Original Research

Study on the Adsorption of Heavy Metals in Sludge by Calcium Alginate Cross-Linked Zeolite Microspheres

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Abstract

This study successfully prepared a calcium alginate cross-linked zeolite microsphere, a heavy metal adsorbent, to reduce the harmful heavy metal content in sludge and improve the efficiency of sludge resource utilization. The effects of temperature, dosage, and stirring time on the adsorption effect were investigated by atomic absorption spectrophotometry and BCR (European Community Bureau of Reference) method, and the ecological risk of heavy metals in sludge before and after treatment was evaluated via the geoaccumulation index. The following results were obtained: after the sludge was treated with calcium alginate cross-linked zeolite microspheres, the total amount of heavy metals decreased, and the proportion of stable state increased. At temperatures within 10ºC-25ºC, the following trend was observed: the higher the temperature, the higher the adsorption efficiency. When the dosage was controlled at 0.5-2 g/500 ml and the stirring time was 2-3 h, a good adsorption effect was achieved. The pollution level of Pb and Zn in the sludge was reduced after adsorption treatment from unpolluted to moderately polluted to unpolluted, and that of Cd and Cu was reduced from moderately to heavily polluted to moderately polluted.

Keywords: sludge, calcium alginate, zeolite, adsorption, heavy metal

Introduction

The acceleration of industrialization and urbanization in recent years has resulted in large amount of sewage that needs to be treated. The amount of sludge produced from the sewage that must be treated is also increasing yearly [1]. By 2025, estimates indicate that China's municipal sludge output will reach more than 70 million tons. Sludge contains not only nutrients, such as N and P, but also persistent organic pollutants, as well as heavy metals, such as Cd, Zn, Cr, and Pb [2, 3]. The proper disposal and conversion of sludge into resources are urgent problems that need to be addressed. However, heavy metals are major obstacles

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to the recycling of sludge. The hazards of heavy metals in municipal sludge are mainly due to unstable heavy metals, such as free heavy metal ions and exchangeable heavy metals, that are easily absorbed by plants, have high mobility, and can undergo substitution reactions with other substances [4]. Given that these metals have a certain degree of mobility and non-biodegradability, they will be inhaled by humans through the enrichment of biological chains, thereby threatening human health and the environment. Therefore, an economical and efficient method for treating heavy metals in sludge must be urgently explored.

At present, adsorption is the most effective method for treating heavy metal pollution. The choice of adsorbent material is a key factor in determining the adsorption effect. As a common heavy metal adsorbent, zeolite is widely used in water treatment [5]. Sludge contaminated by heavy metals has a wide range of sources and usually contains multiple coexisting heavy metals. When zeolite adsorbs sludge with many kinds of heavy metals, it will be restricted by many factors, such as the mutual inhibition of heavy metal ions, resulting in its low adsorbent saturation. Therefore, improving the adsorption efficiency of zeolite is a problem that needs to be solved. Many researchers have modified zeolite to achieve good adsorption performance. The methods used generally include physical, chemical, and biological modifications [6-8].

In recent years, biological modification methods have become a research hotspot. The researchers have used natural sources, including sodium alginate [9], chitosan [10], and lignin [11,12], as raw materials, which were prepared into adsorption materials for removing heavy metal ions in sludge. They are widely used because of their environmental friendliness, non-toxicity, and low cost. As a kind of biosorbent, sodium alginate is a marine natural polymer polysaccharide extracted from the cell wall of brown algae [13]. Sodium alginate is rich in functional groups, such as hydroxyl and carboxyl groups, and can adsorb metal ions well. However, sodium alginate has poor mechanical strength, stability, heat resistance, and mechanical properties. Therefore, Sodium alginate is often grafted and crosslinked to improve its adsorption capacity. The chemical stability and mechanical strength of sodium alginate can be enhanced by cross-linking. Sodium alginate [14] can form a gel with many divalent ions through ion cross-linking. In the field of water treatment, non-toxic ions should be selected for cross-linking to ensure that drinking water is safe. Therefore, calcium ions are often selected to cross-link with sodium alginate. After cross-linking, a stable egg box structure is formed, which further improves the stability and mechanical strength of the material [15].

This study proposed the enhancement of the adsorption of sodium alginate by cross-linking a mixed solution of sodium alginate and zeolite with calcium ions, which utilize the biocompatibility and structural stability of calcium alginate. As a result, a new adsorbent combined with zeolite, which has good metal ion exchange performance, was achieved. After zeolite was added to the sludge and different adsorption conditions were changed, the adsorption effect on heavy metals in the sludge was tested to evaluate the ecological risk of the heavy metals in the sludge. Thereafter, its adsorption mechanism was analyzed. The findings in this work may provide a reliable means of removing heavy metals in the sludge in the future.

