

Lead Removal from Industrial Waste

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ABSTRACT

In this study, the heavy metal removal performance of poly(2-hydroxyethyl methacrylate-N-methacryloyl-(L)-histidine methyl ester), poly(HEMA-MAH) cryogel, a known polymer, in HNO₃ was investigated. To determine the heavy metal removal performance of cryogel, wastewater was used as obtained from an inorganic material manufacturer. The characterization studies using scanning electron microscopy (SEM), Fourier transform infrared (FT-IR) spectroscopy, elemental analysis, water-swelling tests and surface area analysis were conducted. The effect of HNO₃ on the adsorption process, especially for metals, was found very effective even in trace amounts.

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INTRODUCTION

The increasing number of factories with the heavy metal wastes, especially lead, such as a battery, dye, and fertilizer manufacturing, etc. [1], in consequence of the fast developments of agricultural and industrial fields, threaten the ecological environment and human health. The heavy metal ions cannot be degraded, and resulted in an accumulation in the living organism tissues [2]. The lead limits in drinking water allowed by the World Health Organization is 10 µg/L [3]. Moreover, even very little concentration of lead can cause severe consequences for living things including humans [4]. Because its high affinity to enzymes having thiol (-SH) and phosphate ions (PO₄³⁻), ligands and biomolecules inhibiting the haem biosynthesis, Pb²⁺ ions are very hazardous for the permeability of cell membranes in kidney, liver, and brain and likewise toxic for nervous and reproduction system, resulting in abortion, dead and neonatal birth, mental retardation [5, 6], etc. Additionally, it may form complexes with the oxo-groups of enzymes which are very active in porphyrin metabolism and haemoglobin synthesis [7]. Besides the potential neurological and carcinogenic effects of lead, it may cause cognitive and physical retardation in child development, especially in the interval of 0-7 age [8]. Lead has been classified as a carcinogenic

element by the US Environmental Protection Agency and International Agency for Research on Cancer [9].

To date, many of methods were reported on the removal of heavy metal from aqueous solutions such as flocculation, coagulation, electrochemical treatment, and solvent extraction etc. [10-12]. Most of these methods are insufficient and not cost-friendly for controlling heavy metal levels in wastewater, and also for effectivity and environmental care [7]. The affinity adsorption method is the most promising method for the heavy metal removal process [13]. The adsorption technique is simple, cost-friendly and non-toxic [14-17]. Thereupon, useful and easy-to-prepare adsorbents are needed to developed for the heavy metal removal [18] such as iron oxide [19, 20], activated carbon [21], kaolinite [22] and zeolite [23]. On the contrary, these materials have some drawbacks such as aggregation, low adsorption capacity and poor mechanical strength resulting in low yields [24].

In this study, we developed polymeric cryogels, poly(2-hydroxyethylmethacrylate-N-methacryloyl-(L)-histidine methyl ester), poly(HEMA-MAH), for the removal of lead ions from aqueous solution and wastewater obtained from an inorganic material

manufacturer. The aim of the synthesis of this polymeric material was to develop an alternative to conventional methods for heavy metal removal. The application of cryogels is very simple compared to other adsorbents, and thus it may be a good contribution to the literature for the removal of heavy metals.

MATERIALS and METHODS

2-Hydroxyethyl methacrylate (HEMA), ethylene glycol dimethacrylate (EGDMA), lead(II) nitrate, ammonium persulphate, (APS), sodium dodecyl sulphate (SDS), N,N,N',N'-tetramethyl ethylene diamine (TEMED) were purchased from Sigma (St. Louis, USA). N-methacryloyl-(l)-histidine (MAH) was synthesized in accordance with the literature [25]. All other chemicals were in analytical grade and ultra-pure water was used in all experiments.

Synthesis and characterization of poly(2-hydroxyethylmethacrylate-N-methacryloyl-(L)-histidinemethylester cryogels

For the synthesis of poly(HEMA-MAH) cryogels, MAH (200 mg) and HEMA (5 mL) were used as the functional monomer and solid support, respectively. HEMA and MAH were mixed with distilled water of 5 mL before adding to the dispersant phase comprising SDS (1 g), EGDMA (1.2 mL) and distilled water of 18.8 mL. The solution obtained was stirred in a magnetic stirrer for 5 minutes and remained in an ice-bath for 15 minutes before the addition of APS (30 mg) and TEMED (150 μ L). The resulting gel was poured into the two glass plates and remained at -20°C for 24 hours for the cryogelation. A day later, the polymeric cryogel plate was taken, and cut in the shape of a circular disk and washed with distilled water to get rid of unwanted chemicals and foam.

