



## Mathematical Modeling of Ion-Exchange Applications of 2-Hydroxy 4-Methoxyacetophenone-Dithiooxamide-Formaldehyde Resin

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### Abstract

Copolymer resin has been synthesized by the condensation of 2-hydroxy 4-methoxyacetophenone and dithiooxamide with formaldehyde in 2:1:3 molar ratio in presence of 2M hydrochloric acid as catalyst. The newly synthesized copolymer resin has been characterized by UV-visible, IR and proton NMR spectral studies. The copolymer p-HBOF proved to be a selective chelating ion exchange polymer for certain metals. Chelating ion-exchange properties of this polymer were studied for Fe<sup>3+</sup>, Cu<sup>2+</sup>, Ni<sup>2+</sup>, Co<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup> and Pb<sup>2+</sup> ions. A batch equilibrium method has been employed in the study of the selectivity of metal-ion uptake involving the measurements of the distribution of a given metal ion between the copolymer sample and a solution containing the metal ion. The study was carried out over a wide pH range and in media of various ionic strengths. The polymer showed higher selectivity for Fe<sup>3+</sup>, Cu<sup>2+</sup>, Ni<sup>2+</sup> than for Co<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup> and Pb<sup>2+</sup> ions. Study of distribution ratio as a function of pH indicates that the amount of metal ion taken by resin increases with the increasing pH of the medium.

Mathematical modeling: - An attempt has been done to present the metal ion selectivity of the resins with respect to time in the form of mathematical model. The model consists of two straight-line equations, involves all dependent and independent parameters. Graph obtained from actual experimental data is very much comparable to the graph plotted from the data provided by the model. This has been clearly shown by the reliability of the model, which is 94.6%.

**Keywords:** Mathematical model, Ion-exchange resin, polymer, chelation, batch method.

### Introduction

Synthesis, characterization and ion exchange studies of polymeric resins deserves to be investigated because their varied characteristics and beneficial properties. Ion exchangers are widely used in hydrometallurgy, antibiotic purification, analytical chemistry, separation of radioisotopes and also find large scale application in water treatment and pollution control [1]. Resins are found to exhibit better thermal and electrical properties than those of phenol-formaldehyde type copolymer. These resins can be used as high energy materials, ion exchangers, semiconductors, bonding agent/additives, molding material, fungicides in plant and living tissues, biosensors and controlled release devices for pharmaceuticals [2]. Now a day's renewed interest has been evidenced in the context of obtaining materials with high temperature resistance and ion exchangers. Patel and Lad [3] reported the novel terpolymers: poly (keto-amine-ureas) and studied the glass reinforcement of such terpolymer- epoxy systems. Michael and coworkers have reported the synthesis, structural and thermal degradation of a polymer derived from salicylic acid, guanidine and formaldehyde [4]. Synthesis, characterization and ion exchange properties of 4-hydroxyacetophenone, biuret and

formaldehyde terpolymer resin were studied by Gurnule and coworkers [5]. Ion exchange resin derived from semicarbazone and oximes of 2-hydroxy acetophenone-substituted benzoic acid - formaldehyde studied by Nayak et al. [6]. The synthesis and characterization of 2, 4-dihydroxyacetophenone with 1, 4-butanediol copolymer and its ion exchange properties have been reported [7]. Chelation ion exchange resins derived from 2-hydroxy-4-methoxyacetophenone and thiourea with trioxane was investigated by Pancholi et al. [8]. Parmar reported the ion exchange properties of resacetophenone (2, 4 dihydroxyacetophenone) -formaldehyde and Resacetophenone oxime-formaldehyde resins. In our laboratory, extensive research work was carried out on synthesis and characterization of resins and their ion exchange properties. However, the literature studies have revealed that no resin has been synthesized using the monomers 2-hydroxyl 4-methoxyacetophenone, dithiooxamide and formaldehyde. Therefore in the present communication we report synthesis, characterization and analytical application.

### Experimental

The 2-H4-MADF copolymer resin was prepared by condensing 2-hydroxyl 4-methoxyacetophenone (0.3 mol) and dithiooxamide (0.1 mol) with formaldehyde (0.4

mol) in presence of 2M HCl as a catalyst at temperature  $126 \pm 2$  °C in an oil bath for 5 hr. Brown coloured solid product obtained was immediately removed and extracted with diethyl ether to remove excess of 2-hydroxyl 4-methoxyacetophenone,-formaldehyde copolymer, which may be present along with the 2-H4-MADF terpolymer. It was further purified by dissolving in 8 % NaOH and then filtered. The terpolymer was then reprecipitated by dropwise addition of 1:1 (v/v) conc. HCl/water with constant stirring and filtered. The process was repeated twice. The resulting polymer sample was washed with boiling water and dried in a vacuum at room temperature. The purified terpolymer resin was finely ground to pass through 300-mesh size sieve and kept in a vacuum over silica gel. The yield of polymer was found to be about 86 %

#### *Ion exchange properties*

To decide the selectivity of 2-H4-MADF copolymer as an ion exchanger we have studied the influence of various electrolytes using different concentration and at various pH, the rate of metal ion uptake and distribution of metal ion between the terpolymer and solution. The results of the batch equilibrium study carried out with the terpolymer sample.