Materials and Methods

Experimental Materials and Instruments

The following instruments were used: a stirrer, atomic absorption spectrophotometer (TAS-990SVPERF), polarizing microscope (AxioScopeA1), scanning electron microscope (Quanta200), muffle furnace, drying oven, microwave digestion apparatus (MARS-5, CEM), and 5 ml syringe.

The following reagents were used: natural clinoptilolite, sodium alginate (Tianjin Kemiou Chemical Reagent Development Center), calcium chloride (Tianjin Hengxing Chemical Reagent Manufacturing Co., Ltd.), hydroxylammonium hydrochloride, hydrogen peroxide, ammonium acetate, lead nitrate, cadmium nitrate, hydrochloric acid and nitric acid (analytical grade), and hydrofluoric acid and glacial acetic acid (superior grade).

Source and Treatment of Sludge

Sludge was obtained from the A^2/O biological reaction tank in Xi'an Caotan Wastewater Treatment Plant. The heavy metal content in the sludge was determined as follows: the sludge was placed in a drying box for 72 h, dried, passed through a 50-mesh sieve for preliminary screening to remove crushed stones and animal and plant residues, ground into powder, and passed through a 100-mesh sieve. The sieved sludge was sealed for storage and placed in a dry box for backup [16].

Preparation of Calcium Alginate Cross-Linked Zeolite Microspheres

Exactly 15 g of zeolite was obtained, washed with deionized water, stirred with 1 mol•L^{-1} HCL for 1 h, rinsed with deionized water, and heated in a muffle furnace at 550ºC for 2 h. After acid heat treatment, zeolite was obtained, ground into powder, and passed through a 200-mesh sieve for backup. Then, 150 ml of 1.5% sodium alginate solution was mixed with 15 g of zeolite powder with a stirrer at 40ºC and stirred for 1 h. Exactly 0.1 mol•L^{-1} calcium chloride solution was slowly added through the needle tube, stirred for 10 h, and stored in a volumetric flask at room temperature without light for backup.

Characteristic Detection of Calcium Alginate Cross-Linked Zeolite Microspheres

Exactly 20 microspheres were obtained and measured with an outside micrometer, and the average value was determined to obtain the diameter of the microspheres. A certain number of microspheres were added to a graduated cylinder containing a certain amount of water, and the number of microspheres was determined by reading the increase in the graduated cylinder scale to obtain the average volume of the microspheres. The moisture content was calculated by placing a certain quality of microspheres into an oven at 55ºC, drying for 24 h, and weighing [17]. The calcium alginate cross-linked zeolite microspheres were dried at low temperature and examined by scanning electron microscopy.

Total Content of Heavy Metals in Sludge and Determination of Content of their Various Forms

Determination of the Total Amount of Heavy Metals in the Sample Sludge

Exactly 10 g of dry sludge was weighed, added to 100 ml of distilled water, and stirred for 2 h. An atomic absorption spectrophotometer was used to determine the total content of heavy metals in the sludge.

Determination of the Existential form and Content of Heavy Metals in Sludge

The modified BCR method [18, 19] was used to analyze the form and corresponding content of each heavy metal in the sludge. The method divided the heavy metals in the sludge into five forms, namely, water-soluble T1, exchangeable T2, reducible T3, oxidizable T4, and residual T5.

Heavy Metal Adsorption Experiment in Sludge

In the adsorption experiment, calcium alginate cross-linked zeolite microspheres were added into a beaker containing 500 ml of A^2/O biological reaction

tank sludge. Thereafter, the supernatant was removed, the remaining part was evaporated to dry state, and the changes in the total content of the four heavy metals Cu, Cd, Pb, and Zn were determined using an atomic absorption spectrophotometer. Cu, Cd, Pb, and Zn contents in the sludge were measured using the BCR method with three repetitions for each treatment group.

Ecological Risk Assessment of Sludge Treatment with Calcium Alginate Cross-Linked Aeolite Microspheres

The geoaccumulation index method was used to evaluate the pollution level of heavy metals in the sludge before and after microsphere treatment. This method was proposed by the German scholar Muller in 1969 [20] and has been widely used as an index to study the degree of heavy metal pollution in sediments [21, 22]; the specific calculation formula is as follows:

$$I_{geo} = \log_2(C_n/1.5B_n),$$

...where C_n is the content of element n in the sediment (mg·kg^{-1}), B_n is the geochemical background value of the element in the sediment (mg·kg^{-1}).

Data Analysis

The experimental data in this study were analyzed and graphed using Excel 2010 and Origin 2017, respectively.

Results and Discussion

Appearance Characteristics of Calcium Alginate Cross-Linked Zeolite Microspheres

The appearance characteristics of the prepared calcium alginate cross-linked zeolite microspheres were determined. The diameter of the microspheres was 2.15 mm, the monomer volume was 3.95 mm^3, the monomer weight was 4.89 mg, the water content was 79%, and the density was 1.24 mg/mm^3.

Fig. 1 shows that the calcium alginate cross-linked zeolite microspheres are spherical in shape, with

Table 1. The relationship between I_{geo} and pollution level.

