

Removal Efficiency of Cd^{+2} and Pb^{+2} using Polyurea Based on Bis-dithiocarbamate Ligand

Huda M. Nasir, Tahseen A. Saki*, Majeed Y. Al-Luaibi

Department of Chemistry, College of Science, University of Basrah, Basra, Iraq

*Corresponding author E-mail: Tahseensaki@gmail.com

Doi 10.29072/basjs.202037

Abstract

Currently, there is a growing concern and focus on heavy metals due to their detrimental impact on human health, making them one of the most critical environmental issues. To protect humans and the environment, such hazardous heavy metals do not dissolve easily and require removal from contaminated water. This research was aimed at preparing three types of novel polyurea containing bis-dithiocarbamate ligands and using them as chelators to extract cadmium and lead ion from contaminated water. Dithiocarbamates were chosen due to they have strong binding capabilities and can form insoluble stable colored metal ions complexes in water, which make them superior ligands for the removal of heavy metals from polluted water. Generally, these adsorbents exhibit high adsorption capacity, but limitations such as high operational costs, low recyclability and the introduction of a large volume of additional contaminants, have also been found. Therefore, we have been carried out develop more efficient, environmental friendly and inexpensive adsorbents followed by a mechanical separation process, provides one promising solution. The efficiency of metal removal between them is compared and shows that these resins have an excellent ability to give insoluble heavy metal polymers, their efficiency has been studied with different times at a different pH. Activity to the lead ion indicates that (pH=3: H, P > E; pH=5: H, E > P) while behavior to the cadmium ion at all pH values 4, 6 and 8 was: E, P > H.

Article inf.

Received:

16/8/2020

Accepted

10/11/2020

Published

31/12/2020

Keywords:

Removal,
Cadmium, Lead,
Polyurea, Bis-
dithiocarbamate

1. Introduction

Recently, environmental contamination caused by toxic heavy metals has been of great concern and a major problem due to the emission and harmful effects of these heavy metals. These metals produced globally through anthropogenic activities and discharged directly or indirectly into the atmosphere, entering the sources of air, water and food [1-3]. Moreover, most harmful heavy metals tend to build up in living organisms or plants [4, 5]. Cadmium and lead known to have toxicological effects and have adverse effects on human health and living organisms [6-8]. Thus, metal contaminated industrial wastewater must be treated before it is discharged into the environment. For this purpose, various methods were employed to remove heavy metals from industrial wastewater such as chemical precipitation–filtration, electrochemical treatment, extraction by solvents, ion exchange resins and reverse osmosis separation membranes etc. [9-11]. The chemical precipitation method is one of the most common of these methods used to removal of heavy metals from industrial wastewaters. Dithiocarbamates have a high chelating potential against metal ions in different oxidation states, where the presence of N and S atoms in different hybridized states, give an excellent ability to extract heavy metals from aqueous solutions [12-14]. In this scientific paper, three types of dithiocarbamate ligands crosslinking with polyurea were prepared and used for removal of cadmium and lead at different pH and different times. These new resins expect show high efficiency to remove Cd^{+2} and Pb^{+2} ions.

2. Experimental

2.1 Chemicals

Ethylene , propylene and hexamethylene diamines, sodium hydroxide (NaOH), carbon disulfide (CS_2), diisocyanate diphenyl methane (MDI), lead nitrate ($\text{Pb}(\text{NO}_3)_2$) nitric acid (HNO_3), hydrochloric acid (HCl), ethanol ($\text{CH}_3\text{CH}_2\text{OH}$) and cadmium chloride (CdCl_2) were provided from RDH company and used without further purification.

2.2 Physical measurements:

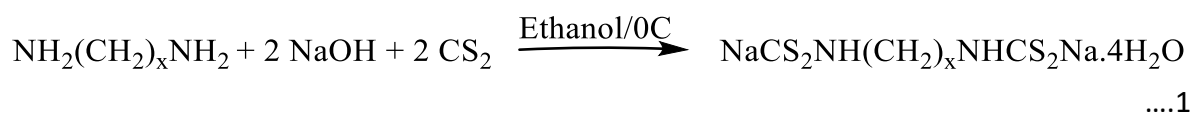
The FTIR spectra were record in the range $400\text{-}4000\text{ cm}^{-1}$ on a FTIR-8400 Shimadzo using KBr discs. Atomic Absorptions were record on AA-7000- Atomic Absorption Spectrometer/Shimadzo, in the Marine Science Laps/University of Basrah, Iraq. Melting points

were measure by a Gallenkamp melting point apparatus and are uncorrected. pH were measured in the Chemistry Department/ College of Science/University of Basrah and with a pH-meter AD –1030 Adwa-Romania.

