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Study on Adsorption Properties of New Sodium Alginate and Chitosan Quaternary Ammonium Salt for Heavy Metal Ions

Chonghua Li

College of Chemical Engineering,Changchun University of Technology, Changchun, China.

20211486@stu.ccut.edu.cn

Abstract. Up against accelerating industrialization, heavy metal pollution has been a global environmental problem. Hence, it is urgent to develop high-efficiency, low-cost and environmentally friendly heavy metal adsorption materials. This study aims to explore sodium alginate and chitosan quaternary ammonium salt (Alg/HTACC), a new biosorption material, and evaluate its adsorbability for heavy metal ions. Alg/HTACC is prepared by solution mixing, with its structure and morphology characterized by Fourier transform infrared spectroscopy and X-ray diffraction. Alg/HTACC is porous in structure, which is beneficial to improving the capture capacity of metal ions. As for the study of adsorption properties, the adsorption behavior of Alg/HTACC for many heavy metal ions such as Cu^{2+}, Cd^{2+} and Pb^{2+} is systematically investigated. According to experimental results, Alg/HTACC has a good adsorption effect on these metal ions. The regeneration ability and recycling potential evaluated by desorption experiments on saturated Alg/Alg/HTACC still maintain high adsorption efficiency, which proves its good usability.

Keywords: Sodium Alginate; Chitosan Quaternary Ammonium Salt; Heavy Metal Ions; Adsorption Property; Desorption Performance.

1. Introduction

With the development of industrialization, heavy metal pollution has been an imperative aspect of global environmental pollution problems [1-5]. Excessive heavy metals will have severe consequences on the human body [6-8], resulting in cell necrosis, kidney disease and other diseases, even carcinogenesis. The accumulation and diffusion of heavy metal ions in the environment pose a great threat to human health and the ecological environment. Thus, the development of efficient heavy metal adsorption materials [9-11] has been the key to solving the content of heavy metals such As Pb, Cd, Hg, Cr and As, which have significant toxicity to people, animals, plants and microorganisms. Given that heavy metal pollution has become a major global environmental problem, the prevention and control of heavy metal pollution has always been a difficulty and research trend in the international environmental protection community [12-13]. Heavy metals can not be degraded by microorganisms and the pollution to environmental media is concealed, long-term and cumulative, so there is no universal and effective treatment till now. Most industrial wastewater can not be treated or the treatment cost is too high, which causes great damage and pollution to the environment. Hence, it is urgent to conduct research on heavy metal pollution control technology and related basic theories to tackle the increasingly serious heavy metal pollution.

Sodium alginate (SA) and chitosan (CS) are two natural polymer materials with good biocompatibility and biodegradability, which are widely used in biomedicine, food processing and environmental protection. Chitosan [14] is a natural basic polysaccharide cationic polymer, which is composed of N-acetyl linked by β-(1-4)glycosidic bond-D-glucosamine. It can be prepared by deacetylation of chitin, providing antibacterial, anti-inflammatory and antioxidant capabilities (CS PACS CM-CTS, etc.) [15]. Sodium alginate is a gel-like substance (SA, PVA/SA, etc.) formed by the combination of natural substances extracted from marine algae and Na^+ [16]. However, the traditional SA/CS hydrogel for heavy metal ions adsorption effect is not ideal with limited adsorbability. It's difficult to meet the needs of daily practical applications [17-18]. Therefore, it is of great significance to improve the adsorption property of heavy metals in SA/CS hydrogel by introducing quaternary ammonium salt functional groups [19].

