

Synthesis, Characterization and Chelation Ion-Exchange Studies of a Resin Copolymer Derived From 8-Hydroxyquinoline-Formaldehyde-Pyrogallol

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Abstract

An ion exchange resin chelator was synthesized from 8-hydroxyquinoline and pyrogallol using formaldehyde as a crosslinking agent to 120°C in a solution of DMF. The resin was characterized by elemental analysis and FTIR. The morphology of the synthesis resin was examined by optical photograph and scanning electron microscopy (SEM). The physicochemical properties of the resin were studied. The cation exchange capacity was measured and the effect of pH and metal ion concentration on the ability of the ion exchange were studied. The ratio of cation exchange reaction and the distribution coefficient in tartaric acid medium at different pH were also studied using the method of batch equilibration.

Keywords: Chelating resin; Batch equilibration; Physico-chemical properties; Distribution coefficient

Introduction

Over the past years, there has been a growing concern for the immobilization of metal ions introduced into bodies of water and wastewater by increasing human technological activities. It has been established beyond doubt that the ions of heavy metals in the environment (air, soil and water) pose a serious threat to human health. With the exponential growth of the population, it is necessary to control the release of toxic heavy metal ions before entering the complex ecosystem.

Separation, removal, and the enrichment of metals in trace amounts in aqueous solutions, have an important role in wastewater, industrial or geological sample analysis. The solid phase extraction on the metal ion was granted fast acceptance due to its various advantages over other the invention also provides methods. The extraction of metal ions using ion exchange resin is a chelating power green analytical method, since it does not involve the use of toxic organic chlorine compounds, which are very frequently used in conventional techniques liquid-liquid extraction.

The main objective of much of the research on chelating resins was the preparation of the insoluble part functionalized polymers that can provide in conjunction with more flexible working conditions good stability and high capacity for metal ions. The use of the modified clay minerals for the adsorption of metal ions from aqueous solutions for purification of industrial water or waste water, the treatment has been widely studied.

These clay minerals, when used as colloids or powders were found to be effective as ion equally exchange resin, but it is difficult to retrieve from these adsorbents filters after use. This regeneration makes very difficult to reuse clay adsorbents. Chelating ion exchange resins have also been prepared by copolycondensing or 8-hydroxyquinoline phenol derivatives such as o-aminophenol, resorcinol or resorcylic acid with formaldehyde [1].

Antico and al synthesized from a gel-type ion exchange resin, Glycol 8-hydroxyquinoline methacrylate and used to investigate separating Pb (II) and Cu (II) in the chloride solution [2]. Chelating ion exchange resins also have been synthesized by the Friedel-Crafts condensation 8-hydroxyquinoline [3] and substituted 8-hydroxyquinoline with [4]

1,2-dichloroethylene. The synthetic resins have been found selective for certain metal ions over a wide pH range. The chelating behavior poly (8-Quinoline-5, 7-dimethylene) [5] and its cross-linked polymer [6] from the reaction with different amounts of bisphenol-a to certain trivalent ions of lanthanides such that La (II) and Gd (II) was investigated by static a load balancing Method. Vernon and al. prepared and studied chelating properties of toxin resin to the transition metal ions [7,8] stability test, they suggested that the gel polymers must never be allowed to dry; otherwise their favorable properties are destroyed.

Shah et al. [9,10] and Warshwsky et al. [11] reported certain resins based on 8-hydroxyquinoline and substituted 8-hydroxyquinoline, respectively, and chelating properties to transition and post-transition metal ions. A chelating ion exchange resin was synthesized from 8-hydroxyquinoline and catechol using formaldehyde have been synthesized by Shah et al. [12].

Until now, no resin based on 8-hydroxyquinoline pyrogallol-formaldehyde in DMF has been inserting for quantitative removal and separation transition metal ions and post transition. As industrial effluents are often rich in transition and transition metal ions after, removing the metals a large industrial task. The study described in the present communication processes of synthesis and characterization of absolvers together with the systematic studies of various properties of ion exchange resin.

Materials and Methods

Materials

8-Hydroxyquinoline (Prolabo, IGT Paris) and formaldehyde were purified by recrystallization method.

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Pyrogallol (Glaxo extra pure) was purified by rectified spirit. Metal ion solutions (KANTO CHEMICAL CO, INC.) were used as received.

