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Studies of Metal Uptake of Copolymer Resin Derived from 8-Hydrxyquinoline, Pyrogallol and Formaldehyde in the Presence of Various Electrolyte

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Abstract— **A resin derived from copolymer of 8-hydroxyquinoline, pyrogallol and formaldehyde (8-HQPF) has already been synthesized by a polycondensation reaction in an acid medium.**

We conducted a study of the nature of variation of effect of different electrolytes ($NaClO_4$, $NaNO_3$, Na_2SO_4 and NaCl) at different concentrations on the amount of metal ions uptake (Cu^{2+}, Zn^{2+} and Pb^{2+}) the copolymer resin.

The copolymer (25 mg) was placed in an electrolyte solution of known concentration. Using a solution of nitric acid HNO_3 (0.1M) or NaOH sodium hydroxide solution (0.1M) was reduced the pH of the mixture to the desired value. The amount of metal ions adsorbed was determined by atomic absorption spectroscopy (AAS). The influence of chloride, nitrate, chlorate and sulfate in different concentrations of the metal-resin interaction was estimated.

Keywords— Metal ion, Copolymer resin, Chelating ion exchange, Electrolyte.

I. INTRODUCTION

Ion exchange is the process by which ions contained in a solution are adsorbed onto a "the ion-exchange resins" material to be replaced by an equivalent amount of other ions of the same polarity. This exchange capacity, specific to each resin is limited. Saturation, it should proceed to the "regeneration" resins to give them back their original exchange potential.

Most of the resins used today are synthetic materials made from polymers. Resins are classified into two categories depending on the nature of the ions that are to be exchanged [1, 2].

Most studies on ion exchange resins seeking to synthesize insoluble functionalized polymers with a good stability and a high ion exchange capacity for certain metal ions [3]. Various physical properties of the resin; Moisture% happy% Solid, true density, apparent density and void volume fraction were investigated [4, 5]. 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) [6] and its cross linked polymer [7] 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 [8, 9, 10] stability test, they suggested that the gel polymers must never be allowed to dry; otherwise their favorable properties are destroyed.

Sharayu s and al. [11] studied the chelating ion-exchange properties of copolymer resin derived from p-cresol, dithio oxamide and formaldehyde. A batch equilibrium method was employed in the study of the selectivity of metal-ion uptake.

For quantitative removal and separation transition metal ions, a previous study [4] has focused on a chelating ion-exchange resin synthesized by the condensation of 8-hydroxyquinoline with pyrogallol using formaldehyde as a cross-linking agent at 120ºC in DMF in the presence of hydrochloric acid catalyst. 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.

The reaction and suggested the structure of the copolymer resin synthesized is shown in Fig. 1.

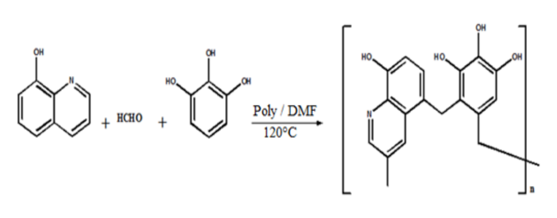

Fig. 1. The reaction and suggested the structure of the synthesized copolymer resin Copolymer Resin Derived from 8-Hydroxyquinoline-Formaldehyde-Pyrogallol

In order to continue this research and to better exploit the chelating properties of the synthesized resin in the environmental field, we investigated in this study of the nature of variation of effect of different electrolytes ($NaClO_4$, $NaNO_3$, Na_2SO_4 and NaCl) at different concentrations on the amount of metal ions uptake (Exchange capacity) (Cu^{2+}, Zn^{2+} and Pb^{2+}) with the copolymer resin.

II. MATERIAL AND METHODS

All chemicals were analytical reagent or pure chemical grade. The electrolyte solution ($NaClO_4$, $NaNO_3$, Na_2SO_4, and NaCl) (KANTO Chemical CO, INC) were used as received.

A. Determination of metal uptake in the presence of various electrolytes

The following experimental study was carried out in order to exploit the effect of the nature of different electrolytes and concentrations on the amount of metal ions adsorbed by the copolymer sample of the synthesized resin.

The copolymer of sample (30 mg) was suspended in an electrolyte solution (30 mL) of known concentration. The pH of the suspension was adjusted to the desired value using 0.1M HCl or 0.1 M NaOH. The mixture was stirred for 24 hours at 30 ° C.