In recent years, researchers have obtained a series of research results on the adsorption of heavy metal ions in SA/CS quaternary ammonium salt hydrogels. For example, Li et al. [20] prepared CS quaternary ammonium salt hydrogel with high absorbability by grafting quaternary ammonium salt functional groups onto the CS chain. The experimental results show that the absorbability of Cu^{2+}, Pb^{2+} and Cd^{2+} on the hydrogel reaches 359.6 mg/g, 314.2 mg/g and 287.1 mg/g respectively, which is significantly higher than that of unmodified CS hydrogel. In addition, Sun et al. [21] prepared an SA/CS quaternary ammonium salt hydrogel through electrostatic interaction and chemical bonding, which was used to adsorb Pb^{2+} and Cd^{2+} efficiently. According to the experimental results, the absorbability of Pb^{2+} and Cd^{2+} by the hydrogel is 480.3 mg/g and 365.2 mg/g respectively, which is much higher than that of traditional SA/CS hydrogel and other researched adsorption materials [22-23].

Although some achievements have been made, the absorbability of SA/CS quaternary ammonium salt hydrogel for heavy metal ions still needs to be further improved. First of all, the structure of sodium alginate [24] has regional and sequence specificity. In other words, the arrangement order and proportion in the chain are different, which determines the difference in its physical and chemical properties. Chitosan is characterized by a large number of amino ($-NH_2$) and hydroxyl (-OH) functional groups [25-26], which make chitosan have good biocompatibility, biodegradability and biological activity [27]. At present, the research mainly focuses on the adsorption of single heavy metal ions, but there are many kinds of heavy metal ions in the actual environment with complicated actual applications. Hence, it is necessary to study the absorbability and mechanism of SA/CS quaternary ammonium salt hydrogel for various heavy metal ions. Secondly, the existing research is mainly about optimizing the preparation methods and adsorption conditions of SA/CS quaternary ammonium salt hydrogel, while the research on its adsorption kinetics and thermodynamic characteristics is relatively few, so it is necessary to further explore the kinetics and thermodynamic characteristics of SA/CS quaternary ammonium salt hydrogel for heavy metal ions [28]. Finally, although studies have shown that SA/CS quaternary ammonium salt hydrogel has certain absorbability, its application and prospect still need to be further expanded. Systematic research is still needed to provide a theoretical basis and technical support for further application of SA/CS quaternary ammonium salt hydrogel [29].

This study aims to investigate the adsorption mechanism, kinetics and thermodynamic properties of SA/CS quaternary ammonium salt hydrogel through the synthesis, structure characterization and heavy metal ion adsorption properties, so as to provide theoretical basis and technical support for its further application. In this study, sodium alginate/chitosan quaternary ammonium salt composite hydrogels with different proportions are synthesized, and then the absorbability of the hydrogels for heavy metal ions such as Cu^{2+}, Pb^{2+}, Cd^{2+} is studied by static adsorption experiments.

2. Materials and Methods

2.1 Materials

Chitosan with 96% deacetylation (CS; Bio Basic, ON, Canada), sodium alginate with 98% purity and a viscosity of 31.5 cps (Techno Pharmchem, India), ultra-pure CaCI2 (Alpha Chemika, India), ureal (Piochem, Egypt), XTT (2, 3-bis (2-methoxy-4-nitro-5-sulfo-phenyl)-2Htetrazolium-caranide; iga1, 111 (Sigma, USA) and acetone (Piochem, Egypt) are used in this study. All other chemicals are supplied by Sigma (USA) and other standard commercial sources.

2.2 Experiments

2.2.1 Preparation of HTACC

3 g CS is suspended in 30 mL of water with 5.2 mL of glycidyl trimethyl ammonium chloride (GTMAC). It is heated to 60 ℃ in a water bath and stirred at 60 ℃ at a rotational speed (200r/min) for 24 hours. The reaction product is precipitated with 2vol acetone. The precipitated product is filtered and dried at room temperature (RT) for 24 hours (Sangeetha et al., 2015). The substitution degree of the quaternized CS is calculated as supplemental material.

