Study on Adsorption Properties of Loess Calcareous Nodules to Heavy Metalions In Aqueous-solution

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Research Article

Keywords: loess calcareous nodules, heavy metal ions, single adsorption, adsorption rate

Posted Date: June 3rd, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-579189/v1>

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Abstract

Using calcareous tuberculosis as adsorbent and heavy metal ions (Cu^{2+} , Zn^{2+} , Cd^{2+} and Pb^{2+}) as adsorbents, different particle size, adsorption time, pH, adsorbent dosage and initial concentration of heavy metals were studied by single heavy metal adsorption test. And the influence of temperature and other factors on the adsorption of heavy metal ions by calcareous nodules, and determine the optimal conditions for the adsorption of heavy metal ions by calcareous nodules. The results show that the adsorption rates of Cu^{2+} , Zn^{2+} and Pb^{2+} decrease gradually with the increase of particle size, but have no obvious effect on Cd^{2+} . With the increase of adsorption time, adsorbent dosage and temperature, the adsorption rates of Cu^{2+} , Zn^{2+} , Cd^{2+} and Pb^{2+} gradually increase. The adsorption rate of Cu^{2+} , Zn^{2+} and Cd^{2+} decreased gradually with the increase of the initial concentration of heavy metal ions, while the adsorption rate of Pb^{2+} increased first and then decreased. With the increase of pH, the adsorption rate of Cd^{2+} increased first and then increased slowly. The adsorption rates of Cu^{2+} , Zn^{2+} and Pb^{2+} increased first and then decreased. The adsorption capacity of calcareous nodules to four heavy metal ions is in the order of $\text{Pb}^{2+} > \text{Zn}^{2+} > \text{Cu}^{2+} > \text{Cd}^{2+}$. When the particle size is 0.25 mm, the adsorption time is 120 min, and the dosage is 0.6 g, the calcareous nodules are Pb^{2+} , Zn^{2+} , Cu^{2+} . And Cd^{2+} can achieve better adsorption, and the adsorption rate can reach 83.33%, 77.78%, 73.81% and 81.93% of its maximum adsorption rate, respectively. The optimal adsorption pH of calcareous nodules to Pb^{2+} , Zn^{2+} , Cu^{2+} and Cd^{2+} was 7, 6, 5 and 8, respectively, and the optimal temperature was 50 °C.

1 Introduction

In recent years, with the rapid development of industrialization and urbanization, a large amount of wastewater containing heavy metal ions such as Cu^{2+} , Zn^{2+} , Cd^{2+} , and Pb^{2+} has entered water ecosystems, and the situation of heavy metal pollution of water body has become increasingly serious (Zhang Z. et al., 2015). Heavy metals have the characteristics of strong toxicity, easy migration and difficult degradation, and will seriously damage human health after entering the water body. Therefore, how to purify water and metal ions has become a hot issue in the treatment of environmental pollution (Wang YY. et al., 2018). Water and metal pollution treatment is a long-term and arduous task, so the cost and environmental friendliness must be fully considered when selecting a treatment method. The adsorption method is more suitable for various low-concentration heavy metal pollution water bodies due to its advantages such as fast treatment rate, simple operation, and good environmental coordination (Zou J. et al., 2018; Li L. I. et al., 2012). In the application of adsorption methods, commonly used adsorbents are activated carbon, chitosan, resin, zeolite, sepiolite, and clay minerals such as kaolinite, vermiculite and montmorillonite (Liu J. et al., 2018). Studies have shown that vermiculite has a strong adsorption capacity for Pb^{2+} , Cd^{2+} , and Zn^{2+} in water (Hu H. et al., 2012; Zehua J. I., 2015), and sepiolite has a good adsorption effect for Ni^{2+} , Cd^{2+} , Zn^{2+} , and Cu^{2+} in water (Sheikhhosseini A. et al., 2013). Studies on the adsorption of heavy metal ions by clay minerals have shown that illite, kaolinite and

montmorillonite have good adsorption effects on Cu^{2+} , Zn^{2+} , Cr^{3+} , Cd^{2+} and Pb^{2+} in water (He H P .et al., 2001).

