AL- Muthanna Journal of Pure Sciences ……Number(2) ….Volume(1)…..
.September/2013…Eng

Synthesis and characterization of copolymer derived from salisylic acid, furfural and resorcinol and its chelating complexation to cationic trace elements.

Abdalhussein A. Khwadem, Faris J. M. Al-Imarah*, and Mohammed A. Muter

Chem. Dept., Educ. Coll., Al-Qadisyah University, Al-Qadisyah-Iraq

****Marine Chem., &Envir. Poll.Dept., Marine Science Centre, Basrah University, Basrah-Iraq***

Abstract:

Terpolymer resins based on Salicylic Acid, Furfural, and Resorcinol (SFR) were synthesized by thecondensation reaction inthe presence of hydrochloric acid as catalyst for their studies as selectivechelatingion exchange terpolymer resins for certain metals. Chelating ion exchangeproperties of these terpolymers were studied for Hg^{2+}, $Cd^{2+}$and Pb^{2+}metal ions uptake. A batch equilibrium method was employed in the study of selectivity and distribution of a given metal ions between the polymersample and a solution containing the metal ion. The study was carried out over a pH range of 5-7 and in a media of various ionic strengths. Cadmium and Lead were determined by means of Atomic Absorbtion Spectrophotometry, while Mercury was determined spectrofluorometry by adopting the method of Mudakavi which modified by Al-Imarahet al., The polymer showed ahigher selectivity for the removal of these ions in the following order$Pb^{2+}>Hg^{2+}>Cd^{2+}$ ions.

Key Words: Terpolymer, Trace ions, selectivity, pollution, removal.

Introduction

Ion exchange may be defined as the reversible exchange of ions between the substrate andsurrounding medium. Ion exchange technique can remove traces of ion impurities fromwater/process liquors and given out a product of ultra pure quality in a single efficient andtechno-economically viable manner. Ion exchangers are widely used in analytical chemistry,hydrometallurgy, antibiotics, purification and separation of radioisotopes and find largeapplication in water treatment and pollution control (Helfferich, 1962; Kunin, 1958). 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,biomolecularseparations, and catalysis (Mueller, et al., 1989).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. Ion exchanges derived from three moieties ae known as terpolymers are found to exhibits better physical properties than those of phenol-formaldehyde copolymer (Masram, et al., 2011). Chelation ion exchange resins derived from 2-hydroxy-4-methoxyacetophenone and thiourea with trioxane was investigated by Pancholi et al., (1991). Masram et al., (2011) have synthesized a number of resins by reacting p-hydroxybenzoic acid with diamines and formaldehyde in a medium of 2M HCl as a catalyst to be selective chelating ion-exchange resins for certain metals. Determination of selected metal ions Cd^{2+}, Hg^{2+}, and Pb^{2+} following the procedure of liquid-liquid extraction by using calyx[n]arenes (Roundhill et al., 2009).

Experimental

Preparation of Salicylic acid Furfural and Resorcinol terpolymer (SFR) by condensation of Salicylic acid (S), Furfural(F), and Resorcinol(R) according to the following procedure: A mixture of Salicylic acid(0.1mol), Furfural (0.2mol), Resorcinol (0.1 mol) and200 mLof 2M hydrochloric acid were taken in a round bottom flask fitted with water condenser and heated in an oil bath at 120 ^{o}C for 10 hours with occasional shaking. The black colored solid product obtained was immediately removed and extracted by diethyl ether to remove excess of salicylic acid, furfural and resorcinol, which might be present along with the SFR terpolymer. It was further purified by dissolving in 8% NaOH and then filtered. The terpolymer was then reprecipited by drop wise 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 yield of the terpolymer was found to be about 85-86%. Other SFR terpolymers were synthesized following the same procedure with different stoicheometric starting materials S, F, and R as listed in table 1.

Table 1: Moles of starting materials and% yields for the synthesize of SFR terpolymer resins.

Terpolymer	Reactants			Catalyst 2M HCl ml	Yield, %
	Salicylic acid moles	Resorcinol Moles	Furfural moles		
SFR-1	0.1	0.1	0.2	200	85
SFR-2	0.2	0.1	0.3	200	86
SFR-3	0.3	0.1	0.4	200	85
SFR-4	0.4	0.1	0.5	200	85

The Infrared spectra for the synthesized SFR terpolymers were recorded in the region of500–4000 cm^{-1} by using Shimadzu FTIR infrared spectrophotometer.