2.3 Preparation of ligands and polyurea

2.3.1 Preparation of sodium bis dithiocarbamate salts:

Sodium (ethylene bis-dithiocarbamate) *hydrate* (I) , Sodium (propylene bis-dithiocarbamate) *hydrate* (II) and sodium (hexamethylene bis-dithiocarbamate) *hydrate* (III) ligands were prepared by the reaction ethanolic solution of the corresponding amine with carbon disulphide (mole ratio1:2) in aqueous solution of sodium hydroxide according to a general literature method (see eq. 1) [15].



Equation 1: preparing sodium bis dithiocarbamate salts

Where:

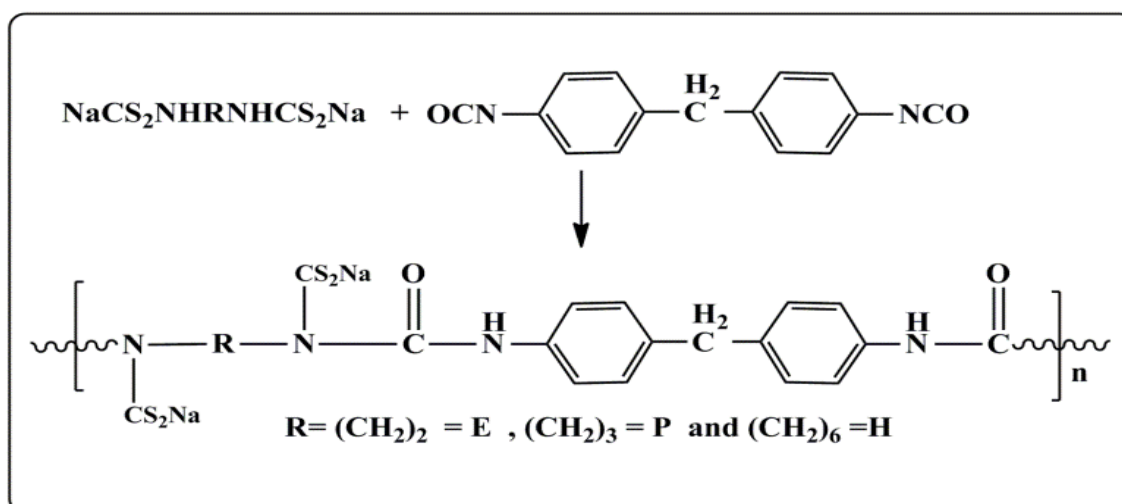
x = 2 Sodium (ethylene bis-dithio carbamate) hydrate (I)

x = 3 Sodium (propylene bis-dithio- carbamate) hydrate (II)

x = 4 Sodium(hexamethylene bis-dithio carbamate) hydrate (III)

2.3.2 Preparation and characterization of polyurea containing bis-dithiocarbamate ligand:

Polyureas (E, P and H) as shown in equation 2 were prepared by mixing (0.1 g) of each sodium bis-dithiocarbamate salts (I, II and III) respectively with (0.3 g) of (MDI) then leaving at room temperature for 24 hours. After heating at 70 °C for 60 min. followed by another 60 min. at 100 °C to complete curing.



Equation 2: Preparing polyurea based on bis-dithiocarbamate ligand

The Table 1 contains the most important FTIR bands shown in the prepared polyureas related to the new groups formed in polyurea and shows the some important physical properties of the prepared polyueas . It is noted from figures (1-3) that a broad band appears at $(3383 - 3340 \text{ cm}^{-1})$ representing the stretch frequency of the N-H group in urea. The emergence of a strong band at 1774 cm^{-1} due to the carbonyl group frequency in urea. Whereas the band at 2280 cm^{-1} is returned to the unreacted NCO groups [16].

