Removal of Heavy Metals From Aqueus Solution Using Activated Carbon Embedded Cryogels

Aktif Karbon Gömülü Kriyojeller Kullanılarak Atık Sulardan Ağır Metal Uzaklaştırılması

Research Article

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ABSTRACT

In this study poly(hydroxyethyl methacrylate) (PHEMA) based activated carbon (AC) embedded cryogel discs were synthesized, characterized and their application for nickel and copper removal from aqueous solutions were investigated. The effect of pH and initial metal concentration on the adsorption capacity of the cryogels were studied in batch systems. Desorption of heavy metal ions was also studied and it was shown that synthesized discs could be repeatedly used without significant loss in the adsorption capacity after five repetitive adsorption–desorption processes.

Key Words
Adsorption, Heavy metals, Activated Carbon, Cryogels.

ÖZ

Bu çalışmada poli(hidroksi metakrilat) temelli aktif karbon gömülü kriyojel diskler sentezlenmiş, karakterize edilmiş ve sulu çözeltilerden ağır metal giderimi incelenmiştir. Sentezlenen kompozit kriyojel disklerin adsorpsiyon kapasitesine pH ve başlangıç metal iyonu derişiminin etkisi kesikli adsorpsiyon süreci kullanılarak incelenmiştir. Metal iyonlarının desorpsiyon çalışmaları gerçekleştirilmiş ve ard arda yapılan beş adsorpsiyon-desorpsiyon döngüsünden sonra kriyojellerin belirgin bir kapasite kaybına uğramadan tekrar kullanılabildiği gözlenmiştir.

Anahtar Kelimeler
Adsorpsiyon, Ağır metal, Aktif karbon, Kriyojel.

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INTRODUCTION

Environmental contamination due to wastewater discharges containing high concentrations of heavy metals is an important environmental issue [1]. Some heavy metals, as trace elements, (e.g. copper, cobalt, iron, manganese, selenium and zinc) are essential to maintain the metabolism of the human body [2]. However, accumulation of those heavy metals in both humans and other living organisms can cause several disorders and diseases [3]. The significant increase in the use of heavy metals in different industrial applications, such as coal combustion, sewage wastewater, automobile emissions, battery industry, mining activities, tanneries, alloy industries, and utilization of fossil fuels results in an increased amount of metal pollution in receiving waters. [4]. Therefore, the Word Heath Organization (WHO) and Environmental Protection Agency (EPA) have regulated the maximum acceptable discharge level into the environment in order to control the water pollution level. According to (WHO), the maximum permissible concentrations for nickel and copper in drinking water are 0.02, and 2.00 mg/L, respectively [5].

Various methods such as; chemical precipitation, ion exchange, membrane filtration, electrolytic methods, reverse osmosis, solvent extraction, and adsorption have been used to remove heavy metals from industrial wastewater. Adsorption has increasingly received much attention in recent years because the method is simple, relatively low-cost and effective in removing heavy metal ions from water [6]. Among these methods, adsorption is widely used to remove heavy metal ions from waters [7–11].

In recent literature, there are several research articles that focus on the development and characterization of new adsorbents such as various polymeric materials, monoliths, cryogels, molecularly imprinted polymers etc. [12–21]. Having many advantages, like structural flexibility, large pores and short diffusion pathways, cryogels can be one of the best choices for adsorption of heavy metal ions. Besides these advantages, they are also cheap, simple to produce in any shape and are not toxic to the environment [10]. However, they have relatively low specific surface area resulting in low adsorption capacity in the adsorption process. In order to overcome this drawback, composite cryogels can be synthesisted by embedding appropriate particles for the desired separation or purification [22, 23].

Activated carbons are versatile adsorbents. Their adsorptive properties are due to their high surface area, a microporous structure, and a high degree of surface reactivity. They can be used to purify, decolorize, deodorize, separate the harmful constituents from liquid solutions [24]. Research has been carried out in the area of activated carbon adsorption during the past four or five decades. In recent literature, activated carbons from different origins have been used for heavy metal removal [25-29].

In this study, high adsorption capacity of activated carbon and unique properties of cryogels are combined and activated carbon embedded, composite PHEMA cryogel discs are sythesized for heavy metal removal. The composite system is characterized using swelling tests and SEM. Nickel and copper adsorption capacities of the composite cryogel discs are tested at various pH and initial metal concentrations.