Loess calcareous nodules, also known as "material ginger stone". It is a soil aggregate of different sizes and shapes under the action of leaching, sedimentation, alteration, and human activities under the conditions of alternating wet and dry conditions and freeze-thaw conditions in the soil on the Loess Plateau(Gong T .et al., 2016). Calcareous nodules are widely distributed in the heavily eroded Loess Plateau, and are mainly composed of primary minerals such as calcite, quartz and feldspar, and layered silicate minerals such as kaolinite, montmorillonite and illite. Among them, illite and montmorillonite have characteristics of huge specific surface area, high activity, and porosity, and can effectively adsorb heavy metal ions in water(Teng Zhihong .et al., 1990). Previous studies on loess calcareous nodules have mainly focused on its origin, distribution, structure, and mechanical properties (Wang Shouyu .et al., 2017;Gong Tiexiong .et al., 2017;Gong T .et al., 2016;Li Chang'an .et al., 1995), but there are few reports on the adsorption characteristics of heavy metal ions on the surface of calcareous nodules. As a natural mineral aggregate, calcareous nodules have the advantages of wide sources, low prices, no secondary pollution when added to water, and easy promotion. In addition, through the method of "treating waste by waste", it not only improves the soil body, but also reduces the heavy metal ions in the water body. It is a material with good environmental coordination. For this reason, this paper studies the adsorption characteristics of loess calcareous nodules on water and heavy metal ions, which can provide a theoretical basis for the application of this adsorbent in removing heavy metals from polluted water.

2 Materials And Methods

2.1 Materials

Test loess calcareous nodules were collected from forest land in Tongchuan City, Shaanxi Province, China ($34^{\circ}99'\text{N}$; $108^{\circ}92'\text{E}$). Calcium nodules of similar size and shape are mainly collected in the surface soil of 0–20 cm and air-dried for later use. The reagents such as $\text{Cu}(\text{NO}_3)_2$, $\text{Zn}(\text{NO}_3)_2$, $\text{Cd}(\text{NO}_3)_2$, $\text{Pb}(\text{NO}_3)_2$, HNO_3 and NaOH are all excellent pure. The test water is distilled water, which is used to prepare standard solutions of different heavy metal concentrations.

2.2 Methods

Scanning electron microscope and microwave digestion test of calcareous tuberculosis

The calcareous tuberculosis powder was prepared into a suspension, and the suspension was evenly coated on a copper table with a pipette. After being naturally air-dried, it was scanned under a high-resolution scanning electron microscope. The chemical composition of calcareous nodules was extracted by aqua regia-hydrofluoric acid microwave digestion method, and the extract was measured by inductively coupled d plasma mass spectrometer (ICP-MS)(Yang L G .et al., 2019).

Test for Calcium Nodule Adsorption to Heavy Metal Ions

A single heavy metal adsorption test was performed under different conditions using calcium nodules as an adsorbent, and an aqueous solution containing heavy metal ions such as Cu^{2+} , Zn^{2+} , Cd^{2+} , and Pb^{2+} as the adsorption target.

The particle size test refers to taking 0.2 g of sieve calcium nodules through 1, 0.5, 0.25, 0.18, and 0.149 mm, respectively. Then, add 50 ml of Cu^{2+} , Zn^{2+} , Cd^{2+} and Pb^{2+} at a concentration of 30 mg / L, shake at constant temperature (25 ± 1 °C) for 120 minutes, centrifuge the supernatant to determine the heavy metal ion content by ICP-MS.

The adsorption time test is to take 0.2 g of calcic nodules through 0.25 mm sieve, and add 50 ml of Cu^{2+} , Zn^{2+} , Cd^{2+} and Pb^{2+} at a concentration of 30 mg / L. Samples were taken at 1, 3, 5, 15, 30, 60, 90, 120 minutes of shaking time, and then the content of heavy metal ions in the supernatant was measured.

pH test: take 0.2 g of calcium nodules through a 0.25 mm sieve and add 30 mg/L of 50 mg solution of Cu^{2+} , Zn^{2+} , Cd^{2+} and Pb^{2+} at pH 5, 6, 7, 8, and 9 respectively. The other test conditions are the same
Diameter test.

Adsorbent dosage test: take 0.2, 0.4, 0.6, 0.8 and 1 g of calcium nodules through a 0.25 mm sieve, respectively, and add 50 mg solutions of Cu^{2+} , Zn^{2+} , Cd^{2+} and Pb^{2+} at a concentration of 30 mg/L, the other test conditions are the same as above .

