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Ion exchange properties of some new chelating resins from cresol urea formaldehyde

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Abstract

Terpolymers resins(o,m,p –C UF) synthesized by the condensation of o,m,p- Cresol and Urea with Formaldehyde in the presence of acid catalyst , FTIR- spectroscopy and thermogravimetric analysis were used to characterize the terpolymers. Chelating ion exchange properties of these polymers were studied for Fe^{2+}, Ni^{2+}, Co^{2+}, Cu^{2+} and Zn^{2+} ions. A batch equilibrium method was employed in the study of the selectivity of metal ion uptake . the study was carried out over a wide pH range and shaking time.The OUF and PUF terpolymers showed highest selectivity for ions being studied.

Keywords: Terpolymers; chelating; ion exchange properties; o, p, m-cresol urea formaldehyde

1. Introduction

Many research works have been carried out on the preparation and characterization of urea containing terpolymers. Terpolymer is found very useful application as adhesives, high temperature flame resistant, fibers, coating materials, semiconductors, catalysis and ion exchange resins [1-5]. Ion exchange resins have attracted much interest in the resent years due to their application in waste water treatment, metal recovery and for the identification of specific metal ions [6,7]. The basic requirement for any polymeric material to be useful as ion exchange resin are: (a) 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, (c) the swollen material must be denser than water. Jadhao and co-worker synthesized a terpolymer resins by condensation of 2, 2′-dihydroxybiphenylandurea with formaldehyde in the presence of 2M hydrochloric acid as a catalyst.The studied chelating ion exchange properties of this polymer for Fe^{3+},Ni^{2+}, Cu^{2+} , Zn^{2+} ,Cd^{2+} and Pb^{2+} ions. A batch equilibrium method and a wide pH rang equilibrium method was employed in the study of selectivity of metal ion up take. The polymer was found to show higher selectivity for Fe^{3+}, Ni^{2+}, Cu^{2+}, than for Zn^{2+}, Cd^{2+} and Pb^{2+} ions [8] .A chelating ion exchange resin was synthesized by condensation of o cresol and urea with formaldehyde in the presence of acid catalyst and the ion exchangecapacity was evaluated with various metal ions Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+} ions [9] . Another chelating polymer synthesized from 2,4-dihydroxy acetophenon and biuret with formaldehyde in 4:1:5 molar ratio in presence of 2M hydrochloric acid as catalyst was also reported to havehigherselectivityforFe^{3+}andCu^{2+}ions[10] .Wasudeo and Deepti reported thesynthesisand characterization of terpolymer resins derived from o-aminophenyl, urea and formaldehyde and studied their ion- exchange properties for Fe^{3+}, Ni^{2+}, Cu^{2+} ,Co^{2+} , Zn^{2+} ,Cd^{2+} and Pb^{2+} ions [11].The present work report the synthesis and characterization of a terpolymer resins from o-cresol, m-cresol and p-cresol with urea and formaldehyde. The work describes the synthesis of the resins in acidic media, characterization, thermal studies of the resins and the systematic studies of various transition metal ion exchange properties of the resins.

2. Materials And Methods:

2.1 chemicals:

o- cresol, m-cresol, p-cresol and urea were of analytical grade . formaldehyde (37% w/v) was received. Metal ion solutions were prepared by dissolving appropriate amount of metal nitrates in double distilled water. The other chemicals and solvents were used as received.

2.2 Synthesis of o,m,p-CUF terpolymers

The terpolymers o, m, p-CUF were synthesized by the condensation of o-cresol, m-cresol, p-cresol and urea with formaldehyde in the mole ratio of 1:1:3, in the presence of 2M HCl as catalyst. The mixture was heated at 120 ^{0}C for 5h. The contents of the flask were shaken periodically to ensure homogenous mixing. After the refluxing period was over , the contents of the flask were poured in to crushed ice with constant stirring and left over night.The separated coloured resin was filtered off and washed several times with cold water followed by hot water and methanol for removing unreacted monomers .Finally the resin was purified by dissolving in 10% NaOH and reprecipitating with 1:1(v/v) conc.HCl/water. The resins thus obtained were washed with cold water followed by hot water and dried in vacuum at 100 ^{0}C the yield of the resins were between 70% to 73% **(12).**

2-3 characterization of the terpolymers were recorded on shimadzu (infinity-1) FTIR spectrophotometer in KBR pallets in the wave number region of 400-4000 cm^{-1} at Basrah university. The thermal analysis of the terpolymers were carried out in air atmosphere at a heating rate of 20 ^{0}C per minute on Perkin Elmere Thermogravimetric Analyzer at Tahran –Iran university.

2-4 Analytical evaluation of the prepared resins as chelating polymers.

The new resins were evaluated analytically by determining their selectivity for metal ions ,time required for chelation equilibrium and the pH working range for each metal ions.

2-4-1 preparation of the standard solutions

The standard solutions were prepared by dilution of standard stock solutions of 1000 ppm metal ion prepared from metal nitrate supplied by Merckand Fluka companies using deionized water in all preparations.

