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Original article

Removal of copper ions from contaminated aqueous solutions through adsorption process using modified polyurethane (PU) as an adsorbent

M. Saghi[a,*], D. Kaviani[b], Z. Bagheri[c], B.Padidaran[d], M.H. Bigtan[a], S. Moghimi[e]

[a]*Department of chemistry, Arak branch, Islamic Azad University, Arak, Iran.*
[b]*Department of chemistry, Science and research branch, Islamic Azad University, Tehran, Iran.*
[c]*Department of laboratory sciences, Varastegan institute for medical sciences, Mashhad, Iran.*
[d]*Education, Maneh and Samalqan, North Khorasan, Iran.*
[e]*Education, Bojnord, North Khorasan, Iran.*

*Corresponding author; Department of chemistry, Arak branch, Islamic Azad University, Arak, Iran; Tel.: +98-9155096870.

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ABSTRACT

Entering the pollutants specially heavy and toxic metals into the water resources has worried the human societies specially those researchers who have been studied much research about this field, this claim of which is proved by the number of valid published articles. Neglecting toxic material removing from water will pose the non-compensable injuries to living organisms and environment. In the paper, the 2- Mercaptobenzothiazole modified polyurethane foam has been used for removal of Cu ion from contaminated water solutions. The continuous experiments have been carried out through preparing adsorption columns for studying and optimizing the effect of primary concentration of the metal, pH, adsorbents used in respect of gram and various conditions for preparing the used polyurethane. The results of the experiments indicated that optimized condition for removing Cu ion with performance of 95 ± 5% includes 5 g modified polyurethane sorbent by modifier with concentration 0.001 M and pH=5.

1. Introduction

38 elements are heavy metals in periodic table which are considered as vital pollutants due to lack of its biodegradability and toxicity feature. The mobility of these metals in the soil was low and does not move to the lower soil layers. Therefore the pollutants accumulate in soil surface layer or at maximum 30cm soil depth when concentration of these elements increases. Hence these elements will further expose under absorbing and transposing to plants and subsequently surface waters or surface waters infiltrated into the underground water. Since these metals could not degrade through chemical or biological processes in nature, if they have entered to food chain, will not be degraded and only will be build up to its quantity. The Lead, Cadmium, Zinc, Mercury, Nickel, Arsenic, Aluminum, Iron, Platinum, Uranium and Copper are the examples of these metals. Most of these elements critically contribute to biological and physiological activity of living organisms and are required in low doses but over-existing some of these elements such as Lead, Cadmium, Mercury, Nickel or silver could be leaded to intoxication or death. Numerous studies carry out about measuring and removing these elements due to importance of control and removal of these elements in environment specially water resources (Eftekharnia, 2010). There are numerous methods for removing heavy metals from polluted water. Chemical sequestration, usingmembranous procedures, reverse osmosis, floating and electrochemical treatment are considered as part of the used methods for removing heavy metals (Kurniawan et al., 2006).These methods are not economically feasible due to high cost especially at industrial scale.Adsorption is a helpful and low cost method for treating contamination resulted from heavy metals. Adsorption is a mass transfer process from liquid or gas to solid phase. In order to enhance adsorption efficiency, this solid surface should be porous and should have high specific area. In recent years, utilizing low price adsorbents has been become common. Some of these adsorbents are waste industrial materials which have suitable functional groupsfor reacting with pollutants. Crabshell, papaya wood, Indian bamboo, cotton, natural zeolites, fish scale and etc. are typical natural adsorbents useful for removing heavy metals (Dhiraj et al., 2008).The synthetic zeolites such as Silicoaluminophosphates (SAPOs) or some polymeric adsorbents could be noted as synthetic adsorbents used in this area.

The development of polyurethanes (PU) began in 1937at I.G.Farbenindutrie where Bayer with coworkers discovered the additionpolymerization reaction between diisocyanates and diols (Cornille et al., 2015).PUs have various applications as different forms such as soft and hard foams, elastomers, thermoplastics elastomers, resin, dye, covering and etc. all around the world. One of the vital application of this polymer is at adsorption process. Since this polymer comprises amide functional groups, it could be used as industrial adsorbent. In the paper, PU modified by 2-Mercaptobenzothiazole(shortly MBT) has been utilized for removing Cu ions from water solutions. In figure .1 the basic molecular structure of PU and its modifier namely MBT have been shown.

