

Thermodynamic and kinetic studies of the removal of Zn^{2+} and Ni^{2+} from their aqueous solution using copolymer resin

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Abstract— Novel polymeric resin was synthesized by polycondensation of 2-dihydroxy 4-methoxybenzophenone and adipamide with formaldehyde in the presence of hydrochloric acid as a catalyst and dimethylformamide (DMF) as a solvent. Chemical, structural and textural characteristics of the resin were determined by FT-IR, 1H -NMR, SEM and EDAX analysis. Adsorption capacity of resin for the removal Ni^{2+} and Zn^{2+} ions was investigated. Adsorption parameters, such as pH, adsorbent dose, contact time, initial metal ion concentration and temperature were optimized. Batch adsorption kinetics have been mathematically described using the pseudo-first order, pseudo-second order, Elovich and intra particle diffusion kinetic models. Adsorption isotherms have also been investigated, using Langmuir and Freundlich isotherm models. Adsorption thermodynamic parameters like enthalpy change (ΔH°), entropy change (ΔS°) and free energy (ΔG°) were calculated from temperature dependent adsorption. Values of (ΔH°) and (ΔG°) suggests that the adsorption of Ni^{2+} and Zn^{2+} ions onto resin is endothermic and spontaneous in nature. Desorption experiments show that the adsorption process of Fe^{3+} and Zn^{2+} ions is reversible and the adsorbent was easily regenerated with 90% adsorption capacity even after four cycles, using 0.2N HCl. Copolymer resin has a good adsorption efficiency for the removal of Fe^{3+} and Zn^{2+} ions compared to other chelating resin.

Keywords- Resin, Copolymer, Condensation, Isotherm, adsorption capacity, Thermodynamic parameters, Thermogravimetry

INTRODUCTION

In recent years, there has been a growing concern for the immobilization of metal ions introduced into water and wastewater bodies by increasing human technological activities. It has been established beyond doubt that heavy metal ions in the environment (water, soil and air) pose a very serious threat to human health. With the exponentially increasing population, there is a need for controlling heavy metal discharge before the toxic metal ions enter the complex ecosystem. Separation, removal, and enrichment of trace metals in aqueous solutions play an important role in the analysis of wastewaters, industrial and geological samples. Solid phase extraction of metal ion has gained rapid acceptance because of its various advantages over other methods. The extraction of metal ions using chelating ion exchange resin is a green analytical method since it does not involve the use of toxic chlorinated organic solvents, which are very frequently used in conventional liquid-liquid extraction techniques. The main objective of most of the research on chelating resins was the preparation of insoluble functionalized polymers that can provide more flexible working conditions together with good stability and high capacity for metal ions. The use of modified clay minerals for the adsorption of metal ions from aqueous solutions for water purification or industrial wastewater treatment has been widely studied. These clay minerals, when used as colloids or powders, have been found to be equally efficient as ion exchange resin but it is difficult to recover such adsorbents from

filters after use. This further renders the regeneration and possible reuse of clay adsorbents very difficult. Chelating ion exchange resins were also prepared by copolycondensation of 8- hydroxyquinoline or phenol derivatives like *o*-aminophenol, resorcylic acid or resorcinol with formaldehyde [1]. Antico *et al.* synthesized a gel type chelating ion exchange resin from glycol methacrylate with 8-hydroxyquinoline and used it to study the separation of Pb(II) and Cu(II) in their chloride solution [2]. The chelating ion exchange resins were also synthesized by Friedel-Craft's condensation of 8-hydroxyquinoline [3] and substituted 8- hydroxyquinoline [4] with 1,2-dichloroethylene. The synthesized resins were proved to be selective for certain metal ions over a wide pH range. Warshwsky *et al.* [5] reported some resins based on 8-hydroxyquinoline and substituted 8-hydroxyquinoline, respectively, along with their chelation properties towards transition and post transition metal ions. So far no resin based on 2-hydroxy 4-methoxy benzophenone-adipamide-formaldehyde in HCl medium has been reported for the quantitative removal and separation of transition and post transition metal ions. As industrial effluents are often rich in transition and post transition metal ions removal of these metals is an important industrial task. The work described in the present communication deals with the synthesis, characterization and thermal studies of the above resin along with the systematic studies of various ion-exchange properties of copolymer resin.

