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# 2,4-Dichlorophenyl Acrylate/8-Quinolinylnyl Methacrylate Copolymers: Ion-Exchange Study

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The chelating ion-exchange properties of the 2,4-dichlorophenyl acrylate (2,4-DCPA)/8-quinolinylnyl methacrylate (8-QMA) copolymers, synthesized using different monomer feed ratios, were investigated by the batch equilibrium method. Five metal ions  $\text{Cu}^{+2}$ ,  $\text{Ni}^{+2}$ ,  $\text{Co}^{+2}$ ,  $\text{Zn}^{+2}$ , and  $\text{Fe}^{+3}$  were used to evaluate the cation-exchanger capability of 2,4-DCPA-co-8-QMA copolymers. The ion-exchange study was carried out for three different experimental variables viz., pH of the aqueous medium, ionic strength of electrolyte and shaking time. It was observed that due to the presence of a pendant ester-bound quinolinylnyl group, the copolymers are better suited as cation exchangers.

**Keywords:** ion-exchange properties; batch equilibration method; ionic strength

## 1 Introduction

Ion-exchange may be defined as the reversible exchange of ions between the substrate and surrounding medium. The ion exchange technique can remove traces of ionic impurities from water/process liquids and produce a product of ultra pure quality in a simple, efficient and techno-economically viable manner. Ion exchangers are widely used in analytical chemistry, hydrometallurgy, antibiotic purification and separation of radio isotopes and find large application in water treatment and pollution control (1, 2).

Ali El-Hag (3) prepared chelating poly(vinyl pyrrolidone/acrylic acid) (PVP/AAC) copolymer hydrogels by radiation induced copolymerization. The removal of Fe(III), Cu(II), and Mn(II) from aqueous solution by the prepared PVP/AAC chelating hydrogel was examined by a batch equilibrium technique. The influence of treatment time, pH and the initial feed concentration on the amount of the metal ions removed was studied. The free radical solution copolymerization of poly(hydroxyethyl methacrylate-co-acrylamide) with monomer feed ratio in the range of 25 to 75% poly(HEMA-co-AAm) was studied by Maranbio et al. (4). They showed that poly(HEMA-co-AAm) can bind metal ions such as Cr(III), Co(II), Zn(II), Ni(II), Cu(II), Cd(II), Pb(II), Hg(II), and Fe(III) in aqueous solution at pH 3.5 to 7.0 and the

interaction of inorganic ion with the hydrophilic polymer was determined as a function of pH and filtration factor. Liang (5) reported a method for  $\text{Ge}^{+4}$  recovery from aqueous solution using crosslinked polystyrene based chelating resin containing 8-hydroxyquinoline moiety. Liu (6) studied the interaction of heavy metal ions and chelating ion exchange resin containing 8-hydroxyquinoline (8-HQ) moiety. The resin has good selectivity to absorb heavy metal ion including Cu(II), Hg(II), Pb(II), and Mg(II) at pH 5.0. These authors suggested that the chelating ion-exchange resin containing 8-HQ could be used to remove heavy metals from water.

Rivas BL (7) synthesized crosslinked poly[3-(methacryloylamino)-propyl]-dimethyl (3-sulfopropyl)ammonium hydroxide-co-2-acrylamidoglycolic acid [PCMAAPDSA-co-AGCO] by radical polymerization and employed the synthesized polymer as an absorbent under competitive and noncompetitive conditions for Cu(II), Cd(II), Hg(II), Zn(II), Pb(II), and Cr(III) by batch and column equilibrium procedures. They reported that resin-metal ion equilibrium was achieved before 1 h. The resin showed a maximum retention capacity value of  $1.084 \text{ meq} \cdot \text{g}^{-1}$  for Hg(II) at pH 2. The recovery of the resin was investigated at  $20^\circ\text{C}$  under different concentrations of  $\text{HNO}_3$  and  $\text{HClO}_4$ .

Hegazy (8) prepared two hydrogels from N-vinyl-2-pyrrolidone/acrylic acid (NVP/AAC) and N-vinyl-2-pyrrolidone/acrylamide (NVP/AAM) for the separation of some heavy metal ions from wastewater. They characterized the polymers and studied some selected properties and the possibility of their practical use in wastewater treatment for heavy metals

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such as Cu, Ni, Co, and Cr. They reported that the maximum uptake for a given metal was higher for a treated NVP/AAC hydrogel than for an untreated NVP/AAC hydrogel and the reverse was true for NVP/AAC copolymers.

Gurnule WB and coworkers (9) synthesized a terpolymer resin by condensation of 2-hydroxyacetophenone and oxamide with formaldehyde in the presence of an acid catalyst. They studied chelating ion-exchange properties of this polymer for  $\text{Fe}^{+3}$ ,  $\text{Cu}^{+2}$ ,  $\text{Ni}^{+2}$ ,  $\text{Co}^{+2}$ ,  $\text{Zn}^{+2}$ ,  $\text{Cd}^{+2}$ ,  $\text{Pb}^{+2}$ , and  $\text{Hg}^{+2}$  ions. A batch equilibrium method was employed in the study of the selectivity of metal ion uptake involving the measurements of the distribution of a given metal ion between the polymer sample and a solution containing metal ions. The study was carried out over a wide pH range and in media of various ionic strengths. They reported that the polymer showed a higher selectivity for  $\text{Fe}^{+3}$ ,  $\text{Cu}^{+2}$ , and  $\text{Ni}^{+2}$  ions than for  $\text{Ca}^{+2}$ ,  $\text{Zn}^{+2}$ ,  $\text{Cd}^{+2}$ ,  $\text{Pb}^{+2}$ , and  $\text{Hg}^{+2}$  ions.