Heavy metal initial concentration test: Take 0.2 g of 0.25 mm sieve calcareous nodules and add 50 ml solutions of Cu^{2+} , Zn^{2+} , Cd^{2+} and Pb^{2+} at concentrations of 10, 20, 30, 50 and 100 mg/L respectively. The other test conditions are the same as above.

Adsorption temperature test: Take 0.2 g of calcium nodules through a 0.25 mm sieve and add 50 mL solutions of Cu^{2+} , Zn^{2+} , Cd^{2+} , and Pb^{2+} at a concentration of 30 mg/L. After shaking for 120 min at the temperature of 20 °C, 30 °C, 40 °C, 50 °C and 60 °C, respectively, the supernatant was centrifuged and the content of heavy metal ions was determined.

Data processing

The adsorption rate can evaluate the adsorption capacity of calcium nodules to heavy metals, and the calculation formula is: $Q = (\text{Ci} - \text{Ce}) / \text{Ci} \times 100\%$

In the formula: Q is the adsorption rate; Ci is the initial concentration of heavy metals; Ce is the equilibrium concentration of heavy metals added to calcareous nodules.

SPSS 18.0 software was used for data analysis, and Origin 8.0 software was used for drawing.

3 Results And Analysis

3.1 Micromorphology and chemical composition of calcareous nodules

Scanning electron microscopy (Fig. 1) shows that the calcareous nodules have a compact texture, a rough surface and a stepped shape, and the particles are smooth and have no obvious rhomboid. Some of the particles have large pores. The particles are of different sizes and shapes, mostly in the form of rods, ellipses, flakes and thin strips, etc. The thin strips and rods may be illite, the oval shape may be iron oxide, and the flakes may be kaolinite and montmorillonite (Gao B Y .et al., 2012). The adsorption of calcium nodules on heavy metal ions in water is related to its mineral type and content. In terms of chemical composition, the main component of calcareous nodules is SiO_2 , followed by CaO , and then Al_2O_3 . The sum of the three is about 90%. In contrast, K_2O , NaO , MgO and Fe_2O_3 are easily leached out with water, and their content is relatively low (Table 1). The ratio of silicon to aluminum in calcareous nodules ($\text{SiO}_2/\text{Al}_2\text{O}_3$) reaches 2.89. Combined with the percentage of each oxide, it can be inferred that the calcareous nodules are mainly 2:1 collision type minerals such as illite and montmorillonite. The 2:1 type mineral has the characteristics of large specific surface area and fine particle size, and has a good effect on the adsorption and precipitation of heavy metal ions. Therefore, calcium nodules can be used to adsorb and remove heavy metal ions in water (Qin H F .et al., 2018)

Table 1
Chemical composition of calcareous nodules

Chemical components	K_2O	CaO	NaO	MgO	Al_2O_3	Fe_2O_3	SiO_2	$\text{SiO}_2/\text{Al}_2\text{O}_3$
Content(%)	2.16	34.57	1.23	1.78	14.36	4.34	41.56	2.89

3.2 Influence of particle size on the adsorption of heavy metal ions by calcium nodules

The adsorption rate of heavy metal ions changes significantly with the size of the calcium nodules (Fig. 2). When the particle size is from 0.149 to 0.25 mm, the adsorption rate of Cu^{2+} , Zn^{2+} and Pb^{2+} decreases slowly. After the particle size is less than 0.25 mm, the adsorption rate decreases greatly. The adsorption rates of Cu^{2+} , Zn^{2+} and Pb^{2+} vary from 20.33–85.00%, 28.67–89.33% and 43.67–82.00%, respectively. When the particle size of Cd^{2+} is from 0.149 to 0.25 mm, the adsorption rate decreases relatively greatly, down by 14.67%. After the particle size is larger than 0.25 mm, the adsorption rate basically stabilizes. As the particle size of calcium nodules increases, the adsorption rate of heavy metal ions gradually decreases. This may be because the larger the particle size of the calcareous nodules of the same mass, the smaller the specific surface area and the relative content of layered silicate minerals such as montmorillonite and illite, thereby reducing the adsorption rate of heavy metal ions. Secondly, the difference in the content of carbonate, sulfate and hydrated oxides of iron, aluminum and magnesium in calcium nodules with different particle sizes will also affect the adsorption effect of heavy metal ions. From visual judgment, the smaller the particle size, the more turbid the solution, and the longer it takes to settle for clarification. It is better to choose calcareous nodules that pass 0.25 mm sieve when carrying out heavy metal ion adsorption.