Experimental Synthesis of Copolymer Resin

A mixture of 2-hydroxy 4-methoxybenzophenone (0.1 mole), adipamide (0.1 mole) and formaldehyde (0.2 mole) in the presence of 200 ml 2M hydrochloric acid (HCl) as a catalyst was heated in an oil bath at 126°C for 5 hrs, with occasional shaking. The separated resinous product (2-H4-MBAF) was washed with hot water and methanol to remove unreacted monomers. The resinous product so obtained was washed with cold water, dried in air and powdered. The powder was washed with hot water and dried. Dried resins were then extracted with diethyl ether followed by petroleum ether to remove 2-hydroxy 4-methoxybenzophenone-formaldehyde copolymer, which might be present along with 2-H4-MBAF copolymer. The resin was purified by dissolution in 8% NaOH and reprecipitation by drop wise addition of 1:1 (V/V) HCl, with constant and rapid stirring to avoid lump formation. The process reprecipitation was repeated twice. The copolymer resin 2-H4-MBAF [Figure 1] so obtained was filtered, washed with hot water, dried in air, powdered and stored in vacuum over anhydrous CaCO₃.

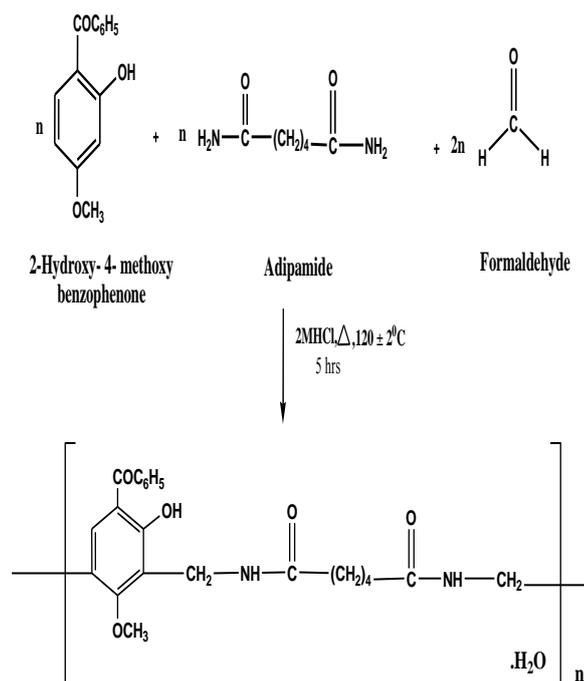


Figure 1. Synthesis of copolymer resin

Results and Discussion

Spectral Characterization of Resin

2-H4-MBAF Copolymer resin synthesized taking various molar ratios of monomers by condensation process are found to be light pink color. These are purified and are found to be soluble in N-N'-

dimethyl formamide (DMF), dimethyl sulphoxide (DMSO), Tetrahydrofuran (THF), aqueous potassium hydroxide and sodium hydroxide and insoluble in common organic solvents.

The IR spectral studies revealed that the copolymer resin give rise to a broad absorption band appeared in the region 3400 cm⁻¹ may be assigned to the stretching vibrations of phenolic hydroxyl (-OH) groups exhibiting intramolecular hydrogen bonding [6]. The band, at 3060 cm⁻¹ indicate the presence of >NH stretching. The sharp and strong band around 3014 cm⁻¹ is assigned to aryl C-H stretching. The weak band around 2944 cm⁻¹ is assigned to -C-H stretching of >CH₂ linkage and the medium band around 2842 cm⁻¹ is assigned to -C-H stretching of -OCH₃ group [7]. The band around 1733 cm⁻¹ is assigned to >C=O stretching of diaryl ketone [7]. The strong band around 1635 cm⁻¹ is assigned to >C=O stretching of amide moiety. The band around 1593-1595 cm⁻¹ may be due to -NH bending and 1505 cm⁻¹ may be due to -C=C- stretching (aromatic vibration). The band at 1434 cm⁻¹ may be ascribed to aromatic skeletal ring. The band at 1380 cm⁻¹ indicate the presence of methylene (-CH₂) bridge. The band around 759-760 cm⁻¹ may be due to -CH₂ bending (rocking) and 1259 cm⁻¹ may be due to -C-N stretching. Tetra substitution in aromatic ring was confirmed by the bands appeared at ~519, ~817, ~950, ~1111 [7].

