

Synthesis and Characterization of Copolymers Derived from Salicylic Acid, Acryloamide, and Furfural (SAF's) and their Study as Ion Exchange Resins for Toxic Divalent Cationic Trace Elements

Al-Imarah F. J. M., Khwedem, A. A. A., and Ibraheem H. K.

Abstract—Terpolymers (SAF's) as an ion exchange resins were synthesized by the condensation of salicylic acid and Acryloamide with furfural in mole ratios of 1:1:2 of the reacting monomers in the presence of hydrochloric acid as catalyst. The resins were characterized by FTIR for the assignment of functional groups and thermogravimetrically analyzed by TGA in which samples were subjected to condition of continuous increase in temperature at linear rate. The thermograms showed that the resin are solids and stabes. The uptake behaviour of synthesized resins for Hg(II), Cd(II) and Pb(II) ions have been studied depending on pH and metal ion concentrations. The study was carried out over a pH range of 5-8 and in a media of certain ionic strengths by using NaNO₃ as an electrolyte. Cadmium and Lead were determined by means of Atomic Absorbion Spectrophotometry, while Mercury was determined spectrofluorometrically by adopting the method of Mudakavi (1984) which modified by Al-Imarah et al (2000). The resin polymer showed a higher selectivity for the removal of these ions in the following order Pb²⁺> Hg²⁺> Cd²⁺ ions. This study could be adopted for industrial waste water treatment.

Keywords— chelating resin, synthesis, distribution ratio, heavy elements, removal of pollutants.

I. INTRODUCTION

The term terpolymerization refers to the simultaneous polymerization of three monomers together (Syed Abuthahir, 2014). On the other hand, The polymer metal complex is a metal complex containing a polymer ligand presenting a remarkably specific structure in which central metal ions are surrounded by an enormous polymer chain (Helfferrich, 1962).

Ion exchange may be defined as the reversible exchange of ions between the substrate and surrounding medium. Ion exchange technique can remove traces of ion impurities from water/process liquors and given out a product of ultra pure quality in a single efficient and techno-economically viable manner. Ion exchangers are widely used in analytical chemistry, hydrometallurgy, antibiotics, purification and

separation of radioisotopes and find large application in water treatment and pollution control (Tarase et al., 2009, Shah et al., 2007). Ion-exchange resins comprise one of the most important scientific developments of the 20th century. Their applicability to water softening, environmental remediation, wastewater treatment, hydrometallurgy, chromatography, bio molecular separations, and catalysis (Shah et al., 2010). Ion exchange is a process in which mobile ions from an external solution are exchanged for ions that are electrostatically bound to the functional groups contained within a solid matrix. When the functional groups are negatively charged the exchange will involve cations and when they are positively charged they involve anions. By taking advantage of the fact that, under certain conditions, ion exchange media have a greater affinity for certain ionic species than for others, a separation of these species can be made; for example, the hydrogen form of a cation exchanger will release its hydrogen ion into solution according to the following equation (Alchin, 2004).

A number of terpolymers derived from phenol derivatives have been studied and reported along with their chelating ion-exchange properties. For example, (Karunakaran, and Burkanudeen, 2002) have synthesized terpolymer from o-nitrophenol-thiourea- formaldehyde and Fe²⁺, Co²⁺, Ni²⁺ and Cu²⁺ were used for chelation. Das, (2000) has derived copolymer from thiosemicarbazone derivatives of phenolic compound. Terpolymers of 8-hydroxy quinoline-formaldehyde-resorcinol/catechol were reported by Shah et al., (2004) and Shah et al., (2003) and chromatographic column separation for various metal ions such as Cu²⁺, Ni²⁺, Zn²⁺, Pb²⁺ and Cd²⁺ have carried out using the quinoline base resins. Rimawi et al., (2004) have studied the chelation behaviour of the phenolic-formaldehyde polymers, poly(2,4-dihydroxybenzoic acid-3,5-dimethylene), poly(2-hydroxybenzoic acid-3,5- dimethylene) and poly(3-hydroxybenzoic acid-4,6-dimethylene) towards the trivalent lanthanide metal ions such as La³⁺, Nd³⁺, Sm³⁺, Gd³⁺ and Tb³⁺ by a static batch equilibrium technique at 25°C as a function of contact time, pH, and concentration. Polymer supported reagents (Beauvais, and Alexandratos, 1998) containing various ligands have been studied for their selective