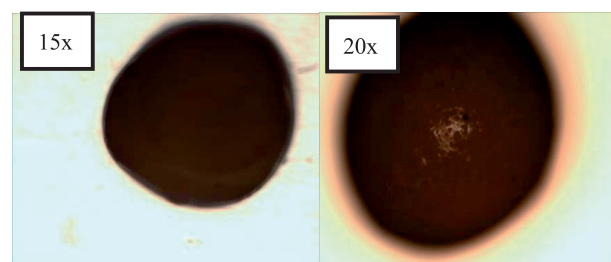| I_{geo}	Pollution level
$I_{geo}<0$	Unpolluted
$0 \leq I_{geo}<1$	Unpolluted to moderately polluted
$1 \leq I_{geo}<2$	Moderately polluted
$2 \leq I_{geo}<3$	Moderately to heavily polluted
$3 \leq I_{geo}<4$	Heavily polluted
$4 \leq I_{geo}<5$	Heavily to extremely polluted
$I_{geo} \geq 5$	Extremely polluted

Fig. 1. Calcium alginate cross-linked zeolite microspheres under polarized light microscope.
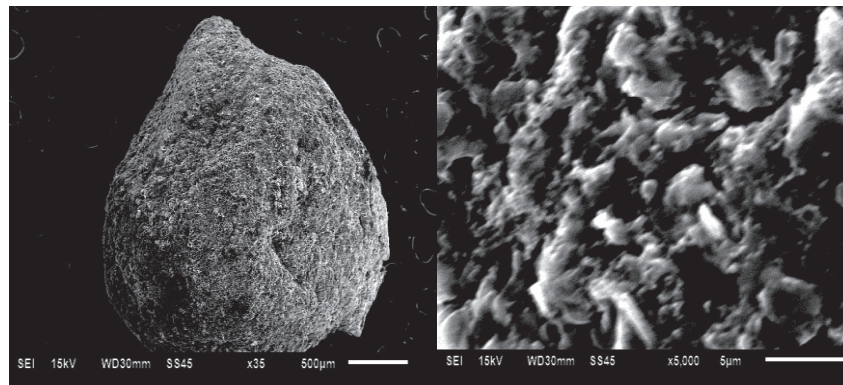
Fig. 2. SEM image of calcium alginate cross-linked zeolite microspheres.

a smooth surface, high water content, higher density than water, stable structure in water, and certain compressive strength.

The calcium alginate cross-linked zeolite microspheres were observed by scanning electron microscopy after dehydration (Fig. 2). The microspheres had a rough surface, many hole-like structures, and are full of gullies and channels. The complex internal structure of the zeolite resulted in its strong ion exchange and adsorption properties [23].

Determination of the Total Content of Heavy Metals in Sludge and the Content of Various Forms

Most of the heavy metals in urban sewage come from the wastewater of factories and enterprises and daily sewage. The sludge of the Xi'an Caotan Sewage Treatment Plant contained a large amount of Cu, Cd, Pb and Zn, and the contents and speciation of heavy metals in sludge from different sources varied. The heavy metal contents of the sludge in the municipal sludge, the sludge in the primary sedimentation tank, and the sludge in the A^2/O biological reaction tank were measured. The results are shown in Table 2 and Fig 3.

Among the five forms of heavy metals, the water-soluble state T1 and the exchangeable state T2 were considered to have high bioavailability and greater harm. Water-soluble T1 can be in an ionic state in a solution where pH is neutral, and heavy metals in this form will be directly absorbed and utilized by plants. The exchangeable state T2 showed great hazard under acidic conditions and easily combined with other

substances to enhance its toxicity, which was extremely harmful to the environment. The reducible state T3 was in the bound state and was relatively stable, but under certain conditions, it still released a certain amount of harmful heavy metal ions through the reaction. The oxidizable state T4 was generally the metal oxide with a stable structure and physical and chemical properties and was not absorbed and utilized by passive plants directly in nature. Only when the surrounding environment changes or the influence of chemical agents can the heavy metals be partially transformed into the forms that can be directly used by passive plants, with certain environmental risks. Residual state T5 was a stable heavy metal in nature, it will not be passively used by plants under normal conditions, and its physical and chemical properties were stable [24]; except under extreme conditions, it did not migrate, was extremely stable and usually not used as an effective content of heavy metals. Therefore, the sum of the content of each heavy metal in water-soluble state T1, exchangeable state T2, reducible state T3, and oxidizable state T4 was taken as the index of unstable heavy metal content in sludge, and the content of the residue T5 was used as the index of the stable content of heavy metals.

Considering that the sludge particles in the primary sedimentation tank were large, the content of residual T5 was high, the moisture content of the sludge was low (93%-96%), the sludge particles in the A^2/O bioreactor were small, the contact area was large, the moisture content was high (99.2%-99.6%), and the content of heavy metal in the bioreactor was higher than that in the primary sedimentation tank. Such conditions are conducive to the adsorption of calcium alginate

Table 2. The content of heavy metals in sludge from different sources.