2-4-2 The analytical methods and measurements:

The batch method was used in this study, thus 0.1 gm of the resin was treated with metal ion solutions of concentration 100 ppm and volume 10 ml at pH range of (1-10) depending on the studied ion and its critical pH beyond which precipitation start to appear.The measurement includes also the effect of treatment time which ranged between 15 min to 24 hrs. the samples treatment was carried out in an orbital shaker at speed of 200 rpm then the solutions were filtered, the concentration of the un combined metal ion remaining in the filtrate was determined by using flame atomic absorption spectrophotometer (Py instrument AA500)the loading capacity of the resin represent the difference between the concentration of the metal ions before and after treatment from relation

$$L.C = V (Co-Ce) /m$$

Were; L.C is the equilibrium loading capacity (mg/ gm), V is the volume of solution (L), m is the weight of the resin (g), Co = initial concentration of Metal ion solution, Ce = concentration of the Metal ion solution after treatment with the resin **(13).**

2-4-3 Regeneration of the loaded resins

The regeneration and the recovery of chelated metal ions were determined by treating 0.1 gm of the loaded resin with 10 ml of 3 N HCl solution as an eluent for different time periods, metal ion concentration in the eluent was determined after treatment and the percentage ion recovery was plotted as function of time.

3. Results And Discussion

The terpolymer resins were dark brown in colour, insoluble in commonly used organic solvents, but were soluble in dimethylformamide, dimethylsulfoxide, and tetrahydrofuran.

3.1 Infrared spectra

The FTIR spectrum of all terpolymer resins are presented in Figure 1 and FTIR spectral data are shown in table 1. The IR spectra revealed that all these terpolymers give rise to nearly similar pattern spectra (table 1).Abroad band appear in the region 3350-3354 cm^{-1}may be assigned to the stretching vibration of the phenolic hydroxyl groups exhibiting intermolecular hydrogen bonding [14] . A band appear in the region 2941-2966 cm^{-1} show the presence of methylene bridge $> CH_2$ in the polymer chain . the appearance of band in the region of 1040-1060 cm^{-1} attributed to the vibration of ether linkage (- CH_2-O-CH_2-) which form during the polymerization.

Table (1) FTIR Spectral data of terpolymer resins

Terpolymer compound	O-H or N-H st. vib. cm^{-1}	C-H st.vib cm^{-1}	C=C st.vib cm^{-1}	C-O st.vib cm^{-1}	Ar.C-H Bending cm^{-1}	C-O-C st.vib cm^{-1}
OUF	3350	2964	1442	1261	880	1060
MUF	3352	2941	1539	1261	748	1040
PUF	3354	2966	1558	1249	817	1040

3-2 Thermogravimetric analysis

The thermograms of the resin samples obtained are shown in Fig.2. The TGA data of the terpolymers are given in table 2. The thermograms of OUF showed two stages of decomposition.The first stage is observed from 185 to 400 ^{0}C.And the second stage was in the temperature range of 400-710 ^{0}C , while for PUF is showed three stages of decomposition and for MUF is showed two stages of decomposition.From the results obtained that the char percentage of terpolymers is from 0.837 to 7.78 due to little amount of aromatic compounds in the terpolymers lattice ,at the other hand the activation energies of these terpolymers which calculated by Arrhenius equation and char content percentage were proportional.Data reveals that the terpolymers are thermally stable.

3.3 Analytical evaluation of terpolymer resins:

The prepared resins were treated with the metal ions Fe^{2+}, Ni^{2+}, Cu^{2+} ,Co^{2+} and Zn^{2+} ions. The factors affecting its L.C. for these ions were evaluated.

3.3.1 The effect of time treatment:

The effects of treatment time on L.C. of terpolymers for metal ions were studied at different pH. Figures (3-11) show the effect of shaking time on the L.C for terpolymers for the studied ions at different pH values. The L.C. presented in these figures indicates the conclusions:

1- Loading capacity increased with increasing treatment time and pH for the studied ions.

2- At higher pH values equilibrium time is shorter than at lower pH values.

3- Equilibrium time varies between 2 to 6 hrs.

4- The total loading capacity of terpolymers for the studied ions was in the following order:

$Cu^{2+} > Zn^{2+} > Fe^{2+} > Ni^{2+} \sim Co^{2+}$ for OUF terpolymer

$Zn^{2+} > Fe^{2+} > Cu^{2+} > Ni^{2+} \sim Co^{2+}$ for PUF terpolymer

$Zn^{2+} > Fe^{2+} > Cu^{2+} > Co^{2+} \sim Ni^{2+}$ for MUF terpolymer

The metal complexing nature of the terpolymers depends not only on the nature of the legand groups but also their accessibility towards metal ions . thus, steric hindrance by the polymeric matrix and hydrophobic nature of the polymer ligands can limit the chelating reaction [15] .

3.3.2 pH effect

Figures (12- 28) show the effect of pH on the loading capacity of terpolymers . the total L.C. sequence of terpolymers from studied ions at different pH values were as follows:

pH=2: Zn^{2+} >Cu^{2+}>Fe^{2+} > Co^{2+} ~ Ni $^{2+}$ for OUF, PUF

pH=2: Zn^{2+} >Fe^{2+} > Co^{2+} > Cu^{2+} > Ni $^{2+}$ for MUF

pH=4: Fe^{2+} ~Cu^{2+} >Zn^{2+} > Co^{2+} ~ Ni^{2+} for OUF, PUF

pH=4: Zn^{2+} > Fe^{2+} > Co^{2+} > Cu^{2+} >Ni^{2+} for MUF

pH =6 Cu^{2+} > Zn^{2+} > Co^{2+} ~ Ni $^{2+}$ for OUF, PUF

pH =6 Zn^{2+} > Cu^{2+} > Co^{2+} ~ Ni $^{2+}$ for MUF

pH =8 Co^{2+} ~ Ni^{2+} for OUF, PUF

pH=8 Ni^{2+}> Co^{2+} for MUF

the obtained relationships are shown in figures(12- 28) selective chelation of some of the studied ions can be achieved by changing the pH of the studied solution. It's clear that L.C. highly increases of certain pH range under constant treatment conditions.