#### *Determination of metal ion uptake in the presence of electrolytes of different concentrations:*

Terpolymer sample (25 mg) was suspended in an electrolyte solution of NaNO<sub>3</sub> (25 ml) of known concentration. The pH of the suspension was adjusted to required value by using either 0.1N HCl or 0.1N NaOH. The suspension was stirred for a period of 24 hrs at temperature 25°C. To this suspension 2 ml of 0.1M solution of the metal ion was added and the pH was adjusted to the required value. The mixture was again stirred at 25 °C for 24 hr and filtered. The solid was washed and the filtrate and washings were combined and the metal ion content was determined by titration against standard EDTA [6]. The amount of metal ion uptake of the polymer was calculated from the difference between a blank experiment without polymer and the reading in actual experiments. Experiment was repeated in presence of other three electrolytes such as NaCl and NaClO<sub>4</sub>, Na<sub>2</sub>SO<sub>4</sub> at different concentration.

#### **Evaluation of the Rate of Metal Uptake:**

In order to estimate the time required to reach the state of equilibrium under given experimental conditions, a series of

experiments of the type described above were carried out in which the metal ion taken up by chelating resins was determined from time to time at 25 °C (in the presence of 25 ml of 1M NaNO<sub>3</sub> solution). It was assumed that under given conditions, the state of equilibrium was established within 24 hrs. Rate of metal ions uptake is expressed as percentage of the amount of metal ions taken up after a certain time.

#### **Evaluation of the Distribution of the Metal Ions at Different pH:**

Distribution of each one of the five metal ions i.e. Fe<sup>+3</sup>, Cu<sup>+2</sup>, Hg<sup>+2</sup>, Cd<sup>+2</sup> and Co<sup>+2</sup> between polymer and aqueous phase was determined at 25 °C in presence of 1M NaNO<sub>3</sub> solution. The experiments were carried out as described above at different pH values. The distribution ratio 'D' is defined by eq. (3).

$$D = \frac{\text{Wt. (mg.) of metal ions taken up by 1 gm. of terpolymer}}{\text{Wt. (mg.) of metal ion present in 1 ml. of terpolymer}} \text{-----} (3)$$

#### **Results and Discussion**

Copolymer which has been used in present investigation as ion exchanger was prepared as shown in reaction scheme. Resin sample was brown in color, insoluble in commonly used solvents but was soluble in DMF, DMSO and THF solvent. No precipitation and degradation of resin occurred in all these solvents. This resin was then purified and analyzed for carbon, hydrogen and nitrogen content and found to be in agreement with calculated value.

#### *Ion-Exchange Properties*

From the study with five metal ions under limited variation of experimental conditions, certain generalization may be made about the behavior of the terpolymer sample.

#### *Effect of electrolytes and their concentration on the metal ion uptake capacity*

We examined the effect of NO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup> and ClO<sub>4</sub><sup>-</sup> at various concentrations on the equilibrium of metal resin interaction of constant pH., which shows that the amount of metal ions taken up by a given amount of copolymer depends on the nature of concentration of the electrolyte present in the solution. In the presence of nitrates, perchlorate and chloride ions the uptake of Fe<sup>3+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup> and Pb<sup>2+</sup> ions increasing with increasing concentration of electrolytes. Whereas in the present of sulphate ions, the amount of above maintained ions taken up by the copolymer resin decreases with increasing concentration of the electrolyte [8]. Above NO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup>, and ClO<sub>4</sub><sup>-</sup> ions form weak complex with the above metal ions, while SO<sub>4</sub><sup>2-</sup> form stronger

complex thus the equilibrium is affected. This may be explained on the basis of the stability constants of the complexes with those metal ions and nature of ligands.

**Rate of metal ion uptake as a function of time**

The rate of metal adsorption was determined to find out the shortest period of time for which equilibrium could be carried out while operating as close to equilibrium condition as possible. During rate of metal ion determination, the concentration of metal ion and electrolyte solution and pH of the solution remain constant and pH of each metal ion is different. As shaking time increases the polymer gets more time for adsorption, hence uptake of metal ions increases. The rate refers to the change in the concentration of the metal ions in the aqueous solution which is in contact with the given copolymer. The figure shows that the time taken for the uptake of the different metal ions at a given stage depends on the nature of metal ions under given conditions. It is found that Fe<sup>3+</sup> ions required about 3 hrs for the establishment of the equilibrium, whereas Cu<sup>2+</sup>, Zn<sup>2+</sup> and Pb<sup>2+</sup> ions required about 6 hrs. Thus the rate of metal ions uptake follows the order Fe<sup>3+</sup> > Cu<sup>2+</sup> > Hg<sup>2+</sup> ≈ Pb<sup>2+</sup> > Zn<sup>2+</sup> > Ni<sup>2+</sup> > Cd<sup>2+</sup> > Co<sup>2+</sup> for the 4-HBPBF copolymer [9].