The achievement on the structure of cryogels was tested via FT-IR (Thermo Scientific Nicolet 6700 FT-IR spectrometer, Waltham, USA) (Figure 1). The stretching (at

3390.05 and 1713.53 cm^{-1}) and amide (at 1650.32 and 1540.38 cm^{-1}) bands were the proof of the MAH incorporation (195 $\mu\text{mole/g}$ polymer, via Elemental analysis (Elementar Vario PYRO cube, Hanau, Germany) into the structure. Because of cryogelic polymerization, there were big cavities formed as a result of water removal at the end of the polymerization. The cavities with rough surface (approximately $3.343\text{ m}^2/\text{g}$, via Quantachrome AutosorbVR iQ-Chemi, Florida, USA, which was comparable with the literature [26-28]) suitable for the adsorption of lead ions could be seen in SEM (Carl Zeiss AG—EVO[®] 50 Series, Germany) images given in Figure 2. The water uptake amount of cryogels was found (376% on average) using the difference between the weights of dry and water retained cryogel according to the formula given by Equation 1. This means that approximately 376 times cryogel mass diffuse into the cryogels with target molecules inside, resulting the long-time interaction, providing high yields in spite of low surface area.

$$\text{Water uptake \%} = \left[\frac{(W_{\text{swollen}} - W_{\text{dry}})}{W_{\text{dry}}} \right] \times 100 \quad (1)$$

Where W_{swollen} is the weight (g) of swollen after removal from the water bath and W_{dry} is the dry weight before entering the water bath.

The Adsorption-Desorption Experiments

The nitric acid solution (5%, v/v) was used as a solvent for the lead removal from aqueous solution. All experiments were performed via a rotator at the speed of 20 rpm for 15 minutes batch wise. The lead adsorption capacities of cryogels were estimated using the formula given by Equation 2.

$$q = \frac{(C_i - C_f) \times V}{m} \quad (2)$$

Where, q , C_i , C_f , V and m are adsorption capacity (mg/g), initial concentration (mg/L), final concentration (mg/L), the volume of the adsorption medium (mL) and amount of cryogel (g), respectively.

The atomic absorption spectrophotometry (Thermo

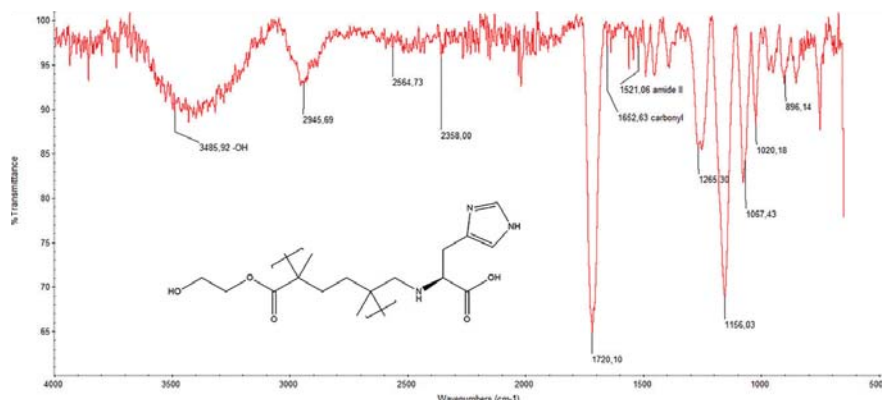


Figure 1. FT-IR spectra of poly(HEMA-MAH) cryogels.