EXPERIMENTAL

Materials

2-hydroxyethyl methacrylate (HEMA) were obtained from Fluka A.G. (Buchs, Switzerland). Ammonium persulfate (APS), N,N′-methylene-bis(acrylamide) (MBAAm) and N,N,N′,N′-tetramethylene diamine (TEMED) were purchased from Sigma (St Louis, USA). Activated carbon in powder form was obtained from Merck AG (Darmstadt, Germany). All other chemicals used were reagent grade and were purchased from Merck AG (Darmstadt, Germany). Standard solutions (1000 mg/L) of Cu^{2+} and Ni^{2+} ions were prepared from their corresponding nitrates obtained from Merck. Water used in the adsorption experiments was purified using a Barnstead (Dubuque, IA, USA) ROpure LPÒ reverse osmosis unit with a high flow cellulose acetate membrane (Barnstead D2731) followed by a Barnstead D3804 NANOpureÒ organic/colloid removal and ion exchange packed-bed system. The resulting

purified water has a specific conductivity of 18 M Ω/cm. All glassware was washed with diute nitric acid solution and rinsed with deionized water before use.

Preparation of PHEMA-AC Cryogel Discs

Production of the PHEMA-AC composite cryogel discs is described below. Monomers (1.6 mL HEMA and 0.3 g N,N-methylene-bis(acrylamide) (MBAAm) were dissolved in deionized water (5 mL) and the mixture was degassed under vacuum for about 5 min to eliminate soluble oxygen. Total concentration of monomers was 16% (w/v). 3.0 mg activated carbon (AC) was added to the resulting solution and stirred until a homogeneous suspension is achieved. The cryogel was produced by free radical polymerization initiated by TEMED and APS. After adding APS (20 mg, 1% (w/v) of the total monomers) the solution was cooled in an ice bath for 2–3 min. Then, TEMED (20 μL, 1% (w/v) of the total monomers) was added and the reaction mixture was stirred for 1 min. Then, the reaction mixture was poured between two glass plates separated with 1.5 mm thick spacers. The polymerization solution in the plates was frozen at –16 °C for 24 h and then thawed at room temperature. The resulting cryogel sheets were cut into circular pieces (2 cm diameter) with a perforator. The cryogels were extensively washed with ethanol and water to remove any unreacted monomer or initiator and then stored in sodium azide 0.02% at 4°C.

Characterization of PHEMA-AC cryogels

Swelling ratios of composite cryogel discs were determined in distilled water. Cryogel disc sample was washed on porous filter paper until washing solution is clear. Then, it was dried to constant mass weight in the oven at 60°C and was weighed carefully (±0.0001 g) before placing in a 50 mL vial containing distilled water (W_0). The vial was put into an isothermal water bath with a fixed temperature (25.0 ± 0.5°C) for 2 h. The cryogel was taken out of the medium, wiped using a filter paper, and weighed (W_S). The swelling ratio was calculated by using Eq.1.

$$Swelling\ Ratio\ \% = \frac{W_S - W_0}{W_0} x100\% \quad (1)$$

Where, W_0 and W_S are the weights (g) of cryogels before and after swelling, respectively.

The surface morphology of the composite cryogel discs were examined using scanning electron microscopy (SEM, JSM-6400, JEOL) at an accelerating voltage of 20 kV after coating the samples with gold. The samples were initially dried in air at 25°C for 7 days before being analyzed. The surface of the sample was then scanned at the desired magnification to study the morphology of the cryogels.

Nickel and Copper Adsorption Studies from Aqueous Solutions

Adsorption of Ni^{2+} and Cu^{2+} ions on the composite cryogels from aqueous solutions was studied in batch systems. The effects of pH and heavy metal ion concentration on heavy metal adsorption on the synthesized cryogels were investigated in a 25 ml buffer solution. The adsorption studies were conducted at different pH values between 4-7 and different concentrations of metal ions (20–300 mg/L). In the adsorption experiments, 0.09 g cryogel discs were added to the corresponding buffer solutions. The flasks were shaken in a 25°C water bath at a speed of 150 rpm. After the desired adsorption period (up to 180 min), the concentration of the metal ions in the aqueous phases was measured using a Perkin–Elmer Model Analyst 800 atomic absorption spectrophotometer including deuterium background correction. The amounts of metal ions adsorbed per unit mass of the cryogel, Q (mg/g), were calculated by using Eq.2.

$$Q = \frac{(C_0 - C) \cdot V}{m} \quad (2)$$

Where C_0 and C are the initial and equilibrium concentrations of the metal ions in the aqueous solution (mg), respectively; V is the volume of the solution (L); and m is the amount of cryogel used (g).