Al-Imarah F. J. M., Khwedem, A. A. A., and Ibraheem H. K , are with Dept. Chem., & Marine Envir. Poll., Marine Science Centre, Basrah University, Basrah-Iraq.

complexation towards various metal ions. Dabrowski et al.(2004) have efficiently removed trace impurities and toxic metals from industrial waste water by various ion exchangers. o-Nitro phenol and thiourea with para-formaldehyde copolymer was identified as an excellent cation exchanger for Zn^{2+} and Co^{2+} ions (Burkanudeen, and Karunakaran, 2002).

A chelating ion exchange terpolymer resin p-NPHXF was synthesized by the condensation of p-nitro phenol and hexamine using formaldehyde as a cross linking agent at 140 °C in a mole ratios of 2:1:4 in presence of glacial acetic acid as a catalyst. The resin was characterized by FTIR and elemental analysis, and its ion exchange study was carried out with Cd^{2+} and Pb^{2+} (Gaitry Copta, 2014).

Among a recent application in medicine to stop or inhibit a certain tumour growth, a terpolymer complex was synthesized via enzyme catalyzed copolymerization of lactone with dialkyle diester and amiondiol, and their hydrophobically adjusted by varying the lactone content and by selecting a lactone comonomer of specific ring size (Zhou, et al., 2012).

Azarudeen and Burkanudeen (2012) prepared a terpolymer derived from anthranilic acid -phenyl hydrazine - formaldehyde and used it as a ligand for a complexation to metal ions Cu^{2+} , Mn^{2+} , and Zn^{2+} . The prepared ligand (terpolymer) and its metal complexes were intended to spectral characterization viz, FTIR, electronic, ESR, 1H NMR for elucidation of the chemical structures.

Certain metal ions such as Ni^{2+} , Cu^{2+} , and Cr^{6+} present as a pollutants in industrial waste waters could be removed by a

TABLE I
MOLES OF STARTING MATERIALS AND % YIELDS FOR THE SYNTHESIZE OF SPFTERPOLYMER RESINS.

Terpolymer	Reactants (moles)			Catalyst 2 M HCl (ml)	Yield, %
	Salicylic acid	Acryloamide	Furfural		
SAF-1	0.01	0.01	0.02	100	85
SAF-2	0.02	0.02	0.04	100	86
SAF-3	0.03	0.03	0.06	100	91
SAF-4	0.04	0.04	0.08	100	92

B. Determination of metal uptake

Metal uptake was determined in different pH media by using the prepared terpolymers according to the following procedure. Terpolymer sample (25 mg) was suspended in 25 ml electrolyte solution of $NaNO_3$ of known concentration. The pH of the suspension was adjusted to the required value by using suitable reagent of 0.1 N HCl or 0.1 N NaOH. The suspension was stirred for a period of 24 h at 25°C. To this suspension 2ml of 0.1 M 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 h and filtered. The solid was washed and the filtrate and washings were combined and the metal ion contents as well as their concentrations were determined by Atomic Absorption spectrophotometry for Cadmium, and Lead. While for Mercury, the procedure of Mudakavi (1984) modified by Al-Imarah et al., (2000) was used. The procedure for Hg^{2+} uptake was conducted in NaCl as an electrolyte, the results were nearly the same as those for $NaNO_3$ electrolyte.

polymerin microfiltration process and adjusted pH (Swaminathan et al., 2012).

In a recent study a noval chelating terpolymer resin has been prepared by terpolymerization of anthranilic acid, salysilic acid, and formaldehyde (ASF) in a molar ratios of 1:1:2, and the prepared terpolymer were studied spectrophotometrically and thermogravimetrically as well as the selectivity and binding capacity towards certain divalent metals (Azarudeen et al., 2010).