2.2.2 Preparation of Sodium Alginate/HTACC Hydrogel

Sodium alginate (Alg) and HTACC are dissolved in 2% w/v distilled water at a mechanical stirring speed (200r/min). The prepared solution is stirred at room temperature for 1 hour, and then the $CaCl_2$ crosslinking solution is added into the mixture until gelation occurs. The hydrogels are dried in a 40 ℃ vacuum oven (BZF-50) for 24 hours. Blends with different mass ratios (60% Ag:40% HTACC, 50% Ag:50% HTACC, 40% Ag:60% HTACC, 30% Ag:70% HTACC) are prepared. The blends are prepared by repeating the above steps with $CaCl_2$ at the following concentrations of 1%, 3% and 5%. Twelve groups of sodium alginate/HTACC hydrogels with different proportions are obtained.

2.3 Experimental Characterization

Fourier Transform Infrared Spectrometer (FTIR) can be used to identify compounds and characterize their molecular structures, which can also be used for quantitative analysis [30-31]. X-Ray Diffraction (XRD) is the main method to study the phase and crystal structure of materials [32]. Inductively Coupled Plasma Emission Spectrometer (ICP) is to analyze the elements to be measured according to the characteristic spectral lines emitted by the atoms of the elements that are measured in the excited state when they return to the ground state. ICP is mainly used in qualitative and quantitative analysis of inorganic elements. ICP-OES can determine most elements in the periodic table (metal elements and non-metal elements such as phosphorus, silicon, arsenic and boron) simultaneously, all of which have good detection limits.

2.4 Determination of Water Absorption of 2.4 Composite Hydrogel

0.1 g composite hydrogel (m_1) is weighed, which is soaked in 100 mL distilled water for 24 hours. Then, the hydrogel is taken out, absorbing the surface moisture and weighing (m_2), so as to calculate the water absorption rate (Water uptake, Wu, $g \cdot g^{-1}$) according to the formula.

$$\mathrm{W}_u = \frac{W_2 - W_1}{W_1}$$

2.5 Adsorption and Resolution of Different Heavy Metal Ions by Composite Hydrogel

$Cu(NO_3)_2 \cdot 3H_2O$, $Cd(NO_3)_2 \cdot 4H_2O$ and $Pb(NO_3)_2$ are used as solute solutions with concentrations of 200 umol·L^{-1}. The original concentrations (c_o) of Cu^{2+}, Cd^{2+} and Pb^{2+} are measured by ICP. 0.1 sample (m) is soaked in distilled water until the water absorption equilibrium is reached. After the surface water is drained, it is put into 50 mL aqueous solution of heavy metal ions (V by volume) and stirred for 12 hours, with the hydrogel taken out to measure the concentration (c_1) of heavy metal ions in the adsorbed aqueous solution. Sorption capacity (Se, $mg \cdot g^{-1}$) is calculated as follows:

$$S_c = \frac{(c_0 - c_1)V}{m_0}$$

The adsorbed hydrogel is soaked in 50 mL^{-1} mol L^{-1} HNO_3 solution for 2 hours, and the content of heavy metal ions (c_2) in the solution is determined.

