	0.1315	0.963	5.01	2.5	0.951

where b is the Langmuir constant (L mg^{-1}) and C_0 is the initial concentration (mg/L)[27]. Separation factor shows the nature of adsorption process and its value indicate the adsorption process could be favourable, linear, unfavourable, when $0 < R_L < 1$, $R_L = 1$, $R_L > 1$, respectively. The values of R_L for the modified XAD-7HP and XAD-761 resins were in the range of 0-1 confirm favourable uptake of Ni(II) by both modified resins.

The Freundlich isotherm is represented by the equation[28]

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

where C_e is the equilibrium concentration (mg/L) and x/m is the amount adsorbed per unit weight of adsorbent. The K_F is the 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 exhibits that the adsorption obeys the Freundlich isotherm. Freundlich constants (K_F and n) calculated from the intercept and slope of the plot from Fig. 6 and presented in Table-1. The values of $1 < n < 10$ indicates high probability of adsorption of Ni(II) on the both modified XAD-7HP and XAD-761 resins.

Adsorption kinetics: In order to clarify the adsorption kinetics of Ni(II) ion onto modified XAD-7HP and XAD-761 resins two kinetic models, which are Lagergren's pseudo-first-order and pseudo-second-order model were applied to the experimental data.

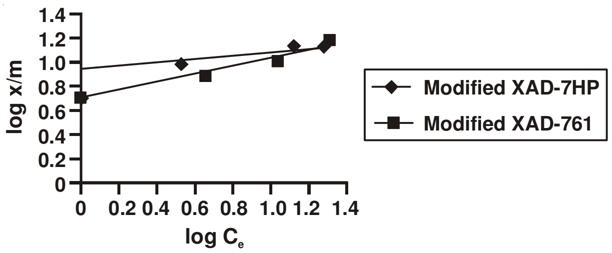
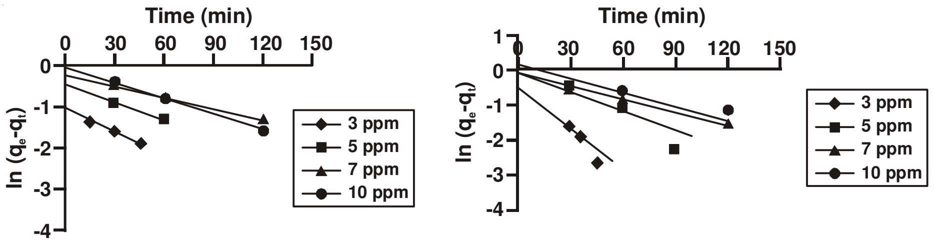


Fig. 6. Application of Freundlich model to the experimental data

The linearized form of the pseudo-first-order rate equation of Lagergren is given as[29]:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (5)$$

where q_e and q_t are the amount of the metal ions adsorbed (mg/g) at equilibrium and t (min), respectively and k_1 is the pseudo-first-order equilibrium rate constant (1/min). A plot of ln (q_e – q_t) *versus* t gives straight line with slope of k_1 and an intercept of ln q_e. It confirms the applicability of the pseudo-first-order rate equation (Fig. 7).



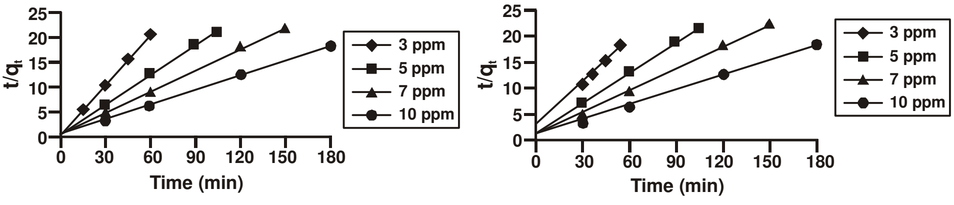
(a) (b)

Fig. 7. Pseudo-first-order kinetics for the adsorption of Ni(II) on modified XAD-7HP (a) and XAD-761 resins (b)

The pseudo-second-order model rate equation may be expressed as[30]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{6}$$

where k_2 is the pseudo-second-order adsorption rate constant (g/mg/min). A plot of (t/q_t) *versus* t produces straight line with slope of $1/q_e$ and intercept of $1/k_2q_e^2$. It indicates the applicability of pseudo-second-order model (Fig. 8).



(a) (b)

Fig. 8. Pseudo-second-order kinetics for the adsorption of Ni(II) on modified XAD-7HP (a) and XAD-761 resins (b)

In order to compare quantitatively the applicability of kinetic models in fitting to data, the per cent relative deviation (P), given by the following equation was calculated:

$$P = \frac{100}{N} \sum \left(\frac{[q_{e(exp.)} - q_{e(theo.)}]}{q_{e(exp.)}} \right) \tag{7}$$

where $q_{e(exp)}$ is the experimental value of q_e at any value of C_e, $q_{e(theo)}$ the corresponding theoretical value of q_e and N is the number of observations. It is found that lower value of percentage deviation (P), better is the fit. It is generally accepted that when P value is less than 5, the fit is considered to be excellent[31]. The results have been analyzed using eqns. 5 and 6. The experimental data fitted well in both the equations. The values of $q_{e(theo)}$ calculated from these models are compared with experimental values $q_{e(exp)}$ in Table-2. It is found that values of $q_{e(theo)}$ calculated from the pseudo-first-order kinetic model differed appreciably from the experimental values $q_{e(exp)}$ for both modified resins. The per cent deviation (P) is also found to be very high for both modified resins. On the other hand, values of $q_{e(theo)}$ are found to be close to $q_{e(exp)}$ when pseudo-second-order rate equation was applied. The percent deviation (P) is well within the range and the values of correlation coefficients (R^2) are also very high to pseudo-second-order kinetics when compared with pseudo-first-order kinetics for both modified resins. These results indicated that the removal of Ni(II) onto both modified XAD-7HP and XAD-761 resins follow well the pseudo-second-order kinetics.

