Journal of Natural Sciences Research www.iiste.org
ISSN 2224-3186 (Paper) ISSN 2225-0921 (Online)
Vol.3, No.11, 2013

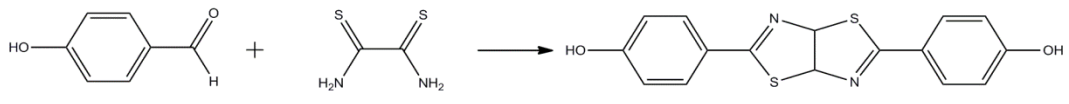
Chelating ion-exchange Properties of Polyurethane Resin Derived from Thiazolo[5,4-D]Thiozole

Einas A. Al-Nasir[1], Dhia A. Hassan[2] , Maher K. Ali[3] and Ali H. Al-Mowali[4*]
1. Department of Chemistry and Polymer Technology, Polymer Research Center, University of Basra, Iraq. 2. Department of Materials Science and Engineering, College of Materials, Xiamen University, Xiamen 361005, China
3. Department of Chemistry,Faculty of Science, Zakho University, Duhok, Iraq.
4. Department of Chemistry, College of Science, University of Basrah, Basrah, Iraq.
* E-Mail of corresponding author:ali_almoali@yahoo.com

Abstract
3,6-dihydrothiazolo [5, 4-d] thiazole which supported on polyurethane was synthesized. The prepared compound was characterized by FTIR and ^{1}H NMR spectroscopy. The chelating properties towards various metal ions Pb^{2+}, Mn^{2+}, Cr^{3+}, $Co^{3+}$and Cd^{+3} was examined. The effects of concentration of metal ions, time of extraction and pH as well as the recovery of ions have been studied. The results showed that the high activity order of resin to extract the metal ions is Pb^{2}> Cd^{+3} > Mn^{2+}>Cr^{3+}> Co^{3+}.
Keywords: thiazole, polyurethane, chelating resin, chelating efficiency, coordination polymers

1. Introduction
In the last years, coordination polymers and metal-organic frameworks have been widely studied, and the number of new species belonging to these categories has impressively risen(Long&Yaghi 2009). This is largely due to the extreme versatility of their chelating properties towards various metal ions(Abed El-Moniem N.M., El-Sourougy M.R.and Shaaban D.A.F. 2005), (Ahmad B.,Hall P.J.& Heslop J. 2007), (Singanan & P. Edward 2013), (Murthy K.S.R. & Marayya R. 2011).Various new chelating polymeric resins have been reported and found use as ion exchangers (Treavor H. & Philips B. 2007),(Shah B.,Shah A. &Patel N 2008), (Tarase M.V., Zade A.B.&Gurnule W.B. 2008). However , no work has been carried out on synthesis ,characterization and ion exchange properties of the 3,6-dihydrothiazolo(5,4-d) thiazole supported on polyurethane. The purpose of the present study ,is to explore the chelating properties of five metal ions Pb^{2+} , Cd^{3+} , Mn^{2+} Cr^{3+} and Co^{3+} on the newly synthesized thiazole supported on polyurethane as a function of pH values, concentration of metal ions and time of extration.This work is described in detail in the following sections.

