HEAVY METAL REMOVAL BY POLYMER – ZEOLITE BASED ADSORBENT

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Abstract: Water resources are threatened by a lot of pollutants such as heavy metals. Copper, a heavy metal, is quite toxic at high concentrations similar to the other heavy metals. These metals can also accumulate fatty tissues of livings. Due to these reasons heavy metals should be removed from wastewaters before being discharged. There are many methods to remove heavy metals such as chemical precipitation, ion exchange, membrane technologies, etc. Adsorption is an alternative method which is cheap, easy to apply and effective. Various adsorbents including biopolymers are used efficiently for heavy metal removal. Alginate is one of them composed of mannuronic and guluronic acid monomers. Alginate can form beads by adding mostly calcium which were used for heavy metal removal. Recent studies were particularly focused on improvement of these beads by adding some materials capable of capturing heavy metals such as clay, bentonite, activated carbon, etc. In this study, a natural zeolite, clinoptilolite was used to increase copper removal capacity of alginate beads. For copper removal, series of adsorption experiments were performed under constant temperature and mixing rate. Alginate-clinoptilolite beads were found to be more effective (almost 20 % of higher copper removal) compared to alginate beads alone. Adsorption of copper was equilibrated after about 8 hours of incubation and the highest copper reduction was observed as 87 mg Cu^{2+}/g alginate-clinoptilolite beads at initial Cu^{2+} concentration of 100 mg/L.

Keywords: Alginate, Clinoptilolite, Copper, Toxicity

Introduction

Environmental pollution is particularly get worse by industrial evolution. A lot pollutants become wide spread in the biosphere, such as heavy metals. Heavy metals are generally toxic even at considerably low concentrations. Also, they can accumulate in fatty tissues which resulted increase in heavy metal levels in the food web. Therefore, heavy metals are required to be treated before discharge into the environment (Papageorgiou et al, 2008). There are many methods used for the treatment of heavy metals such as chemical precipitation, filtration, ion exchange, membrane technologies and adsorption. One of the alternatives is adsorption by natural polymers. For instance, alginates are found to be effective in heavy metal uptake (Vieira and Volesky, 2000).

Alginates are polysaccharides composed of mannuronic (M) and guluronic (G) acid monomers. These monomers can be arranged as MM-, MG- and GG-blocks (Hay et al, 2010). Carboxylic acid groups linked to these monomers are claimed to be the main functional groups in heavy metal removal. Also, complexation reactions together with divalent cations might have a role in heavy metal uptake. Alginates with high GG-blocks content can form strong gels with divalent ions particularly calcium ions (Davis et al, 2003). Generally alginate beads formed by gelation investigated in related studies. However, in recent years, studies especially focused on improving heavy metal removal capacity of alginate beads by forming composite structures. For example, heavy metals like Pb^{2+}, Mn^{2+}, Cd^{2+}, Cu^{2+}, Zn^{2+}, Fe^{2+}, Al^{3+} and Hg^{2+} were removed by magnetic alginate beads (Bee et al, 2011; Idris et al, 2010; Idris et al, 2012; Ngomsik et al, 2009; Park et al, 2007), alginate montmorillonite beads (Shawky, 2011), pectin alginate beads (Harel et al, 1998) and ceramic membrane alginate beads (Athanasekou et al, 2009). Similarly, this study aimed to improve heavy metal uptake capacity of alginate beads by combining alginate and clinoptilolite.

Clinoptilolite is a natural zeolite having ability to remove metals from wastewaters by ion exchange. Cd^{2+}, Cu^{2+}, Ni^{2+}, Cr^{3+}, Pb^{2+}, Fe^{3+} could be removed by using clinoptilolite effectively (Kocaoba et al, 2007; Inglezakis et al, 2002; Inglezakis et al, 2003; Iznaga et al, 2007; Petrus et al, 2005; Sprynskyy et al, 2006). Also, it is a cheaper source and very abundant in Turkey (DPT, 1996). As a result, the main purpose of this study is determination of optimal conditions for composite alginate-clinoptilolite beads formation and then testing these beads for their ability to take copper from a synthetic wastewater. It is thought that this study might be useful in order to have a new designed and effective adsorbent for heavy metal removal by using cheaper and natural materials, one of which has major sources in our country.