Synthesis method

8-hydroxyquinoline (14.5 g, 0.1 moles) has been ground into fine powder and taken in a (250 ml) round bottom balloon and dissolved in DMF (25 ml) to give a clear yellow solution. Formaldehyde (7.5 ml, 0.25 mol as 37%) added and stirred until a solution of red color.

A pyrogallol solution (11 g, 0.1 mole) in (10 ml) DMF has been added to above the solution and stirring for 3 h. Then, the mixture has been heated to reflux on a water bath at 90°C under constant stirring for 3 to 5 h.

Condensation reagents was carried out in the presence of an acid HCl 2M on sand bath by heating to 120°C during 7 -8 h until a viscous solution with formation of a hard mass of brown colored resin has been obtained.

The synthetic resin has been removed from the reaction vessel and cured in an oven at 70-80°C during 12 h. The resulting resins having been washed with DMF and deionized water to remove unreacted monomers and impurities. After the complete washing cycle, the reaction yield production of the resin synthesized was 50% (15 g).

The resin sample has been purified and dried finely crushed and sieved to obtained uniform particles of 50-70 mesh and stored in polyethylene bottle. The resin has been then screened characterized using different instrumental analysis techniques and was used for the entire experiments during the search period. Testing of solubility of the resin in a different solvent was performed at room temperature and pressure with intermittent agitation. The resin has been found being insoluble in all common organic solvents such as acetone, ethanol, benzene, chloroform etc. and all acids and alkalis of higher strengths.

Infra-Red spectra of the synthesized resin sample have been carried out without solvent on a Thermo Scientific Nicolet spectrometer IR-200 FT-IR, which is the measurement accuracy of 4 cm⁻¹ in the area 400-

4000cm⁻¹. The allocation FTIR spectra peaks are presented in Figure 1. Elemental analysis was performed on Carlo ZAF EDAX quantification (Standard Less). The results of the elemental analysis are in good accordance with the calculated values of %C, % H and % N which is presented in Table 1.

To convert the resin sample in its H⁺ form, it has been equilibrated with a solution of HCl 1M for 24 h and washed with deionized water until it is free from chloride by testing with silver nitrate solution. The H⁺ form of the resin have been used for subsequent studies. The batch equilibrium method has been adopted for studying the ion-exchange properties. Physico-chemical properties such as moisture and solid contents, apparent density, true density and void volume fraction have been studied by the methods of the literature [13].

The sorption properties such as exchange rate, pH effect on the exchange capacity, effect of the cation concentration on the exchange capacity and distribution coefficient (K_d) values for various metal ions as a function of pH and concentration of the electrolyte have been studied with the literature methods [13,14]. The value of the void volume fraction has been found 0.36, while other resins signaled 8-hydroxyquinoline formaldehyde [8], 8-hydroxyquinoline formaldehyde resorcinol [9] and 8-hydroxyquinoline formaldehyde catechol [12] exhibited void volume fraction values of 0.54, 0.59 and 0.36, respectively.

Rate of exchange of metal ions

For the experiment, an accurately weighed (0.250 ± 0.001 g) dry resin in the H⁺ form was taken into different glass bottles stoppered and equilibrated with a desired pH values with buffer solution for 24 h. After decanting of the buffer solution, 50 ml (0.2 M) of metal ion solution was added with the same pH. The amount of non-chelated metal ion has been determined by Atomic Absorption Spectroscopy (AAS) at fixed time intervals. The results are shown in Figure 2.

Effect of pH on metal ion exchange capacity

To study the pH effect on absorbing metal ions, it is necessary to buffer the resin and solutions used. For this purpose, buffer solutions of