¹H NMR spectra of copolymer was scanned in DMSO-d₆. The singlet obtained in the region 2.48 (δ) ppm may be due to the methylene proton of Ar-CH₂-Ar bridge [8]. The weak multiple signals (unsymmetrical pattern) in the region of 6.50 (δ) ppm may be attributed to aromatic proton (Ar-H) [8]. The signals in the range at 8.89 (δ) ppm may be due to phenolic hydroxyl protons. The much downfield chemical shift for phenolic -OH indicates clearly the intramolecular hydrogen bonding of -OH group [9]. The signal appeared in the region at 5.51 (δ) ppm is due to the proton of -NH bridge. The signal appeared in the region at 3.80 (δ) ppm is due to the methylene proton of Ar-CH₂ bridge [9]. The methyl protons of the Ar - O - CH₃ moiety may be identified by the intense peak at 3.30 (δ) ppm.

SEM analysis is a useful tool for the analysis of the surface area and structure morphologies of adsorbent. SEM images of resin was analyzed using a Leo Gemini 1530 scanning electron microscopy at an acceleration voltage of 10 kV and with working distance 20 μm. SEM images of resin, Ni²⁺ and Zn²⁺ loaded resin indicates that an asymmetric surface and

open pore structure are present, which may provide high internal surface area (means high metal ion adsorption capacity) in the resin adsorbent. The presence of pores suggests that there is a good possibility for the metal ions to be trapped and adsorbed onto the surface of resin. The mean size of surface cavities was measured on the image and the average diameter was less than 2 μ m. These cavities are large enough to allow the metal ions to penetrate into the resin surface and interact therein with the surface groups. The surface morphology of treated resin is different, before and after adsorption of metal ions. The pores were completely filled, after adsorption of metal ions[9].

Effect of solution pH

Effect of solution pH on nickel and zinc uptake by resin was studied, varying solution pH from 3 to 9 at adsorbent dosage 50 mg/L using initial concentration of Ni²⁺ and Zn²⁺ 100 mg/L for 90 min. Amount of adsorbed heavy metals (nickel and zinc) were calculated from the difference of initial and final metal ion concentration in the solution. The highest adsorption capacity (>96%) was recorded, at the neutral pH (~7) of the metal solution and it decreases as the solution pH increases or decreases. The neutral pH may be attributed to the presence of free lone pair of electron on nitrogen atom as well as on sulphur atom suitable for the coordination with the metal ions to give the corresponding resin-metal complexes and the mechanism. The higher adsorption capacity for the Ni²⁺ and Zn²⁺ ions at neutral pH, can be attributed to the interaction of free metal ions with the resin adsorbent. Hence optimum pH 7 was maintained, for further batch adsorption studies. The concentration of heavy metal ions in the solutions, before and after equilibrium was determined by AA6300 Atomic absorption spectrometer (Shimadzu- AA6300, Japan) and load parameters of AAS for Ni²⁺ and Zn²⁺ ions are given in Table (1). The pH of solution was measured with a Hanna pH meter, using a combined glass electrode and pH was maintained using 0.1 N HCl and NaOH solution[8-9].

Effect of adsorbent dosage

The adsorbent dosage is also an important factor in the batch adsorption studies shows the effect of adsorbent dosage (50 – 300 mg) on metal ion removal. Adsorption experiment was carried out using 100 ml of 200 mg/L of metal ion solution in solution pH of 7 at 180 rpm agitation speed for 90 min. Adsorption capacity increases, when adsorption dosage is increased because active sites of adsorbent surface increase to interact with the metal ions. The rapid increase in adsorption, with the increase in the adsorbent dose, can be attributed

to greater surface area and availability of additional adsorption sites. The maximum adsorption efficiency of both metal ions was found to be at 2 g/L of resin adsorbent. There was a non-significant increase in the percentage removal of metal ions, when the resin dosage was increased beyond the 2 g/L, because the adsorbent sites were saturated with metal ions already. Hence further adsorption of metal ions was not possible. The results of effect of adsorbent dosage suggest that after a certain adsorbent dose, maximum adsorption is attained and hence the amount of ions remain constant, even with further addition of dosage of adsorbent.