II. EXPERIMENTAL

A. Polymer syntheses

Starting materials Salicylic acid (0.01 M, 1.38g), Acryloamide (0.01 M, 0.71g) and Furfural (0.02 M, 1.92 ml) were mixed in a round bottom flask. 100 ml of 2 M HCl was added slowly to the reaction mixture and the contents were refluxed at 100-120°C for 8-10 hours on an oil bath with periodic shaking. After completion of the reaction, the mixture was poured in ice cold water, filtered and then washed with hot water to remove unreacted starting materials. Finally, the product was washed with alcohol and dried in vacuum. The yield of the terpolymer was found to be about 85-86%. Other SAF terpolymers were synthesized following the same procedure with different stoicheometric starting materials S, A, and F as listed in table 1.

III. RESULTS

The FTIR spectra for typical terpolymer SAF is shown in figure 1, and the typical thermogravimetric analysis curve for SAF resin is shown in figure 2. For the studies of divalent metals uptake by the prepared resin SAF for the ions Hg^{2+} , Cd^{2+} , and Pb^{2+} are given in figures 3,4, and 5 respectively.

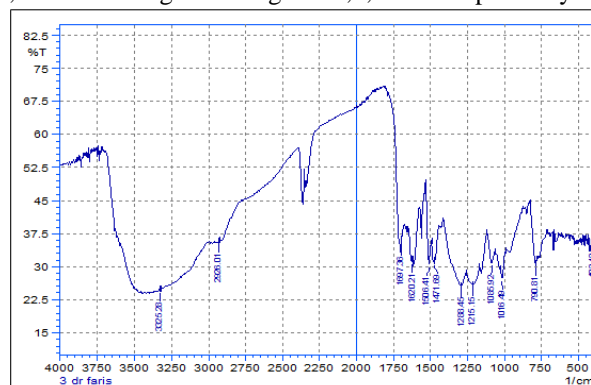


Fig. 1: The FTIR spectrum of SAF terpolymer

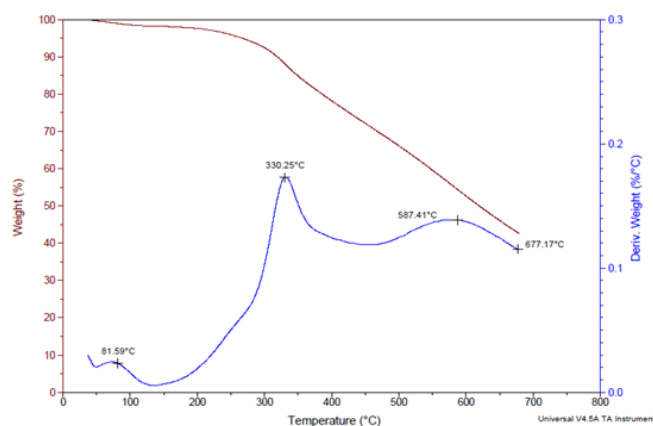
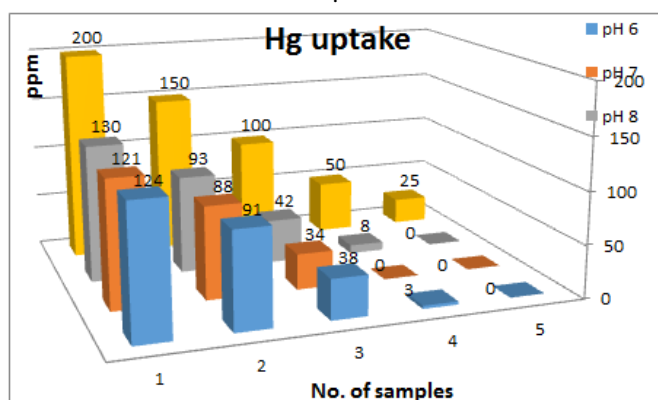
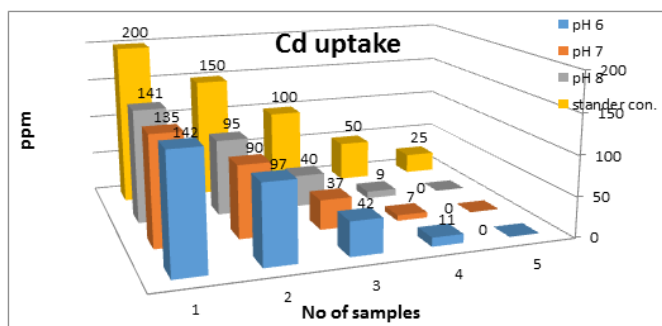
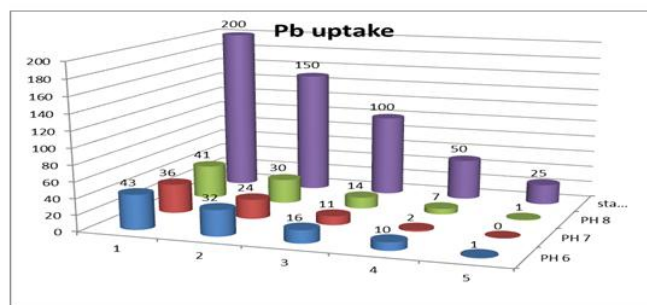
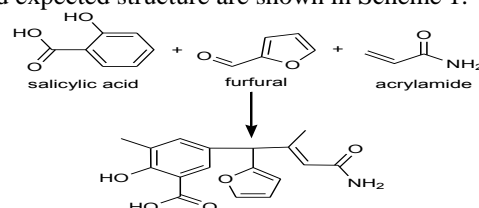