Determination of metal uptake

Metal uptake was determined in different pHmedia 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 byusing suatible reagent of 0.1 N HCl or 0.1 N NaOH. The suspension was stirred for a period of 24 h at25°C. To this suspension 2 ml of 0.1 M solution of the metal ion was added and the pH wasadjusted 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 ioncontents as well as their concentrations were determined byAtomic Absorption spectrophotometery 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 Na NO_3 electrolyte.

Exchange capacity between metal ions and synthesized terpolymers.

The capacity of the terpolymers to bind metal ions were studied as follows b: A 5 ml metal standard solution in 2% nitric acid was added to approximately 15 ml of water. Then, 10 mg of terpolymer dissolved in 5 ml of water was added to the metal ion solution by adopting the procedure of Sauer et al., (2004). The pH slowly adjusted to the required value with dilute NaOH solution, and the volume was completed to 25 ml with water. After 24 h of mixing the solution was ultrfiltrated on an appropriate filter paper to retain the terpolymer-metal ion complex. Both the initialsolution and the permeate solution were analyzed for metal and the retained, bound metal then calculated as:

$$\text{Loading capacity} = \frac{\text{mmol of metal}}{\text{g terpolymer}} = \frac{(C_i - C_p) X V}{1{,}000 X p X A}$$

where C_i= the initial concentration of metal ion,

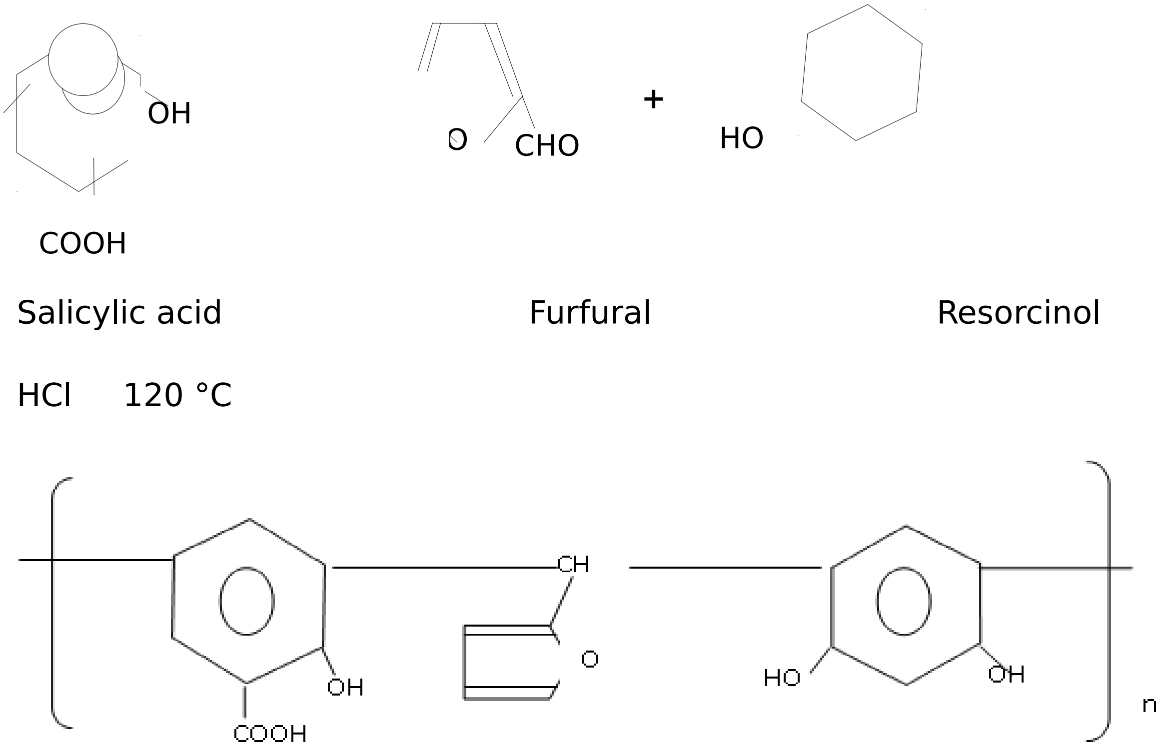
C_p = concentration of metal ion in the permeate (ppm),

V =volume of initial solution(ml),

P = amount of terpolymer used (gm),

A = Atomic weight of the metal ion (g/mole).