Materials and Methods

Alginate was purchased and used directly. Clinoptilolite was first ground and then sieved into different sizes. The lowest size clinoptilolite (<100 µm) was selected due its possible higher surface area. It was washed with 2M NaCl solution for 1 day at 150 rpm in order to increase heavy metal uptake capacity. After that, it was washed with distilled water, then dried at 100 ºC for 1 day and stored in a desiccator.

Essentially, alginate beads are produced by pouring alginate solution drop by drop into $CaCl_2$ solution. However, there is no standard procedure for the production these beads. For this reason, 1, 2 and 4% alginate solutions were prepared and added dropwise into 50, 100, 250 mM $CaCl_2$ solutions by using a peristaltic pump under constant stirring at 50 rpm. After that these beads were incubated overnight for hardening and separated by filtration through 0.45 µm filter under vacuum by washing with distilled water. At the end, optimal concentrations for alginate and calcium ion were selected for bead preparations. This procedure was used for both alginate and alginate-clinoptilolite (1g / 1g) beads formation.

For the removal of copper, first, the efficiencies of alginate and alginate-clinoptilolite beads were compared by using 100 mg (i) alginate beads and (ii) alginate-clinoptilolite beads. These beads were added into 100 mg/L Cu^{2+} solution (100 mL in 250 mL erlenmeyer flasks) at pH 4, 25 °C and 200 rpm for 72 hours. Two samples, collected at time zero and 72 hours, were filtered through 0.45 µm filter and acidified by HNO_3. Finally, copper analyses were performed by Inductive Coupled Plasma-Mass Spectroscopy (ICP-MS).

In the second experimental set, the kinetics of copper adsorption by alginate-clinoptilolite beads were followed by using 100 mg alginate-clinoptilolite beads. These beads were added into 100 mg/L Cu^{2+} solution (100 mL in 250 mL erlenmeyer flasks) at pH 4, 25 °C and 200 rpm for 72 hours. Samples, collected at 1, 4, 8, 12, 24 and 72 hours, were filtered through 0.45 µm filter and acidified by HNO_3. Finally, copper analyses were performed by ICP-MS.

Results and Discussion

Optimization of the Procedure Used for Alginate Beads Production

Essentially, alginate beads are formed by combining two solutions under constant and gentle stirring: alginate and calcium salts. However, there is no standard procedure for the bead production. For this reason, first different concentrations of alginate and $CaCl_2$ solutions were prepared and alginate beads were formed. Second, the results were evaluated in terms of homogeneity of the beads' size, shape and hardness of the beads. For this purpose, three different alginate solutions, 1, 2 and 4 %, dropped into 50, 100 and 250 mM calcium ion containing solutions.

Alginate solution at 4 % concentration showed considerably high viscosity, probably because of its polymeric nature. In general, solution of a polymer has high viscosity particularly when the polymer has high polymerization degree. If this kind of a polymer is used at high concentration, the solution would have high viscosity. Thus, the beads formed by alginate solution at 4 % concentration had irregular shapes independent of calcium concentration. When the beads produced by 1 and 2 % of alginate solutions were compared, the ones formed by 2 % of alginate solutions were found hard enough to use in the experiments although beads formed by 1 % of alginate solutions were a bit softer.

On the other hand, there were no obvious variations between the beads formed at different calcium ion concentrations. Only the beads formed at 50 mM of $CaCl_2$ solutions seemed to have smaller and more homogenous size distribution when they were observed visually. This could also reduce the chemical usage compared to other calcium doses tested (100 and 250 mM) in the study. As a result, alginate beads were determined to produce by dropping 2 % of alginate solution into 50 mM of $CaCl_2$ solutions (Figure 1). This procedure was also utilized for the production of alginate-clinoptilolite beads.