Sample source	Total heavy metals (mg/kg)			
	Cu	Cd	Pb	Zn
Municipal sludge	158.17	2.96	79.12	560.32
Primary settling tank	142.29	2.15	65.48	530.66
A^2/O biological reaction tank	144.36	2.74	70.21	496.74

cross-linked zeolite microspheres. Therefore, the sludge in the A²/O biological reaction tank was studied to explore the effects of changing temperature, dosage, and stirring time on the adsorption of heavy metals in the sludge.

Effect of Temperature on the Adsorption of Heavy Metals in Sludge by Calcium Alginate Cross-Linked Zeolite Microspheres

The effect of calcium alginate cross-linked zeolite microspheres on the adsorption of heavy metals in sludge at different temperatures (0ºC, 10ºC, 20ºC, 25ºC, 30ºC, and 40ºC) was explored. At different temperatures, the same amount of 2 g microspheres were added into the beaker containing 500 ml of sludge and stirred for 4 h at the speed of 500 r·min⁻¹. The metal content of the sludge after adsorption treatment was dºetermined. The changes in the total content of heavy metals and the proportion of stable state are shown in Figs 4 and 5.

Temperature change had a certain influence on the adsorption effect of calcium alginate cross-linked zeolite microspheres. Under the premise of rising
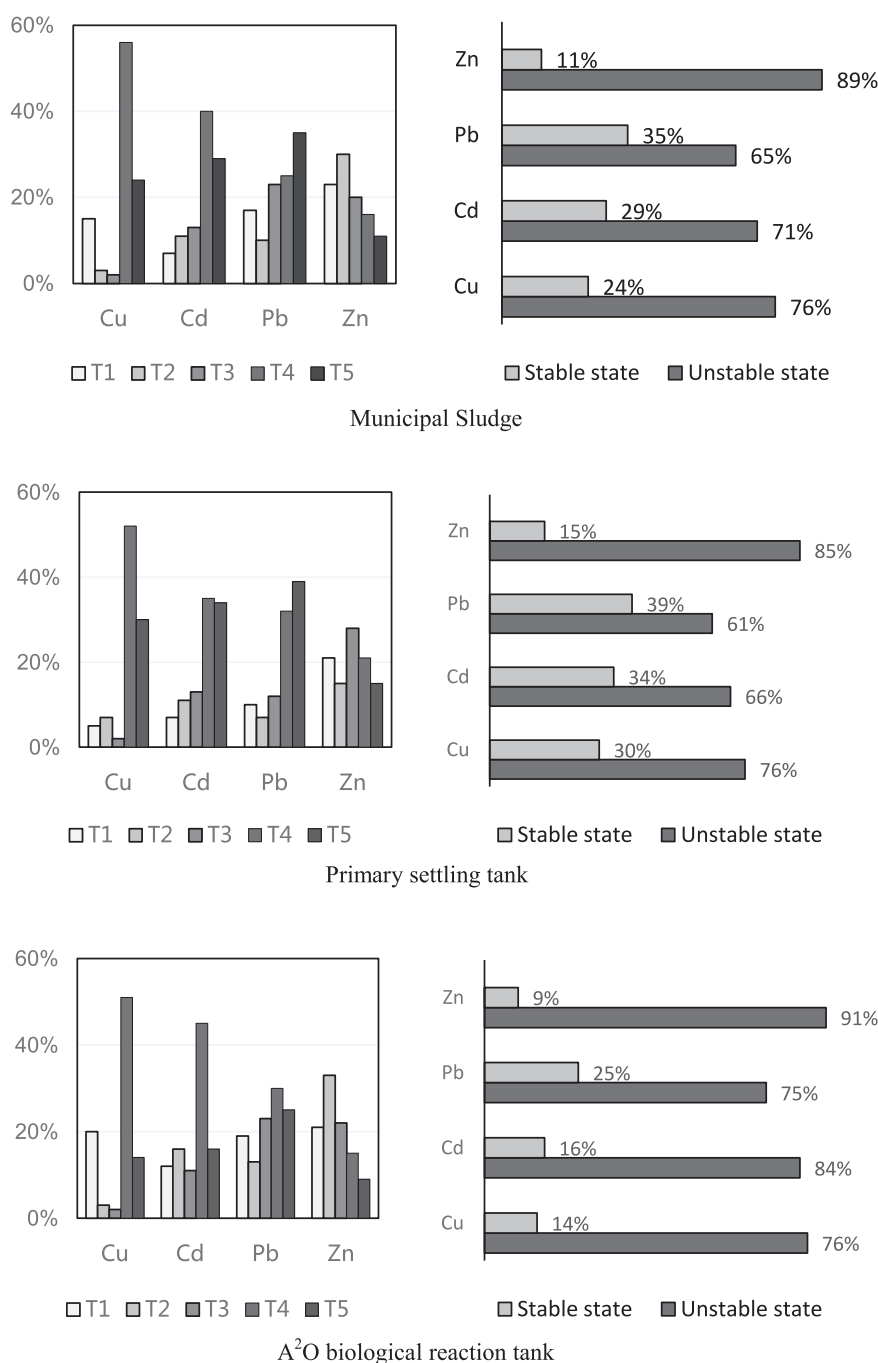