The resin samples wereblack in color, insoluble in commonly used solvent, but soluble in strong base. Noprecipitation and degradation occurs for resins in all solvents.



Scheme 1. Reaction between Salicylic acid (S), Furfural (F), and Resorcinol (R) and

expected structure for the synthesized SFR's terpolymers (Alchin, 2004).

Table 2: physicochemical properties for the synthesized SFR terpolymers.

Polymers Solvents	SFR-1	SFR-2	SFR-3	SFR-4
Color	**Black**	**Black**	**Black**	**Black**
Melting point	**-**	**-**	**-**	**-**
Water	**-**	**-**	**-**	**-**
NaOH 10%	**+**	**+**	**+**	**+**
DMF	**-**	**-**	**-**	**-**
DMSO	**-**	**-**	**-**	**-**
H_2SO_4	**-**	**-**	**-**	**-**
CCl_4	**-**	**-**	**-**	**-**
Benzene	**-**	**-**	**-**	
Methanol	**-**	**-**	**-**	**-**
CS_2	**-**	**-**	**-**	**-**
$CHCl_3$	**-**	**-**	**-**	**-**

Infrared spectra

FTIR Spectrum for SFR-1 is shown in Figure 1.

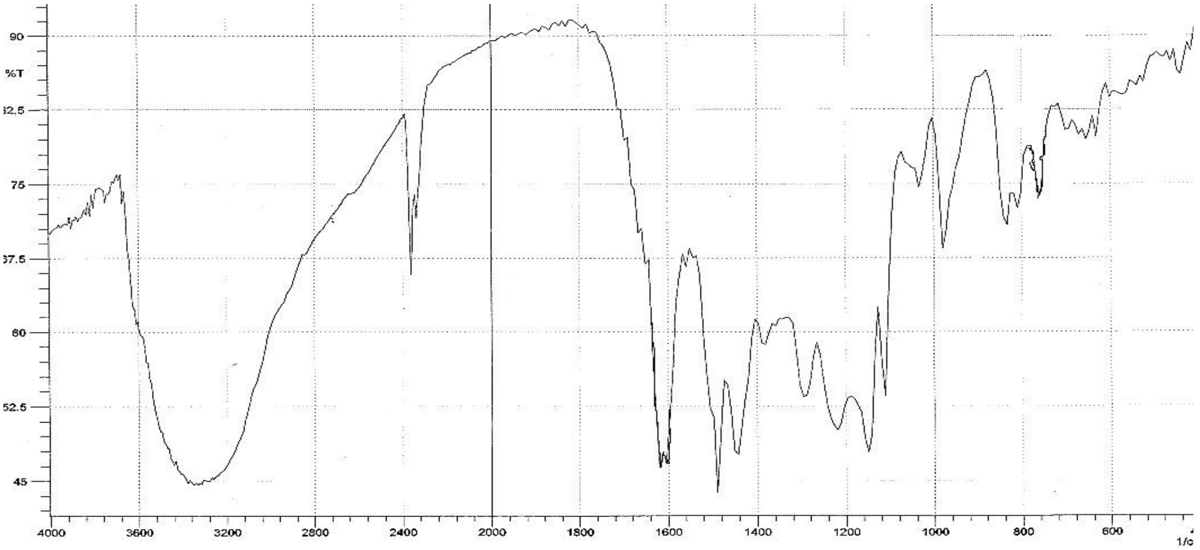


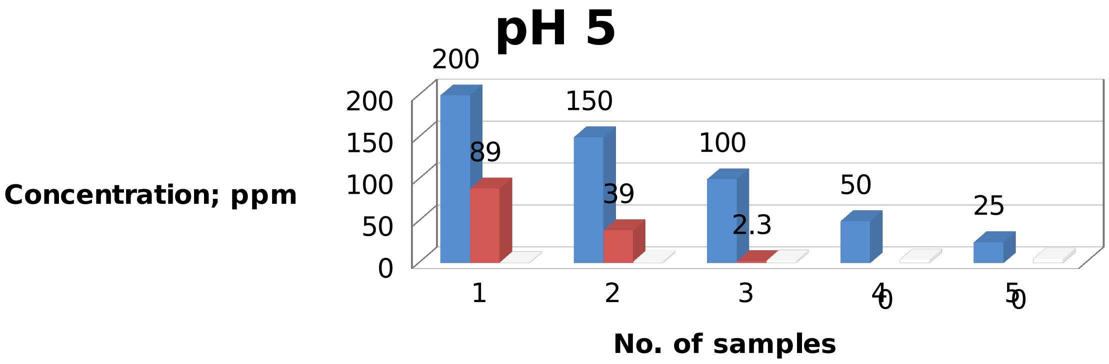
Figure 1: The IR spectrum of SFR-1 terpolymer.