Copper Removal by Alginate-Clinoptilolite Beads

The main goal of this study is to form a new composite alginate bead by cheaper and possibly local sources which is more effective in heavy metal uptake. Clinoptilolite is selected for this purpose since it is a low cost material with abundant sources in Turkey. Then, in order to determine the effectiveness of zeolite addition into alginate beads, first, copper removal capacities of alginate beads and alginate-clinoptilolite beads were investigated for 72 hours at constant temperature and mixing rate. Results showed that both alginate and alginate-clinoptilolite beads could remove copper efficiently from the synthetic wastewater having about 100 mg/L of Cu^{2+}. Alginate-clinoptilolite beads had higher heavy metal uptake capacity. About 20 % more copper removal could be achieved by new composite beads after 72 hours (Table 1). Therefore, there should be no diffusional limitations for copper migration due to clinoptilolite addition and functional groups of clinoptilolite appeared to be used for the exchange of copper.

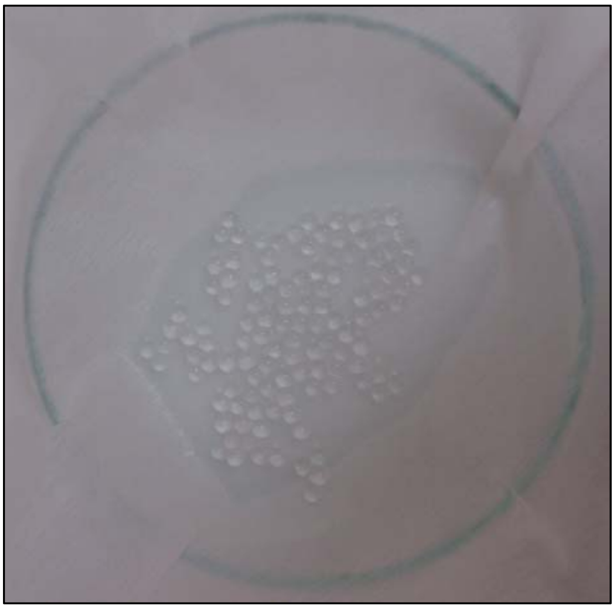


Figure 1. Alginate beads produced by 2% alginate and 50 mM Ca^{2+}

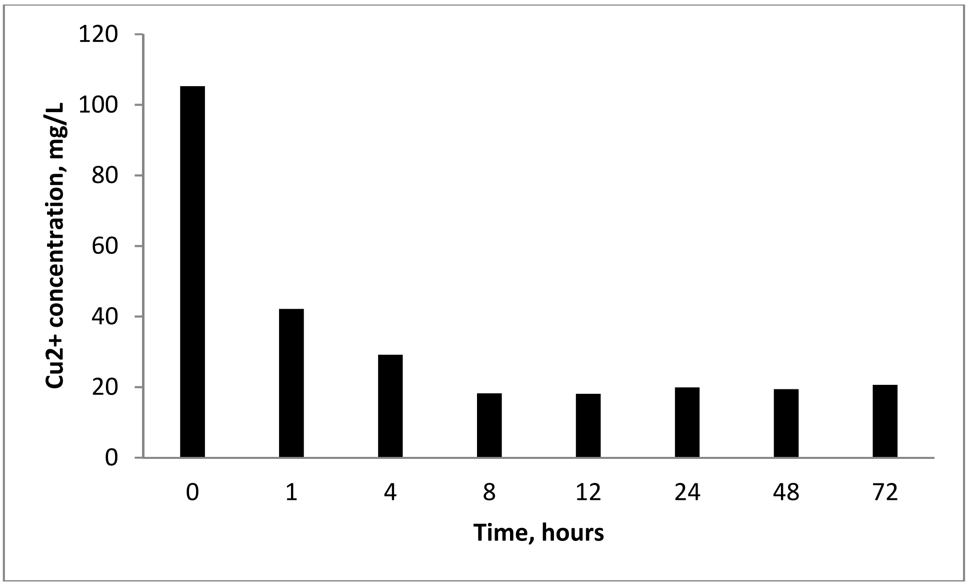
Table 1. Copper removal by alginate and alginate-clinoptilolite beads

Bead type	Initial copper concentration (mg/L)	Final copper concentration (mg/L)	Removal (%)
Alginate	103.3	37.5	64
Alginate-clinoptilolite	107.5	18.4	83

Since alginate-clinoptilolite beads were found to be more efficient compared to alginate beads alone, this combination was subjected to further experiments. For these experiments, first, kinetics of copper removal by alginate-clinoptilolite beads were investigated during 72 hours. The main purpose was to determine the equilibrium time for adsorption process at which there should be no drastic change of copper concentration in the solution.