Table 1: Some physical properties of polyurea along with some important bands in FTIR for polyurea

Polyurea symbol	Weight (gm.)	Color	Important bands in FTIR spectra for polyurea in cm^{-1} unit				
			C=N	N-C	C=O	N-H	Unreacted NCO
E	0.374	Dark yellow	1597	1266	1774	3340	2280
P	0.331	Light yellow	1597	1202	1774	3379	2280
H	0.348	Light yellow	1597	1258	1774	3383	2280

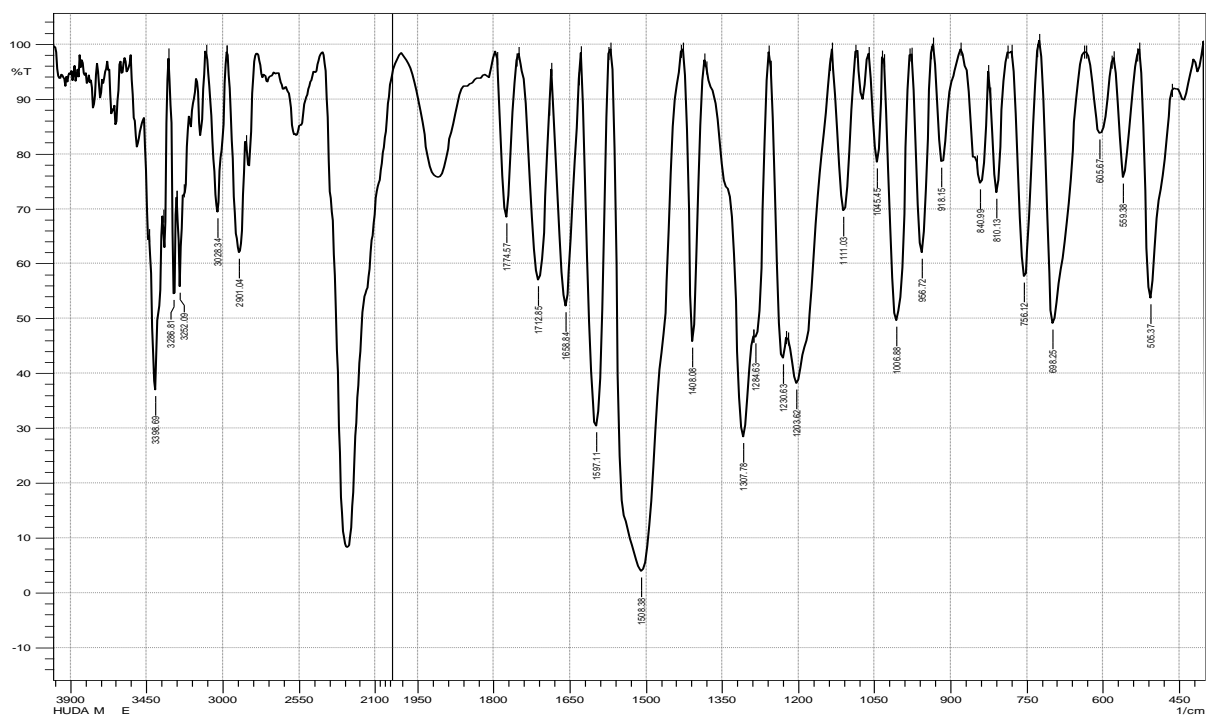


Figure 1: FTIR spectrum for polyurea E

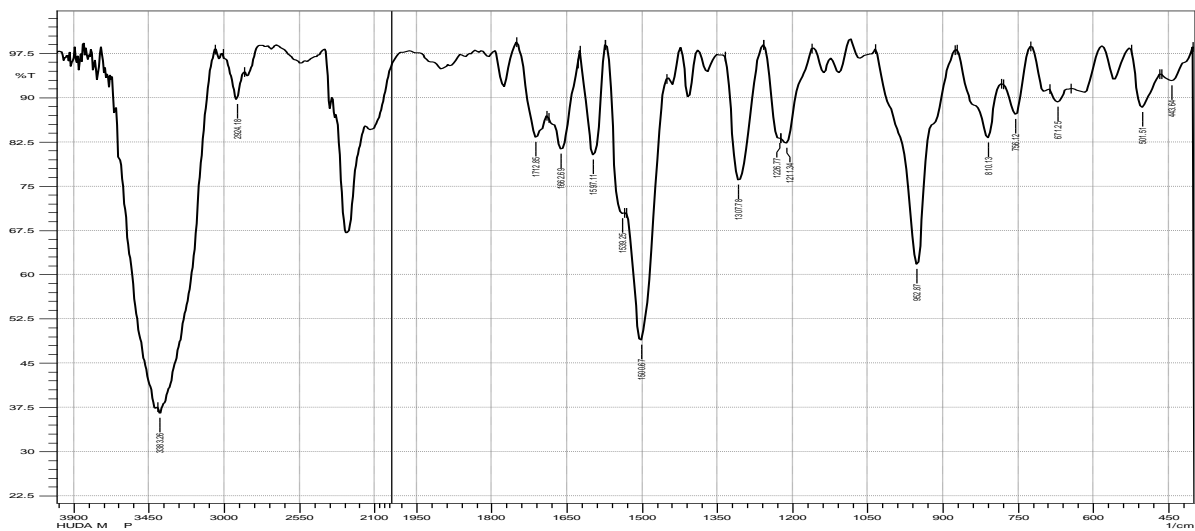


Figure 2: FTIR spectrum for polyurea P

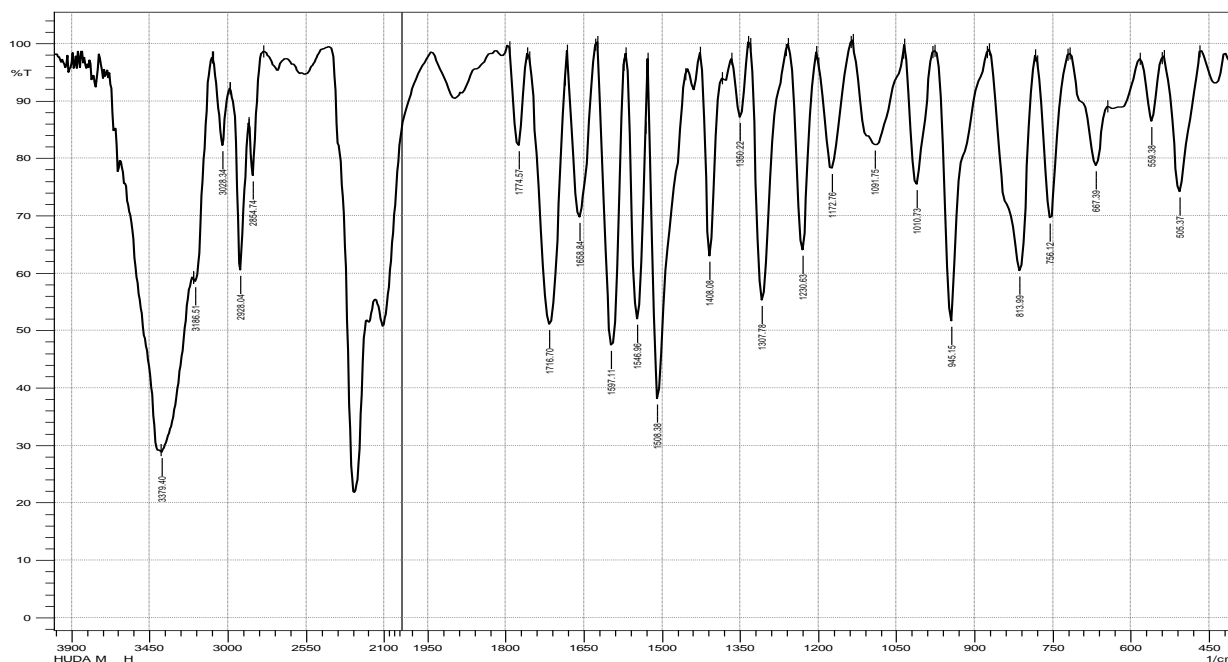


Figure 3: FTIR spectrum for polyurea H

3. Analytical study

The standard solutions of the studied ions were prepared according to the known literature as follows [17]:

- a. The standard solution of lead ions at a concentration of (1000 mg/l) was prepared by dissolving (1g) of $\text{Pb}(\text{NO}_3)_2$ in a little distilled water in a (1000 ml) volumetric flask and add (2 ml) of nitric acid, completing the volume to (1000 ml). Dilute it to a solution with a concentration of (30 mg/l) and other lower concentrations with a range that guarantees the linear behavior of the Beer-Lambert Law.
- b. The standard solution of cadmium ions at a concentration of (1000 mg/l) was prepared by dissolving (1g) of CdCl_2 in a little distilled water in a (1000 ml) volumetric flask and adding (2 ml) of hydrochloric acid, completing the volume to (1000 ml). Then it was diluted to a solution with a concentration of 3 mg/l and other lower concentrations with a range that guarantees the linear behavior of Beer-Lambert Law. Figure 4 shows standard calibration curves for the ions under study.

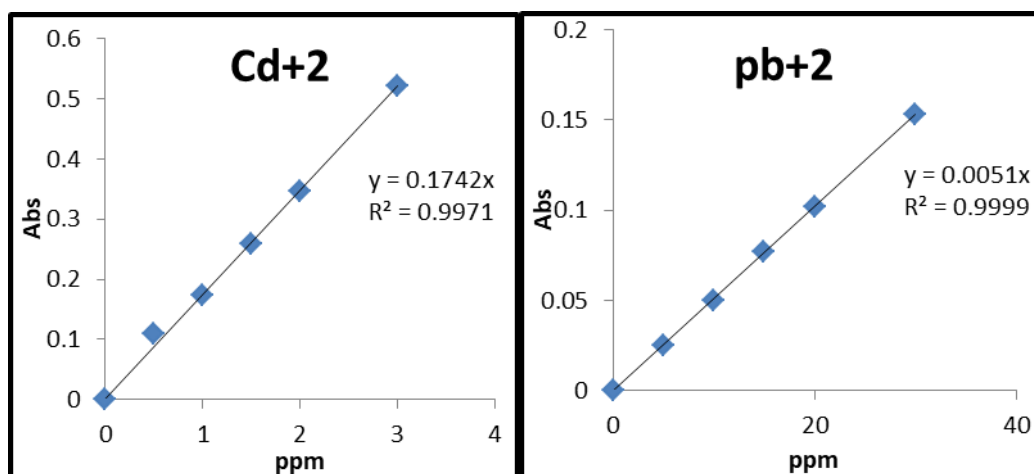


Figure 4: Standard calibration curves for the studied ions

3.1. Analytical measurements:

The analytical efficiency of polyureas (E, P and H) towards ions of some heavy elements (Pb^{+2} and Cd^{+2}) were studied using the batch method by treating (0.1 g) of the polyurea with (25 mL) of the element's ion solution studied for (24 hours). At the highest acidic function in which the metal ions can be found at the concentration used in an elegant and non-turbid manner depending on the studied ion, after which the element's hydroxide precipitate begins to appear [18]. Moreover, by using an electric vibrator at a speed (200 r/min) and at 25 °C. Compared the solutions absorbance with the absorbance of the standard concentration of the studied ion and the neglect of solutions with equal or close readings with the absorption of the standard concentration since the metal ion was not bound to the polyurea and can be satisfied with this stage of the study and to say that the polyurea is not effective towards that element. In the event that the absorbance of the filtrate is less than the absorbance of the standard concentration, this indicates an association between the element and the polyurea, and therefore the optimum conditions for their binding can be deduced by studying the influence of time factors and the acidic function. Absorbance was measured by the technique of flame atomic absorption (FAA) because it is highly sensitive and requires a short time and is characterized by the accuracy of its measurements compared to other spectral techniques [19]. Lead and cadmium ions were chosen as the most toxic elements.

1. The effect of treatment time and acid function on the efficiency of polyureas E ,P and H to withdraw cadmium ions Cd^{+2} :

The effect of the change in the treatment time and the acidic function factors on the efficiency of polyureas to withdraw the cadmium ion was studied by treating (0.1 g) of them with 25 ml of cadmium ion solution at a concentration of (30 ppm) and at an acid function (4, 6, 8) and promoted using electrical vibrator for different times periods (0.5, 1, 3, 6 and 24) hours then were filtered, the absorbance of the filtrates was measured. Then reusing the same process with polyurea P and H and the polyureas' efficiencies for binding was calculated and was as shown in figure 5. From the resulting measurements we find that the optimum conditions from the treatment time and the acidic function of these polyureas to withdraw cadmium ion can be summarized in Table 2.