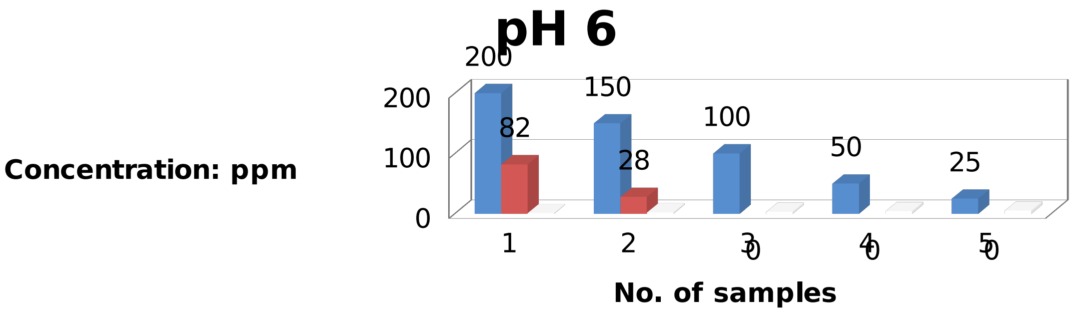
cm

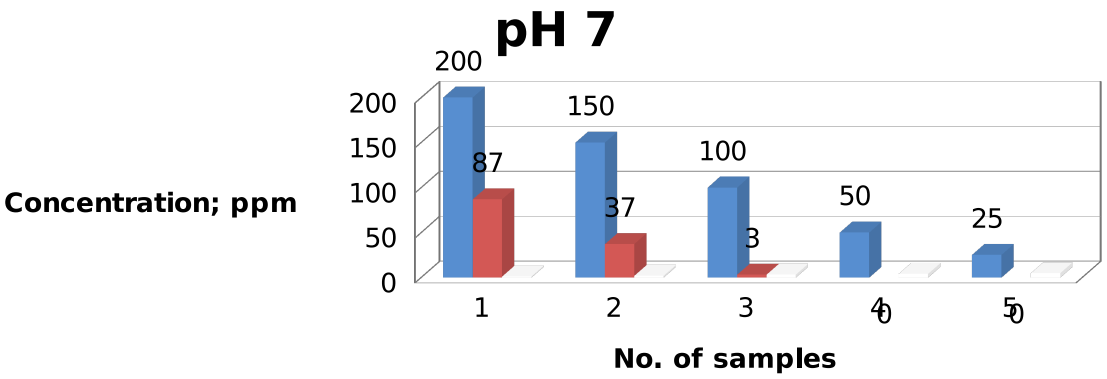
All IR Spectra for SFR's terpolymers which are recorded in a KBr matrix showed a peak in the range of 3500 to 3200 cm^{-1}(Kattamwar, et al., 2009). Those peaks are Attributed to the stretching vibration of the -OH group of the polymeric associated phenolic group and the intermolecular H bonding between the hydroxy group of -COOH from different acid units in the polymeric chain. The band at 1640 cm^{-1} was observed because of >C=O (carboxylic kitone) stretching (Shah, et al., 2009). A peak at 2930.7 cm^{-1} are due to aromatic skeletal ring stretching modes (Shah, et al., 2009). The band in 2350 cm^{-1} refers to presence CO_2.The band observed between 1200 and 800 cm^{-1}could be caused by a 1, 2, 3, and 5-tetra substituted benzene ringGurnule and Dhote, 2012).The inflections around 1464, 787 and 1321.6 cm^{-1} were due to the stretching, and bending of -CH which suggested the presence of methylene bridges in the terpolymer (Shah, et al., 2007).