3.3.4Regenerationoftheloadedterpolymers

3M of HCl was used for the regeneration of terpolymers, several factors affecting the regeneration of metal ions from loaded resins, namely treated time, concentration of the eluent and the nature of the studied ions

Figure (29) shows that increasing the treatment time increases the percentage ion recovery. The amount of the recovered ions depends mostly on the nature of the ion itself.the percentage ion recovery of the studied ions was in the following order:

Zn^{2+} > Cu^{2+} >Fe^{2+} > Co^{2+} > Ni $^{2+}$ for OUF, PUF

Cu^{2+} > Zn^{2+} > Fe^{2+} > Co^{2+} > Ni $^{2+}$ for MUF

Table (2) some thermal stability characteristics determined from TGA thermograms

Resin name	TG/DTG				ΔE (kj/mole)	Temp. of 50%Wt loss. °C	Char% at 700 °C
	step	Ti°C	T_o(DTG $_{max}$) °C	T_f °C			
OUF	1 st	80	185 250 335	400	28.165		
	2 nd	405	540 590	710	84.549	445	7.7838
PUF	1 st	30	115	165	50.1425		
	2 nd	170	230 270	330	75.3124	385	3.194
	3 d	335	425 520	585	68.9425		
MUF	1 st	35	250 280 325	360	34.5739		
	2 nd	365	555 585	620	80.7643	450	0.837

Table 3 The loading capacity and recovery data of terpolymers

Ion	Zn^{2+}	Cu^{2+}	Fe^{2+}	Ni $^{2+}$	Co^{2+}	Resin name
Optimum L.C mg ion/gm resin	9.576	9.84	9.233	9.3	9.296	OUF
	9.799	9.632	7.56	8.799	8.571	PUF
	9.331	4.941	8.998	3.799	3.865	MUF
Best pH	6	6	4	8	8	OUF
	6	6	4	8	8	PUF MUF
% ion recovery	93	89.5	86.4	83	84.6	OUF
	92.6	91.5	88.5	85	87.6	PUF
	85.6	87.5	84	81.4	82.5	MUF