Shah Bhavna and coworkers (10) reported the preparation of chelating ion exchange resin containing 8-hydroxy quinoline and separation of metal ions by selective adsorption in this resin column. They measured the physicochemical properties like % moisture content, void volume fraction, total exchange capacity, rate of exchange, thermal stability and effect of metal ion concentration on exchange capacity. The quantitative separation of Cu(II)-Ni(II) and Zn(II)-Ni(II) was accomplished by selective adsorption in column.

The basic requirements that are essential for any polymeric material to be useful as an ion-exchange resins are:

- It must be sufficiently hydrophilic to permit diffusion of ions through the structure at a finite and usable rate.
- It must contain sufficient number of accessible ion exchangeable groups which do not undergo degradation during use, and
- The swollen material must be denser than water.

## 2 Experimental

### 2.1 Materials

2,4-dichloro phenol (S.D. Fine Chemicals), 8-hydroxy quinoline (Merck), 2,2'-azobisisobutyro nitrile (Aldrich), Benzoyl chloride (S.D. Fine Chemicals) were used as received. Solvents purified by fractional distillation were used in the reaction.

### 2.2 Synthesis of 2,4-Dichlorophenyl Acrylate (2,4-DCPA)

Acryloyl chloride was prepared as reported (11) and used for further reaction. The esterification was performed with acryloyl chloride and 2,4-dichloro phenol. Absolute alcohol (400 ml) and NaOH (0.2 mol) were added to a three-necked flask, equipped with stirrer, condenser and thermometer, and the contents were stirred until all NaOH dissolved. 2,4-Dichloro phenol was added and the reaction mixture was heated to  $60^\circ\text{C}$  for 30 min with stirring, cooled to room

temperature and then to  $0-5^\circ\text{C}$  by ice. Freshly prepared acryloyl chloride (0.21 mole) was added dropwise to the cooled reaction mixture and stirred for 90 min. It was then poured into a crushed ice-water mixture when a light brown color liquid settled down. It was then extracted with ether. The ether layer was separated out and evaporated. The liquid monomer obtained after evaporation of ether was dried over anhydrous calcium chloride in a vacuum desiccator. The product yield was 82%.

### 2.3 Synthesis of 8-Quinolinyl Methacrylate (8-QMA)

Synthesis and characterization of 8-QMA is already discussed in our earlier publication (12).

### 2.4 Copolymerization

The homo and copolymers with different feed ratio were synthesized by free radical polymerization of 2,4-DCPA with 8-QMA using DMF as a solvent and AIBN as an initiator at  $70^\circ\text{C}$  with constant stirring. The resulting polymer solution was slowly poured into large volume of methanol with stirring when the polymer was precipitated out. It was filtered and washed with methanol. Solid polymers were purified by repeated precipitation by methanol from solution in DMF and finally dried under vacuum. The reaction scheme of the copolymer is shown in Figure 1.

### 2.5 Ion-Exchange Study

The ion-exchange properties of 8-QMA homo- and copolymers were investigated by batch equilibration method (13, 14). The polymer samples were ground to a fine powder and dried in a vacuum at  $60^\circ\text{C}$  for 24 h. (Semi-solid samples were not taken for the study). The finely powdered and dried polymers were used for the ion-exchange study. Five metal ions  $\text{Cu}^{+2}$ ,  $\text{Ni}^{+2}$ ,  $\text{Zn}^{+2}$ ,  $\text{Co}^{+2}$ , and  $\text{Fe}^{+3}$  in the form of aqueous metal nitrate solution were used. The ion-exchange study was carried out using three experimental variables: (i) pH of the aqueous medium, (ii) electrolyte and its ionic strength and, (iii) shaking time. Among these three variables, two were kept constant and only one was varied at a time to evaluate its effect on metal uptake capacity of the polymers. The details of experimental procedure are as given below.

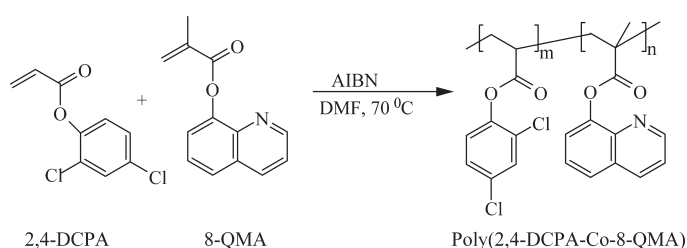


Fig. 1. Reaction scheme of copolymer.

**2.6 Effect of pH of the Aqueous Medium on Metal Binding Capacity**

The effect of pH on the metal binding capacity of the polymers was studied at room temperature in the presence of 1.0 M NaNO<sub>3</sub> solution as an electrolyte.

The polymer sample (50 mg) was suspended in the electrolyte solution (1.0 M NaNO<sub>3</sub>, 40 ml) and the pH of the suspension was adjusted to the required value by the addition of either a 0.1 M HNO<sub>3</sub> or 0.1 M NaOH solution. The conical flask with this content was stoppered and placed on the mechanical stirrer for 24 h to allow the swelling of the polymer at room temperature. The metal ion solution (0.1 M metal nitrate, 2 ml) was added, and the pH of the content was adjusted to the required value. The content was mechanically stirred for 24 h again and then filtered and washed with the distilled water. The filtrate was collected in a conical flask and the unadsorbed metal was estimated by back titration with standard EDTA solution using the appropriate indicator. A separate blank experiment (without adding polymer sample) was also carried out in the same manner. From the difference between a sample and blank reading, the amount of metal adsorbed by the polymer was calculated and expressed in terms of milliequivalent per gram of the polymer (meq · g<sup>-1</sup>).