Municipal Sludge

Primary settling tank

A²O biological reaction tank

Fig. 3. The percentage content of heavy metal species in the sludge of each sample and the content of stable and unstable states (T1:water-soluble state, T2:exchangeable state, T3: reducible state, T4: oxidizable state, T5: residual state).

temperature with other conditions unchanged, the total content of heavy metals in sludge gradually decreased, the percentage of stable state increased, and the total amount of heavy metals showed a downward trend. These phenomena were most obvious in the temperature range of 10ºC-25ºC. The adsorption effect of Zn is the most obvious, and its steady state content increased from 19% to 34%. The adsorption efficiency of calcium alginate cross-linked zeolite microspheres decreased when the temperature exceeded 25ºC, which may be related to the decrease in the permeability of alginate caused by the increase in temperature. When alginate gel is heat treated, shrinkage caused by water discharge is detected, Alginate density increases, resulting in improved resistance to gel and decreased permeability, The temperature and duration of heat treatment will lead to the rearrangement of polysaccharide structure [25]. Other studies have shown that the lower temperature reduces the diffusion rate of calcium ions

and results in a more regular microstructure of calcium alginate particles than before [26], and the decrease in temperature increases the fracture strength of calcium alginate particles. This factor may explain the decreased adsorption efficiency of the calcium alginate cross-linked zeolite microspheres when the temperature increased.

Effect of the Dosage of Calcium Alginate Cross-Linked Zeolite Microspheres on the Adsorption of Heavy Metals in Sludge

The effect of the dosage of calcium alginate cross-linked zeolite microspheres on the adsorption of heavy metals in the sludge was studied by adding 0.5, 1, 2, 3, and 4 g of calcium alginate cross-linked zeolite microspheres into a beaker containing 500 ml of muddy water mixture and stirred at the rate of 500 r·min⁻¹ at 25ºC for 4 h. The metals in the sludge and the changes
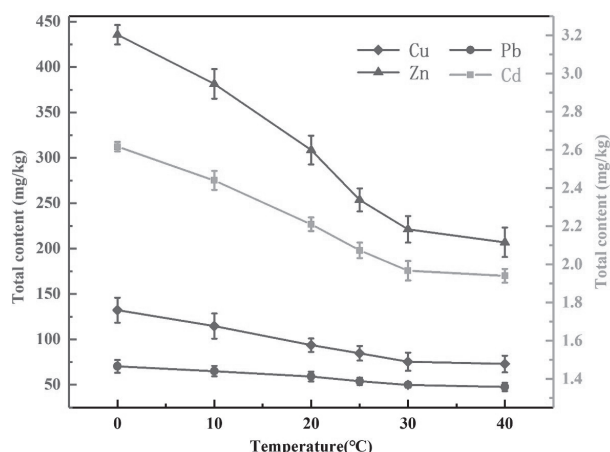

Fig. 4. Effect of temperature on heavy metals in sludge treated with calcium alginate cross linked zeolite microspheres.
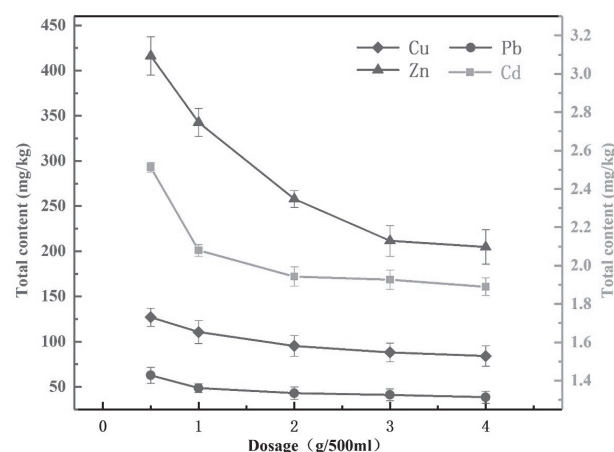