Adsorption kinetic studies

Contact time is an important factor in the batch adsorption process, because this parameter can affect the adsorption kinetics of an adsorbent for a given metal ion concentration. Kinetic studies for Ni²⁺ and Zn²⁺ were performed by using different concentrations (100, 150 and 200 mg/L). The experiment was conducted by mixing 100 mL of Ni²⁺ and Zn²⁺ solutions with 50 mg/L of resin. The mixture was shaken in a thermostatic shaker (Orbitek) at 180 rpm. Samples were taken at different time intervals ranging between 15 to 120 min.. It is seen that the adsorption efficiency increases rapidly during the initial adsorption stage and it continues to increase at a relatively slow speed with contact time and reaches equilibrium at 90 min, beyond which constant adsorption was noticed. It was found that the maximum Ni²⁺ and Zn²⁺ ion adsorption onto the resin was attained at 90 min. Hence 90 min was fixed, for further adsorption experiments.

Adsorption kinetics provides valuable information about the controlling mechanism of adsorption process. Reaction rate of adsorbate uptake, which is required for selecting optimum operating conditions for the fullscale batch process, can be elucidated with adsorption kinetics studies. Adsorption kinetic models such as pseudo-first order [10], pseudo-second order [11], Elovich [12] and interparticle diffusion [13] models were applied for experimental data.

Pseudo-first order kinetic model

Pseudo-first order equation relates the adsorption rate to the metal adsorbed amount at time t as:

$$\frac{dq_t}{dt} = k_1(q_e - q_t)$$

where q_e and q_t are the adsorbed amount of metal ions at equilibrium and time (t) respectively, expressed as mg/g, k_1 is the pseudo-first order kinetic constant,

expressed as (min-1). Equation integration and rearrangement yield the linear form:

$$\log(q_e - q_t) = l$$

shows that the plotting of $\log(q_e - q_t)$ versus t , gives straight lines for pseudo-first order model.

Values of slope (k_1) and intercept ($\log q_e$) of these lines were calculated. The values for overall adsorption rate constant (k_1), theoretical equilibrium adsorption capacity (q_e) and correlation coefficient (R^2) values are reported in Table (2). It is seen that, the values of q_e are not generally comparable to the experimental data obtained. The correlation coefficients values are also low when compared to pseudo-second order and Elovich kinetic coefficients values. The results indicate that the adsorption process does not proceed well following pseudo-first order kinetics.

Pseudo-second order kinetic model

Pseudo-second order kinetic equation may be written in the form:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2$$

where k_2 ($g\ mg^{-1}\ min^{-1}$) is second order kinetic constant, the differential equation is usually integrated and transform in its linear form:

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

shows that the plots of t/q_t versus t give a straight linearity; implying that the adsorption system studied follows the pseudo-second order kinetic model. The q_e and k_2 values were calculated from slope and intercept of the plots respectively and are listed in Table (1). The adsorption data were treated according to pseudo-second order kinetic model using equation (4). As Table (2) shows, the correlation coefficients (R^2) are high compared to the other kinetic coefficients values. Moreover, the values of q_e , calc, as estimated from the pseudo-second order model are close to those q_e , exp values (Table 1). The pseudo-second order model is better than the other kinetic models. The result suggests that the adsorption data well fit with pseudo-second.

order kinetic model. So, it is possible to suggest that the adsorption of Cu^{2+} and Mn^{2+} metal ions onto resin follows a second order kinetic reaction.

Elovich kinetic model

The experimental data were also applied to Elovich kinetic models, which is given in the equation given below;

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln(t)$$

where α is the initial adsorption rate constant ($mg/(g\ min)$) and the parameter β is related to extent of surface coverage activation energy for chemisorptions

(g/mg). The plots obtained from the graphical interpretation of the data for the Elovich kinetic model. The values of α , β and R^2 were calculated from plot of q_t against $\ln(t)$ and the constants are given in the Table (2). This kinetic model does not predicts any definite mechanism but has been found useful in describing chemical adsorption on highly heterogeneous adsorbents. The correlation coefficient (R^2) is lower than the pseudo-second order kinetic model. The Elovich kinetic model results suggest that the adsorption process does not fit well with the experimental data.