Fig. 2: A typical thermogravimetric analysis curve for SAF resin

Fig. 3: Metal uptake of 25, 50, 100, 150, and 200 µg/ml Hg²⁺ by SAF terpolymer at pH's 6, 7, and 8.Fig. 4: Cd uptake of 25, 50, 100, 150, and 200 µg/ml Cd²⁺ by SAF terpolymer at pH's 6, 7, and 8.Fig. 4: Pb uptake of 25, 50, 100, 150, and 200 µg/ml Pb²⁺ by SAF terpolymer at pH's 6, 7, and 8.

IV. DISCUSSION

The reaction sequence of the synthesis of SAF terpolymer resin and expected structure are shown in Scheme 1.



Scheme 1. Reaction between Salicylic acid (S), Furfural (F), and acrylamide (A) and expected structure for the synthesized SAF's as concentration

According to table 1, the stoichiometric ratios of monomers of S, A, and F were the same leading to increase percent yeild as concentrations of starting materiale were increased (Khwedem, 2013).

The important IR bands which appeared in the recorded FTIR spectrum of the SAF terpolymer resin along with their assignments are tabulated in Table 2. The spectrum shows a broad band at 3325.28 cm⁻¹ due to the (O-H) stretching vibration of Ar-OH involved in the intramolecular hydrogen bonding with Ar-COOH. The strong band appeared at 1288.45 cm⁻¹ is due to (C-N) stretching vibration of Ar-NH₂(Shah et al., 2008). The strong band at 1620.21 cm⁻¹ may be assigned to (C=O) stretching vibration of the carboxyl group present in the resin molecule (Shah et al.,2006). The NH-stretching vibration of amino group seems to be merged with a broad band of -OH group of -COOH groups. The tetra-substitution in the benzene ring is established by the presence of the medium bands at 1016.49 and 790.81 cm⁻¹ which are attributed to (C-H) bending vibration(Raj et al., 2010). The weak band at 2926.01 cm⁻¹ is due to the (C-H) stretching vibration of methylene group (Shah et al., 2008).

TABLE II
FTIR SPECTRAL DATA FOR SAF TERPOLYMER.