2 ml of 0.1 M metal ion solution and the mixture was again stirred at 30 ° C for 24 hours and then filtered. The solid was filtered and washed and the amount of adsorbed metal ions with the polymer was estimated by atomic absorption spectroscopy (AAS).

The experiment was repeated in the presence of several electrolytes of different ionic strength.

The estimate of the exchange capacity was according to the following relationship:

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

B. Evaluation of the rate of metal-ion uptake

To estimate the time needed to reach the state of equilibrium in appropriate experimental conditions, a series of experiments were conducted. Metal exchange rate was estimated at a temperature of 27 ° C in the presence of 25 ml of a solution of $NaNO_3$ used as electrolyte. Steady state is reached within 24 hours. The adsorption rate of the metal was estimated by atomic absorption spectroscopy (AAS) as the percentage of the amount of chelated metal ion after a period of time related to that of the equilibrium state.

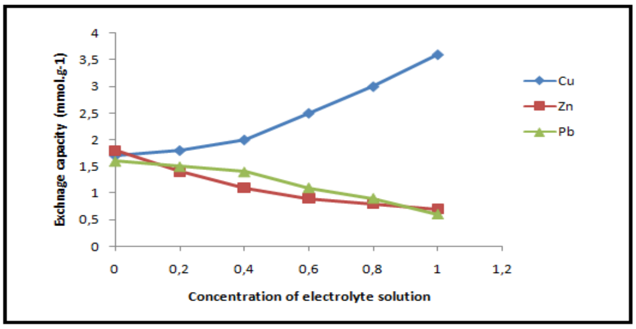

Fig. 2. Exchange capacity of metal ions by 8-HQPF copolymer resin at different concentration of electrolyte solution $NaClO_4$

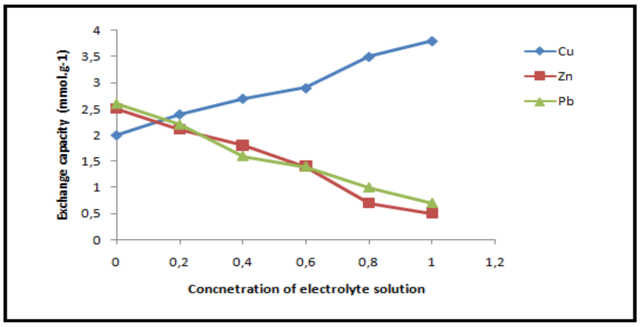

Fig. 3. Exchange capacity of metal ions by 8-HQPF copolymer resin at different concentration of electrolyte solution $NaNO_3$

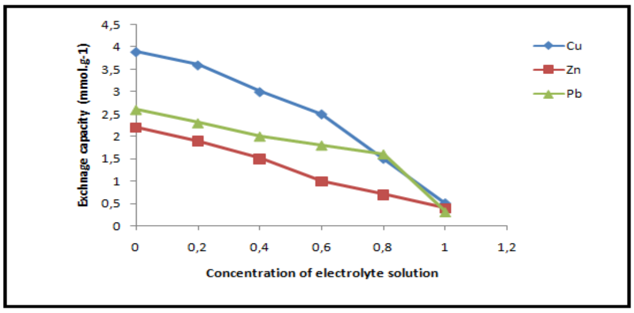

Fig. 4. Exchange capacity of metal ions by 8-HQPF copolymer resin at different concentration of electrolyte solution Na_2SO_4

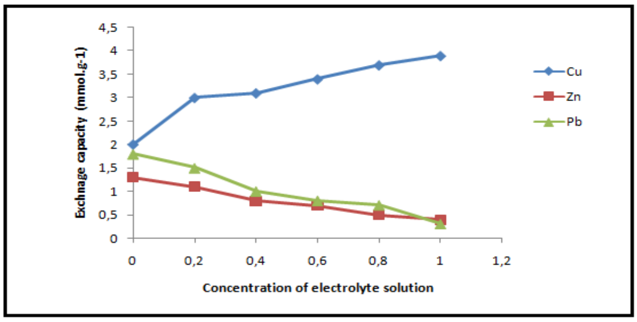

Fig. 5. Exchange capacity of metal ions by 8-HQPF copolymer resin at different concentration of electrolyte solution NaCl