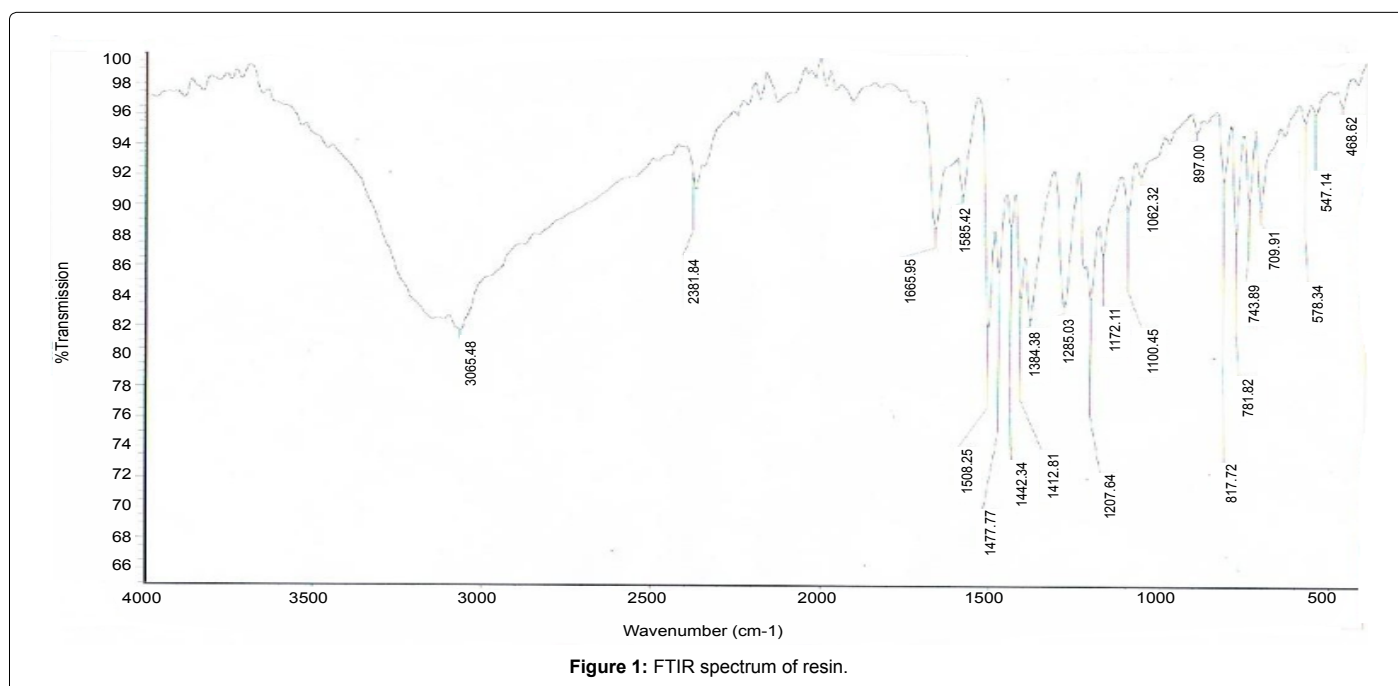
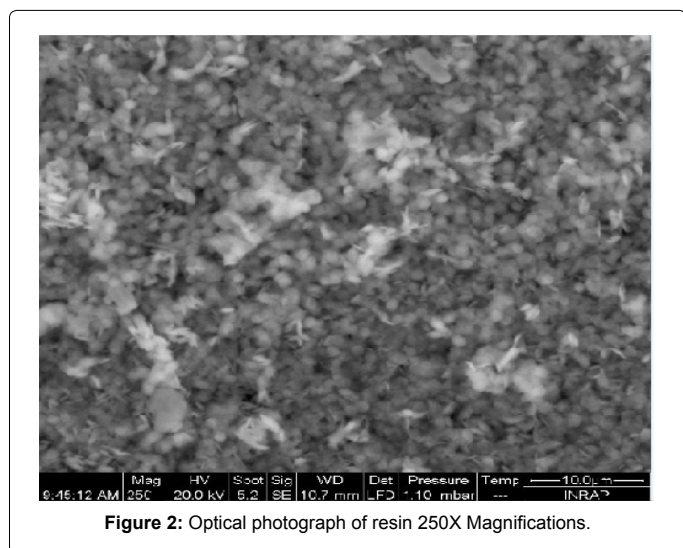


Figure 1: FTIR spectrum of resin.

% Calculated (% Found)		
C	H	N
69.15	4.04	4.74
68.15	3.98	4.65

Table1: Element Analysis of the Resin.



Property	Values (S.D)
% Moisture content	5.25 (±0.05)
% Solid	93 (±0.05)
True density	0.95 (±0.01) g.cm ⁻³
Apparent density	0.51 (±0.01) g.cm ⁻³
Void volume fraction	0.38 (±0.025)

Table 2: Physicochemical Properties of the synthesized Resin.

pH 3-6 have been prepared from 0.2 M acetic acid and 0.2 M sodium acetate solutions [15].

A pH-meter (Elico, model CL-44) has been used for measuring the pH. Different weighing assemblies (0.250 ± 0.001 g) dry resin have been equilibrated with buffer in different bottles closed during 24 h, so that the resin attained the desired pH value.