**Distribution ratios of metal ions at different pH**

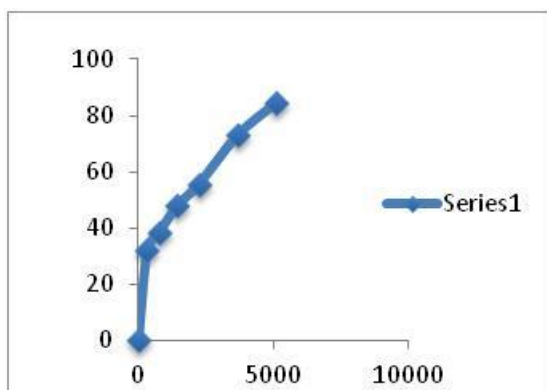
The distribution of metal ion depends upon pH of the solution. By increasing pH, the H<sup>+</sup> ion concentration in the solution decrease and only metal ion in the solution available for adsorption which increase uptake of metal ions.

The effect of pH on the amount of metal ions distributed between two phases can be explained by the results. The data on the

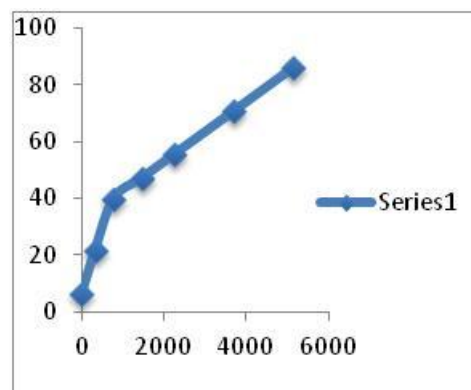
distribution ratio as a function of pH indicate that the relative amount of metal ions taken up by the copolymers increase with increasing pH of the medium [30]. The magnitude of increase, however, is different for different metal cations. The study was carried out from 2.5 up to pH 6.5 to prevent hydrolysis of metal ions at higher pH. The selectivity of Fe<sup>3+</sup> ion is more for the 2-H4-MADF copolymer resin as compare to the any other metal ions under study. The order of distribution ratio of metal ions measured in the range, 1.5 to 6.5 is found to be Fe<sup>3+</sup> > Cu<sup>2+</sup> > Ni<sup>2+</sup> > Zn<sup>2+</sup> [38]. Thus the results of such type of study are helpful in selecting the optimum pH for a selective uptake of a particular metal cation from a mixture of different metal ions [10]. For example, the result suggests the optimum pH 2.5 for the separation of Fe<sup>3+</sup> and Zn<sup>2+</sup> with distribution ratio 'D' is 480.2 and 685.7 respectively using the 4-HBPBF copolymer resin as ion exchange. Similarly for the separation of Fe<sup>3+</sup> at the optimum pH is 2.5 with distribution ratio is 480.2 for 2-H4-MADF copolymer. The lowering in the distribution ratios of Fe<sup>3+</sup> was found to be small hence, efficient separation could be achieved. The order of distribution ratio of metal ions measured in pH range 2.5 to 6.5 is found to be Fe<sup>3+</sup> > Cu<sup>2+</sup> > Ni<sup>2+</sup> > Cd<sup>2+</sup> > Zn<sup>2+</sup> > Co<sup>2+</sup> > Pb<sup>2+</sup>.

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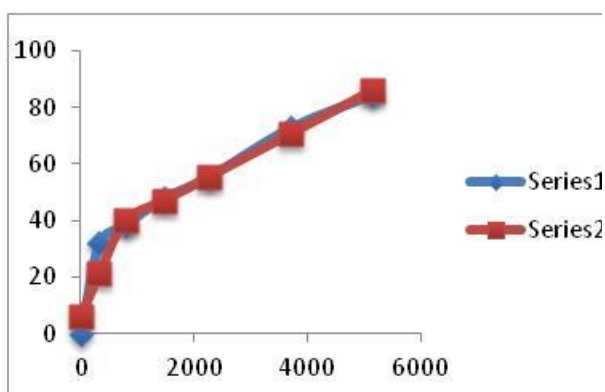
Graph from experimental data



Graph from model



## Comparison of graphs



### Conclusions

2-H4-MADF copolymer resin was prepared from 4-hydroxybenzophenone and biuret with formaldehyde in hydrochloric acid medium by condensation technique. The amorphous nature of the 2-H4-MADF copolymer resins were confirmed by the SEM studies and reveals that the copolymer can act as an effective ion exchanger for trivalent and divalent metal ions such as  $\text{Fe}^{3+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Hg}^{2+}$  and  $\text{Pb}^{2+}$  ions. This study of ion-exchange reveals that 2-H4-MADF copolymer resin is proved to be an eco-friendly cation exchange resin and can be used for the removal of hazardous metal ions from the environmental area, for the purification of industrial waste solution and for the purpose of purification and desalination of water.

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