$$\mathrm{E_p} = \frac{(c_1 - c_2)V}{S_c \times m_0} \times 100\%$$

3. Results and Discussion

3.1 FITR Infrared Data Analysis

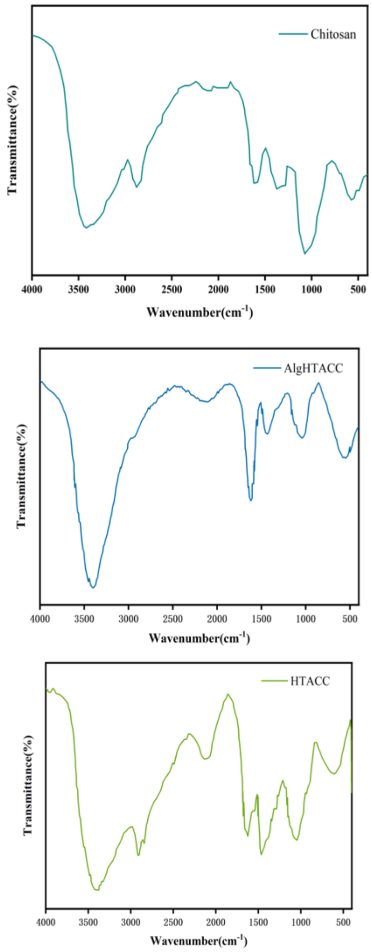

Figure 1 FTIR is (a) chitosan, (b) HTACCC, (c) Alg/HTACCC

For chitosan quaternary ammonium salt, the main functional groups [33-35] are as follows. The $-NH_3^+$ group is the most vital functional group of chitosan quaternary ammonium salt, which can be identified by the N-H stretching vibration absorption band (about 3400 cm^{-1}) in the infrared spectrum. The -OH group is the quaternary ammonium salt of chitosan, which still retains a part of the -OH group and can be identified by the O-H stretching vibration absorption band (about 3200-3600 cm^{-1}) in the infrared spectrum. -C=O group is the interaction between the -C=O group and the $-NH_3^+$ group in chitosan quaternary ammonium salt, which can be identified by C=O stretching vibration absorption band (about 1650-1700 cm^{-1}) in the infrared spectrum.

Chitosan: 3416cm^{-1} is N-H stretching vibration, 1600cm^{-1} is N-H deformation vibration in the presence of $-NH_3^+$ group, 2879cm^{-1} is C-H stretching vibration, 1374cm^{-1} is C-H bending vibration in the presence of acetyl group, 1072cm^{-1} is a strong characteristic peak of fatty ether. **HTACC:** 3400cm^{-1} is N-H stretching vibration, 1622cm^{-1} is N-H deformation vibration in the presence of $-NH_3^+$ group, 2916 cm^{-1} is C-H stretching vibration, 2114 cm^{-1} is alkyne triple bond stretching vibration, 1464cm^{-1} is C=C skeleton vibration, 1045cm^{-1} is C-O stretching vibration. **Ag-HTACC:** 3400cm^{-1} is N-H stretching vibration and 1616 cm^{-1} is N-H deformation vibration. 1432cm^{-1} is C-H flexural vibration and 1050 cm^{-1} is aromatic ether R-O stretching.

3.2 XRD Data Analysis

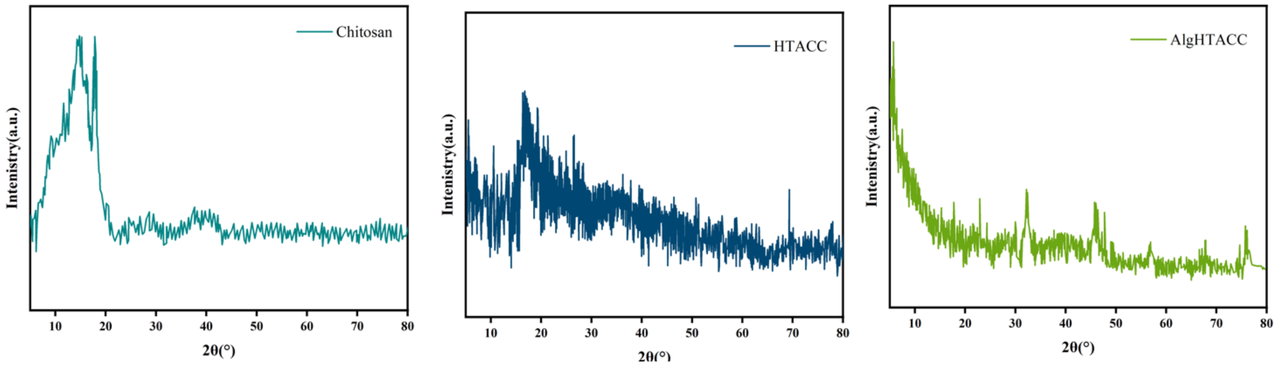

Figure 2 XRD is Chitosan, HTACCC and AlgHTACCC

HTACC: XRD of quaternary ammonium salted chitosan can provide information about its crystal structure, such as crystal structure type, lattice parameters, crystal plane spacing and unit cell volume. However, the specific degree and crystal plane analysis need to be determined according to the experimental data, and the structure of chitosan quaternary ammonium salt may change with its degree of substitution and molecular weight.