Fig. 6. Effect of dosage on heavy metals in sludge treated with calcium alginate cross linked zeolite microspheres.
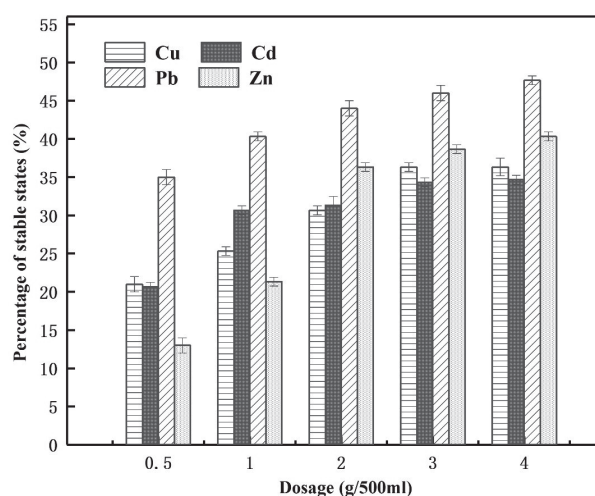

Fig. 5. The relationship between temperature and percentage of stable states.
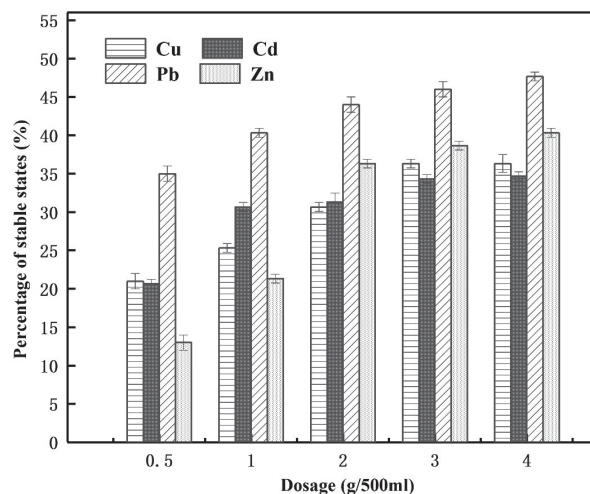

Fig. 7. The relationship between dosage and percentage of stable states.

in the total content of heavy metals were determined after adsorption treatment. The changes in the steady state ratio are shown in Figs 6 and 7.

With the increase in dosage, the total content of each heavy metal in the sludge continued to decrease, and the percentage of the steady state continued to rise. This result is attributed to the phenomenon in which the more adsorbents were added, the more adsorption sites became available. This condition is conducive to the adsorption of heavy metals. When the dosage was controlled at 0.5-2 g/500 ml, the total content of each heavy metal decreased the fastest, and the adsorption effect of Zn was the most obvious. The high content of T1 and T2 forms of Zn may have made it easy for calcium alginate cross-linked zeolite microspheres to react, so the stable state content of Zn also increased the fastest. Considering economy and ensuring good adsorption effect, the dosage should be controlled at 1.5-2 g/500 ml.
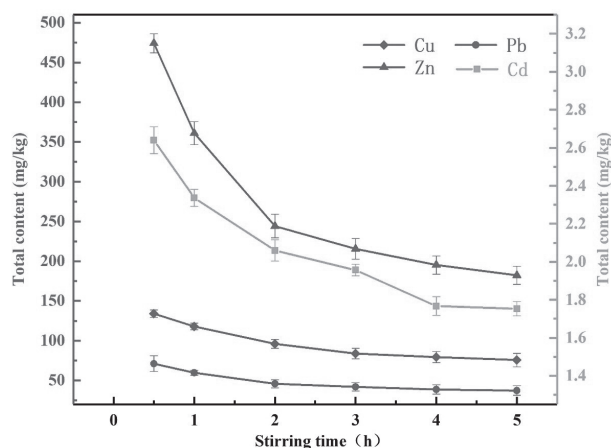

Fig. 8. Effect of stirring time on heavy metals in sludge treated with calcium alginate cross-linked zeolite microspheres.
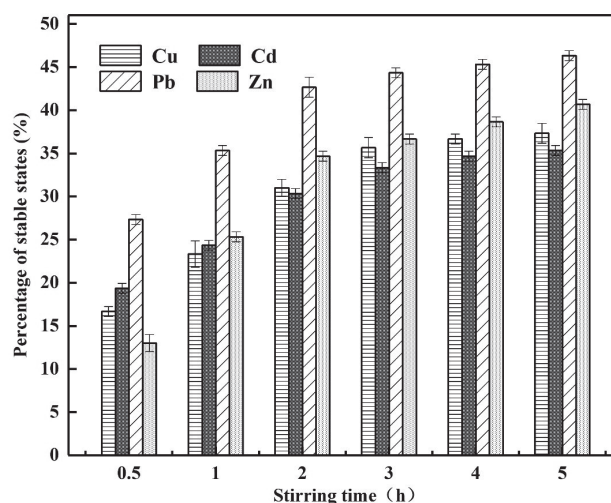

Fig. 9. The relationship between stirring time and percentage of stable states.

Effect of Stirring Time on the Adsorption of Heavy Metals in Sludge by Calcium Alginate Cross-Linked Zeolite Microspheres

Under the same conditions, 2 g of microspheres were added into the beaker with 500 ml mud-water mixture at 25ºC and stirred at the speed of 500 r·min⁻¹. The stirring time was changed to 0.5, 1, 2, 3, 4, and 5 h, and the heavy metal content in the sludge after adsorption treatment was measured. The changes in total heavy metal content and the proportion of stable state are shown in Figs 8 and 9.