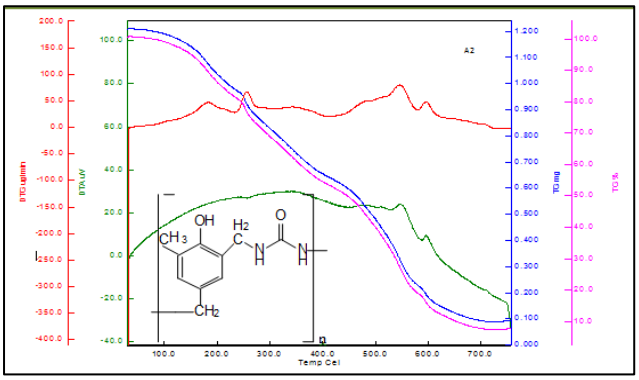

Figure 1: Typical thermogravimetric curve (DTGA) of OUF terpolymer

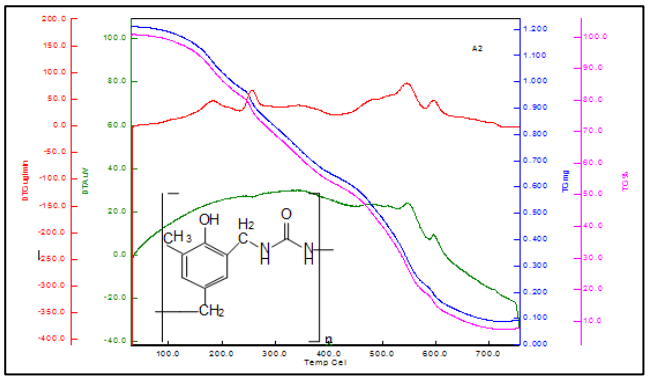

Figure 2: Typical thermogravimetric curve (DTGA) of PUF terpolymer

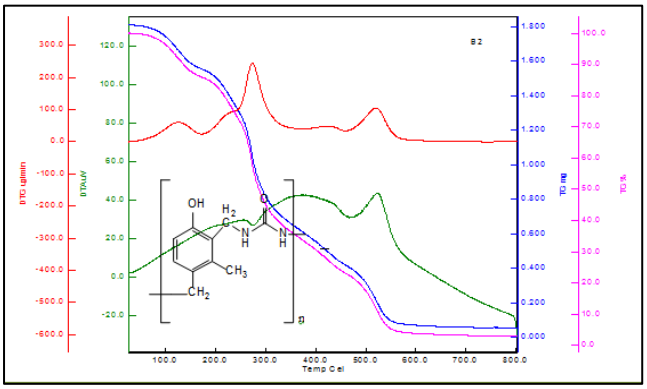

Figure 3: Typical thermogravimetric curve (DTGA) of MUF terpolymer

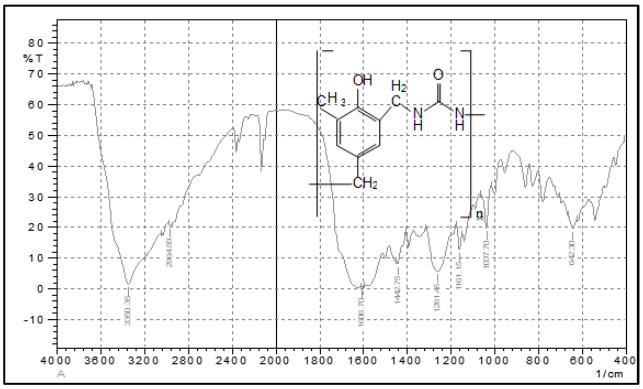

Figure 4 : typical IR Spectra of OUF terpolymer

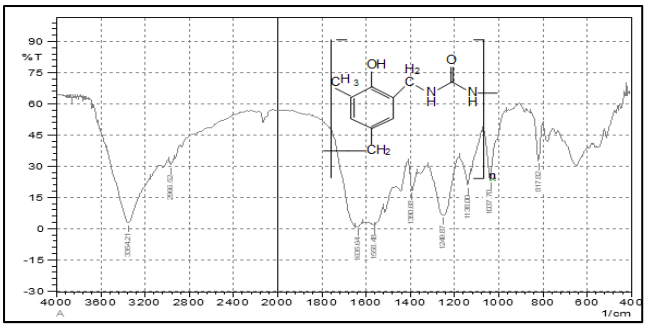

Figure 5 : typical IR Spectra of PUF terpolymer

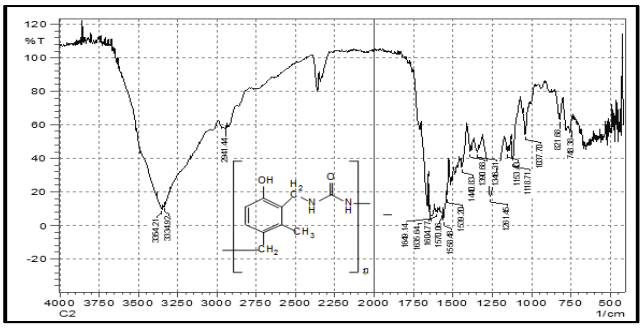

Figure 6 : typical IR Spectra of MUF terpolymer

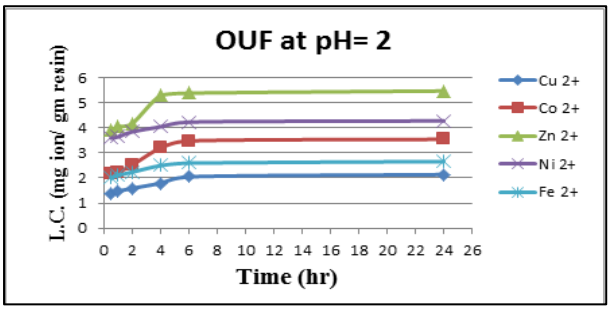

Figure 7:The effect of treatment time on the loading capacity of resin OUF towards Cu^{2+}, Co^{2+}, Zn^{2+}, Ni^{2+} and Fe^{2+} ions at pH =2

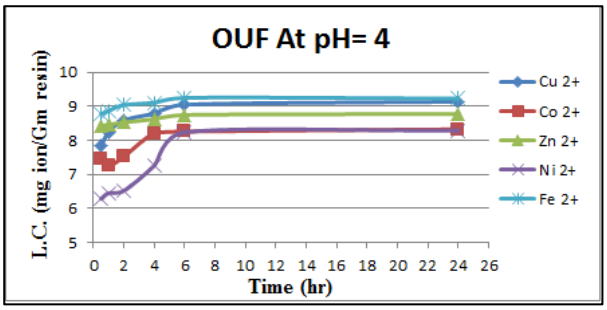

Figure 8:The effect of treatment time on the loading capacity of resin OUF towards Cu^{2+}, Co^{2+}, Zn^{2+}, Ni^{2+} and Fe^{2+} ions at pH =4

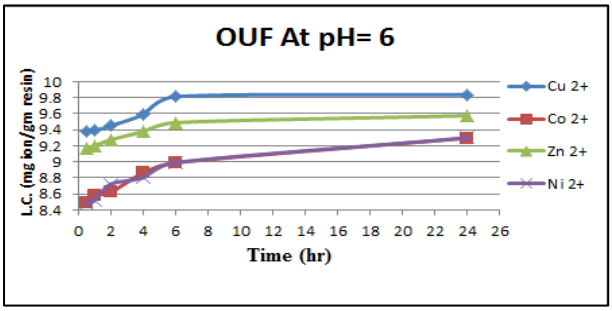

Figure 9:The effect of treatment time on the loading capacity of resin OUF towards Cu^{2+}, Co^{2+}, Zn^{2+}, Ni^{2+} and Fe^{2+} ions at pH =6

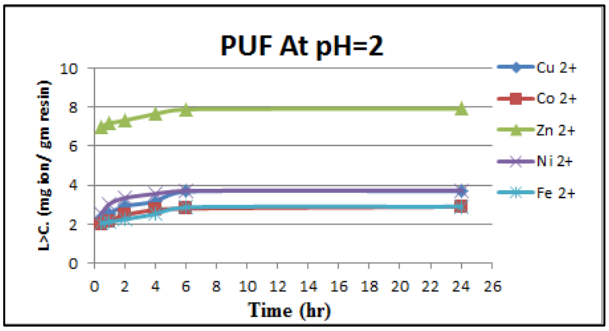

Figure 10:The effect of treatment time on the loading capacity of resin PUF towards Cu2+, Co2+, Zn2+, Ni2+and Fe2+ions at pH =2