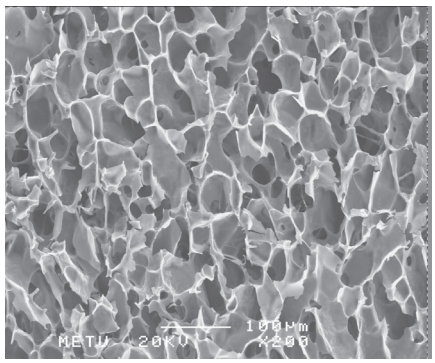
Heavy metal ion desorption studies were also performed in a batch system using a 10 mL HNO_3 solution having a concentration of 0.1 M. Cryogels were placed in the desorption medium and shaken in a water bath shaker at a rate of 150 rpm for 60 min. The concentration of metal ions in desorption

medium were obtained as described before. The desorption ratio was calculated from the amount of metal ions adsorbed on the cryogels and the final metal ions concentrations in the desorption medium.

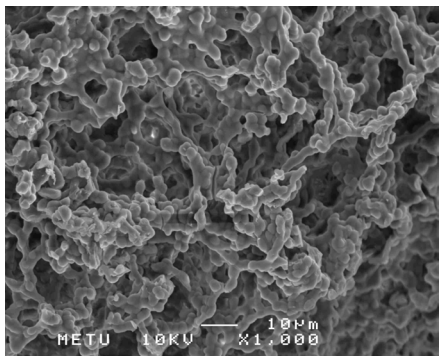
RESULTS AND DISCUSSION

Characterization of Synthesized PHEMA-AC Cryogel Discs

Supermacroporous composite cryogel discs were synthesized by polymerization in the frozen state of monomers HEMA with MBAAm as a cross linker in the presence of APS/ TEMED as initiator/ activator pair. Activated carbon (AC) particles were embedded in the structure of the cryogel. Even after the addition of AC particles, the discs maintained their elastic, sponge-like structure. However, when compared with the plain PHEMA cryogels, they were less elastic. The swelling ratio and equilibrium swelling degree of PHEMA-AC cryogel discs were and 626 % and 6.42 g H_2O / g cryogel respectively. The synthesized cryogel discs were also characterized by SEM method. The SEM images of the plain PHEMA discs and PHEMA-AC discs were given in figure 1 a-b, respectively.



(a)



(b)

Figure 1. SEM images of plain PHEMA discs (a) and PHEMA-AC composite discs (b)

In the figure, both of the cryogels have interconnected continuous pores between 10-100 μm. These interdependent flow channels and supermacroporosity provide easy diffusion of heavy metal ions into the structure and may lead to effective interactions between the heavy metal ions and composite cryogel discs. It was observed from figure 1b that the activated carbon particles were successfully embedded to the structure of PHEMA cryogel.

Nickel and Copper Adsorption on PHEMA-AC Cryogel Discs

In order to obtain the suitable conditions for maximum adsorption of Ni(II) and Cu(II), adsorption behavior of the heavy metal ions on the synthesized cryogel discs at different initial metal concentration and pH were tested by batch adsorption experiments.

Effect of pH

The pH of solutions is known to be one of the major parameters controlling metal adsorption processes on both nonspecific and specific adsorbents. In the absence of metal chelating groups, the concentration and the form of soluble metal species affect the precipitation of the metal ions. It is known that precipitation of metal ions becomes significant generally above pH 7.0. Therefore, the effect of pH on the adsorption capacity of the composite cryogels was investigated in the pH range between 4.0 and 7.0.

Figure 2 and 3 demonstrate the effect of pH on Ni and Cu adsorption on the composite cryogel discs, respectively. For the entire metal ion concentrations for both of the target metal ions, composite cryogel exhibited a low affinity for heavy metal ions in acidic conditions. Heavy metal adsorption increased as the pH of the solution increased. This behavior may be explained by investigating the interaction between the activated carbon and metal ions. A perusal of the literature indicates that the more important parameters that influence and determine the adsorption of metal ions on the activated carbon surface from aqueous solutions are the carbon-oxygen functional groups present on the carbon surface and the pH of the solution. At low pH values, the surface of the activated carbon can