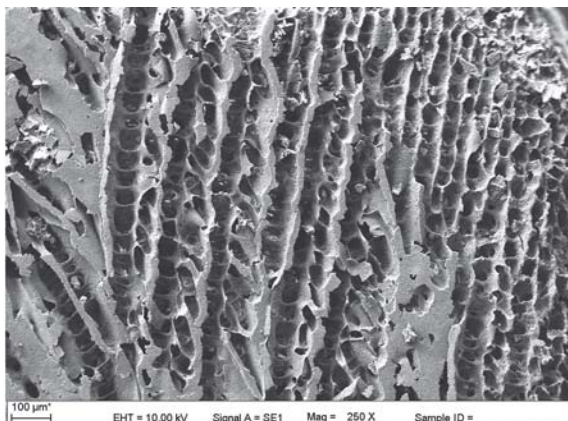
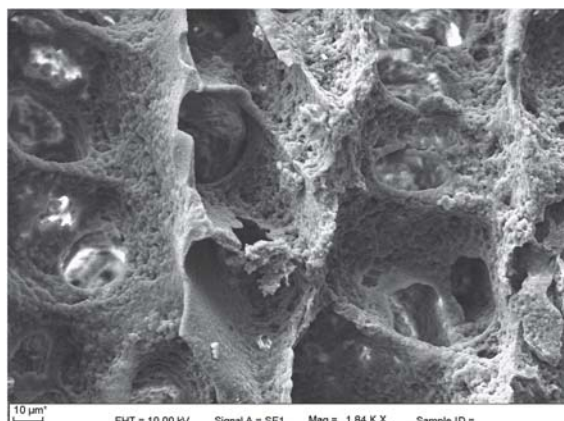


Figure 2. SEM images of poly(HEMA-MAH) cryogels.



Scientific / ICE 3500, UK) and inductively coupled plasma optic emission spectrophotometry (Thermo Scientific / ICAP 6500, UK) were used for the determination of lead amount adsorbed, and each experiment was repeated thrice for the statistical reliability.

RESULTS and DISCUSSION

To determine the lead amount adsorbed onto the cryogels, wastewater sample was obtained from an inorganic material manufacturer. The electrostatic interaction was dominant throughout all experiments.

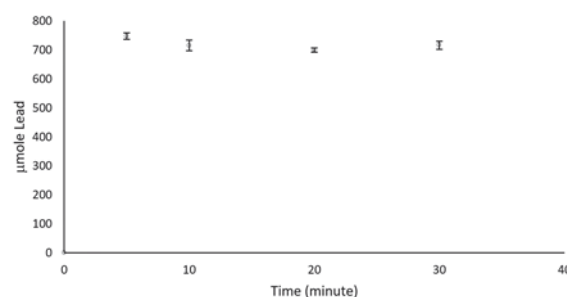
The Adsorption-Desorption Experiments

Because of highly recommended electrostatic interaction between the ligand and target molecules was achieved during this study, the interaction between cryogels and lead was almost completed in 5 minutes. (Figure 3). The plateau observed after 5th minute was because all binding sites were engaged with the lead atoms in the solution and no more interaction can occur. On the contrary, the adsorption onto poly(HEMA-MAH) cryogels was increased with increasing concentration with no plateau observed up to 1000 ppm due to the fact that the number of ligands attached to the structure was high and also the target lead ion was quite small as compared to a polymeric structure resulting high number of interactions with each functional group on the polymeric cryogel (Figure 3).

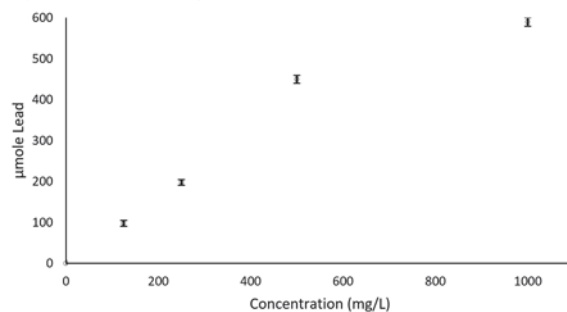
The poly(HEMA-MAH) cryogels had uptake lead of approximately 747 μmole in a fast and cost-friendly single step process for the removal of Pb^{2+} ions.

The Pb^{2+} adsorption capacity of poly(HEMA-MAH) cryogel was determined from a sample of wastewater from a local fabric manufacturer. To run the experiment, sample and HNO_3 ratio was specified in the ratio of 1:1. The lead adsorption capacity of cryogel was determined as approximately 34% of all wastewater which is quite high.

The lead-adsorption behaviour of cryogel was ascertained by the isotherm estimation. For that purpose, the Langmuir and Freundlich adsorption isotherm constants were calculated primarily. According to the graphs given in Figure 4 (time and concentration versus adsorbed lead amount), the single layer interaction was preponderant on the homogeneous surface (Table 1). The adsorption isotherm constants can be found in Table 1. The Redlich-Peterson adsorption isotherm model was also investigated which gave quite an effective result, especially for heavy metal adsorption interactions. In Table 1, β (0.36) value was in good agreement with the Langmuir adsorption model. In this adsorption system, the dominating model is the pseudo-second-order kinetic model due to the higher correlation coefficient value (1.00) meaning that the process was run as chemically controlled.