3.3 The effect of adsorption time on the adsorption of heavy metal ions by calcium nodules

As time goes by, the adsorption rate of heavy metal ions gradually increases, but the adsorption curve is quite different (Fig. 3). The adsorption rate of Cd^{2+} and Pb^{2+} increased significantly within the adsorption time of 1 to 60 minutes, and the increase of adsorption rate decreased significantly when the adsorption time continued to be prolonged. Compared with Cd^{2+} and Pb^{2+} , Cu^{2+} and Zn^{2+} can reach a higher adsorption rate in a short time (within 15 min). Cu^{2+} , Zn^{2+} , Cd^{2+} and Pb^{2+} can reach the maximum adsorption rate of 78.21%, 93.33%, 78.26% and 84.55% respectively at 30 min. The maximum adsorption rates are 26%, 30.00%, 15.33% and 41.00%, respectively. Cu^{2+} , Zn^{2+} , Cd^{2+} and Pb^{2+} can achieve better adsorption effects within 60 minutes. This may be caused by the combination of mineral types and contents in calcareous nodules. Due to the large concentration gradient between the calcium nodules and the heavy metal adsorption solution, the adsorption rate is relatively fast. The adsorption rate of calcium nodules to 4 kinds of heavy metal ions increased relatively smoothly after 60 min. The adsorption time can determine the degree of adsorption of heavy metal ions to a certain extent, and affect the adsorption effect of heavy metal ions. When the time exceeds 60 min, the adsorption rate of 4 kinds of heavy metal ions increases little with time. This study shows that the adsorption time is not the main factor affecting the adsorption rate of heavy metal ions. As long as the appropriate adsorption time is selected, a higher adsorption rate can be achieved. It is more appropriate to extend the adsorption time appropriately. Choose 120 min for comprehensive comparison.

3.4 The effect of pH on the adsorption of heavy metal ions by calcium nodules

pH is an important factor affecting the adsorption rate during the adsorption process, which may be related to the chemical properties of different heavy metal ions and their existence in the solution. Figure 4 shows that when $\text{pH} = 4$, the adsorption rate of calcium nodules on Cu^{2+} , Zn^{2+} , Cd^{2+} and Pb^{2+} is the smallest, which are 16.00%, 19.67%, 9.67% and 10.33%, respectively. At this time, the calcium carbonate, iron, aluminum, magnesium and other oxides in the calcareous nodules begin to decompose under the action of H^+ , causing damage to their structure and properties. At the same time, the concentration of Ca^{2+} , Fe^{2+} , Al^{3+} and Mg^{2+} in the solution is increasing continuously, forming a competitive relationship with Cu^{2+} , Zn^{2+} , Cd^{2+} and Pb^{2+} in the solution, which in turn affects the adsorption of heavy metal ions. With the gradual increase of pH, the adsorption rate of Cd^{2+} increases firstly and then slowly, and the maximum adsorption rate is 30.33% ($\text{pH} = 8$). The adsorption rates of Zn^{2+} and Pb^{2+} first increase and then decrease, the maximum adsorption rates are 40.67% ($\text{pH} = 6$) and 49.67% ($\text{pH} = 7$), respectively. When the pH is 5, the adsorption rate of Cu^{2+} reaches the maximum, when the $\text{pH} > 5$, the adsorption rate is significantly reduced, and when the $\text{pH} = 6\text{--}8$, the adsorption rate is basically stable.

Studies have shown that under different pH, the existence of metal ions is different. The Cd^{2+} adsorption process is mainly complex and potential adsorption (Li L I. et al., 2012), so the higher the pH, the more helpful the Cd^{2+} adsorption. Cu^{2+} , Zn^{2+} and Pb^{2+} are mainly adsorbed by precipitation. With the increase of pH, heavy metal ions are gradually converted into hydroxide complex ions. Among them, Cu^{2+} begins to precipitate after $\text{pH} = 5$, and Zn^{2+} begins to precipitate after $\text{pH} = 6$. After $\text{pH} = 7$, Pb^{2+} began to

precipitate, so with the increase of pH, the changes in the adsorption rates of the four heavy metal ions were inconsistent (Tsao TM .et al., 2012;Zhu H .et al., 2006;Zhang Z Y .et al., 2017;Chou YM .et al., 2014).