Alg/HTACC: XRD of chitosan films have peaks at 18.7° and 22.5°, which represent the existence of hydrated and dehydrated crystals respectively. The XRD [37-38] of sodium alginate film showed crystallization peaks at 15.2° and 22.5°. These results confirm the existence of crystal structure in these two biopolymers, and different treatment processes will affect their crystal morphology and stability.

3.3 Water Absorption of Composite Gel

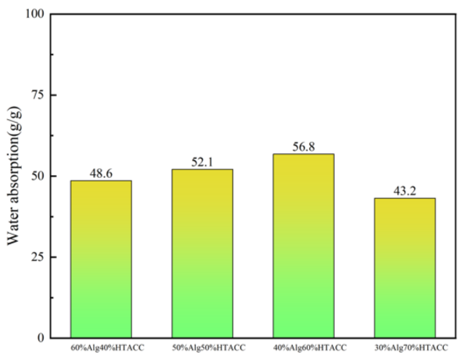

Figure 3 Water Absorption of Alg/HTACC Composite Gel

The composite gel is composed of two or more different gels, and its water absorption [39-40] is one of the important indexes to measure its performance. The water absorption rate affects the application effect of composite gel, such as the application in agriculture, medical treatment, cosmetics and other fields. The water absorption of composite gel is related to the hydrophilicity of its constituent materials. Generally speaking, the stronger the hydrophilic material, the higher its water absorption. Alg/HTACC composite gel is rich in hydrophilic groups with strong hydrophilicity. As for the material structure, quaternary ammonium chitosan and sodium alginate are both hydrophilic structures, while the composite hydrogel prepared by them has a porous network structure, which forms a special crosslinking network through process control and the water absorption has been greatly improved. The water absorption test is conducted by immersion method as shown in Figure 3.

With the increasing HTACC, the water absorption of the composite hydrogel first increased to 56.8%, and then decreased to 43.2%. This is because the addition of HTACC makes Alg/HTACC form a microscopic macroporous structure, which is beneficial to the absorption of water by composite gel. However, with the increasing HTACC to a certain extent, the filler in the pore increases and the water absorption decreases slightly.

3.4 Adsorption of Cu^{2+}, Cd^{2+} and Pb^{2+} by Alg/HTACC

As a polymer material with a three-dimensional network structure, the composite hydrogel has good water absorption, water retention and biocompatibility. In recent years, composite hydrogels have been widely studied and applied in the adsorption and resolution of heavy metal ions [41-42]. Composite hydrogels can adsorb heavy metal ions by physical adsorption, chemical adsorption and biological adsorption. Physical adsorption is mainly through the porous structure and surface active sites of hydrogel to adsorb heavy metal ions. Chemical adsorption is mainly through the formation of stable chemical bonds between functional groups in hydrogel and heavy metal ions. Biosorption is through the specific binding of biomolecules such as proteins, polysaccharides, etc. in hydrogels with heavy metal ions.

The adsorption and desorption experiments of Cu^{2+}, Cd^{2+} and Pb^{2+} ions are implemented several times. With the increasing HTACC, the adsorption experiments of the three ions increased to a certain extent at first and then decreased. The adsorption of heavy metal ions by Alg/HTACC composite hydrogel is mainly chemical adsorption, supplemented by physical adsorption. With the increasing HTACCC content, S_c increases first, which is due to the increasing pore number, surface active sites and functional groups that can form stable chemical bonds with heavy metal ions. When the content of HTACC increases to a certain extent, S_c decreases, which is due to the formation of macro-pore structure and the elastic pore, leading to the decreasing surface active sites and functional groups.