After 24 h, buffer solutions have been decanted and (50 ml) of 0.2 M metal ion solutions pH ranging from 3 to 6 have been added. Metal ion solutions have been equilibrated at room temperature for 24 h with intermittent agitation.

After 24 h, the solutions were decanted and metal ion concentration in the supernatant was measured by a method Atomic absorption spectroscopy (AAS) which is a spectral procedure for the quantitative determination of chemical elements employing the absorption of optical radiation (light) by free atoms in the gaseous state.

The same method was followed throughout the study to calculate the ion exchange capacity of the resin as:

$$\text{Exchange capacity (mmol.g}^{-1}\text{)} = \frac{([\text{Initial molarity of the metal ion}] - [\text{Remaining molarity of the metal ion}])}{(\text{Atomic molar mass of the metal} * \text{Weight of the resin sample})}$$

Effect of metal ion concentration on exchange capacity

To study the metal ion concentration effect on uptake of different metal ions by the resin, the resin has been equilibrated with an acetate buffer to desired pH (pH value of highest exchange) for 24 h and buffer

solutions were then decanted. An accurately weighed (0.250 ± 0.001 g) dry resin has been equilibrated with metal ion solutions (50 ml) with variant mass concentration (e.g., 1 ppm, 2 ppm, 3 ppm, 4 ppm to 5 ppm) at the same pH value at room temperature during 24 h with intermittent agitation.

After 24 h, the metal ion solutions were decanted and non-chelated metal ions have been estimated by atomic absorption spectroscopy (AAS).

K_d Values for metal ions in presence of electrolyte (tartaric acid) solution

Measurement of distribution coefficient of metal ions over a wide range of condition is the best method to avoid choosing elution conditions for separation columns by a strictly trial and error process. The batch distribution coefficient, K_d is defined as:

$$K_d = \frac{\text{mmole of metal ion on resin} * \text{volume of metal ion solution}}{\text{mmole of metal in solution} * \text{weight of dry resin}}$$

Although this distribution coefficient is measured on a base discontinuously, it can be used to predict elution behavior metal ions eluted from an ion-exchange column. For separating two substances, the conditions should be chosen such that the distribution coefficient of one of them is small (preferably 1 or less) so that it eluting the column is fast, while the distribution coefficient of the other substance, under the same conditions should be as large as possible (more than 10 times) such that the substance is firmly held by the resin [16].

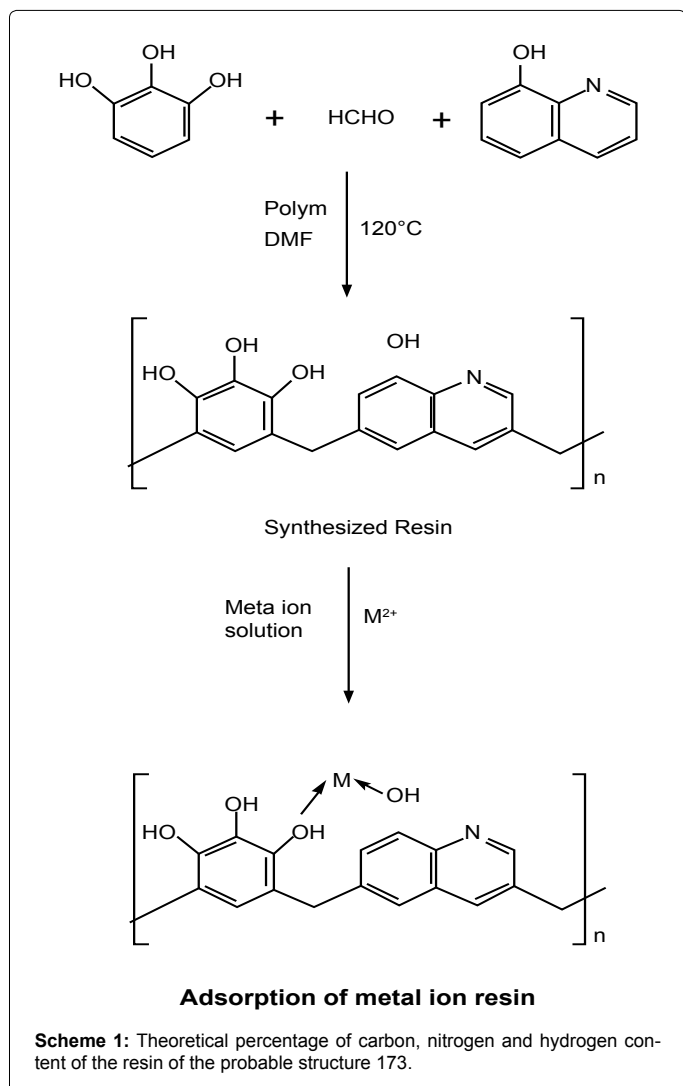
Effect of different concentrations and pH of the electrolyte (tartaric acid) to adsorbing metal ion the synthetic resin was investigated. A dry resin sample weighed exactly (0.250 ± 0.001 g) has been suspended in the electrolyte solution (tartaric acid) of 50 ml different known concentrations (e.g. 0.1 M, 0.2 M, 0.3 M, 0.5 M and 1 M). The pH of the suspension was adjusted to the desired value using acetate buffer and the resin has been equilibrated for 24 h. To the suspension, 2.0 ml of different metal ion solutions under study (5 mg.ml⁻¹) was added to be equilibrated for 24 h with intermittent agitation. After 24 h, the solutions were decanted and unadsorbed metal ions were estimated.