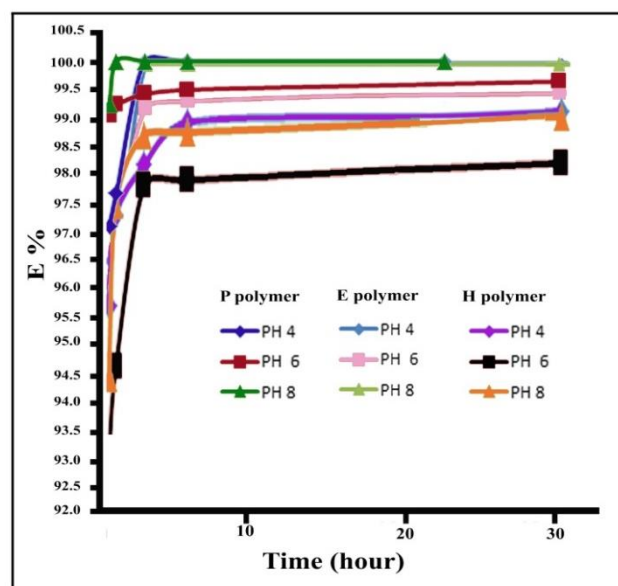


Figure 5: Efficiency of polyureas E,P and H to withdraw cadmium ion in acidic function pH=4,6 &8 at different processing times

Table 2: Optimum conditions for E, P, H polyureas to withdraw cadmium ion

Optimum Conditions	polyurea H		polyurea P		polyurea E	
Acidic function (pH)	8	4	8	4	8	4
Treatment time (hour)	3	6	1	3	1	3
Removal efficiency %	98.6	98.8	100	100	100	100

2. The effect of the processing time and acidic function on the efficiency of the polyurea E, P and H withdrawal of lead ions Pb^{+2}

The effect of the change in the treatment time and the acidic function factors on the efficiency of polyurea E to withdraw the lead ion was studied by treating (0.1 g) of them with (25 ml) of lead solution at a concentration of (30 ppm) and at the acidity (3 and 5) and shaken using electrical vibrator for different time periods (0.5, 1, 3, 6 and 24 hours) were filtered and the absorbance of the filtrates was measured. Then reusing the same process with polyurea P and H and the polyureas' efficiencies for binding was calculated and was as shown in figure 6. From the resulting measurements, we find that the optimum conditions from the treatment time and the acidic function of these polyureas to withdraw lead ion can be summarized in table 3.

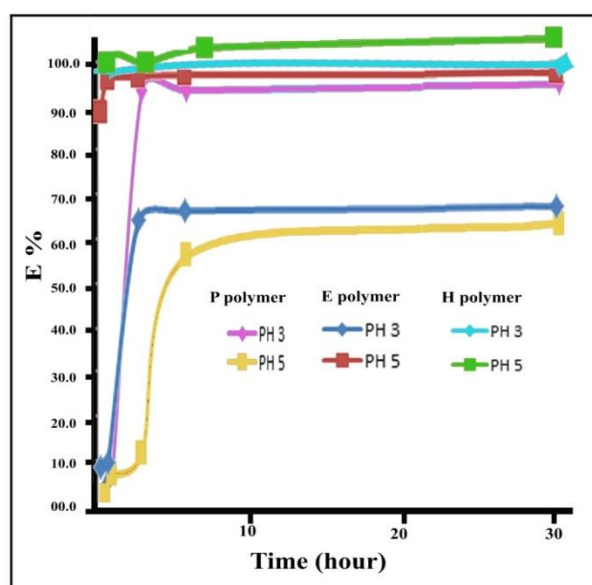


Figure 6: Efficiency of polyureas E, P and H to withdraw lead ion in acidic function pH= 3&5 at different processing times