The above experiment was performed using 0.1 M metal nitrate solutions of Cu<sup>+2</sup>, Ni<sup>+2</sup>, Co<sup>+2</sup>, Zn<sup>+2</sup>, and Fe<sup>+3</sup> in the presence of 1 M NaNO<sub>3</sub> as an electrolyte at the pH values of 3.0, 3.5, 4.0, 5.0, 5.5, and 6.0. For Fe<sup>+3</sup>, the experiments were carried out at a pH of 1.5, 2.0, 2.5, 3.0, and 3.5. The results of these experiments are presented in Tables 1 to 5.

**2.7 Effect of Electrolyte and its Ionic Strength on Metal Uptake**

The effect of electrolyte and its ionic strength on metal uptake by polymers was investigated at pH 5.5 for Cu<sup>+2</sup>, Ni<sup>+2</sup>, Co<sup>+2</sup>, Zn<sup>+2</sup>, and at pH 3.0 for Fe<sup>+3</sup> using three different electrolytes with four different concentrations of each.

The polymer sample (50 mg) was suspended in the electrolyte solution (40 ml) of a known concentration. The pH of the

**Table 1.** Effect of pH on Cu<sup>+2</sup> metal ion binding capacity of poly(8-QMA) and poly(2,4-DCPA-co-8-QMA)

Sample code no.	Metal ion uptake (meq · g <sup>-1</sup> )					
	pH of the medium					
	3.0	3.5	4.0	5.0	5.5	6.0
2	0.80	1.40	1.89	2.10	2.54	2.82
3	0.59	0.93	1.26	1.67	2.12	2.58
4	0.48	0.87	1.16	1.53	2.08	2.41
5	0.35	0.43	0.68	0.97	1.05	1.18
6	0.18	0.20	0.23	0.25	0.28	0.32
7	1.06	1.65	1.95	2.42	2.56	2.68

Weight of polymer: 50 mg; Electrolyte: 1.0 M NaNO<sub>3</sub> (40 ml).

**Table 2.** Effect of pH on Ni<sup>+2</sup> metal ion binding capacity of poly(8-QMA) and poly(2,4-DCPA-co-8-QMA)

Sample code no.	Metal ion uptake (meq · g <sup>-1</sup> )					
	pH of the medium					
	3.0	3.5	4.0	5.0	5.5	6.0
2	0.85	1.28	1.57	2.08	2.90	3.34
3	0.67	0.93	1.23	1.76	2.28	2.87
4	0.53	0.87	0.98	1.53	2.03	2.56
5	0.38	0.48	0.75	1.21	1.42	1.68
6	0.23	0.26	0.32	0.38	0.43	0.48
7	0.98	1.62	2.13	2.89	3.32	3.65

**Table 3.** Effect of pH on Co<sup>+2</sup> metal ion binding capacity of poly(8-QMA) and poly(2,4-DCPA-co-8-QMA)

Sample code no.	Metal ion uptake (meq · g <sup>-1</sup> )					
	pH of the medium					
	3.0	3.5	4.0	5.0	5.5	6.0
2	0.51	0.63	0.98	1.36	1.78	2.14
3	0.43	0.58	0.76	1.02	1.34	1.89
4	0.38	0.42	0.68	0.93	1.28	1.52
5	0.18	0.25	0.34	0.51	0.65	0.83
6	0.09	0.12	0.18	0.23	0.25	0.31
7	0.75	0.98	1.48	1.83	2.12	2.48

suspension was adjusted to the required value by the addition of either 0.1 M HNO<sub>3</sub> or 0.1 M NaOH and the contents were mechanically stirred for 24 h. To this, metal nitrate solution (0.1 M, 2 ml) was added and the pH of the content was adjusted to the required value. The content was mechanically stirred for another 24 h and then filtered and washed with the distilled water. The filtrate was collected in a conical flask and the unadsorbed metal was estimated by back titration with a standard EDTA solution using the appropriate indicator. A separate blank experiment (without adding polymer sample) was also carried out in the same manner. From the difference

**Table 4.** Effect of pH on Zn<sup>+2</sup> metal ion binding capacity of poly(8-QMA) and poly(2,4-DCPA-co-8-QMA)

Sample code no.	Metal ion uptake (meq · g <sup>-1</sup> )					
	pH of the medium					
	3.0	3.5	4.0	5.0	5.5	6.0
2	0.53	0.68	0.93	1.12	1.65	2.03
3	0.48	0.52	0.78	0.98	1.23	1.65
4	0.36	0.44	0.65	0.83	1.18	1.43
5	0.23	0.28	0.47	0.59	0.88	1.02
6	0.10	0.14	0.19	0.25	0.32	0.41
7	0.58	0.75	1.03	1.42	1.83	2.12

**Table 5.** Effect of pH on Fe<sup>+3</sup> metal ion binding capacity of poly(8-QMA) and poly(2,4-DCPA-co-8-QMA)

Sample code no.	Metal ion uptake (meq · g <sup>-1</sup> )				
	pH of the medium				
	1.5	2.0	2.5	3.0	3.5
2	0.78	0.98	1.32	1.83	2.14
3	0.63	0.78	0.98	1.46	1.93
4	0.58	0.65	0.83	1.28	1.65
5	0.32	0.41	0.58	0.69	0.90
6	0.12	0.15	0.23	0.28	0.32
7	0.89	1.12	1.46	2.01	2.33

between a sample and blank reading, the amount of metal adsorbed by the polymer was calculated and expressed in terms of milliequivalent per gram of the polymer (meq · g<sup>-1</sup>).