C_{pb} : 10 mg/L, T: 25°C, a in HNO_3 of 5 % (v/v)



$t_{\text{adsorption}}$: 30 minutes, T: 25°C, in HNO_3 of 5 % (v/v)

Figure 3. Lead adsorption onto poly(HEMA-MAH) cryogel.

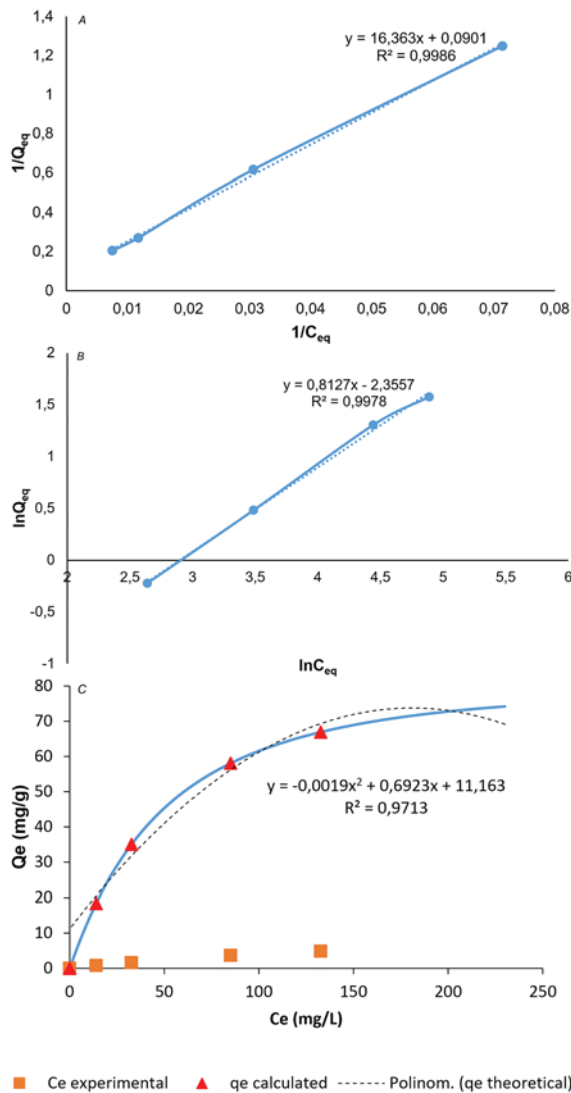


Figure 4. A) Langmuir, B) Freundlich and C) Redlich- Peterson Adsorption Isotherms.

Table 1. Adsorption isotherm and kinetic parameters for the aluminium adsorption process.

| Langmuir Isotherm | | | | Freundlich Isotherm | | | Redlich-Peterson Isotherm | | | |
|--------------------|-----------------|----------------|--------|---------------------|-------------------|--------|---------------------------|------|------|--------|
| Q_{exp} | Q_{max} | b | R^2 | n | K_f | R^2 | K | a | b | R^2 |
| 6,12 | 11,98 | 0,005 | 0,9986 | 0,812 | 0,118 | 0,9978 | 0,18 | 0,69 | 0,36 | 0,9713 |
| Pseudo-First-Order | | | | Pseudo-Second-Order | | | | | | |
| $Q_{exp} (mg/g)$ | $q_{eq} (mg/g)$ | $k_1 (1/min.)$ | R^2 | $q_{eq} (mg/g)$ | $k_2 (g/mg.min.)$ | R^2 | | | | |
| 1,96 | 3,58 | 0,0044 | 0,81 | 1,90 | 0,3792 | 1,00 | | | | |

CONCLUSION

The importance of lead removal is getting more and more increased because of increasing number of diseases, especially anaemia, encephalopathy, and colic disease. We are exposed to heavy metals, especially lead, every day from air, water, soil and food products. In this study, poly(HEMA-MAH) cryogel was synthesized to provide a polymeric material for the removal of lead from wastewater. It was observed that chemical dynamics were dominated during adsorption occurring in one layer homogenously. The wastewater sample obtained from the manufacturer was the important target medium to see the lead adsorption performance of the cryogel to see whether this polymeric material will run or not. A cost-effective, short-timed and simple method was applied in this study. As a concluding remark, it can be said that the poly(HEMA-MAH) cryogel is promising alternative for efficient heavy metal, especially Pb^{2+} removal, contrary to conventional techniques.

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