As shown in Figure 4, the composition of 40%Alg60% HTACC has the best adsorption effect on three metal ions. At this time, the content of HTACC in the structure composition of composite hydrogel is the most suitable, and the size of elastic pore, the number of surface active sites and functional groups are all the most conducive to the adsorption of heavy metal ions, which has critical research significance for the subsequent industrial treatment of industrial wastewater with sodium alginate and chitosan quaternary ammonium salt.

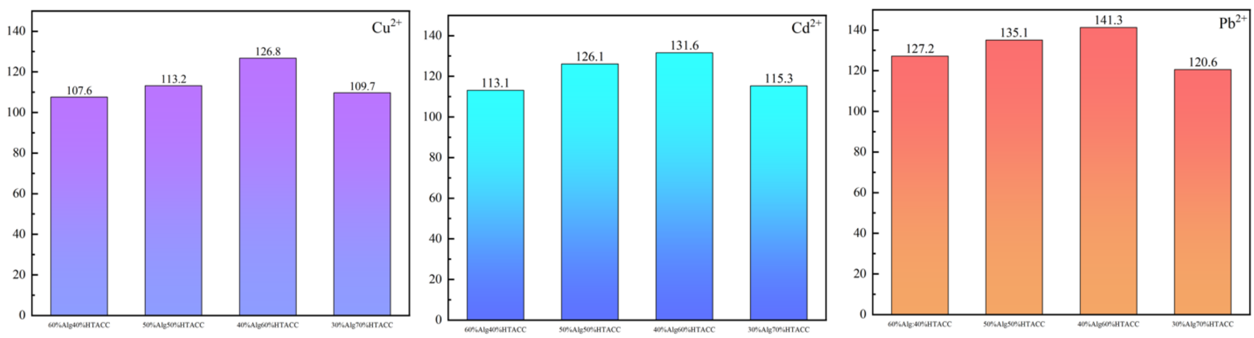

Figure 4 Adsorption of Cu^{2+}, Cd^{2+} and Pb^{2+} by Alg/HTACC

3.5 Desorption of Cu^{2+}, Cd^{2+} and Pb^{2+} by Alg/HTACC

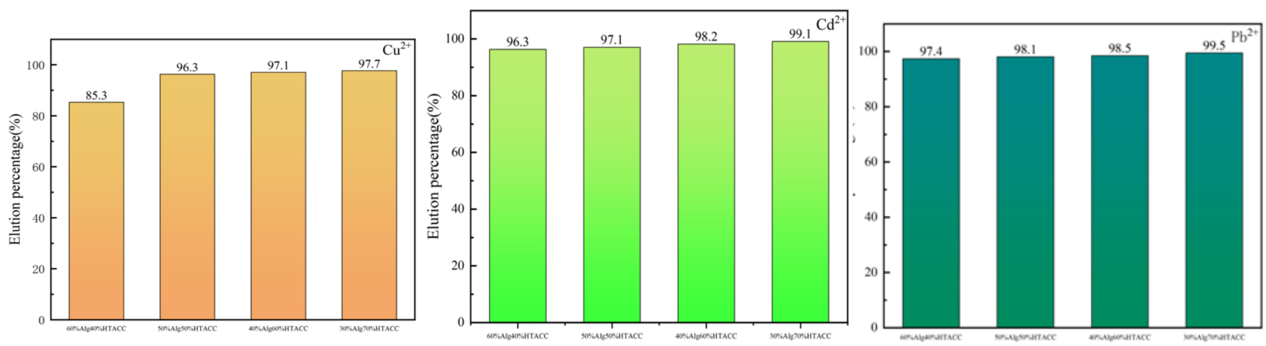

Figure 5 Desorption of Cu^{2+}, Cd^{2+} and Pb^{2+} by Alg/HTACC

The analysis of heavy metal ions by composite hydrogel mainly includes acid washing, alkali washing, salt washing and solvent washing [43]. These methods are mainly by changing the pH ionic strength or solvent properties of the solution to destroy the adsorption equilibrium between the hydrogel and heavy metal ions, thus realizing the resolution of heavy metal ions. In addition, heavy metal ions can be resolved by adding competitive adsorbents or using biological enzymes.