Metal uptake by SFR's terpolymer:

The chelating ion exchange properties of the SFR's terpolymers were examined for metal ions Cd^{2+}, Hg^{2+}, and Pb^{2+} uptake at different pH, the study was proceeded for pH's 5, 6, and 7. Figures 2-4 shows the metal ion uptake ofmercury by SFR1 terpolymer at different pH in which uptake was increased from pH 5 to pH 6 then decreased at pH 7.

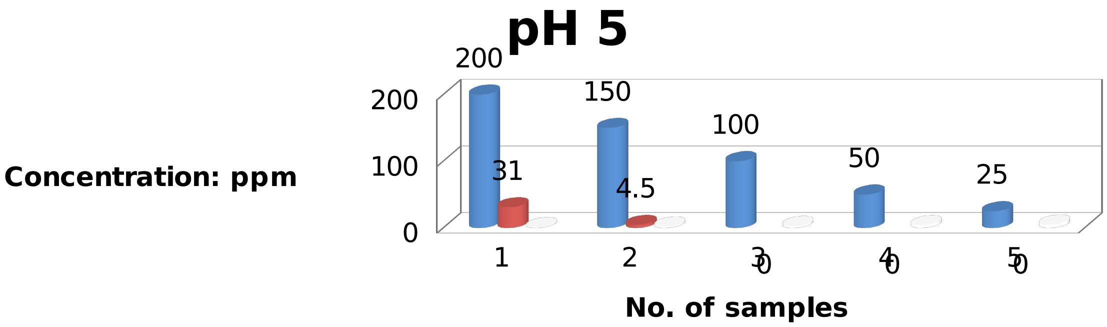