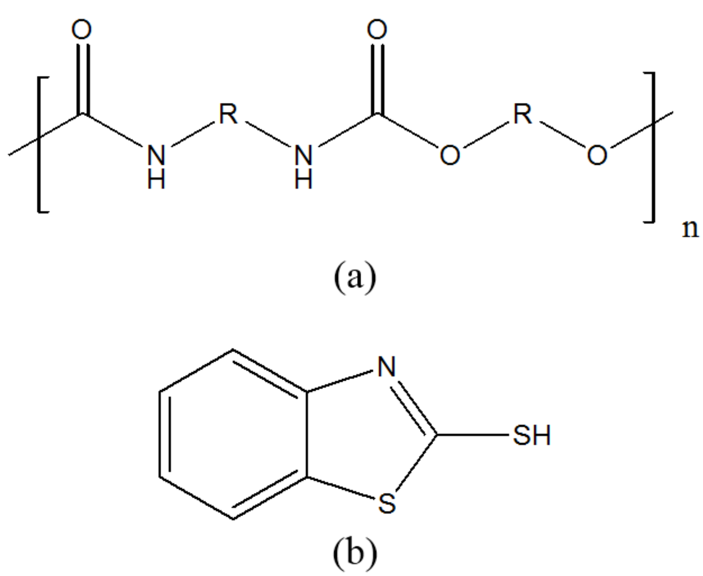

Fig.1. Basic molecular structure of PU (a) and MBT (b).

2. Experimental

2.1. Materials and methods

All chemicals used in the paper were prepared from German company Merck. In order to prepare the Cu metal ion in samples, the salt of copper nitrate was utilized. The stock solution made from the salt of copper nitrate was prepared to make other required solutions from it through dilution method. DilutedHCl solution was used for pH adjustment. Also organic solution for modifying the used formulas was prepared through solving specific amount of MBT inside the methanol.

2.2. Continues adsorption method

Firstly 3 gadsorbent was soaked in MBT for 2 hours. After filtering the extra solvent, the modified PU was placed in the column and 100ml solution containing copper has been passed through the column. In order to determine the concentration of the metal ion existed in the solution, the concentration of this ion was measured before and after passing through the column using atomic absorption device. The relation corresponding to adsorption capacity calculation and adsorption percent has respectively been shown in equation 1 and 2. In this relations Q_t is the adsorption capacity, C_t the equilibrium concentration of metal, C_0 the primary concentration, V solution volume and W is the mass of the used adsorbent.

$$Q_t = \frac{(C_O - C_t)V}{W} \quad (1)$$

$$\%\, E = \frac{(C_O - C_t)}{C_O} \times 100 \quad (2)$$

3. Results

3.1. Effect of PU surface modification

Figure .2shows the effect of chemical modification of PU surface to use in metal ion removal. As it can be found if the used PU is soaked in MBT with concentration of 0.001 M, then greatest percent of adsorption will be achieved. While it is not case for water and methanol and the adsorption value is less. The results indicate that if the used PU had been soaked before being used in the solution, then the efficiency of removal will be increase.

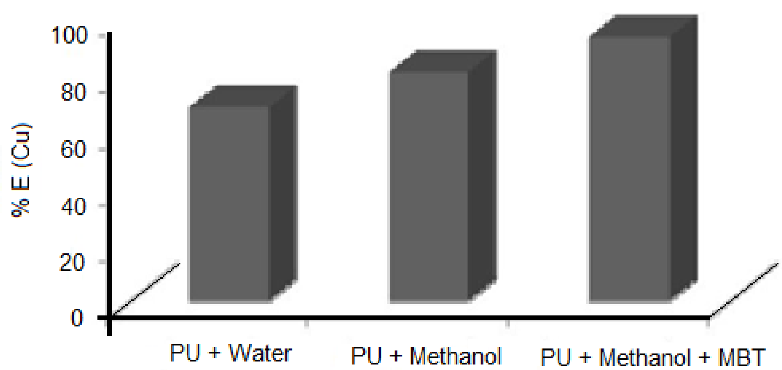

Fig.2. Effect of chemical modification of PU surface on the Cu adsorption.
Modifier: MBT 0.001 M in methanol solvent, Solution volume: 100 ml,Adsorbent amount: 3 g, Temperature: 28 °C.

3.2. Effect of pH

The vital factor in adsorption capability is the pH.Dependence of adsorption to pH is due to competition for area places among the metal ions and hydrogen ions. In pHs less than 2 which are strongly acidic, the hydrogen ion will win in the competition. For the same reason, the removal efficiency is very low. Increasing the removal efficiency with increasing the pH due to mechanism of cation exchange for ligand MBT is illustrated in figure .3. According to figure .3, adsorption rate increase with increasing pH but it become constant after about a pH of 5. Therefore as shown in figure .3, the best pH for better adsorption is 5.