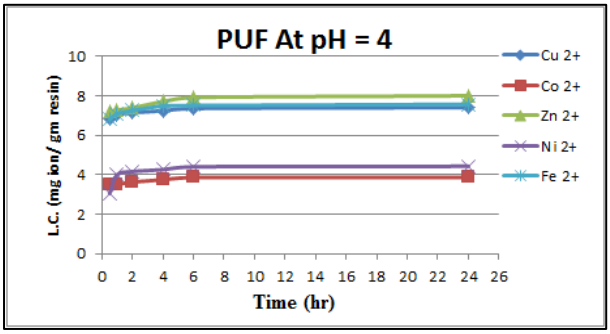

Figure 11:The effect of treatment time on the loading capacity of resin PUF towards Cu2+, Co2+, Zn2+, Ni2+ and Fe2+ions at pH =4

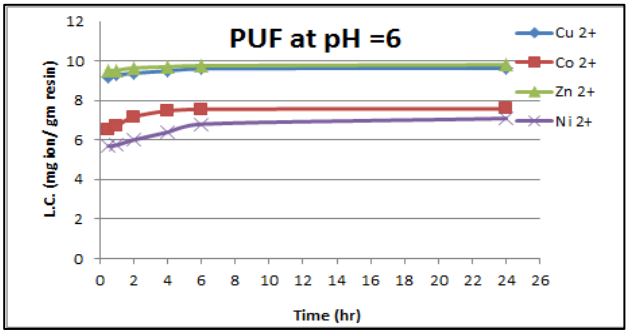

Figure 12:The effect of treatment time on the loading capacity of resin PUF towards Cu^{2+}, Co^{2+}, Zn^{2+}, Ni^{2+} and Fe^{2+} ions at pH =6

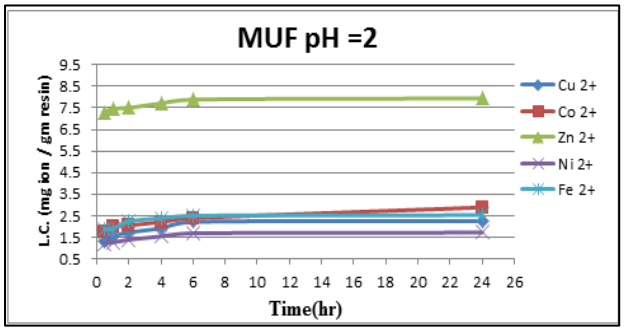

Figure 13:The effect of treatment time on the loading capacity of resin MUF towards Cu2+, Co2+, Zn2+, Ni2+and Fe2+ions at pH =2

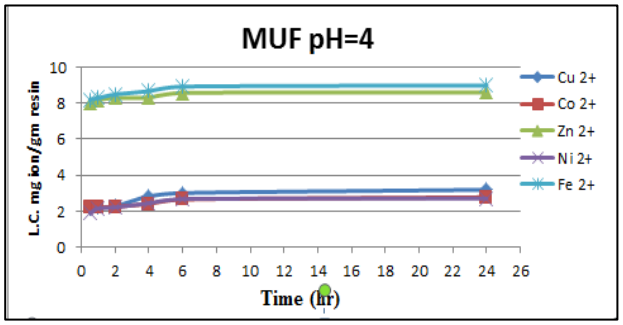

Figure 14:The effect of treatment time on the loading capacity of resin MUFtowards Cu2+, Co2+, Zn2+, Ni2+and Fe2+ ions at pH =4

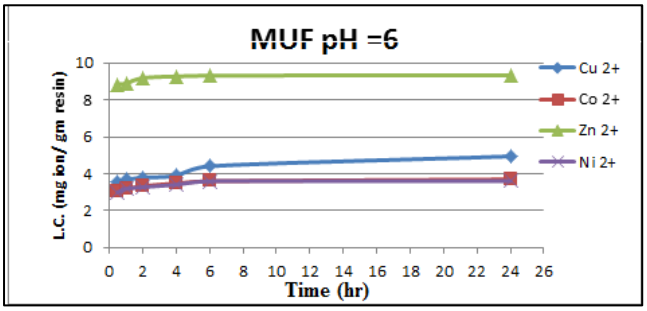

Figure 15:The effect of treatment time on the loading capacity of resin MUF towards Cu^{2+}, Co^{2+}, Zn^{2+}, Ni^{2+} and Fe^{2+} ions at pH =6

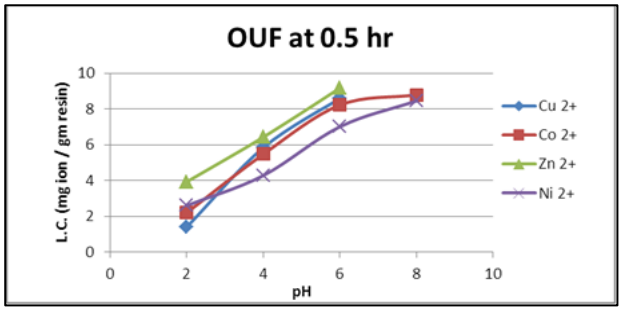

Figure 16: pH effect on total loading capacity of resin OUF towards Cu2+, Co2+, Zn2+ and Ni 2+ ions at 0.5 hr