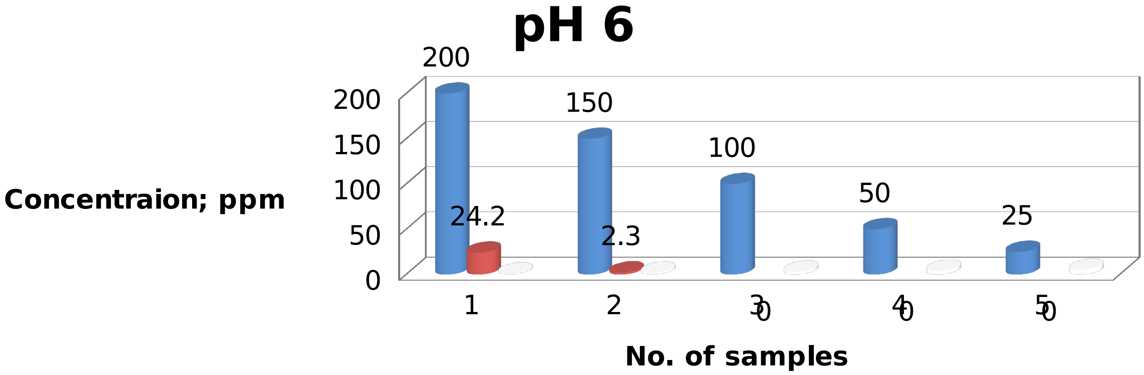


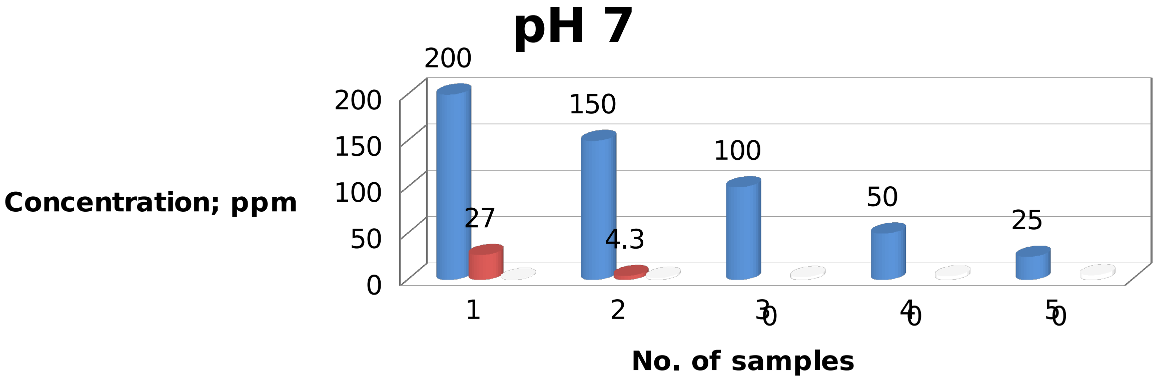


Figure; 2: Metal uptake of 25, 50, 100, 150, and 200 µg/ml Hg^{2+} by SFR1 terpolymer at pH's 5, 6, and 7.

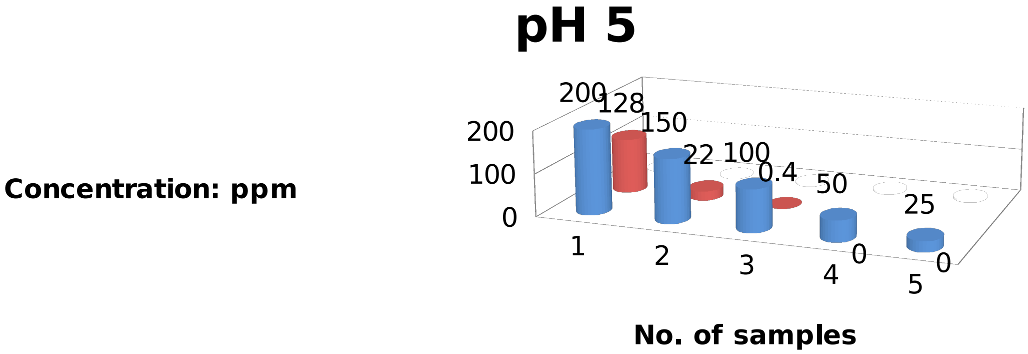
For Pb^{2+} and Cd^{2+} uptake at pH's 5, 6, and 7 by SFR1 terpolymer showed the same behavior as that for Hg^{2+} as shown in Figs. 3 and 4 respectively.