The above experiment was performed using 0.1 M metal nitrate solutions of Cu<sup>+2</sup>, Ni<sup>+2</sup>, Co<sup>+2</sup>, Zn<sup>+2</sup>, at pH 5.5 and of Fe<sup>+3</sup> at pH 3.0 in the presence of three different electrolytes (NaNO<sub>3</sub>, Na<sub>2</sub>SO<sub>4</sub>, and NaCl) each with four different concentrations (0.05, 0.1, 0.5, and 1.0 M). The results of these experiments are presented in Tables 11 to 14.

### 2.8 Estimation of the Rate of Metal Uptake as a Function of Time

In order to estimate the time required to attain the state of equilibrium under the prescribed experimental conditions, a series of experiments were conducted in which the amount of metal ion adsorbed by the polymer was estimated at specific time intervals. The polymer sample (50 mg) was mechanically stirred with 1.0 M NaNO<sub>3</sub> solution (40 ml) at required pH value for 24 h to allow the swelling of the polymer. Metal ion solution (0.1 M metal nitrate, 2 ml) was added to this and pH of the content was adjusted to the required value by addition of either 0.1 M HNO<sub>3</sub> or 0.1 M NaOH. The contents were mechanically stirred for different time intervals (1, 2, 3, 4, 5, 6, 7, and 24 h). After the

**Table 6.** Distribution ratio of Cu<sup>+2</sup> ion adsorbed by the polymer and remained in the solution at equilibrium

Sample code no.	Distribution ratio (K <sub>D</sub> )					
	pH of the medium					
	3.0	3.5	4.0	5.0	5.5	6.0
2	108	158	223	293	348	403
3	93	126	138	235	290	375
4	62	102	123	175	258	315
5	43	58	72	108	120	185
6	12	15	23	28	35	43
7	113	193	245	323	389	445

Weight of polymer: 50 mg; Electrolyte: 1 M NaNO<sub>3</sub> (40 ml).

**Table 7.** Distribution ratio of Ni<sup>+2</sup> ion adsorbed by the polymer and remained in the solution at equilibrium

Sample code no.	Distribution ratio (K <sub>D</sub> )					
	pH of the medium					
	3.0	3.5	4.0	5.0	5.5	6.0
2	105	165	265	375	468	585
3	85	123	247	328	389	498
4	69	105	180	265	325	355
5	53	65	93	138	165	183
6	20	23	28	32	38	45
7	120	182	308	381	605	718

**Table 8.** Distribution ratio of Co<sup>+2</sup> ion adsorbed by the polymer and remained in the solution at equilibrium

Sample code no.	Distribution ratio (K <sub>D</sub> )					
	pH of the medium					
	3.0	3.5	4.0	5.0	5.5	6.0
2	79	85	165	243	323	361
3	65	78	132	190	245	293
4	41	69	118	163	205	256
5	23	35	63	74	89	98
6	8	11	15	18	25	28
7	89	102	183	283	365	404

specific time interval, the particular suspension was filtered and washed with the distilled water. The filtrate was collected and the unadsorbed metal was estimated by titration with standard EDTA solution using appropriate indicator. From the difference between the original amount of metal added at the beginning of the experiment and the amount of unadsorbed metal, the amount of metal adsorbed by the polymer after a specific time interval was calculated. It was assumed that, under the prescribed experimental conditions, the system attains the state of 100% equilibrium after 24 h.

**Table 9.** Distribution ratio of Zn<sup>+2</sup> ion adsorbed by the polymer and remained in the solution at equilibrium

Sample code no.	Distribution ratio (K <sub>D</sub> )					
	pH of the medium					
	3.0	3.5	4.0	5.0	5.5	6.0
2	59	83	115	165	209	262
3	48	53	93	131	178	198
4	36	43	66	85	125	165
5	21	29	43	58	75	102
6	5	7	10	15	20	23
7	85	98	123	185	238	283

**Table 10.** Distribution ratio of Fe<sup>+3</sup> ion adsorbed by the polymer and remained in the solution at equilibrium

Sample code no.	Distribution ratio (K <sub>D</sub> )				
	pH of the medium				
	1.5	2.0	2.5	3.0	3.5
2	65	98	125	168	182
3	58	83	102	131	150
4	43	58	78	105	134
5	28	35	49	63	71
6	7	10	14	23	28
7	71	109	143	195	208

**2.9 Distribution Ratios of Metal Ions as a Function of pH**

The distribution of each metal ion (Cu<sup>+2</sup>, Ni<sup>+2</sup>, Co<sup>+2</sup>, Zn<sup>+2</sup>, and Fe<sup>+3</sup>) between polymer and aqueous phase was estimated at different pH, using 1 M NaNO<sub>3</sub> solution. 50 mg polymer was stirred in a 1 M NaNO<sub>3</sub> solution (40 ml) at required pH value for 24 h. To the swelled polymer, a 0.1 M metal ion solution (2 ml) was added and the pH was adjusted to the required value by addition of either 0.1 M HNO<sub>3</sub> or 0.1 M