Intra particle diffusion kinetic model

The intra particle diffusion model is expressed with the equation given by Weber and Morris.

$$q_t = k_p t^{1/2} + C$$

k_p is the intra-particle diffusion rate constant ($mg/g\ min$), t is the time (min). The constants of the intra-particle diffusion model were obtained from the linear plots q_t against $t^{1/2}$ using the experimental data. The intra-particle diffusion straight line does not pass through the origin. The results show that intra particle diffusion is not the only rate controlling step. The kinetic constants and correlation coefficients of all isotherm models are given in Table (1). Highest correlation coefficients were obtained for the pseudo-second order kinetic model, which shows that the adsorption process follows the pseudo-second order rate expression.

Adsorption isotherm studies

The effect of the initial metal ion concentration was varied in the range of 25-150 mg/L at a constant pH 7, using an adsorbent dose of 50 mg and reaction mixture were shaken for 90 min at room temperature. The removal efficiencies were high ($> 90\%$) at lower initial metal ion concentration ($< 75\ mg/L$). The available adsorption sites were easily occupied by M^{2+} ion resulting higher removal efficiency. The non-linear forms of Langmuir [14] and Freundlich [15] adsorption isotherm models were used to evaluate the adsorption experimental data using MATLAB R2009a.

Langmuir isotherm model

The Langmuir isotherm model is a commonly applied model for adsorption on a completely homogenous surface with negligible interaction between adsorbed molecules. This model assumes uniform adsorption energies onto the surface and maximum adsorption depends on saturation level of monolayer. The mathematical description of this model is

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$$

where C_e is the equilibrium concentration of metal ion in the solution (mg/L), q_e is the adsorbed value of metal ion at equilibrium concentration (mg/g), q_m is the maximum adsorption capacity (mg/g) and K_L is the Langmuir binding constant which is related to the energy of adsorption. The data obtained q_e , K_L and correlation coefficients (R^2) values are reported in Table (2)

Freundlich isotherm model

Freundlich isotherm model is related to multilayer adsorption and for the adsorption on heterogeneous surface.

Non-linear form of the Freundlich equation is given by the following equation

$$q_e = K_f C_e^{\frac{1}{n}}$$

where K_f is the Freundlich constant ((mg/g)(L/mg)^{1/2}) which indicate the adsorption capacity and represents the strength of the adsorption bond. n is the heterogeneity factor which represents the bond distribution. The values of n , between 1 to 10 indicate favourable adsorption in nature. For the present study the value of n was found to be greater than 1, which indicates that the adsorption of Ni^{2+} and Zn^{2+} metal ions is a favourable adsorption. All the constants and parameters of Freundlich isotherm models are listed in Table (2). It can be seen that the experimental data fitted well with the Freundlich isotherm model than Langmuir isotherm model (due to the poor correlation coefficient (R^2) value of Langmuir isotherm model). Based on these results, it can be inferred that the adsorption process is a heterogeneous surface adsorption rather than a monolayer one. The reason might be related to such factors as the heterogeneous distribution of active sites onto resin adsorbent [16-17].

Adsorption thermodynamics studies

The effect of temperature on the adsorption of resin has been investigated at 303, 308, 313, 318 and 323 K. Thermodynamic considerations of an adsorption process are necessary, to conclude whether the adsorption process is spontaneous or not. The thermodynamic parameter such as Gibbs free energy change (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) were calculated using the following equation [18-19].

$$\Delta G = -RT \ln K$$

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ$$

where ΔG° is the standard free energy change (J/mol), R the universal gas constant (8.314 J/mol K), and T is the absolute temperature and K is equilibrium constant. ΔG° were calculated using Gibbs free energy

equation. ΔH° and ΔS° were obtained from the slope and intercept of the plot of $\log K$ Vs $1/T$. The thermodynamics calculated values are reported in Table (3).