TABLE-2
PSEUDO-FIRST-ORDER AND PSEUDO-SECOND-ORDER KINETIC CONSTANTS FOR THE ADSORPTION OF Ni(II)) ON MODIFIED XAD-7HP AND XAD-761 RESINS

		Pseudo-first-order kinetics					Pseudo-second-order kinetics				
Adsorbent	Conc. (mg/L)	k_1 (L/min)	$q_{e(theo)}$ (mg/g)	$q_{e(exo)}$ (mg/g)	R^2	P	k_2 (g/mg min)	$q_{e(theo)}$ (mg/g)	$q_{e(exo)}$ (mg/g)	R^2	P
Modified XAD-7HP	3	0.0200	0.3678	2.90	0.999	87.31	0.2222	3.00	2.90	0.999	3.44
	5	0.0166	0.6065	4.95	0.941	89.80	0.0800	5.00	4.95	0.999	0.84
	7	0.0148	0.7408	6.90	0.991	89.26	0.0148	7.20	6.90	0.999	4.34
	10	0.0121	0.9512	9.90	0.998	90.39	0.0100	10.00	9.90	0.999	1.01
Modified XAD-761	3	0.0466	0.7408	2.95	0.990	74.88	0.0740	3.00	2.95	0.999	1.69
	5	0.2420	0.9048	4.90	0.991	81.53	0.0333	5.00	4.90	0.999	2.04
	7	0.0166	1.0000	6.80	0.998	85.29	0.0265	6.85	6.80	0.999	0.83
	10	0.0133	1.2214	9.80	0.998	87.53	0.1666	10.00	9.80	1.000	2.04

The free energy of adsorption (ΔG°) can be related with the equilibrium constant K (L/mol), corresponding to the reciprocal of the Langmuir constant, b, by the following equation[32,33]:

$$\Delta G^{o} = -RT \ln b \qquad (8)$$

where R is the universal gas constant (8.314 J mol^{-1} K^{-1}) and T is the absolute temperature (K). Gibbs free energy change (ΔG°) was calculated to be -28.78 kJ mol^{-1} for modified XAD-7HP resin and -22.54 kJ mol^{-1} for modified XAD-761 resin. Negative values of ΔG° indicated that the adsorption process was found to be spontaneous in nature. However, the removal mechanism of Ni(II) adsorption is not well understood. It may further be added that the modified resin extracts nickel ion from solution by ion exchange/chelation through electrostatic attraction.

Desorption studies: Desorption studies were conducted to recover the Ni(II) from the modified XAD-7HP and XAD-761 resins. Attempts were made to desorb Ni(II) from the spent resins using sodium chloride (1-10 %). The final Ni(II) concentration in the aqueous phase was determined by using atomic absorption spectrophotometer. Results showed that 99 % of Ni(II) desorbed from the modified resin under optimum concentration of 5 % NaCl for modified XAD-7HP resin and 3 % NaCl for modified XAD-761 resin. After the extraction of Ni(II) on modified resins, they were washed completely with distilled water. The adsorption capacity of the modified XAD-7HP and XAD-761 resins were again tested for about five cycles of operation. Results showed that adsorption capacity of NaCl regenerated modified XAD-7HP and modified XAD-761 resins were maintained over the range 99-87 and 99-92 %, respectively even up to I-V cycles of operation and the results are shown in Table-3.

TABLE-3
EFFICIENCY OF MODIFIED RESINS ON THE REMOVAL OF Ni(II) USING NaCl AS REGENERANT UNDER CYCLES

Cycle	Percentage of Ni(II) removed by modified XAD-7HP	Percentage of Ni(II) removed by modified XAD-761
I	99.10	99.80
II	96.50	98.40
III	93.50	96.50
IV	89.50	94.70
V	87.50	92.50

Conclusion

In present study, two new simple and eco-friendly modified Amberlite XAD-7HP and Duolite XAD-761 resins were prepared and found to be useful for separating the nickel ion from aqueous solution. Separation media could be prepared by mixing the resins in aqueous solutions of anionic surfactant and EDTA, without any chemical synthesis, thereby chelating functionality was easily introduced on the solid surface. It is further added that XAD-7HP was found to remove nickel ions over a large pH range when compared with XAD-761. Both the modified resins could be regenerated by using inexpensive regenerant such as 3-5 % of NaCl. It has been found out that the regenerated modified resins could be again and again used for at least five cycles of operation without major loss in adsorption capacity and loss of material. Hence it may be concluded that both modified resins can be used for nickel removal from aqueous system.

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