**Table 11.** Effect of electrolyte concentration on metal ion adsorption capacity of poly(8-QMA) and poly(2,4-DCPA-co-8-QMA)

Sample code no.	Electrolyte concentration (mol · lit <sup>-1</sup> )	Metal ion uptake (meq · g <sup>-1</sup> )				
		Cu <sup>+2</sup>	Ni <sup>+2</sup>	Co <sup>+2</sup>	Zn <sup>+2</sup>	Fe <sup>+3</sup>
2	0.05	1.83	1.93	1.12	3.03	3.38
	0.10	2.39	2.18	1.43	2.83	2.83
	0.50	2.43	2.33	1.69	2.54	2.36
	1.00	2.54	2.89	1.78	1.65	1.83
3	0.05	1.48	1.56	0.98	2.85	2.94
	0.10	1.93	2.03	1.06	2.59	2.58
	0.50	2.05	2.16	1.23	2.18	2.03
	1.00	2.12	2.28	1.34	1.23	1.46
4	0.05	1.12	1.23	0.75	2.17	2.63
	0.10	1.68	1.77	0.96	1.94	2.19
	0.50	1.86	1.93	1.16	1.68	1.60
	1.00	2.08	2.07	1.28	1.18	1.28
5	0.05	0.36	0.83	0.23	1.94	1.68
	0.10	0.53	1.05	0.36	1.76	1.43
	0.50	0.79	1.22	0.49	1.42	1.02
	1.00	1.05	1.42	0.65	0.88	0.69
6	0.05	0.08	0.16	0.03	1.62	0.83
	0.10	0.15	0.23	0.12	1.46	0.69
	0.50	0.21	0.38	0.19	0.89	0.42
	1.00	0.26	0.43	0.25	0.32	0.28
7	0.05	2.01	2.08	1.36	3.38	3.83
	0.10	2.24	2.41	1.58	2.93	3.05
	0.50	2.48	2.83	1.83	2.65	2.56
	1.00	2.56	3.32	2.12	1.83	2.01

Weight of polymer: 50 mg; pH of the medium: 5.5 (for Cu<sup>+2</sup>, Ni<sup>+2</sup>, Zn<sup>+2</sup>, and Co<sup>+2</sup>) and 3.0 (for Fe<sup>+3</sup>).

**Table 12.** Effect of electrolyte concentration on metal ion adsorption capacity of poly(8-QMA) and poly(2,4-DCPA-co-8-QMA)

Sample code no.	Electrolyte concentration (mol · lit <sup>-1</sup> )	Metal ion uptake (meq · g <sup>-1</sup> )				
		Cu <sup>+2</sup>	Ni <sup>+2</sup>	Co <sup>+2</sup>	Zn <sup>+2</sup>	Fe <sup>+3</sup>
2	0.05	1.83	1.93	1.12	3.03	3.38
	0.10	2.39	2.18	1.43	2.83	2.83
	0.50	2.43	2.33	1.69	2.54	2.36
	1.00	2.54	2.89	1.78	1.65	1.83
3	0.05	1.48	1.56	0.98	2.85	2.94
	0.10	1.93	2.03	1.06	2.59	2.58
	0.50	2.05	2.16	1.23	2.18	2.03
	1.00	2.12	2.28	1.34	1.23	1.46
4	0.05	1.12	1.23	0.75	2.17	2.63
	0.10	1.68	1.77	0.96	1.94	2.19
	0.50	1.86	1.93	1.16	1.68	1.60
	1.00	2.08	2.07	1.28	1.18	1.28
5	0.05	0.36	0.83	0.23	1.94	1.68
	0.10	0.53	1.05	0.36	1.76	1.43
	0.50	0.79	1.22	0.49	1.42	1.02
	1.00	1.05	1.42	0.65	0.88	0.69
6	0.05	0.08	0.16	0.03	1.62	0.83
	0.10	0.15	0.23	0.12	1.46	0.69
	0.50	0.21	0.38	0.19	0.89	0.42
	1.00	0.26	0.43	0.25	0.32	0.28
7	0.05	2.01	2.08	1.36	3.38	3.83
	0.10	2.24	2.41	1.58	2.93	3.05
	0.50	2.48	2.83	1.83	2.65	2.56
	1.00	2.56	3.32	2.12	1.83	2.01

Weight of polymer: 50 mg; Electrolyte: NaNO<sub>3</sub> solution (40 ml); pH of the medium: 5.5 (for Cu<sup>+2</sup>, Ni<sup>+2</sup>, Zn<sup>+2</sup>, and Co<sup>+2</sup>) and 3.0 (for Fe<sup>+3</sup>).

NaOH. The content was mechanically stirred for 24 h. The experiments were carried out from 3.0 to higher permissible pH for Cu<sup>+2</sup>, Ni<sup>+2</sup>, Co<sup>+2</sup>, and Zn<sup>+2</sup>. In the case of Fe<sup>+3</sup>, the study was carried out from pH 1.5 to 3.5.

After 24 h, the mixture was filtered. The filtrate and washings were collected. The amount of the metal ion which remained in the aqueous phase was estimated by back titration with standard EDTA solution using appropriate indicator. Similarly, a blank experiment was carried out without adding the polymer sample. The amount of metal adsorbed by the polymer was calculated from the difference between sample and blank reading. The original metal ion concentration is known and the metal ion adsorbed by the polymer was estimated. The distribution ratio 'K<sub>D</sub>' is calculated from the following equation:

$$K_D = \frac{\text{Amount of metal adsorbed on resin}}{\text{Amount of metal in solution}} \times \frac{\text{Volume of solution}}{\text{Weight of resin}}$$

The results are presented in Tables 6 to 10.