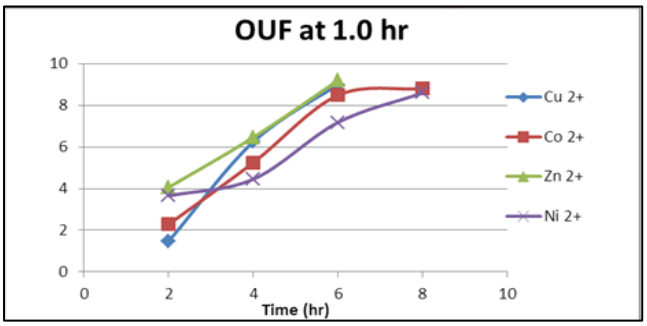

Figure 17: pH effect on total loading capacity of resin OUF towards Cu^{2+}, Co^{2+}, Zn^{2+} and Ni^{2+} ions at 1.0 hr

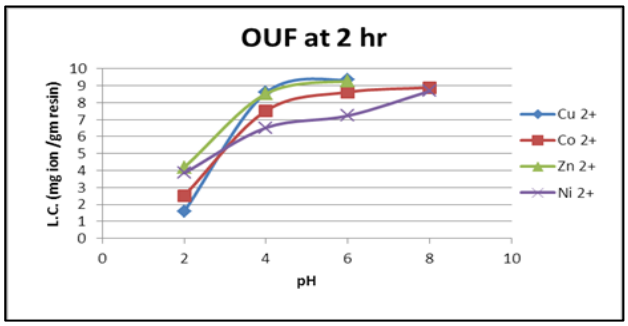

Figure 18: pH effect on total loading capacity of resin OUF towards Cu^{2+}, Co^{2+}, Zn^{2+} and Ni^{2+} ions at 2.0 hr

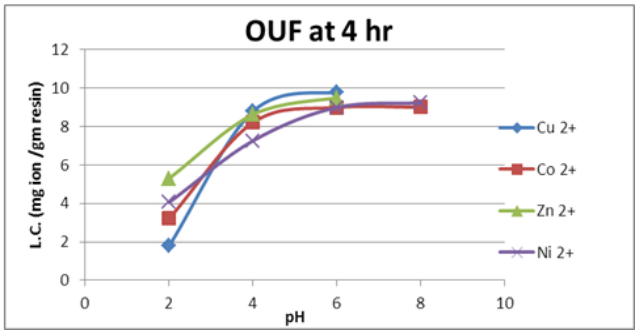

Figure 19: pH effect on total loading capacity of resin OUF towards Cu^{2+}, Co^{2+}, Zn^{2+} and Ni^{2+} ions at 4.0 hr

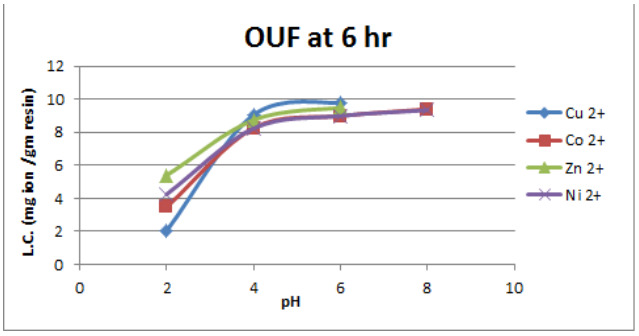

Figure 20: pH effect on total loading capacity of resin OUF towards Cu^{2+}, Co^{2+}, Zn^{2+} and Ni^{2+} ions at 6.0 hr

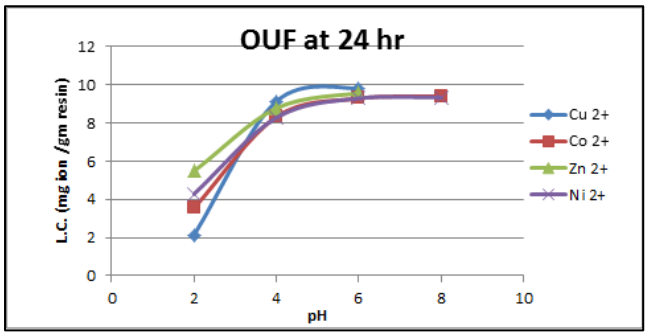

Figure 21: pH effect on total loading capacity of resin OUF towards Cu2+, Co2+, Zn2+ and Ni2+ ions at 24 hr

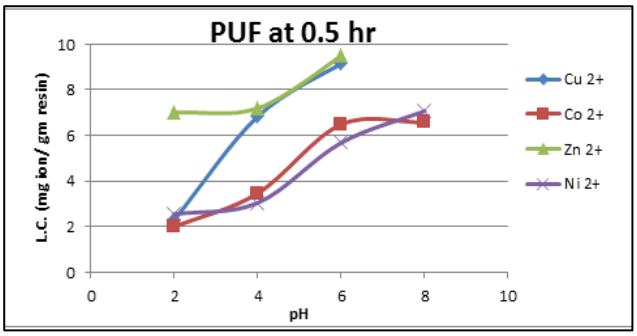

Figure 22: pH effect on total loading capacity of resin PUF towards Cu2+, Co2+, Zn2+ and Ni2+ ions at time = 0.5 hr