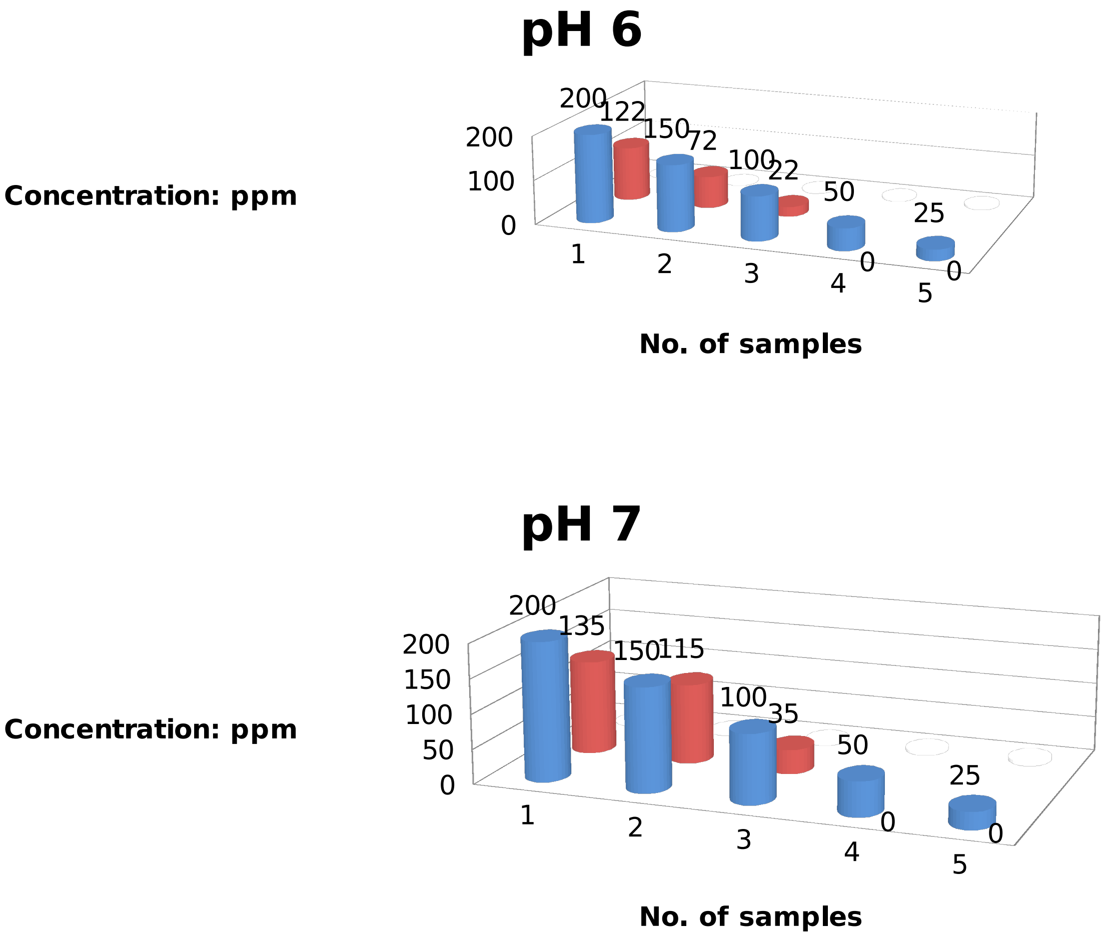






Figure; 3: Metal uptake of 25, 50, 100, 150, and 200 μg/ml Pb^{2+} by SFR1





Figure; 4: Metal uptake of 25, 50, 100, 150, and 200 µg/ml Cd^{2+} by SFR1 terpolymer at pH's 5, 6, and 7.

The exchange capacity determines how much metal ions the terpolymer could be bind. For complete removal of mercury ions from the solution it is found that capacity of terpolymer SRF-1 was 147.53mg/ml at pH 6, Table 2, for lead it is found to be 217.557 mg/ml at pH 6, Table 3, while for cadmium it is found to be 97.55mg/ml at pH 6, Table 4.

Table 2.Capacity of SFR-1 terpolymer to mercury ions at different pH.

pH	5	6	7
Capacity mg/g	138.69	147.53	141.3
Distribution Percentage Ratio	55.5	59	56.5

Table 2.Capacity of SFR1 terpolymer to lead ions at different pH.

pH	5	6	7
Capacity mg/g	217.557	217.557	216.315
Distribution Percentage Ratio	84.5	87.9	86.5

Table 2.Capacity of SFR1 terpolymer to cadmium ions at different pH.

pH	5	6	7
Capacity mg/g	90.05	97.55	81.2
Distribution Percentage Ratio	36	39	32.5

The data on the distribution ratios of the studied metal ions as a function of pH indicate that the amount of metal ions taken up by the SFR terpolymers increase with increasing pH of the medium to a certain extent (pH 6) then it will decrease (Tarase et al.,2009) . This fact indicate that the distribution of metal ions depend upon pH of the solution. By increasing pH, the H^+ ion concentration in the solution decrease and only metal ion in the solution available for adsorption which increase uptake of metal ions (Patle, et al., 2011). The order of the distribution ratio of studied metal ions within SFR terpolymers measured in the pH range 5-7 found to be $Pb^{2+} > Hg^{2+} > Cd^{2+}$. The study was carried out only to pH=7 in order to prevent hydrolysis of the metal ion at higher pH (Masram et al., 2011).

Conclusion

The synthesized resins were proved to be selective for certain metal ions over a wide pH range. Because of their highly insolubility, terpolymers provide good stability and good flexibility in working conditions.

References

Alchin, D.(2004). Ion exchange resins. Service Chemist, Drew New

Zealand.pp 7

Al-Imarah, F. J. M., Jawad, A. H. M., and Kevork,S. A.,(2000). Levels of
mercury in ground water at Zubair and Safwan, South of Iraq. Basrah J.
Sci., 16:1-6.