Vibrational mode	Wave number (cm ⁻¹)	
	Reported	Observed
-OH of Ar-OH group involved intramolecular hydrogen bonding with Ar-COOH	3500 - 3200	3325.28
Methylene(-CH ₂) stretching	3000 - 2850	2926.01
>C=O Stretching (carboxylic ketone)	1690 - 1620	1620.21
1,2,3,5-Substitued benzene ring	1200 - 800	1016.49 & 790.81
(C-N) Stretching of Ar-NH ₂	1200 - 1300	1288.45
Aromatic ring stretching (C-H)	2700 - 3000	2900

The thermogravimetric analysis is an effective tool to assess the thermal stability of the terpolymer resin. The thermogram of the terpolymer resin SAF which is shown in Figure 2 from which the thermogravimetric data are extracted and tabulated in Table 3, revealed that the SAF resin exhibits three stages of degradation pattern. The first degradation stage begins at 81.59°C and it extends to 330.25°C with the weight loss of 20% which corresponds to the loss of carboxylic group attached to the aromatic ring as CO₂ [Azarudeen et al., 2009.]. The second degradation takes place from 330.25°C and ends at 587.41°C with the weight loss of 35% which may be due to the elimination of side chain attached to the aromatic ring. Finally the third degradation stage starts at 587.41°C and the complete degradation takes place at 677.17°C. After 700 °C almost the entire resin was lost and decomposition could be taken place (karunakaran and Magesh, 2011).

TABLE III
THERMOGRAVIMETRIC DEGRADATION OF TERPOLYMER RESIN SAF

Temperature, °C	Weight loss of resin %
100	-
200	5
300	20
400	25
500	30
600	40
700	60
800	100

The chelating ion-exchange property of the ASF terpolymer resin was adopted for uptaking Hg²⁺, Cd²⁺, and Pb²⁺ ions in a certain concentration of NaNO₃ electrolyte and at a pH range of 5-8 as well as a concentration range for the metal ions in the range 25, 50, 100, 150, and 200 µg/ml. The results for the removal of divalent ions Cd²⁺, Hg²⁺, and Pb²⁺ which are shown in figures 3, 4, and 5 indicate that the amount of metal ions uptake for a given amount of terpolymer resin SAF depends on the nature of the divalent ion and the pH of the medium.

Sodium nitrate was preferred as an electrolyte for uptake of divalent ions Cd²⁺, Hg²⁺, and Pb²⁺ by terpolymer resin SAF due to the formation of weak chelates between the nitrate anion and metal ions (Ahmed et al., 2010). Moreover, the upon the metal Pb²⁺ could be due to the presence of amino and hydroxyl groups in the structure of the resin (Shah et al., 2008, Singru et al., 2008).

The amount of Pb²⁺ ions uptake by the SAF terpolymer resin is higher than that for the ions Hg²⁺, and Cd²⁺, this may be due to the relative weak chelation of Pb²⁺ ions with the anion NO₃ of the used NaNO₃ electrolyte compared to that of the Cd²⁺, and Hg²⁺ ions (Azarudeen, et al., 2008).

The uptake of metal ions by terpolymer resin depend upon the distribution of these metals between the polymer phase and the aqueous phase. Within this study the pH range used were 5-8, higher pH will lead to hydrolysis of metal ions and the formation of metal hydroxide interferes with the ion exchange process (Azarudeen, et al., 2008). For the terpolymer resin SAF, the pH showed a great effect upon the uptake of the

metal ions Hg²⁺, Cd²⁺, and Pb²⁺. The results revealed that the optimum pH value was 7 in which the uptake was completely leading to zero concentrations of the metal ions and the order of the removal of the toxic metal ions was Pb²⁺ > Hg²⁺ > Cd²⁺.

V. CONCLUSION

The distribution of metal ions between terpolymer phase and the aqueous phase depend upon the metal ion, terpolymer resin, and the pH of the solution. All of these electrolyte parameters have a great effect upon the ion exchange resins, the removal or uptake of the toxic trace element ions by a certain terpolymer ion exchange resins. According to this study, the prepared terpolymer SAF could be used to remove toxic elements Cd²⁺, Hg²⁺, and Pb²⁺ ...etc which may exist in the industrial waste water before water recycling or discharging directly into surface water. For even more effective removal of toxic ion pollutants, this procedure could be adopted together with any other technique such as RO, Ultrafiltration, membrane separation ... etc. Furthermore, the results of this study revealed that the most effective composition for the removal of toxic ions is the following: SAF terpolymer resin, at pH 7 and NaNO₃ as an electrolyte.

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