**Table 13.** Effect of electrolyte concentration on metal ion adsorption capacity of poly(8-QMA) and poly(2,4-DCPA-co-8-QMA)

Sample code no.	Electrolyte concentration (mol · lit <sup>-1</sup> )	Metal ion uptake (meq · g <sup>-1</sup> )				
		Cu <sup>+2</sup>	Ni <sup>+2</sup>	Co <sup>+2</sup>	Zn <sup>+2</sup>	Fe <sup>+3</sup>
2	0.05	3.75	2.42	2.01	1.46	2.22
	0.10	3.34	2.12	1.63	1.12	1.48
	0.50	2.83	1.36	1.28	0.93	1.09
	1.00	2.42	1.23	0.93	0.79	0.88
3	0.05	3.57	2.11	1.64	1.15	1.98
	0.10	3.14	1.82	1.18	1.01	1.25
	0.50	2.68	1.08	1.08	0.83	0.78
	1.00	2.21	0.96	0.71	0.62	0.70
4	0.05	2.48	1.63	1.16	1.30	1.08
	0.10	2.19	1.27	0.96	1.10	0.84
	0.50	1.53	0.89	0.78	0.98	0.64
	1.00	1.34	0.85	0.53	0.67	0.52
5	0.05	1.24	0.93	0.88	0.98	0.93
	0.10	1.08	0.65	0.73	0.86	0.56
	0.50	0.83	0.43	0.51	0.57	0.43
	1.00	0.80	0.39	0.35	0.40	0.28
6	0.05	0.65	0.44	0.38	0.29	0.25
	0.10	0.53	0.28	0.21	0.25	0.10
	0.50	0.32	0.15	0.08	0.16	0.05
	1.00	0.28	0.09	—	0.05	2.28
7	0.05	3.98	2.68	2.26	1.58	1.63
	0.10	3.43	2.49	1.87	1.23	1.31
	0.50	2.98	1.87	1.42	1.02	0.95
	1.00	2.45	1.53	1.17	0.85	2.40

Weight of polymer: 50 mg; Electrolyte: Na<sub>2</sub>SO<sub>4</sub> solution (40 ml); pH of the medium: 5.5 (for Cu<sup>+2</sup>, Ni<sup>+2</sup>, Zn<sup>+2</sup>, and Co<sup>+2</sup>) and 3.0 (for Fe<sup>+3</sup>).

### 3 Results and Discussion

The synthesis of the monomer 2,4-DCPA was confirmed by IR and <sup>1</sup>H-NMR techniques. All the expected signals for 2,4-DCPA were observed.

*IR of 2,4-DCPA (cm<sup>-1</sup>):* 3015 ( $\nu_{\text{C-H}}$ ), 2978 ( $\nu_{\text{CH}_3}$ ), 1756 ( $\nu_{\text{C=O}}$ ), 1640 ( $\nu_{\text{C=C}}$ ), 1230 (asymmetric  $\nu_{\text{C-O-C}}$ ), 1150 (symmetric  $\nu_{\text{C-O-C}}$ ), 890 (-CH bending mode of vinyl group), 730 (rocking mode of vinyl group), 667 ( $\nu_{\text{C-Cl}}$ ). The two absorption bands at 1593 and 1480 cm<sup>-1</sup> may be assigned as the characteristic absorption of o-substituted phenyl ring.

*<sup>1</sup>H-NMR of 2,4-DCPA ( $\delta$  ppm) (60 MHz):* 5.98 (1H, -CH=), 6.36 (1H) and 6.53 (1H) (non-equivalent methylene protons), 7.16–7.43 (3H, aromatic protons).

The formation of polymers was confirmed by IR spectral data. The C=C stretching peak of monomer 2,4-DCPA at 1640 cm<sup>-1</sup> is absent as expected in the polymers formed by the monomers 2,4-DCPA and 8-QMA. The copolymers show the two medium bands at 2993 and 2947 cm<sup>-1</sup> that are attributed to the asymmetric and symmetric stretching vibrations due to C-H of methylene moiety. A strong absorption at 1471 cm<sup>-1</sup> is due to  $\nu_{\text{C-H}}$  bending vibration of the -CH<sub>2</sub>- group. Two sharp and distinct bands at 1770 and

**Table 14.** Effect of electrolyte concentration on metal ion adsorption capacity of poly(8-QMA) and poly(2,4-DCPA-co-8-QMA)