2-Materials and Methods
2-1Materials
Cadmium nitrate tetrahydrate, chromium nitrate, cobalt nitrate hexahydrate, lead nitrate and manganese chloride were obtained from Fluka, 2-chloroethanol, 4-hydroxybenzaldehyde, chloroform, dithiooxamide**,** hydrochloric acid, methylene diphenylisocyanate , polyester polyol and potassium carbonate were obtained from Merck. Solvents were used after being purified according to the standard method.
2- 2 Instruments
Melting points were determined with a BUCHI apparatus. IR spectra were recorded on FTIR spectrophotometer Shimadzu model affinity (as KBr disks).^{1}H NMR spectrum was recorded on Varian unity 200 MHz. The flame atomic absorption spectroscopy Phoenix – 986 AA model.
2-3 Preparation Methods
2-3 -1 Synthesis of 4,4'-(3a, 6a-dihydro thiazolo [5, 4-d] thiazole-2, 5-diyl) diphenol (1)
As reported earlier (Long&Yaghi 2009) , the synthesis reaction of compound (1) was carried out in three necks round bottom flask with condenser, 3.61 g (30mmol) of dithiooxamide and 4.32 g (60 mmol) of 4-hydroxybenzaldehyde were stirred under reflux temperature at oil bath for 2 hours. The hot mixture was cooled to room temperature, the obtained crystal product has yellow color which was filtered, washed three times by ethanol and dried at room temperature for 48 hour, mp: 220 C^o. The synthetic rout is shown in scheme 1.

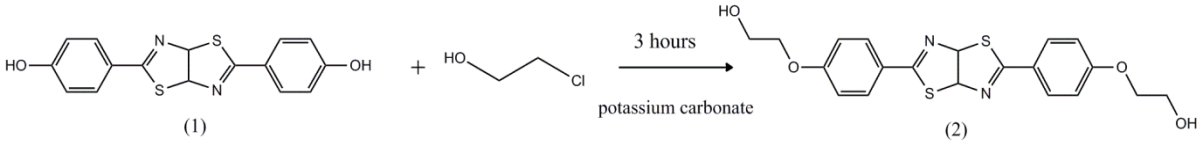


(1)

Scheme 1: Synthesis of compound (1).

2-3-2 Synthesis of 2,2'-(4,4'-(3a,6a-dihydrothiazolo[5,4-d]thiazole-2,5-diyl)bis(4,1-phenylene)) bis(oxy)diethanol (2)

Three necks round bottom flask with condenser was charged with 9.85 g (30 mmol) of compound (1), 4.15 g (30 mmol) potassium carbonate and 4.83 g (60 mmol) 2-chloroethanol. 25ml of ethanol was added to reactants and mixed by mechanical stirrer under reflux temperature at oil bath for 3 hours. The hot mixture was filtered and concentrated then extract from chloroform, yellow viscous product was obtained from the aqueous layer, and the synthetic rout is shown in scheme 2.



Scheme 2: Synthesis of compound (2).

2-3-3 Supported the compound (2) on polyurethane

0.25 g of compound (2) and 0.4 g polyester polyol were mixed with water as a swelling agent and then 0.6 g of methylene diphenylisocyanate (MDI) was added to the mixture and the product foam left for 24 hours to complete the process of hardening at room temperature; the resulting foam was crushed and characterized by infrared spectroscopy.

2-3-4 Preparation of the metal ion solution with polyurethane foam.

The solutions of 100 ppm of metal Ions were prepared in different PH (2, 4, 6,and 8) .10 ml of the prepared solutions were mixed with0.1 gm of polyurethane foam for different time (0.5, 1, 2, 3, 4, 5, and 24) hours.This solution was filtered and isolated; the concentration of metal ions was measured by flame atomic absorption spectroscopy.

2-3-5 Reactivate the resin and the percentage of recovery.

0.1 g of resin was mixed with an ion solution at best condition to give the highest load capacity of the ion solution element100 ppm for 24 hours. The solution was filtered, and the resin was collocated.After drying 10 ml of 3N HCl in round bottom flask was re-shaked and the concentration of the element was determined by flame atomic absorption spectroscopy.

3. Results and Discussion

3-1 Structur Characterization of 3, 6-dihydrothiazolo [5, 4-d]thiazolederivatives.

The 3,6-dihydrothiazolo [5, 4-d] thiazole derivatives compound (2) was established from their IR spectrum as shown in Table 1. The IR spectrum (Figure 1) exhibited a broad band at 3500- 3140 cm^{-1} which was referred to the O-H stretching, the band of aromatic and aliphatic C-H stretching was appeared at 3100- 3000 cm^{-1} and 3000-2900 respectively. Two weak bands at 2000-1800c m^{-1} are reffered to an ovrton transitions for aromatic ring . C=N stretching has a strong band apperead at 1650 cm^{-1}.