Table 3: Optimum conditions for E, P, H polyureas to withdraw lead ion

Optimum Conditions	polyurea H	polyurea P	polyurea E
Acidic function (pH)	5	3	5
Treatment time (hour)	1	3	1
Removal efficiency %	99.3	93.4	96.7

4. Result and discussion

From this study, we result that efficiency of polyureas E; P; H can be arranged to withdraw cadmium ion as follows:

At pH = 4 then: E; P > H

At pH = 6 then: E; P > H

At pH = 8 then: E; P > H

That is, the efficiency of polyureas E and P was higher in the three acidic functions while polyurea H was slightly less than them and the efficiency of the three did not less than 92% at 30 min. and this gives an indication of the possibility of using any of the polyureas prepared to withdraw the cadmium from the contaminated water in a relatively short time And in acidic, basic and neutral environments.

And the efficiency of polyureas E; P; H can be arranged to withdraw the lead ion as follows:

At pH = 5 then: H; E > P

At pH = 3 then: H; P > E

It is noted that the efficiency of polyurea H was the highest in both acidic functions, while the efficiency of polyureas E and P was affected by the change of the acid function, as the performance of polyurea P decreased at pH=5 unlike polyurea E, that is, polyurea H can be used to withdraw the lead element with different acidic functions and at a treatment time it was estimated half an hour

5. Conclusions

This study showed high efficiency in removing (Cd^{+2}) and (Pb^{+2}) ions from aqueous solution at short time and different pHs by using three resins of polyurea containing bis dithiocarbamate ligand due to their high bonding capacity for heavy metals and this suggests the use of these resin for trace concentration from natural sample.

References

- [1] S.A. Zabin, M.A. Foaad, A.Y. Al-Ghamdi, Non-carcinogenic risk assessment of heavy metals and fluoride in some water wells in the Al-aha region, Saudi Arabia. *Hum. Ecol. Risk Assess.*, 14 (2008)1306–1317.
- [2] A. Zahra, M.Z. Hashmi, R.N. Malik, Z. Ahmed, Enrichment and geo-accumulation of heavy metals and risk assessment of sediments of the Kurang Nallah – feeding tributary of the Rawal Lake reservoir, Pakistan. *Sci. Total Environ.*, 470–471(2014) 925–933.
- [3] S. Balakrishnan, S. Duraisamy, M. Kasi, S. Kandasamy, R. Sarkar, A. Kumarasamy, Syntheses, physicochemical characterization, antibacterial studies on potassium morpholine dithiocarbamate nickel (II), copper (II) metal complexes and their ligands. *Heliyon*, 5 (2019) e01687.
- [4] N. Rascio, F. Navari-Izzo, Heavy metal hyperaccumulating plants: how and why do they do it? And what makes them so interesting?. *Plant Sci.*, 180(2011) 169–181.
- [5] H. Ali, E. Khan, M.A. Sajad, Phytoremediation of heavy metals – concepts and applications. *Chemosphere*, 91(2013) 869–881.
- [6] D.K. Mohan, H. Umar, A. Sarswat, M. Alexandre-Franco, U.J. Charles, Cadmium and lead remediation using magnetic oak wood and oak bark fast pyrolysis bio-chars. *Chem. Eng. J.*, 236(2014) 513–528.
- [7] N.A. Mohd Zahria, S.N.A. Jamilb, L.C. Abdullaha, S.J. Hueyd, T.C.S. Yawa, M.N. Mobarekehe, N.S.M. Rapeia, Equilibrium and kinetic behavior on cadmium and lead removal by using synthetic polymer. *J. Water Pro. Eng.*, 17(2017), 277–289.