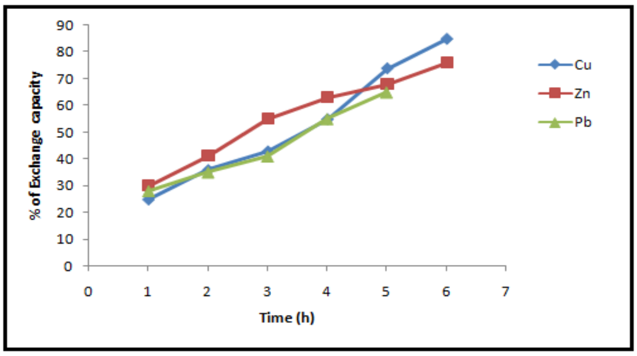

Fig. 6. Comparisons of the rate of metal ion uptake by 8-HQPF copolymer resin

III. RESULTS AND DISCUSSION

The resin was found to be insoluble in all common organic solvents such as acetone, ethanol, benzene, chloroform, etc [4].

A. Ion-exchange properties

On the figures Fig. 2 to Fig. 5, there is shown the results of the study of the properties of ion- exchange with the 8-HQPF. This study was conducted with three metal ions (Cu^{2+}, Pb^{2+} and Zn^{2+}) in the appropriate experimental conditions.

B. Influence of electrolytes on the metal-ion uptake

The effect of chlorate, nitrate, sulfate and chloride in different concentrations on the interaction of the metal-resin equilibrium was studied. As shown in figures 2 to 5, the amount of metal ions adsorbed by an amount of the copolymer sample is strongly dependent on the nature and concentrations of the electrolyte present in the solution. The metal ions fixing performance will be controlled by the presence of large excess of competitor's ions (anions such as: chlorate, nitrate, sulfate and chloride).

The analysis of Fig. 2 shows, that in the presence of chlorate ions, the adsorption of Cu (II) increases with the increase of the concentration of $NaClO_4$ electrolyte. However, the adsorption of Zn (II) and Pb (II) ions decreases with increasing concentration of the same electrolyte.

Fig. 3 shows that in the presence of nitrate ions, the adsorption of Cu (II) increases with the increase of the concentration of $NaNO_3$ electrolyte.

Fig. 4 shows that in the presence of sulfate ions, the adsorption of Cu (II), Zn (II), and Pb (II) decreases with increasing electrolyte concentration of Na_2SO_4.

Fig. 5 shows that in the presence of chloride ions, the adsorption of the Cu (II) increases with the increase of the concentration of the NaCl electrolyte. However, the adsorption of Zn (II) and Pb (II) ions decreases with increasing concentration of the electrolyte.

The polymer adsorption performance of the synthetic resin with metal ions can be evaluated on the basis of the kinetics of binding and the presence of electrolytes.

When chloride ions are added in a metal solution, a significant improvement in the fixation occurs when the chloride ion concentration reached 0.1 M; the excess chloride ions is reflected in a competition effect which progressively limits the uptake ability. The presence of an optimal concentration of chloride ions to promote the formation of adsorbent species (without exercise of competitors ion effect) is therefore a key parameter in the optimization of the binding of these metal ions (Fig. 5).

Whereas, in simple solutions (sulfate, nitrate or chlorate .), the metal is adsorbed by chelating at a neutral pH, but in the presence of a ligand (8-HQPF) forming anionic species metal-resin allows the attachment of the metal on the resin (electrostatic attraction on the protonated functions).

It is concluded that the optimum operating condition depends on the nature of the ligand, its complex stability constants with these metal ions and the nature and concentration of electrolytic solution.

The choice of the optimum pH for selective adsorption of a particular metal cation from a mixture of different metal ions has already been studied and the results of the separation of metal ions based on the distribution coefficient K_d were also analyzed [4].

C. Evaluation of the rates of metal uptake

The metal adsorption rate by the resin copolymer 8-HQPF resin samples were measured for Cu (II), Zn (II) and Pb (II) to determine the time required to reach the state of equilibrium.

Fig. 6 shows that the rate of metal up-take is strongly dependent on the nature of the metal ion in indicated conditions. Experimental results show that the rate of metal exchange capacity can follow the following order : Cu (II)> Zn (II)> Pb (II).

IV. CONCLUSION

This study addresses a method for decontaminating industrial wastewater as it covers a wide area of environmental investigations.

The copolymer 8-HQPF showed a higher selectivity for Cu^{2+} for Pb^{2+} and Zn^{2+} in the presence of different electrolyte solutions, this selectivity may be related to setting mechanisms: as it has been mentioned above, the resin 8 -HQPF has a high affinity for these metals. This property allows a first form of selectivity of particular interest for industrial application in decontamination for ions which can be adsorbed easily on the resin.

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