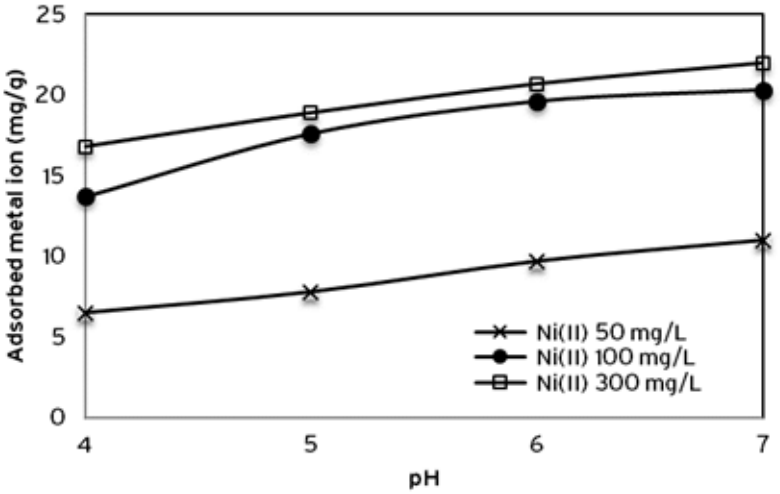


Figure 2. Effect of pH on adsorption of Ni(II) ions on PHEMA-AC composite cryogel at 25°C.

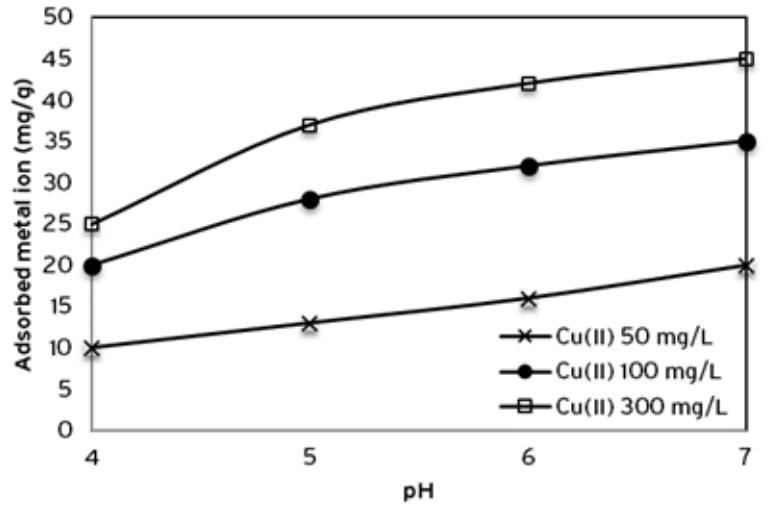


Figure 3. Effect of pH on adsorption of Cu(II) ions on PHEMA-AC composite cryogel at 25°C.

be excessively protonated resulting in a decrease in metal ion adsorption. At higher pH values, the carbon surface has a negative charge, due to the ionization of acidic carbon- oxygen surface groups, leading in an increase in metal ion adsorption [24].

When figure 2 and figure 3 were compered, it was observed that for all of the pH range and metal ion concentrations, synthesized composite cryogel system had a higher affinity to Cu(II) ions than Ni(II) ions.

Figure 4 shows the Cu(II) and Ni(II) adsorption curves for PHEMA-AC cryogels. These adsorption curves were obtained by the adsorption of single metal ions to the aqueous solutions. The initial heavy metal concentrations were changed between 20-300 mg/L. The amount of metal ions adsorbed per unit mass of the cryogel (adsorption capacity) increased first with the initial metal ion concentration then reached a plateau value, which represents the saturation of the active sites available for metal ions adsorption on the PHEMA-AC cryogel. Adsorption of both heavy metal ions reached a saturation level at a bulk concentration of approximately 300 mg/L. The maximum adsorption capacities of the PHEMA-AC composite cryogel were 22 mg/g for Ni(II) and 45 mg/g for Cu(II). It was observed that PHEMA-AC cryogel had more affinity towards Cu(II) ions.

Non-specific adsorption of heavy metal ions onto the PHEMA cryogel without including AC was also performed under the same experimental conditions (pH=7, initial metal ion concentration of 300 mg/L). The heavy metal ion adsorption capacities on the PHEMA cryogel are relatively low, about 0.4 mg/g for Cu(II), 0.16 mg/g for

Ni(II). Since PHEMA cryogel is highly porous, it may absorb heavy metal ions within those pores. In addition, the hydroxyl and carbonyl groups of HEMA may also interact with the heavy metal ions causing this non-specific adsorption.