The ^{1}H NMR spectrum of compound 2 was recorded at 200 MHz in $CDCl_3$ and characterized by three groups, aliphatic CH_2 group which showed triplet signals at 3.646 ppm and at 3.93 ppm, The signals of the proton adjacent to aromatic rings appears at 6.88 and 7.52 ppm by two doublet signals with coupling constant of 8.8Hz, the signal at 5.07 ppm attributed to the alcoholic OH.

3-2 Chelating efficiency of the prepared resins.

Figures(3-7) Show that, the exchange capacity for Pd^{2+} , Mn^{2+} , Cr^{3+}, $Co^{3+}$and Cd $^{3+}$ by the prepared resin as a function of PH and the effect of treatment time. The chelating capacity of the metal ions toward prepared resin is slightly effected by the change of PH values in the range of (1-8). The maximun exchange capacity of Mn $^{2+}$,Cr $^{3+}$ and Co $^{3+}$ is higher than that of pd $^{2+}$ and Cd $^{3+}$.The transition elements pd^{3+} and Cd $^{3+}$ having greater hydrated ion radius than 3d series transition metal ions (Mn $^{2+}$, Cr $^{3+}$ and $^{Co3+}$) under study. This will results in electrostatic attraction between the metal and coordination group ,lower the comples stability and hence lower the capacity (Shah etal 2013).

The effect of treatment time As shon in figures (3-7) indicates pronounced loading capacity at each PH value,while controlling other variable such PH, temperature, metal ion concentration and volume of the studied solution.

The process of restoring the ions from the resin loaded, and the difference between the concentration of the down trend with acid 3N HCl component and focus associated with the resin percentage calculated to recover the element at 24h is shown in the Table(2)

4.Conclusion

From the above results it may concluded that the chelating polyurethane resin derived from thiazolo(5,4-d) thiazole may be used to recover certain metal ions from waste solutions and used for the purpose of purification

of waste water.

References

Long J.R. and O.M. Yaghi (2009),The pervasive chemistry of metal–organic frameworks, *Chem. Soc. Rev*.,38(12),1213-1214.

Abd El-Moniem N.M.,El-Sourougy M. R.and Shaaban D.A.F.(2005), Heavy metal ions remaval by chelating resin,pigment and resin technology,34(6) 332-339.

Baraka A., Hall P.J. and Heslop M.J.(2007),Melamine-formaldhyde-NTA chelating gel resin:synthesis,characterisation and application for copper(II) ion removel from synthetic wastewater, J. Hazardous Materials ,140(1-2),86-94.

Singanan and Peters E(2013), Removel of toxis heavy metals from Synthetic wastewater using a novel biocarbon technology, J. Enviromental Chemical Engineering, 7,30-38.

Murthy K.S.R. and Marayya R. (2011),Studies of the Removal of Heavy Metal Ions from industrial effluents using ammonium pyrrolidine dithio carbamate loaded polyurethane foams, Applied Sciences Journal,12(3),358-363.

Treavor H. and Boyer C. (2007), A pilot-scale evaluation of magnetic ion treatment for removal of natural organic materials and inorganic ions, Water research,40,2865-2876.

Shah B., Shah A. and patel N.A Bengin(2008). Approach of microwave assisted synthesis of Co polymeric resin with improved thermal, spectral and ion-exchange properties, Iranian polymer j.,17,3-17.

Tarase M.V.,Zade A.B. and Gurnule W.B.(2008), Resin: Synthesis, Characterization and ion exchange,108,738-746.

Shah P. M.,Shah B.A.and Shah A.V.(2008),Selective sorption of heavy metal ions from aqueous solutions using m-cresole based chelating resin and its analytical applications,Iranian J. Chem.Eng.29(2),49-58.