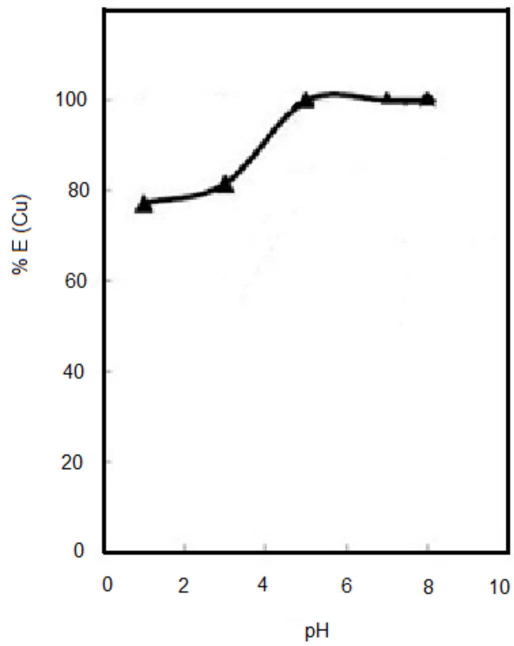

Fig.3. Effect of pH on theCu adsorption (pH optimization).

3.3. Effect of adsorbent dose

By increasing the amount of adsorbent, the adsorption efficiency will increase. As shown in figure .4, for Cu ion, the adsorption efficiency decrease at low adsorbent and it increase with increasing the amounts of adsorbent. But according to the figure .4, it is clear that if adsorbent amount exceeds to specific value then it will not effect on the adsorption amount and the curve will be almost as straight line.

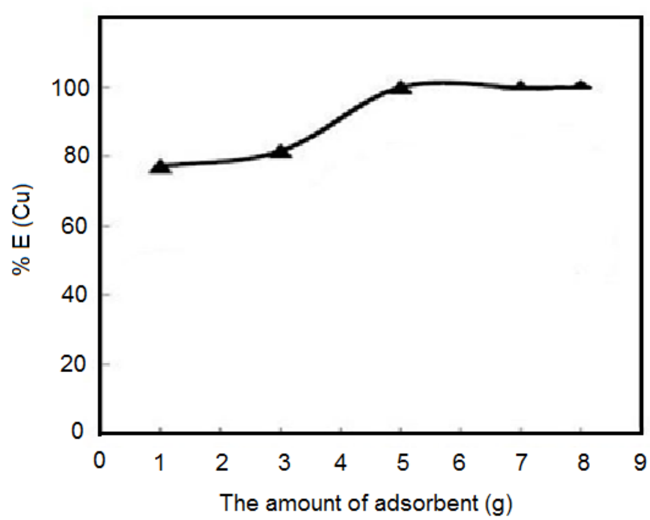

Fig.4. Effect of adsorbent dose on the Cu adsorption.

3.4. Effect of initial concentration

The primary concentration of analyte is of another factors which could affect on the adsorption process. The removal efficiency decreases with increasing the initial concentration of ion. The reason is that with increasing the concentration of adsorbing materials, adsorption site will quickly be saturated on the adsorbent and the removal efficiency will reduce. Figure .5 shows the effect of initial concentration on the Cu adsorption. As shown in figure .5, with increasing the initial concentration of the solution, the adsorption efficiency will decrease.

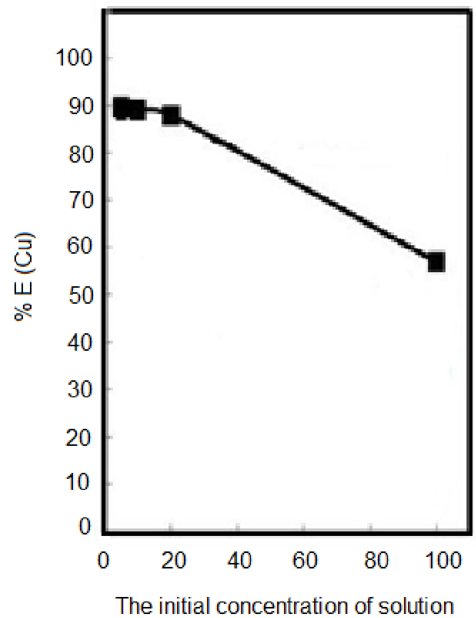

Fig.5. Effect of initial concentration on the Cu adsorption.

4. Discussion

In the paper, the modified PU foam has been used along with MBT to remove the copper ions from contaminated aqueous solutions.In order to carry out the adsorption as best as possible, it is necessary to identify the factors affecting on the adsorption efficiency and they should then be optimized. By doing this research, the results indicated that best possible state for removing the Cu ions from the solution with efficiency of $95 \pm 5\%$ occurred under the conditions which 5 g PUadsorbent modified by MBT (0.001M) are utilized and the environment pH equals to 5.

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