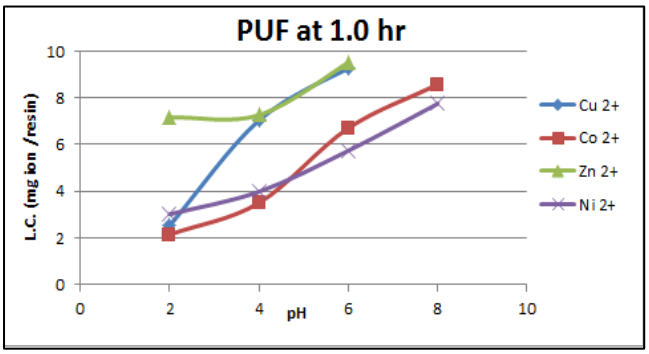

Figure 23: pH effect on total loading capacity of resin PUF towards Cu2+, Co2+, Zn2+ and Ni2+ ions at time = 1.0 hr

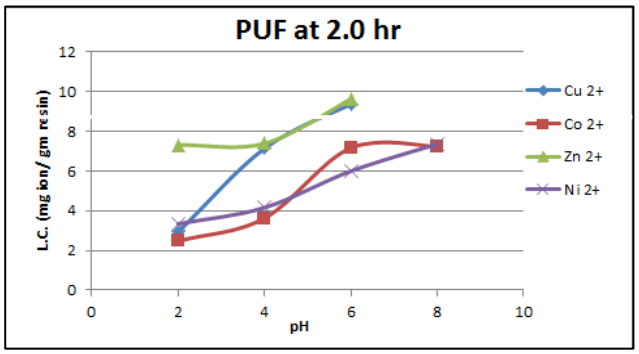

Figure 24: pH effect on total loading capacity of resin PUF towards Cu2+, Co2+, Zn2+ and Ni2+ ions at time = 2.0 hr

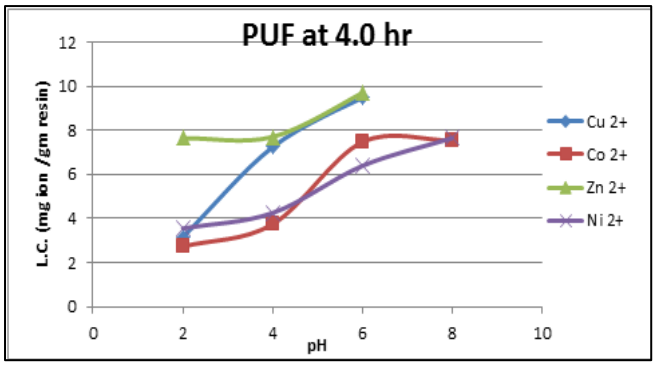

Figure 25: pH effect on total loading capacity of resin PUF towards Cu^{2+}, Co^{2+}, Zn^{2+} and Ni^{2+} ions at time = 4.0 hr

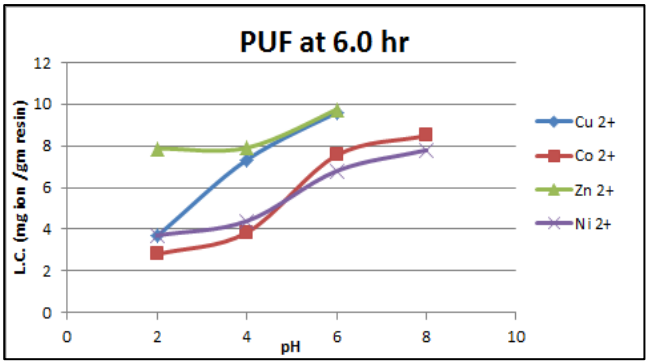

Figure 26: pH effect on total loading capacity of resin PUF towards Cu 2+, Co 2+, Zn 2+ and Ni 2+ ions at time = 6.0 hr

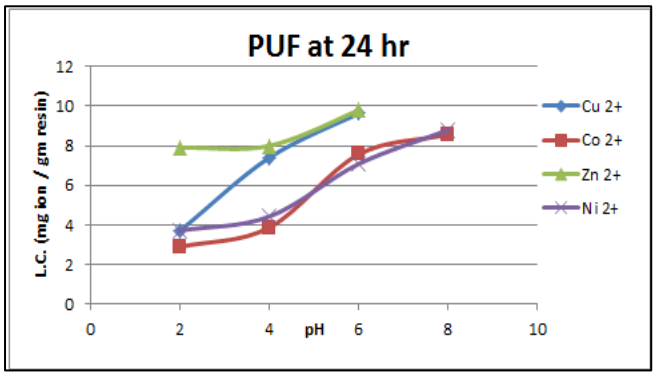

Figure 27: pH effect on total loading capacity of resin PUF towards Cu 2+, Co 2+, Zn 2+ and Ni 2+ ions at time = 6.0 hr

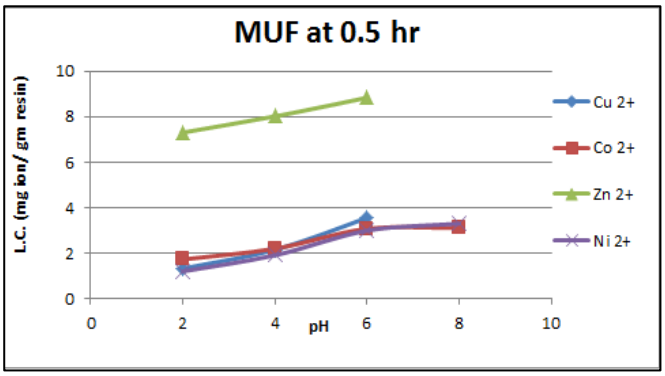

Figure 28: pH effect on total loading capacity of resin MUF towards Cu 2+, Co 2+, Zn 2+ and Ni 2+ ions at time = 0.5 hr