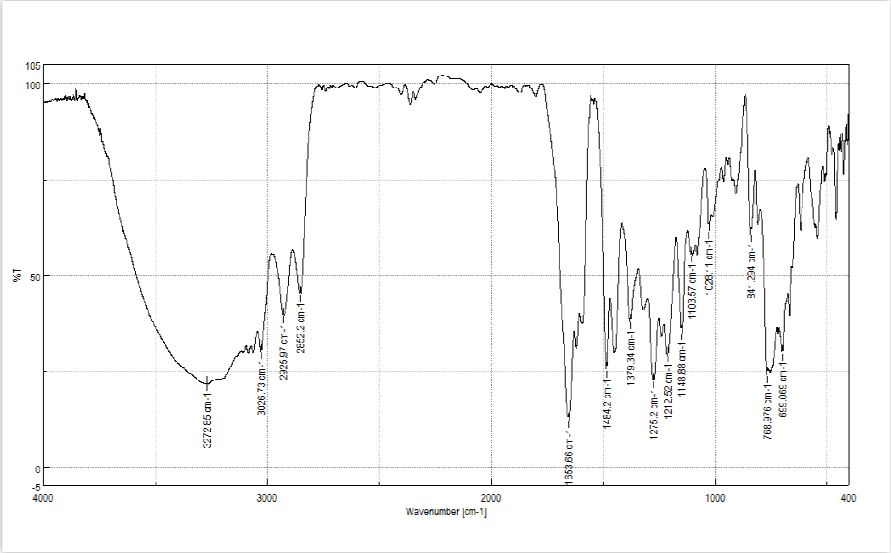


Figure 1. IR spectrum of compound (2).

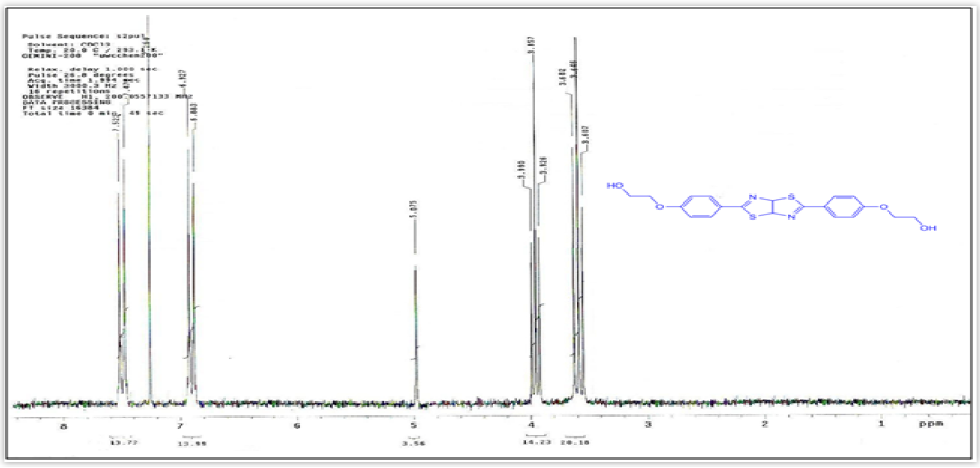


Figure 2. Proton NMR spectrum of compound (2).