The adsorption and resolution properties of composite hydrogels for different heavy metal ions are affected by many factors, such as composition, structure, surface properties, pore size and so on. By adjusting and controlling these factors, composite hydrogels with high adsorption and resolution properties can be prepared, which provides an effective means for the treatment of heavy metal pollution.

3.6 Repeated Adsorption and Desorption of Pb^{2+} by 40%Alg60%HTACC

After Pb^{2+} are adsorbed on the pore surface, the porosity of the material increases, but a small amount of Pb^{2+} remain in the pore after each desorption, so the sorption capacity S_c decreased when it was adsorbed again. But after 5 times of adsorption, the sorption capacity S_c remains stable, and the remaining Pb^{2+} in the pore tends to be stable, which shows a high desorption effect. In the same way, the porosity of the material increases when Pb^{2+} are adsorbed on the pore surface, but a small amount of Pb^{2+} remain in the pore after each desorption. Thus, the sorption capacity S_c will decrease when it is adsorbed again, but it remains stable after 5 times of adsorption with a high desorption effect. The results of five repeated adsorption experiments for Pb^{2+} are 141.3, 139.7, 138.1, 137.2 and 136.5 respectively. The desorption rate of Pb^{2+} is 95.8%, 97.9%, 96.2%, 95.9%, 93.4%. Therefore, it can be inferred that the new sodium alginate and chitosan quaternary ammonium salt has good stability, and the composite hydrogel may have repeated adsorption and desorption properties, which is of great significance for recycling the material, and the limit of repeated adsorption needs further discussion.

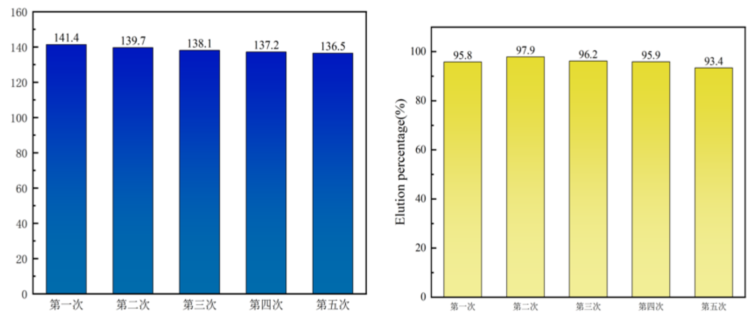

Figure 6 Multiple Adsorption and Desorption of 40%Alg60%HTACC and Pb^{2+}

4. Conclusion

This aims to investigate the absorbability of a new sodium alginate and chitosan quaternary ammonium salt for heavy metal ions. After a series of adsorption experiments and instrumental characterization analysis, the following conclusions are drawn. The new sodium alginate and chitosan quaternary ammonium salt has good adsorption performance for heavy metal ions. According to the experimental results, the material can adsorb a variety of heavy metal ions, including Cu^{2+}, Cd^{2+} and Pb^{2+} with the remarkable adsorption effect. The analysis of influencing factors shows that different mass ratios of Alg:HTACC have a significant influence on the adsorption effect. Under proper conditions, the adsorption effect is the best. According to the reusability experiments, the new sodium alginate and chitosan quaternary ammonium salt has good stability with sustainable high absorbability after many adsorption-desorption cycles. To sum up, the new sodium alginate and chitosan quaternary ammonium salt has excellent absorbability of heavy metal ions, which has potential application prospects. However, further research is needed to optimize the adsorption conditions, improve the adsorption efficiency and explore the performance of practical applications.

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