Samples were collected at previously determined time intervals and variation of copper concentration in solution is presented in Figure 2. When the results were evaluated, adsorption of copper seemed to be considerably fast onto alginate-clinoptilolite beads. For example, only after 1 hour, copper removal efficiency was reached up to 60 %. In addition, copper concentration decreased from 100 to 30 mg/L after 4 hours of incubation period while it was measured around 18 mg/L after 8 hours. Then, until 72 hours, there were no significant changes in copper concentrations. As a result, the maximum copper removal was observed around 83 % and the equilibrium time for the adsorption phenomena was about 8 hours.

Amount of adsorbed copper per mass adsorbent is an important indication for adsorption capacity. In literature, it is generally noted as q_e (mg/g), which is defined as the amount of metal adsorbed per unit mass of adsorbent. The changes of q_e are also illustrated in Figure 2. As it is shown in the figure, at the beginning, the trend is opposite to copper concentration in the solution as expected. Thus, q_e values were first increased and then it was somehow fixed through the end of the experiment. The maximum q_e value was reached around 8 hours that is corresponded to 87 mg Cu^{2+}/g alginate-clinoptilolite beads.



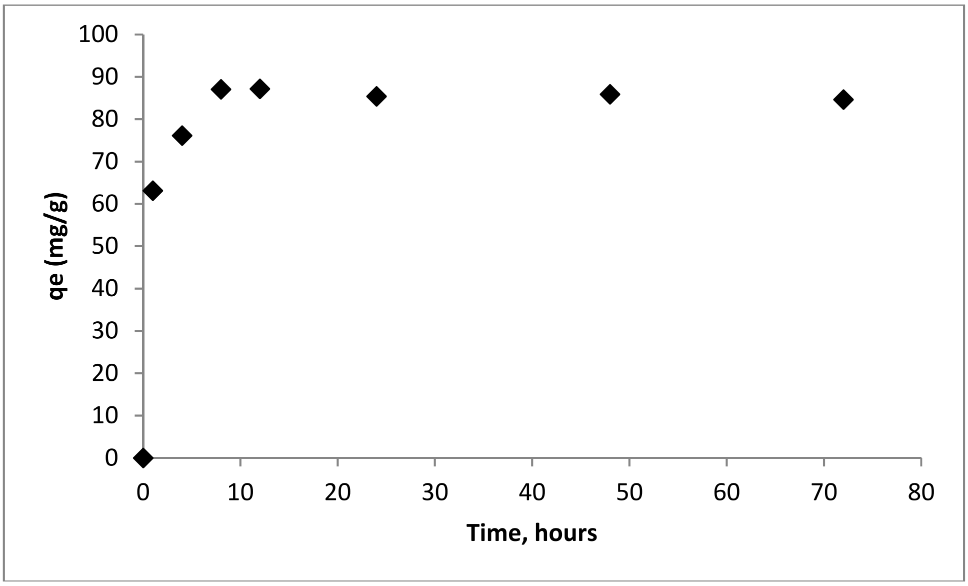


Figure 2. Changes in copper concentration and adsorption with time by alginate-clinoptilolite beads

Conclusion

Heavy metals are one of the major pollutants in industrial wastewater streams. They are required to be treated so that these metals are not harmful for the livings. Alginate – clinoptilolite beads are found to be effective combinations for heavy metal removal according to the results of the current study. These composite alginate beads can be suggested to use as alternative adsorbents since clinoptilolite is one of the local and cheaper sources in Turkey. Also, the results of the study might be helpful for further investigations particularly for column adsorption systems operated in continuous mode.

Acknowledgements

This study is funded by Scientific and Technological Research Council of Turkey – 2209/A University Students National Research Projects Funding Program.

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