Results and Discussion

Physico-chemical properties

Physicochemical properties of the synthesized resin are presented in Table 2. Moisture content of a resin providing a measure of its water swelling capacity or its loading capacity. The water content depends on numerous factors, such that the composition of the resin matrix, the cross-linking degree or the nature of the active groups and the ionic resin form. The degree of cross-linking a resin has an effect on the moisture content and moisture content of the resin, and therefore, has an effect on the selectivity. In a high moisture content of the resin, the active groups are more spaced apart, e.g. strong acid cation resins contain about 50% moisture. The water content percentage of synthetic resin, as shown in Table 2 is 5.25%. Therefore, the resin has a low moisture percentage range relative to the commercial resins. Resins synthesized from salicylic acid and furfural-benzidine p-hydroxybenzoic acid-furfural-benzidine [17] has lower moisture contents (4.01 and 4.9% respectively) than the synthesized resin.

The resin synthesized from 8-hydroxyquinoline-pyrogallol-formaldehyde [12] and salicylic acid formaldehyde-m-cresol [18] had slightly higher moisture content (5.64 to 9.4%, respectively). The moisture differential may be caused by different experimental conditions, such as carriers, wherein the resins have been synthesized,



the polymer backbones, the cross-linking degree and the functional groups involved.

The true density of the synthetic resin is 0.95 g.cm^{-3} , which is given in Table 2. The actual density commercial resins are generally between 1.1 to 1.7 g.cm^{-3} . To prevent flutter of resin particles, the actual density floating must be greater than a resin particles is not desirable in chromatographic studies, as disturbs forming a compact column. The optimum density and size uniform particles allow the perfect column packing and column performance.

Measuring the density of the column or the apparent density is necessary that the resins are commercially available on a volume basis and packed on a weight basis. The bulk density of the polymer synthesized is given in Table 2, from which to see that the apparent density of the resin is in the range of 0.51 g cm^{-3} , which is comparable to the density commodity resins. This can be due to changes in the polymer matrix, different functional groups and the synthesis process. The apparent density parameter gives an indication of the required length of a column packed with a study of the ideal chromatographic column.

The value of the void volume fraction resin is also given in table a vacuum volume fraction of the synthetic resin was the order of 0.38.

The sensitive value the void volume fraction is broadcast on the resin and exchangeable ion exchange rate increases leaving ions. The essential minimum void volume has an improved diffusion exchangeable ion and gives the feasibility of the operation of the column thereby.

Spectral characterization of resin

The FTIR spectrum of the resin is shown in Figure 1. A strong band at 3300 cm^{-1} is due to the $\nu(\text{O-H})$ stretching of phenolic group, a medium band at 3066 cm^{-1} is due to the $\nu(\text{C-H})$ stretching of aromatic ring and the presence of a medium-strong band at 2900 cm^{-1} is due to the $\nu(\text{C-H})$ stretching of methylene group. The bands at 1666 , 1585 and 1447 cm^{-1} can be assigned to $\nu(\text{C=N})$ heterocyclic ring and $\nu(\text{C=C})$ aromatic ring stretching, respectively. A band at 1442 cm^{-1} is also due to $\delta(\text{C-H})$ deformation of methylene group [9]. The presence of a medium-strong band at 1384 cm^{-1} can be assigned to in plane $\delta(\text{O-H})$ bending of aromatic and a band at 1285 cm^{-1} is due to aromatic $\nu(\text{C-O})$ stretching. A sharp single band at 781 cm^{-1} , which can be assigned to the presence of 1,2,3,4,5-penta substituted benzene ring [10], confirms the polymerization of monomers.