The positive values of enthalpy indicate that the adsorption reaction is endothermic in nature. The negative values of ΔG° suggest that the adsorption reaction is generally a spontaneous process in nature and thermodynamically favorable. The positive entropy values indicate the increase of randomness at the solid–liquid interface during the adsorption process [19].

Conclusions

On the present study, the resin adsorbent was synthesized characterized and an adsorption process was developed for the removal of Ni^{2+} and Zn^{2+} ions from aqueous solution. The FT-IR and ¹H-NMR confirmed that the synthesis of resin was achieved successfully. The maximum adsorption capacity of Ni^{2+} and Zn^{2+} ions were attained at pH approximately 7. The resin resin dosage increased the percentage removal of metal ions, due to increasing surface area. The adsorptions of metal ions significantly decreased, by the further addition of same metal ions. The adsorption kinetic studies, showed good correlation coefficients were obtained in the pseudo-second order kinetic model and the metal ion uptake process followed the pseudosecond order rate expression. Isotherm experimental results showed that the adsorption data fitted well with Freundlich isotherm and the maximum adsorption capacities of resin for Ni^{2+} and Zn^{2+} ions as calculated from Langmuir isotherm model occurred at 212.8 and 226.32 mg/g respectively. The adsorption of Ni^{2+} and Zn^{2+} ions, increased as the temperature is increased from 30 to 50° C and the adsorption has been found to be an endothermic reaction.. The overall results, one may state that the chelating resin can be used in the treatment of wastewater from industry.

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Table.1. Kinetic models and other statistical parameters for Ni²⁺ and Zn²⁺ adsorption

Kinetic model	Parameters	Ni ²⁺ ion			Zn ²⁺ ion		
		100 mg/L	150 mg/L	200 mg/L	100 mg/L	150 mg/L	200 mg/L
Pseudo-firstorder equation	kad (min-1)	1.53 X10-2	1.64 X10-2	1.81 X10-2	1.87 X10-2	1.94 X10-2	1.90 X10-2
	qe,cal (mg/g)	427.80	398.16	401.90	446.69	420.61	436.95
	R2	0.958	0.955	0.901	0.915	0.925	0.892
Pseudo-secondorder equation	k (g mg-1 min-1)	1.21 X10-4	1.08 X10-4	0.95 X10-4	0.88 X10-4	0.86 X10-4	0.85 X10-4
	qe ,cal (mg/g)	196.04	198.04	219.00	227.76	227.60	240.96
	qe,exp (mg/g)	227.27	232.55	243.90	256.41	259.74	263.15
	R2	0.990	0.986	0.993	0.993	0.992	0.990
Elovich equation	α (mg/g.min)	9.92	10.71	12.86	10.29	10.72	12.12
	β (g/mg)	0.0124	0.0126	0.0128	0.0141	0.0121	0.0118
	R2	0.969	0.976	0.972	0.989	0.975	0.982
Intraparticle diffusion	kp (mg/g.min 1/2)	22.24	23.06	20.26	24.56	23.61	20.36
	C	12.54	19.76	14.30	16.16	15.27	12.49
	R2	0.984	0.984	0.992	0.989	0.990	0.984

Table.2 The value of parameters for two isotherm models used in this study

Isotherm Model	Cu ²⁺ ion		Mn ²⁺ ion	
	Parameter	R2	Parameter	R2
Langmuir	qm= 212.8	0.896	qm= 226.32	0.886
	KL = 0.223		KL = 0.2825	
	SSE = 1863		SSE = 2034	
	RASE = 21.58		RASE = 22.55	
Freundlich	KF= 72.61	0.992	KF= 81.74	0.974
	n = 3.75		n = 3.58	
	SSE = 374.7		SSE = 1094	
	RASE = 9.679		RASE = 16.54	

Table.3. Thermodynamic data for Ni²⁺ and Zn²⁺ adsorption onto resin

Metal ion		ΔG (kJ/mol)	ΔH(kJ/mol)	ΔS (kJ/mol)
Ni ²⁺	100 mg/L	-5.024	27.18	0.147
	200 mg/L	-2.805	19.39	0.103
Zn ²⁺	100 mg/L	-6.210	21.34	0.119
	200 mg/L	-3.372	17.64	0.093