Gurnule, W. B., and Dhote, S. S., (2012). Preparation, Characterization and
Chelating Ion-exchange Properties of copolymer Resin Derived from
2,4-Dihydroxy Benzoic acid, Ethylene Diamine and Formaldehyde. Der
PharmaChemica, 4 (2):791-799
Helfferich F,(1962). Ion Exchange Resins, Mc-Grow Hill:New York.S. S. Kattamwar, A. B. Zade, S. S. Rahangdale and W. B. Gurnule(2009).
Terpolymer resin-III: synthesis and characterization of 8-
hydroxyquinoline-dithiooxamide-formaldehyde terpolymer resin. J.
Appl. Polym. Sci. (113): 3330-3335.
Kunin R,(1958). Ion Exchange Resins, 3rd Ed; Wiley:New York.
Masram, D. T., Kariya, K. P., and Bahave, N. S. (2011).Physicochemical and
ion exchange studies of resin derived from p-hydroxybenzoic acid and
phenlenediamine with formaldehyde.Adva. Appl. Sci. Res. 2(4):156-
165.
Mudakavi, J. R. (1984). Spectrophotometric determination of trace amount
of mercury with phenanthroline and eosin. Analyst, 109:1577-1599.Mueller, C. S.,Romelowand, G. J., and Beck, J. N., Bull(1989). Environ.
Contam.Toxic. pp, 42-56.
Patle, D. B., Gurnule, W>B., and Zade, A. B. (2011). Synthesis,
characterization and ion-exchange properties of a terpolymer derived
from 4-hydroxybenzophenone, biuret and formaldehyde. Der Pharma
Chemica, 3(3):341-353.
Sauer, N. N., Ehler, D. S., and Duran, B. L. (2004). Lead extraction from

contaminated soil using water-soluble polymer. J. Envir. Engin. 130(5) :585-588.

Shah, B., A., Shah, A. V., and Patel N. B. (2008). A Benign Approach of Microwave Assisted Synthesis of Copolymeric Resin with Improved Thermal, Spectral and Ion-exchange Properties. Iranian Polymer Journal. 17 (1): 3-17

Shah, B. A., Shah, A. V., and Bhatt, R. R.,(2007). Studies of chelation ion exchange properties of resin copolymer derived from salicylic acid and its analytical applications, Iran Polym. J, 16, 173-184.

Tarase, M. V., Gurnule, W. B., and Zade, A. B. (2009). Ion exchange properties of a terpolymer resin derived from 2, 4-dihydroxybenzaldehyde, oxamide and formaldehyde. E. J. Chem., 6(3):639-650.

تخليق و تشخيص راتنج بوليمر ثلاثي من حامض السلسليك والفورفورال والريسورسينول ودراسته كمعقد مخلبيا نتقائي لعدد منايوناتال معادن النزرة الموجبة.

عبدالحسين عليعل خويدم , فارس جاسم محمد الأمارة * ومحمد علي مطر

جامعة القادسية / كلية التربية / قسم الكيمياء

* جامعة البصرة / مركز علوم البحار / قسم الكيمياء البيئية والتلوث

الخلاصة

تم تخليق راتنج البوليمرالثلاثي والمتكون من حامض السلسليك والفورفورال و الريسورسينول حيث تفاعلت المواد المذكورة اعلاه على طريقة بلمرة التكثيف بوجود حامض الهيدروكلوريك كعامل محفز للتفاعل. ودرست خصائص البوليمر الثلاثي كمعقد مخلبي انتقائي لأيونات الزئبق, والرصاص والكادميوم الثنائية التكافؤ. درست خصائص البوليمر الثلاثي ومدى امتصاصة لهذه الأيونات من خلال تحضير مجموعة من المحاليل المحتوية على هذه الأيونات بتراكيز مختلفة ثم معاملتها مع البوليمر وتحديد الأمتصاصية لة من خلال فرق التركيز قبل وبعد المعالجة وقد اجريت هذه القياسات على مدى من الدالة الحامضية تراوح 5-7 ثم تم تحديد عملية توزيع الأيونات بين البوليمر والمحلول. تم قياس ايونات عنصر الزئبق على طريقة Mudakavi والتي تم تعديلها من قبل Al-Imarah et al.,
بواسطة جهاز التفلور اما ايونات عناصر الرصاص والكادميوم فقد قيست بواسطة جهاز طيف الأمتصاص الذري. وقد كانت قدرة البوليمر على ازالة هذه الأيونات على الترتيب التالي $Cd^{2+} >$ $Hg^{2+} < Pb^{2+}$