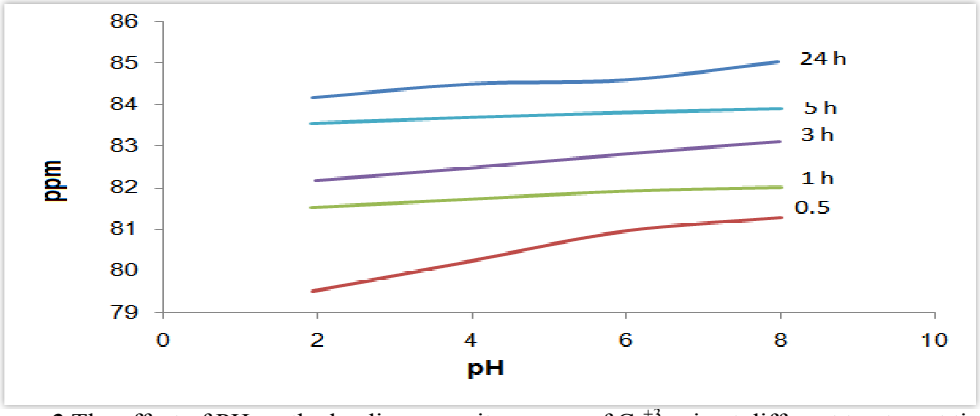


Figure 3. The effect of PH on the loading capacity curves of Cr^{+3}resin at different treatment times.

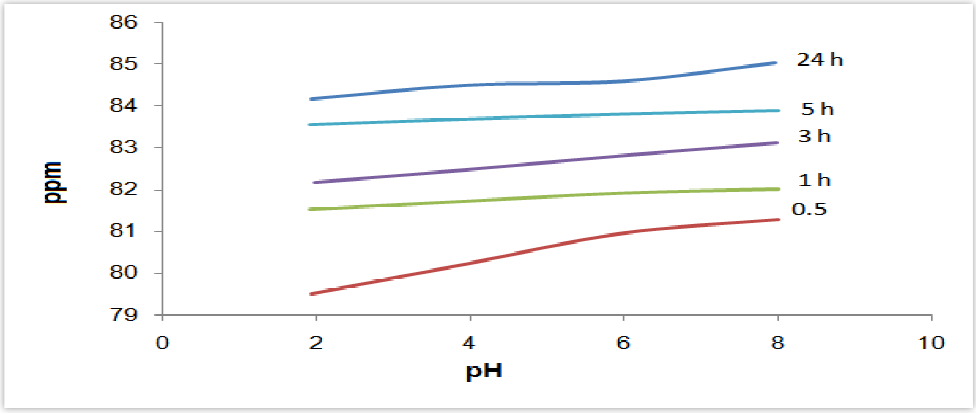


Figure 4. The effect of PH on the loading capacity curves of Co^{+2}resin in different treatment times.

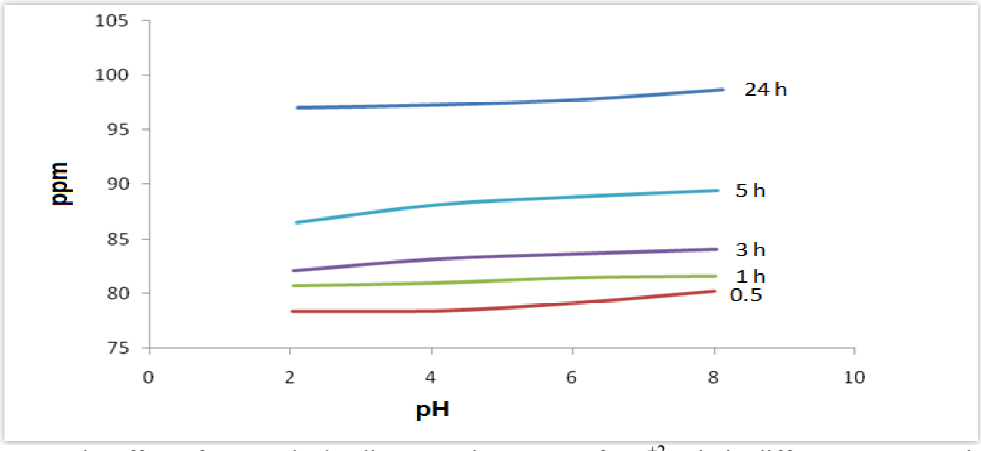


Figure 5. The effect of PH on the loading capacity curves of Mn^{+2}resin in different treatment times.