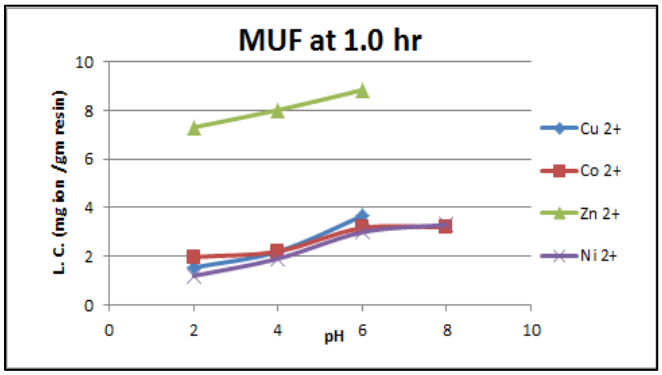

Figure 29: pH effect on total loading capacity of resin MUF towards Cu^{2+}, Co^{2+}, Zn^{2+} and Ni^{2+} ions at time = 1.0 hr

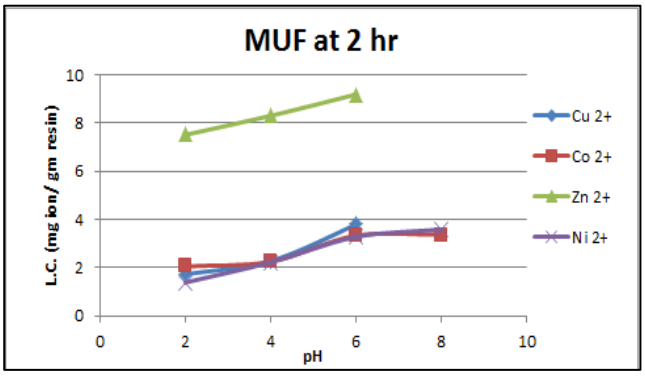

Figure 30: pH effect on total loading capacity of resin MUF towards Cu 2+, Co 2+, Zn 2+ and Ni 2+ ions at time = 2.0 hr

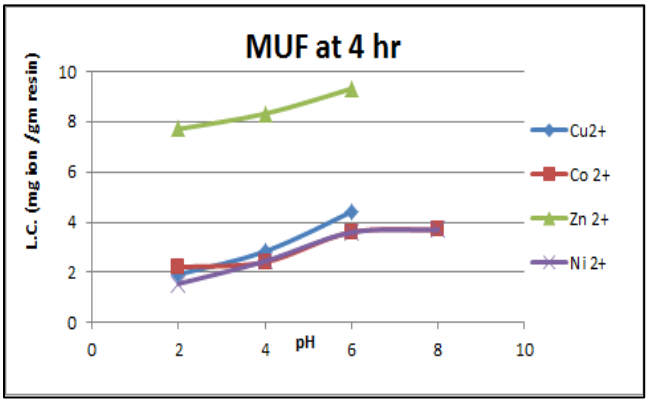

Figure 31: pH effect on total loading capacity of resin MUF towards Cu2+, Co2+, Zn2+and Ni 2+ ions at time = 4.0 hr

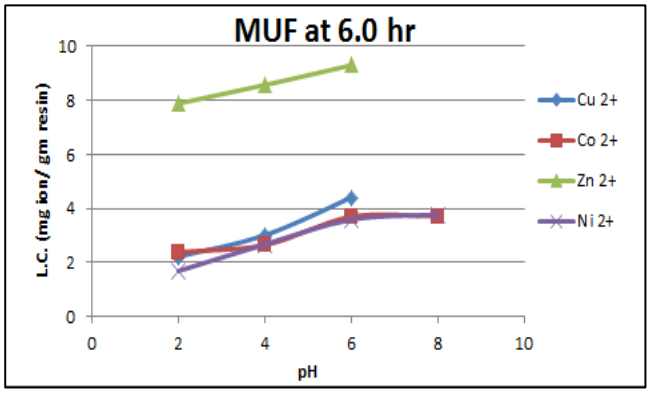

Figure 32: pH effect on total loading capacity of resin MUF towards Cu2+, Co2+, Zn2+ and Ni 2+ ions at time = 6.0 hr

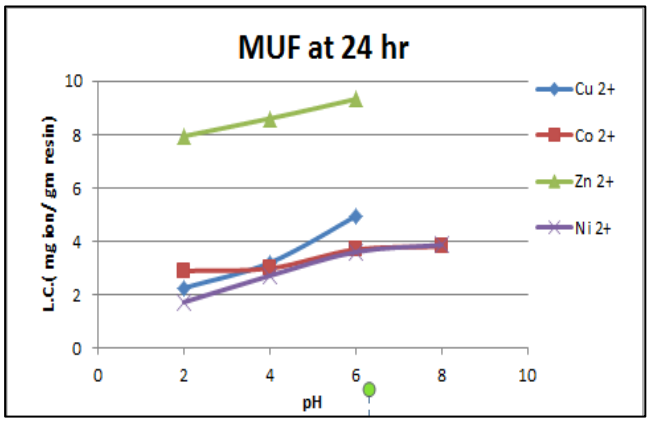

Figure 33: pH effect on total loading capacity of resin MUF towards Cu2+, Co2+, Zn2+ and Ni2+ ions at time = 24 hr

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