Sample code no.	Electrolyte concentration (mol · lit <sup>-1</sup> )	Metal ion uptake (meq · g <sup>-1</sup> )				
		Cu <sup>+2</sup>	Ni <sup>+2</sup>	Co <sup>+2</sup>	Zn <sup>+2</sup>	Fe <sup>+3</sup>
2	0.05	1.35	1.30	0.53	1.88	2.48
	0.10	2.43	2.34	0.99	1.63	1.53
	0.50	2.79	2.70	1.34	1.10	1.25
	1.00	3.12	3.19	1.58	0.73	0.83
3	0.05	1.23	1.02	0.45	1.54	1.98
	0.10	2.34	1.81	0.83	1.32	1.23
	0.50	2.42	2.32	1.12	0.89	0.98
	1.00	2.70	2.78	1.33	0.53	0.65
4	0.05	0.84	0.93	0.38	1.26	1.75
	0.10	1.12	1.20	0.56	0.98	0.78
	0.50	1.63	1.65	0.89	0.64	0.60
	1.00	1.75	1.78	1.01	0.53	0.45
5	0.05	0.53	0.64	0.22	0.69	0.93
	0.10	0.68	0.90	0.35	0.58	0.62
	0.50	0.73	0.98	0.42	0.41	0.47
	1.00	0.78	1.04	0.46	0.32	0.33
6	0.05	0.08	0.10	—	0.10	0.12
	0.10	0.12	0.18	0.02	0.06	0.09
	0.50	0.15	0.20	0.05	0.03	0.04
	1.00	0.17	0.22	0.06	—	—
7	0.05	1.78	1.46	0.62	2.12	2.66
	0.10	2.58	2.38	0.98	1.84	1.85
	0.50	2.98	2.88	1.48	1.03	1.30
	1.00	3.32	3.65	1.64	0.78	1.00

Weight of polymer: 50 mg; Electrolyte: NaCl solution (40 ml); pH of the medium: 5.5 (for Cu<sup>+2</sup>, Ni<sup>+2</sup>, Zn<sup>+2</sup>, and Co<sup>+2</sup>), and 3.0 (for Fe<sup>+3</sup>).

1215 cm<sup>-1</sup> have contributions, respectively from  $\nu_{\text{C=O}}$  and  $\nu_{\text{C-O}}$  stretching vibration of the ester group. The vibrations due to the phenyl ring are assigned to strong absorptions at 1461 and 1582 cm<sup>-1</sup>. The  $\nu_{\text{C-Cl}}$  stretching frequency is assigned to the band at 670 cm<sup>-1</sup>. The polymers have three strong bands at 1474, 1505, and 1605 cm<sup>-1</sup> which are due to the characteristic absorption of the 8-o-substituted quinoline ring system.

The presence of a pendent quinolinyl group in the polymer chain imparts ion-exchange properties to the polymer. Tables 1 to 5 show the effect of pH on the metal binding capacity of the synthesized polymers. It is observed that the relative amount of metal ion adsorbed by the polymers increase with increasing pH of the medium. The result of distribution ratios (Tables 6 to 10) also indicates that at equilibrium, the distribution of each metal between the polymeric phase and aqueous phase increase with increasing pH of the medium. The data clearly indicates that Ni<sup>+2</sup> gets adsorbed selectively to the highest extent whereas Zn<sup>+2</sup> adsorbed to the least extent over the entire pH range studied. The lowest affinity of the Zn<sup>+2</sup> ions may be attributed to the very low stability constants of Zn complexes with ligands. Tables 11 to 14 show the effect of the type and concentration of an electrolyte on the amount

**Table 15.** Rate of Cu<sup>+2</sup> metal ion uptake by poly(8-QMA) and poly(2,4-DCPA-co-8-QMA) as a function of time

Sample code no.	% Attainment of equilibrium						
	Time (hrs)						
	1.0	2.0	3.0	4.0	5.0	6.0	7.0
2	35.8	38.3	41.8	58.2	88.3	94.3	96.1
3	30.3	34.8	42.3	60.1	82.8	96.8	97.3
4	28.6	31.3	40.2	62.3	80.5	93.5	94.5
5	25.4	27.6	35.7	58.7	81.3	88.9	90.4
6	23.6	25.2	28.9	50.5	79.5	98.2	—
7	33.4	36.8	42.2	63.4	80.0	90.2	94.9

Weight of sample: 50 mg; Metal ion: 0.1 M Cu(NO<sub>3</sub>)<sub>2</sub> (2 ml); Electrolyte: 1.0 M NaNO<sub>3</sub> (40 ml); pH of the medium: 5.5.

**Table 16.** Rate of Ni<sup>+2</sup> metal ion uptake by poly(8-QMA) and poly(2,4-DCPA-co-8-QMA) as a function of time

Sample code no.	% Attainment of equilibrium <sup>a</sup>						
	Time (hrs)						
	1.0	2.0	3.0	4.0	5.0	6.0	7.0
2	28.0	30.7	38.6	49.9	72.8	87.1	94.3
3	26.7	29.8	34.5	51.2	77.9	85.2	95.8
4	25.4	28.0	35.1	55.8	76.8	88.3	95.2
5	20.2	21.8	28.7	60.6	70.4	81.8	90.1
6	19.9	21.0	26.8	50.3	71.2	89.0	91.8
7	26.1	29.9	36.8	49.2	73.5	86.8	96.4

<sup>a</sup>With respect to 100% equilibrium after 24 h. Weight of sample: 50 mg; Metal ion: 0.1 M Ni(NO<sub>3</sub>)<sub>2</sub> (2 ml); pH of the medium: 5.5.

of different metal ion adsorption by the polymer from their solutions at room temperature. It is observed that the amount of Cu<sup>+2</sup>, Ni<sup>+2</sup>, and Co<sup>+2</sup> ions adsorbed increases, whereas that of Zn<sup>+2</sup> decreases with increasing the concentration of

**Table 17.** Rate of Co<sup>+2</sup> metal ion uptake by poly(8-QMA) and poly(2,4-DCPA-co-8-QMA) as a function of time

Sample code no.	% Attainment of equilibrium <sup>a</sup>						
	Time (hrs)						
	1.0	2.0	3.0	4.0	5.0	6.0	7.0
2	23.4	30.1	37.8	55.8	67.8	86.2	92.3
3	22.9	28.3	34.5	58.9	69.9	88.5	91.4
4	21.2	24.7	29.6	49.6	63.2	82.3	90.3
5	18.5	23.2	28.9	51.2	62.5	81.5	92.6
6	12.8	19.5	24.7	43.5	58.8	79.8	90.8
7	21.8	26.7	39.3	60.1	75.4	83.4	93.4

<sup>a</sup>With respect to 100% equilibrium after 24 h. Weight of sample: 50 mg; Metal ion: 0.1 M Co(NO<sub>3</sub>)<sub>2</sub> (2 ml); Electrolyte: 1.0 M NaNO<sub>3</sub> (40 ml); pH of the medium: 5.5.