The repeated use (regeneration) of the polymeric adsorbents is likely to be a key factor in improving process economics [30]. PHEMA-AC cryogel loaded with the maximum amounts of the target metal ions were placed in the desorption medium containing 0.1 M HNO_3 and the amount of metal ions desorbed in 2 h was measured. High desorption ratios up to 99% were obtained for both of the metal ions with the desorption agent. Adsorption-desorption cycle was repeated five times using the same cryogel to investigate the reusability of the composite cryogels (Figure 5). Adsorption capacity of the PHEMA-AC cryogel did not change significantly during the repeated adsorption-desorption operations, showing that the synthesized cryogel can repeatedly be used in the target metal adsorption process without loosing its adsorption capacity.

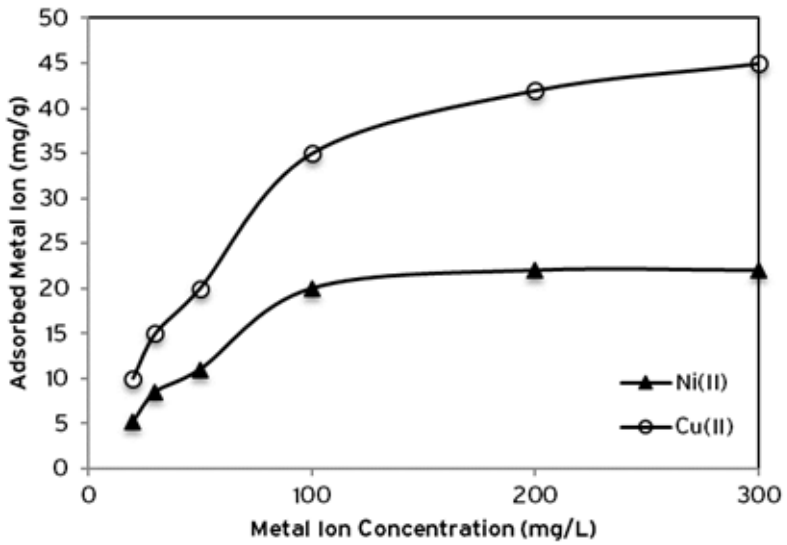


Figure 4. Effect of initial metal ion concentration on the adsorption of target metal ions on PHEMA-AC composite cryogel at pH=7 and T= 25ºC.

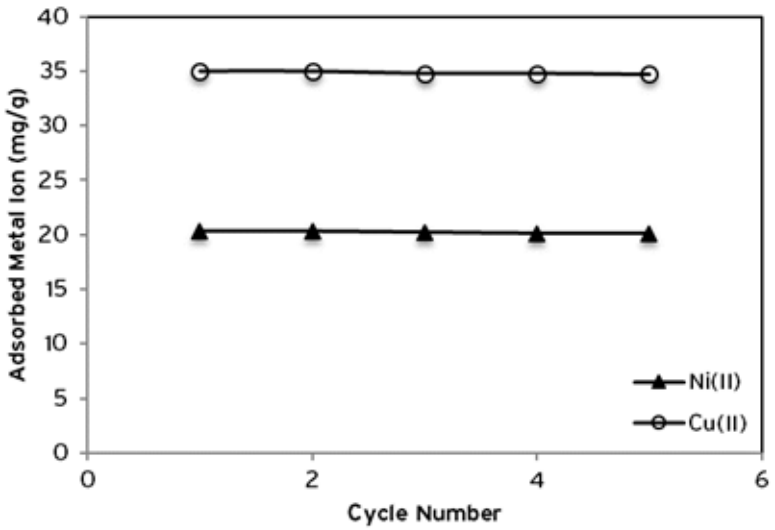


Figure 5. Adsorption–desorption cycle of PHEMA-AC composite cryogels. Metal ion concentration: 100 mg/L; pH: 7; temperature: 25ºC.

CONCLUSIONS

Cryogels can be one of the best choices for adsorption of heavy metal ions based on their advantages like structural flexibility, large pores, short diffusion pathways, easy implementation and cost friendly scale up potential for industrial applications. However, they have relatively low specific surface area resulting in low adsorption capacity in the adsorption process. In order to overcome this drawback, in this study, activated carbon having high adsorption capacity was embedded in the structure of PHEMA cryogel discs. Plain PHEMA discs had very low nickel and copper adsorption capacities. The addition of AC in the structure of PHEMA increased the adsorption capacities significantly. It can be concluded that embedding plays an important role for the increase in the adsorption capacity of a cryogelic adsorbent and proposed material can be classified as an efficient adsorbent and an alternative for the control of heavy metal ion pollution.

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