- [8] G. Zhao, J. Li, X. Ren, C. Chen, X. Wang, Few-layered graphene oxide nanosheets as superior sorbents for heavy metal ion pollution management. *Environ. Sci. and Technol.*, 45(2011) 10454–62.
- [9] R. Say, E. Birlik, A. Denizli, A. Ersöz, Removal of heavy metal ions by dithiocarbamate-anchored polymer/organosmectite composites. *Appl. Clay Sci.*, 31(2006) 298–305.
- [10] L. Danyang, N. Lanli, D. Yimin, Z. Jiaqi, C. Tianxiao, Y. Zhou, Synthesis of poly(amidoamine) dendrimer-based dithiocarbamate magnetic composite for the adsorption of Co^{2+} from aqueous solution. *J. Mat. Sci.: Mat. Elec.*, 30 (2019) 1161–1174.
- [11] B. Liu, X. Lv, X. Meng, G. Yu, D. Wang, Removal of Pb(II) from aqueous solution using dithiocarbamate modified chitosan beads with Pb(II) as imprinted ions. *J. Chem. Eng.*, 220(2013) 412–419.
- [12] L. Bai, H. Hu, W. Fu, J. Wan, X. Cheng, L. Zhuge, L. Xiong, Q. Chen, Synthesis of a novel silica-supported dithiocarbamate adsorbent and its properties for the removal of heavy metal ions. *J. Hazard. Mater.*, 195(2011) 261–275.
- [13] J. Gaur, S. Jain, R. Bhatia, A. Lal, N.K. Kaushik, Synthesis and characterization of a novel copolymer of glyoxal dihydrazone and glyoxal dihydrazone bis(dithiocarbamate) and application in heavy metal ion removal from water. *J. Therm. Anal. Calorim.*, 112(2013) 1137–1143.
- [14] J.O. Adeyemi, D.C. Onwudiwe, Organotin(IV) Dithiocarbamate Complexes: Chemistry and Biological Activity. *Molecules*, 23(2018) 2571-2597.
- [15] H.M. Nasir, T.A. Saki, M.Y. Al-Luaibi, Synthesis, identification and thermal study of some new inorganic polymers based on bis-dithiocarbamate ligands with silicone, tellurium and some transition metals. *Innovaciencia*, 7(2019) 1-13.

- [16] A. Wolinska-Grabczyk, B. Kaczmarczyk, A. Jankowski, Investigations of hydrogen bonding in the poly(urethane-urea)-based membrane materials by using FTIR spectroscopy. Polish J. Chem. Tech., 10(2008)53-56.
- [17] H. Chen, Y. Zhao, Q. Yang, Q. Yan, Preparation of poly-ammonium/sodium dithiocarbamate for the efficient removal of chelated heavy metal ions from aqueous environments. J. Env. Chem. Eng., 6 (2018) 2344-2354.
- [18] B. Konar, S. Basu, Use of chelating resin containing thioacetamide groups for the separation of copper. J. Anal. Chem., 348(1994) 281-283.
- [19] D. Skoog , F. Holler, Crouch S, "Principled Instrumental Analysis" 6th edition, Thomson-Brooks/Cole, United State (2007).

المستخلص

يوم بعد يوم يتزايد القلق من تزايد تراكيز المعادن الثقيلة السامة في البيئة بسبب آثارها الصحية على الكائنات الحية حيث تعد من أكثر الملوثات البيئية خطورة. تشمل الدراسة تحضير ثلاثة أنواع من البوليمرات الجديدة المتضمنة روابط الثايوكاربامات الثنائية التي استخدمت كمخالب للتأصر مع ايونات المعادن الثقيلة الأكثر سمية وهي الكادميوم والرصاص الثنائية. تم اختيار الثايوكاربامات الثنائية نظرًا لامتلاكها مجاميع فعالة قادرة على الارتباط مع الايونات المعدنية وتكوين معقدات مستقرة وغير قابلة للذوبان في المياه الملوثة. حضرت في هذه الدراسة بوليمرات البولي يوريا التي تمتاز بالكفاءة العالية للامتصاص والصدقية للبيئة وغير مكلفة اقتصادياً حيث تم مقارنة كفاءة إزالة الايونات باستخدام هذه البوليمرات المتضمنة مجاميع الثايوكاربامات الثنائية. أظهرت النتائج قدرة ممتازة على سحب الايونات من خلال دراسة كفاءتها عند دوال حامضية مختلفة وبأوقات زمنية مختلفة. سحب أيون الكادميوم في جميع قيم الدالة الحامضية (4, 6, 8) كانت الكفاءة للبوليمرات $P & E > H$. بينما كفاءة البوليمرات لسحب ايون الرصاص عند الدالة الحامضية 3 كانت كالتالي $H & P > E$ وعند الدالة الحامضية 5 كانت الكفاءة $E & H > P$.