Elemental analysis

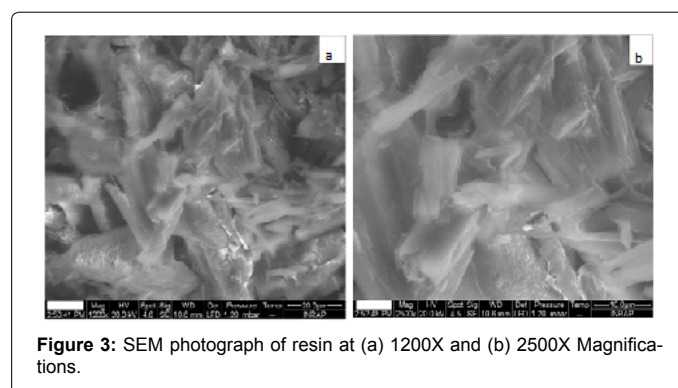
The theoretical percent of carbon, nitrogen and hydrogen content of the resin have been calculated from the general formula ($\text{C}_{17}\text{H}_{13}\text{NO}_4$) of the repeating unit of the structure likely (Scheme 1). Table 1 show that the results of the elemental analysis are in good accordance with the calculated values. The elemental analysis results are supported the proposed structure of the resin presented in Scheme 1.

Optical and SEM photographs

The morphology of the insert resin sample was investigated by scanning electron micrographs, which are represented in Figure 2 and Figure 3, respectively. The synthetic resin optical photographing showed that it is of a brown color. The morphology of the resin shows a fringed model of the, crystalline-amorphous structure.

The fringes represent transition state between the crystalline and amorphous phase [19]. The resin exhibits more amorphous character with closed packed surface having deep pits (Figures 3a and 3b) as it compared with anthranilic acid-formaldehyde-resorcinol resin and 8-hydroxyquinoline-formaldehyde-pyrogallol resin reported earlier [12-19].

Surface analysis has been found to be useful in the understanding surface features of the material. The morphology of the resin parts crystal growth from polymer solutions corresponding to the largest organization large scale in polymers, e.g. in size spherulites of a few millimeters. Ideally, the spherulites are aggregates of size sub-



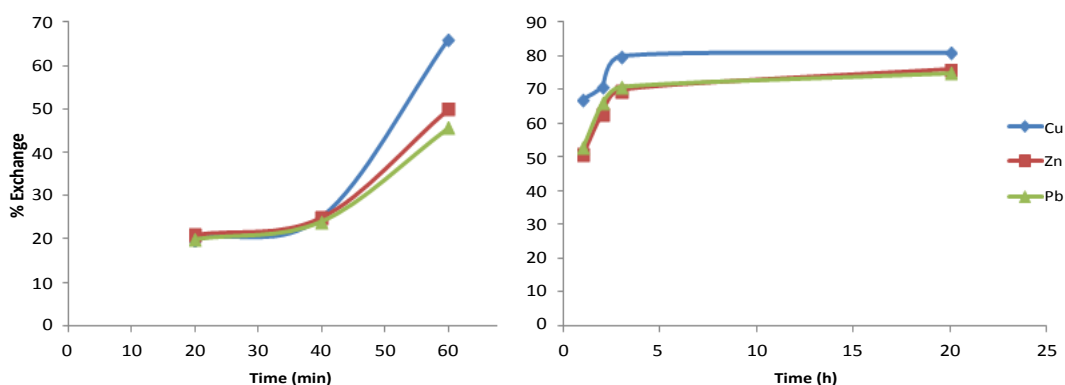


Figure 4: Rate of exchange of cations on resin.

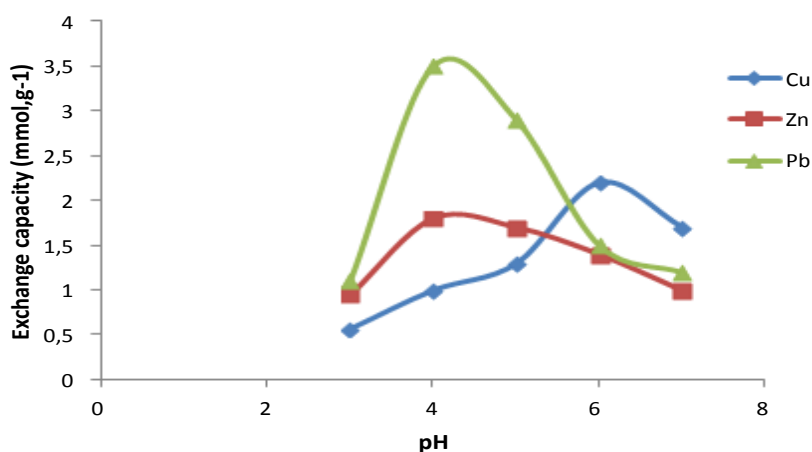


Figure 5: Effect of pH on cation exchange capacity.