As an important parameter in the liquid phase reaction, stirring time has a considerable influence on improving the adsorption effect. Prolonging stirring time will increase the possibility of collision and aggregation between particles [27]. Figs 8 and 9 show that with prolonged stirring time, the heavy metals are better adsorbed by calcium alginate cross-linked zeolite microspheres, and the total amount of heavy metals decreased with prolonged stirring time. The proportion of stable heavy metals in the sludge showed an upward trend, and the heavy metals under stable state increased the fastest within 2 h after the stirring time was controlled. After 3 h, the growth rate under the stable state gradually stabilized, when the adsorption sites were occupied by heavy metal particles, the adsorption effect would not be significantly improved by prolonging the stirring time. The adsorption of heavy metals by calcium alginate cross-linked zeolite microspheres in sludge was completed. Thus, the stirring time should be controlled at 2-3 h.

Adsorption Treatment of the A²/O Bioreactor Sludge Microsphere before and after Ecological Risk Assessment

When the dosage of microspheres was 2 g/500 ml, the temperature was 25ºC, the stirring speed was 500 r·min-1, and the stirring time was 3 h, the sludge collected from the A²/O bioreactor was tested for adsorption. The geoaccumulation index method was used to evaluate the pollution level of heavy metals in the sludge before and after microsphere treatment, and the results are shown in Fig. 10.

Fig 10 shows that when the background value of soil chemistry in Xi'an WAS Bn [28, 29], the I_{geo} values of Pb and Zn in the sludge treated by microsphere were -0.26 and -0.93, respectively, and the pollution level was zero. This result suggested that treatment with microspheres did not harm the soil in the Xi'an area. The pollution level of Cu and Cd in the sludge before treatment was moderately to heavily polluted, which indicates that pollution was strong. Although these two heavy metals are not highly toxic, they will cause harm to animals and plants if they accumulate in the organism and enter the ecological environment. After treatment, the pollution level of Cu and Cd was reduced to moderately polluted, which has less harmful effects
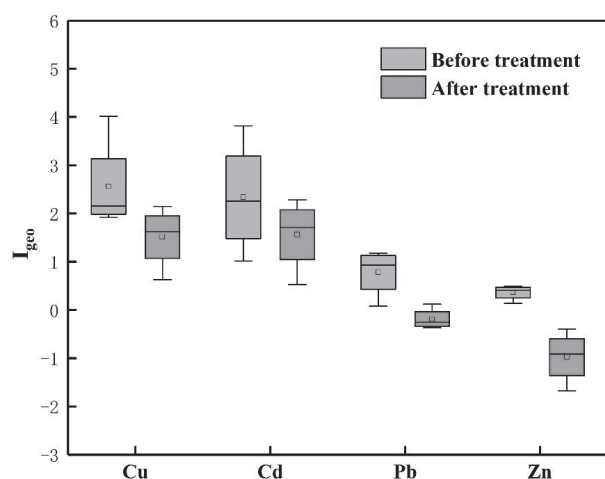
Fig. 10. Impact on environmental risk assessment before and after application of calcium alginate cross-linked zeolite microspheres.

to the environment. Treatment of sludge with calcium alginate cross-linked zeolite microspheres can reduce the harmful effects of heavy metals in the sludge to the environment, which has practical guiding value for the recycling of sludge in the Xi'an area.

Analysis of Adsorption Mechanism

Combined with the process flow of the sewage plant, before the sludge enters the A²/O biological reaction tank, some residues and their organic combined states in the primary sedimentation tank easily form large particles and precipitate in the sludge. Therefore, the content of residual T5 and oxidizable T4 in the primary sedimentation tank sludge was high. Compared with the A²/O biological reaction tank, the primary sedimentation tank had a lower pH and slightly acidic

sewage. The partial exchangeable state T2 of heavy metals was transformed into water-soluble T1 in the sewage that entered into the A²/O biological reaction tank together with the sewage. Table 2 and Fig. 3 show that the water-soluble T1 content of each heavy metal in the A²/O biological reaction tank was higher than that in the primary sedimentation tank. This result may be attributed to the A²/O bioreactor that can absorb and utilize the water-soluble T1 of heavy metals through microorganisms and fix them in the microorganisms that enter the sludge. However, when microorganisms die, the heavy metals in water-soluble T1 will be released into the sludge. If calcium alginate cross-linked zeolite microspheres, possessing both physical and chemical adsorption features, are added to the A²/O biological reaction tank in practical applications, the high water content of the sludge in the A²/O biological reaction tank combined with aeration allows the microspheres to become in full contact and react with the heavy metals in the sewage. The calcium alginate in microspheres contains a large number of carboxylic acids and can combine with heavy metal ions [30]. The heavy metal salt precipitate of alginate is stored in the capsule cavity and is independent of the active site of zeolite, which weakens the mutual inhibition of heavy metal adsorption [31].