**Table 18.** Rate of Zn<sup>+2</sup> metal ion uptake by poly(8-QMA) and poly(2,4-DCPA-co-8-QMA) as a function of time

Sample code no.	% Attainment of equilibrium <sup>a</sup>						
	Time (hrs)						
	1.0	2.0	3.0	4.0	5.0	6.0	7.0
2	39.5	47.1	66.5	80.1	91.3	98.3	—
3	40.1	46.2	62.9	79.4	92.4	97.5	—
4	38.6	49.4	65.8	82.2	93.8	94.6	99.8
5	41.2	47.8	62.2	84.8	97.7	99.8	—
6	32.8	36.4	58.9	72.9	89.0	96.4	—
7	42.3	44.8	66.8	82.7	92.5	99.4	—

<sup>a</sup>With respect to 100% equilibrium after 24 h. Weight of sample: 50 mg; Metal ion: 0.1 M Zn(NO<sub>3</sub>)<sub>2</sub> (2 ml); Electrolyte: 1.0 M NaNO<sub>3</sub> (40 ml); pH of the medium: 5.5.

**Table 19.** Rate of Fe<sup>+3</sup> metal ion uptake by poly(8-QMA) and poly(2,4-DCPA-co-8-QMA) as a function of time

Sample code no.	% Attainment of equilibrium <sup>a</sup>						
	Time (hrs)						
	1.0	2.0	3.0	4.0	5.0	6.0	7.0
2	48.9	59.5	74.5	89.1	98.9	—	—
3	51.2	61.2	76.8	89.3	98.2	—	—
4	45.6	58.4	79.9	92.4	97.5	—	—
5	50.1	60.3	83.2	93.5	99.2	—	—
6	43.8	55.6	78.5	89.6	96.7	99.7	—
7	51.5	60.1	83.5	94.0	99.8	—	—

<sup>a</sup>With respect to 100% equilibrium after 24 h. Weight of sample: 50 mg; Metal ion : 0.1 M Fe(NO<sub>3</sub>)<sub>3</sub> (2 ml); Electrolyte: 1.0 M NaNO<sub>3</sub> (40 ml); pH of the medium: 3.0.

NO<sup>-3</sup> and Cl<sup>-1</sup> ions whereas that of Zn<sup>+2</sup> decreases with increasing the concentration of NO<sup>-3</sup> and Cl<sup>-1</sup> ions. But, in the case of SO<sub>4</sub><sup>-2</sup>, the adsorption of all the metal ions studied decreases with increasing the concentration of SO<sub>4</sub><sup>-2</sup> ions which may be explained in terms of the stability constant of the complexes of studied metal ions with NO<sup>-3</sup>, Cl<sup>-1</sup>, and SO<sub>4</sub><sup>-2</sup> anions (12). Tables 15 to 19, show the results of the rate of metal uptake by the polymers as a function of time. It is observed that among the five metal ions studied, Zn<sup>+2</sup> and Fe<sup>+3</sup> ions required the shortest time (about 4–5 h) whereas Cu<sup>+2</sup>, Ni<sup>+2</sup>, and Co<sup>+3</sup> requires 6–7 h to reach the state of equilibrium. Due to this difference in the uptake rate of the metals, it may be possible to use these polymers to separate Zn<sup>+2</sup> and Fe<sup>+3</sup> ions from their mixtures with Cu<sup>+2</sup>, Ni<sup>+2</sup>, and Co<sup>+2</sup> ions.

#### 4 Conclusions

Since the pendent quinolinyl group plays a key role in the ion-exchange phenomena, the amount of metal adsorbed by each



sample depends upon its 8-QMA content. As the pH of the medium increases, the amounts of metal adsorbed by the polymers also increase and follow the trend of  $\text{Ni}^{+2} > \text{Cu}^{+2} > \text{Co}^{+2} > \text{Zn}^{+2}$ . It has been found that the adsorption of  $\text{Fe}^{+3}$  studied in the pH range of 1.5 to 3.5 increases with increasing pH. The adsorption of  $\text{Cu}^{+2}$ ,  $\text{Ni}^{+2}$ , and  $\text{Co}^{+2}$  at pH 5.5 increases with increasing  $\text{NO}^{-3}$  and  $\text{Cl}^{-}$  ion concentration in the aqueous phase, whereas that of  $\text{Zn}^{+2}$  and  $\text{Fe}^{+3}$  decrease with increasing  $\text{NO}^{-3}$  and  $\text{Cl}^{-}$  ion. From the results of the distribution ratio, it can be observed that all the polymers show the highest affinity for  $\text{Ni}^{+2}$  and the least affinity for the  $\text{Zn}^{+2}$ . Due to the considerable difference between the adsorption capacity at different pH, the rate of metal uptake and distribution ratio at equilibrium, it may be possible to use the polymers for separation of particular metal ions from their mixture.

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