microscopic particles. Spherulites are characterized by the secondary structure features, such as faint corrugations. The higher magnification 500 \times shows the coexistence of an appreciable amorphous fraction with a small amount of shallow pits. The surface of the resin (Figure 3) contributes greater segments of crystalline regions.

Rate of exchange for metal ions

As the base resin structure is important in physical absorption metal ions by the different copolymers of the resin. From the results, viewed that the metal ion exchange rate is faster at the beginning and then slow. These occur due to the removal or exchange of ions of the solution the surface of the resin and after the entire available site (group) were occupied resin. It results in slower rate of the exchange. Figure 4, shows the rate of exchange of the metal ion of the synthetic resin.

Metal ion exchange on the resin has a time dependent phenomenon. The rate of different metal ion exchange was to determine the shortest time interval for which equilibrium can be performed [20]. The graph represented on Figure 4 indicates that time required for the exchange of 50% ($t_{1/2}$) for Cu (II) is 30 min and Zn (II) and Pb (II) are 50 and 56 min, respectively. This is assigned to the Cu (II) hydrated have radii smaller (0.419 nm) than hydrated Zn (II) (0.430 nm) and thus have greater access to the resin surface. The order of the exchange capacity is: Cu (II)>Zn (II)>Pb (II).

Rapid exchange rate in the beginning can be explained on the basis of mass action of the law and the equilibrium state. The exchange rate greater facilitates the chromatographic separation column. Metal ion exchange kinetics mainly depends on various physical properties, including the particle size distribution, the size pores, the physical base structure and diffusion of counterion [12,13].

Effect of pH on exchange capacity

Metal removal ions from an aqueous solution by sorption are strongly dependent on pH of the solution which influences the surface charge of the sorbent [19]. Chelating ligands form complexes with various metal ions in specific pH conditions [20]. Therefore, the synthesis resin has been used to study the effect of varying pH on its chelating ability to various metal ions. The results of the exchange capacity depending on the pH for different metal ions are presented in Figure 5. The results show that the sorption metal ions is increased with increasing pH to a maximum value and thereafter decreased. Maximum sorption occurred Cu (II) at pH 6, Zn (II) at pH 4 and Pb (II) at pH 4. The order of selectivity for the metal ions is: Cu (II)>Zn (II)>Pb (II). An increase in pH increases the negatively charged nature of the sorbent surface. This leads to an increase in the electrostatic attraction between positively charged metal ions and negatively charged sorbent and results in increased sorption of metal ions. At lower pH, the removal

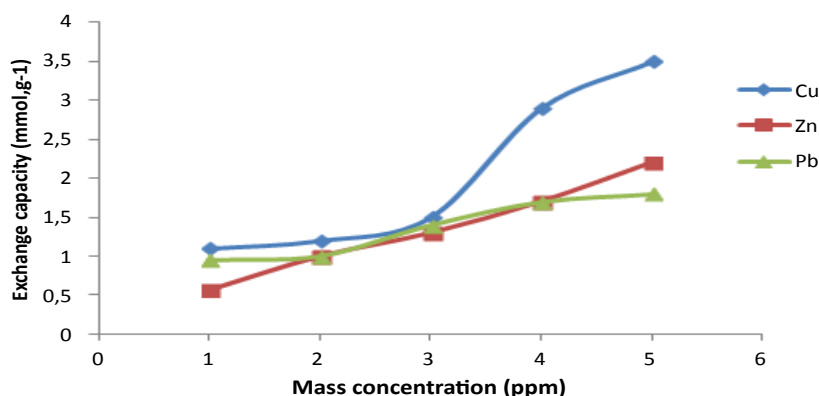


Figure 6: Effect of cation concentration on exchange capacity.