The compositional characteristics of the basic structure of zeolite suggest its good heavy metal ion exchange performance [32]. Zeolite has a stable structure, many internal pores, large surface area, and wide external contact surface, and its framework is negatively charged and forms a charge balance with metal cations on the surface. However, the metal cations on the surface and the negative electricity in the lattice framework are not spatially symmetrical, so the surface of the zeolite has a strong electrostatic force. When the pores in the zeolite are vacant, they will be subjected to the action of electrostatic force from the
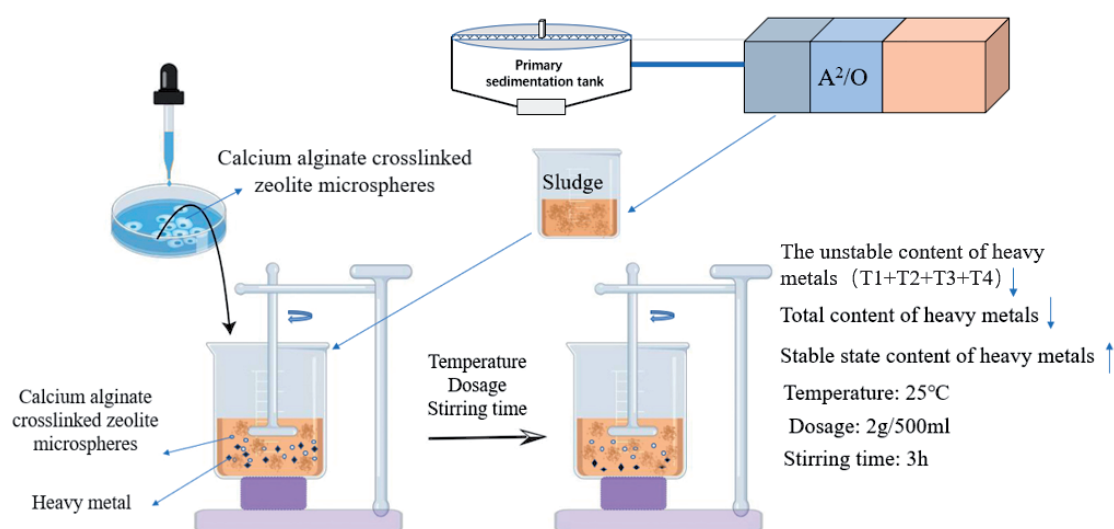

Fig. 11. Schematic diagram of the removal of heavy metals from sludge by calcium alginate cross-linked zeolite microspheres.

surface of the pore wall, showing strong adsorption performance. The zeolites in the microspheres can adsorb the exchangeable heavy metals through active sites and ion exchange and the reducible T3 and oxidizable T4 particles through their own channels; however, the residual T5 particles are large and difficult to be adsorbed. The total amount of water-soluble state T1, exchangeable state T2, reducible state T3, reducible state T3, and oxidizable state T4 represents the amount of unstable state of heavy metals. The microspheres adsorb the four types of heavy metals in the sludge. This phenomenon reduces the total amount of heavy metals and the unstable content of heavy metals and the harmful environmental effects of heavy metals in the sludge.

Conclusions

In this study, a sodium alginate solution was mixed with modified zeolite powder and added dropwise to calcium chloride solution. A metal adsorbent was prepared through cross-linking reaction. The sludge from the A²/O bioreactor of Xi'an Caotan Sewage Treatment Plant was added with microspheres adsorb heavy metals. The effects of changing temperature, dosage, and stirring time on the adsorption efficiency of microspheres on the adsorption of heavy metals were explored, and ecological risk assessment was conducted. The conclusions are as follows:

(1) When the temperature was within 0ºC-25ºC, the adsorption efficiency of the microspheres gradually increased as the temperature increased, the total amount of heavy metals decreased, and the steady state content increases. When the temperature was higher than 25ºC, the adsorption efficiency decreased. The larger the dosage and the longer the stirring time, the higher the adsorption efficiency. When the dosage was greater than 2 g/500 ml, the adsorption efficiency would decrease. Considering the actual cost and efficiency, the adsorption effect was the best when the control temperature was 25ºC, the dosage was 2 g/500 ml, and the stirring time was 3h.

(2) The ecological risk of heavy metals in sludge was assessed samples after adsorption treatment by using the geoaccumulation index method. The Cd and Cu pollution level in sludge decreased from moderately to heavily polluted to moderately polluted, and that of Pb and Zn decreased from unpolluted to moderately polluted to unpolluted. In this study, the adsorption experiment of calcium alginate cross-linked zeolite microspheres provides a new method for removing heavy metals in sludge.

Acknowledgements

Conflict of Interest

The authors declared no conflict of interest.

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