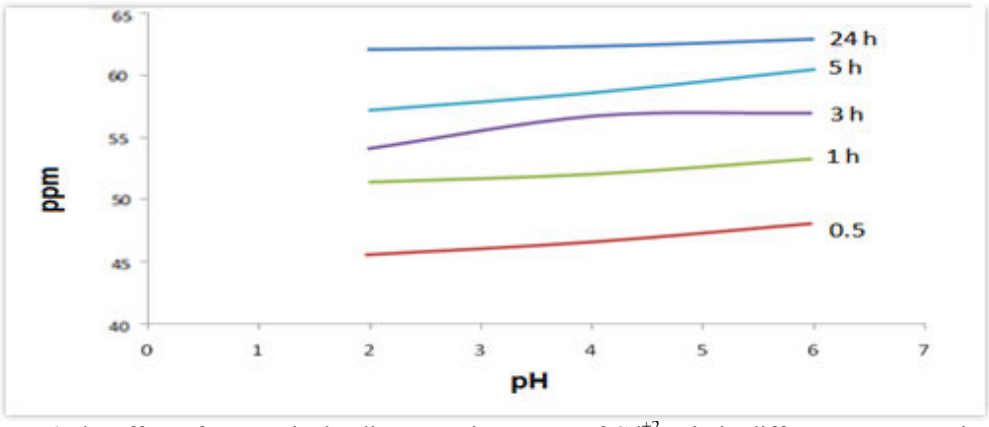


Figure 6. The effect of PH on the loading capacity curves of Cd^{+2}resin in different treatment times.

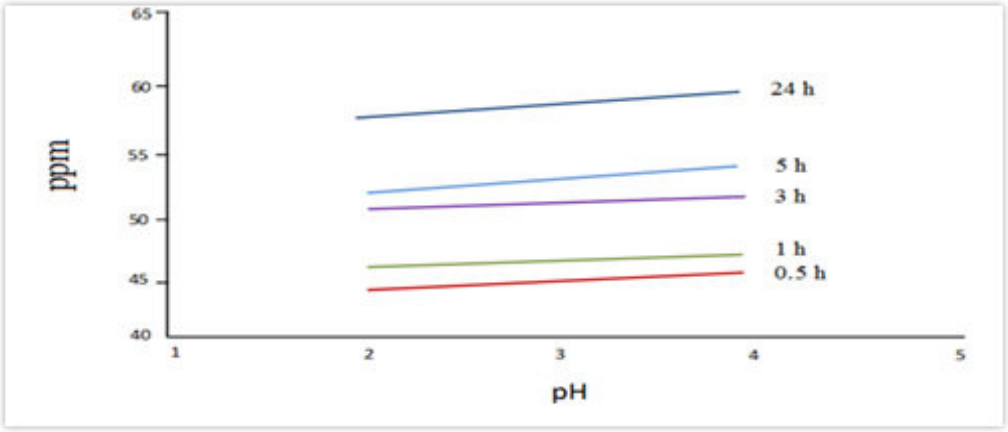


Figure 7. The effect of PH on the loading capacity curves of Pb^{+2} resin in different treatment times.

Table 1. IR absorption bands (cm^{-1}) of 3, 6-dihydrothiazolo [5, 4-d] thiazole (Compound 2).

υ cm^{-1}	Assignment
3272.8	υ(O–H) stretching Hydrogen bonding
3026.7	Ar.(C–H) stretching
2925.9	Al.(C–H) stretching
1653.6	υ (C=N) stretching
1484.2- 1028.1	υ (C=C) bending
1275.2,1212.5	υ(C–O) stretching

Table 2. Loading rate and the percentage of recovery elements of ions loaded resin at the maximum loading time (24) hour

Percentage of recovery %	Metal Ion
98.6	Mn^{+2}
63.3	Cd^{+2}
85.2	Cr^{+3}
84.4	Co^{+2}
58.1	Pb^{+2}

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