Metal ion	[Tartaric acid] (M)	K _d values at different pH				
		3	3.5	4	5	6
Cu(II)	0.1	1101	671	527	202	155
	0.2	698.3	320	130	110	79.7
	0.3	250.1	106	80.5	50.8	38.9
	0.5	55.6	55.6	39.7	52.3	55
	1	14	19.3	11.8	8.4	6.5
Zn(II)	0.1	1800	1320	432	402	200
	0.2	640.7	618	220	111	131
	0.3	588.2	300	95	71.8	59
	0.5	134	115	74	28.1	36.8
	1	81	35.5	25.2	11.8	5.3
Pb(II)	0.1	2221	980	610	421	261
	0.2	668.4	640	231	116	142
	0.3	435.9	341	95.3	82.2	30.4
	0.5	130.2	82.5	80	40.3	4.7
	1	10.8	45.4	34.9	17	2.8

Table 3: K_d Values of Metal Ions at Various Tartaric Acid Concentrations and pH Values.

of metal ions is decreased due to the higher concentration of H⁺ ions present in the reaction mixture which compete with the metal ions for the sorption sites at the surface.

Meanwhile, the observed decrease in sorption capacity is due to the formation of insoluble metal ion hydroxides [21].

In the case of Pb(II) purely electrostatic factors are responsible. Due to the less deep pits, resin exhibits lower ion exchange capacity for Pb(II). Pb(II) has bigger hydrated radii, so it cannot easily penetrate to originate in more crystalline region of the polymeric network. Therefore, the cleaner separation can be obtained from the browser binary mixture Pb (II) with transition metal ions such as Cu (II) or Zn (II).

Effect of metal ion concentration on exchange capacity

Examination data presented in Figure 6 shows that the amount of adsorbed metal ions increases with increasing concentration of metal ions in the solution to a maximum value, and will remain constant while new increase of metal concentration. A low concentration of metal ions, the available number of metal ions in the solution is low relative to the arrangement sites on the sorbent [21]. However, at higher concentrations, the sorption available sites remain same as more metal ions are available for sorption and subsequently sorption becomes almost constant then after [9,10].

Effect of electrolyte concentration and pH on distribution coefficient (k_d) values

Batch process of equilibrium is useful to determine the distribution coefficient (K_d) for the metal ions depending on the concentration of tartaric acid. Tartaric acid is a potent chelating elution agent. It contains six oxygen atoms with unshared electron pairs, which from complexes of chelating metal ions more stable with resin-metal complexes. Tartaric acid can easily eluting resin metal ions and give clear separation.

Distribution coefficient values (K_d) for different metal ions have been determined by the batch equilibration method. The K_d values have been investigated metal ions depending on pH and the concentration of the electrolyte solution and the results are shown in Table 3. The present survey limit distribution studies to a certain pH to each metal ion to avoid hydrolysis metal ions at a pH above [9]. As is evident from the following Table 3, any electrolyte concentrations and the entire pH range, the values of K_d decrease in order Pb (II)>Zn (II)>Cu (II).

Meanwhile, in all cases, the K_d values decrease with increasing electrolyte concentration and increase with increasing in pH. It is expected that distribution coefficients metal ions can vary depending on the stability metal complexes with chelating groups of the resin. Best results for stabilizing higher distribution coefficients. This study limit distribution studies to a certain pH to each metal ion to avoid hydrolysis metal ions at a higher pH.

It is evident that to obtain sharper separation metal ions, large values of ΔK_d should selected from the same experimental conditions [16].

Analytical Application

Removal of toxic metal from industrial effluents

The chelated lead has been eluted with a tartaric acid solution to 1 M to pH 3. It has been found that removal and recovery of copper from the effluent were quantitative.

The pH of the industrial effluent containing Zn (100 cm³) has been adjusted to 3 using a buffer solution and passed through the resin column at a rate of 1 cm³ min⁻¹ stream, followed by washing with water carefully.

The results showed 92% Pb (II) and 89% Pb (II) recovery of industrial effluents using the resin. The synthetic resin may be adopted for the industrial processing (treatment) of wastewater.

Conclusions

In conclusion, the chelating resin derived from Pyrogallol and 8-Hydroxyquinoline with formaldehyde was useful cation exchanger for divalent metal ions. A SEM image of the resin establishes the amorphous nature of the resin which helps for the higher metal ion uptake. The synthesized resin can be used for the removal of toxic heavy metals from aqueous media and industrial wastewater containing Cu(II) and Pb(II). The recovery of the metals from Industrial effluents gives an indication of the utilization potential of the synthesized resin for wastewater treatment.

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