3.5 Effect of the amount of adsorbent on the adsorption of heavy metal ions by calcium nodules

The adsorption rate of calcium nodules on Cu^{2+} , Zn^{2+} , Cd^{2+} and Pb^{2+} in the solution gradually increases with the increase in the amount of calcium nodules (Fig. 5). When the dosage is increased to 0.6 g, the adsorption rate of the calcium nodules on the 4 kinds of heavy metal ions gradually slows down. The amount of calcareous nodules has a weak effect on the adsorption rate of Cd^{2+} , with a range of only 16.00–27.67%, and the most obvious impact on Pb^{2+} , with a range of change from 43.00–76.00%, which is nearly doubled. The order of the adsorption effect of calcareous nodules on the four heavy metal ions is $\text{Pb}^{2+} > \text{Zn}^{2+} > \text{Cu}^{2+} > \text{Cd}^{2+}$, in which the maximum adsorption rates of Cu^{2+} and Cd^{2+} are both lower than 40%, and the adsorption rate of Pb^{2+} is as high as 80%. This may be related to the difference in electronegativity of Cu^{2+} , Zn^{2+} , Cd^{2+} and Pb^{2+} (Tao, Ye .et al., 2017). Although the high dosage of calcium nodules is beneficial to increase the adsorption rate of heavy metal ions, it will cause turbid water quality and poor visual effect. Considering the adsorption effect and visual senses, 0.6 g is more suitable for practical applications.

3.6 Influence of the initial concentration of heavy metals on the adsorption of heavy metal ions by calcium nodules

With the increase of the initial concentration of heavy metal ions, the adsorption rate of calcium nodules on Cu^{2+} , Zn^{2+} and Cd^{2+} showed a significant downward trend, while Pb^{2+} first increased and then decreased (Fig. 6). This may be because the initial concentration is low, there are many adsorption sites on the surface of calcareous nodules, and the concentration of heavy metal ions in the solution is different, so the adsorption rate is large. As the initial concentration of heavy metals increases, the adsorption sites are saturated, resulting in a decrease in the adsorption rate. The initial concentration of heavy metal ions has much greater influence on the adsorption rate of Cu^{2+} , Cd^{2+} and Pb^{2+} than Zn^{2+} . In the range of 100 mg/L, the adsorption rate of Zn^{2+} changed the most slowly, only decreasing by 27.80%, while the adsorption rate of Cu^{2+} , Cd^{2+} and Pb^{2+} decreased greatly, decreasing by 84.60%, 70.80% and 69.00% respectively. The adsorption rate of 4 kinds of heavy metal ions is better at lower concentration, and worse at higher concentration. As far as Pb^{2+} is concerned, in the range of 30 mg/L, although the adsorption rate has a downward trend, it still remains above 40%. For Cu^{2+} , the change trend is similar, the adsorption rate remains above 40% in the range of 20 mg/L, and the adsorption rate remains above 30% in the range of 30 mg/L. The adsorption rate of Cd^{2+} and Zn^{2+} is lower than 30% in the range of 20 mg/L, and the adsorption rate reaches the maximum at 10 mg/L, 74.00% and 38.00% respectively. Comprehensive consideration of calcium nodules is more suitable for treating low-concentration wastewater.

3.7 The effect of temperature on the adsorption of heavy metal ions by calcium nodules

With the increase of temperature, the adsorption rate of calcium nodules on Cu^{2+} , Zn^{2+} , Cd^{2+} and Pb^{2+} all increase (Fig. 7), indicating that heating is helpful to the advancement of the adsorption process. When the temperature is in the range of 20–40 °C, the adsorption rate increases slowly, and when the temperature reaches 40 °C, the adsorption rate increases sharply. This may be because the higher the temperature, the higher the adsorption and exchange rate of heavy metal ions. The order of the influence of temperature change on the adsorption of heavy metal ions by calcium nodules is $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+} > \text{Cd}^{2+}$. Among them, in the range of 20–40 °C, the change of temperature has a weak effect on the adsorption rate of Pb^{2+} , and the adsorption rate only increases by 5.67%. When the temperature reaches 60 °C, the adsorption rate increases by 46.00%. The adsorption rate of Cu^{2+} , Zn^{2+} and Cd^{2+} increases linearly with the increase of temperature. When the temperature reaches 60 °C, the adsorption rate increases by 55.67%, 66.33% and 73.67%, respectively. When the temperature is 50°C, the adsorption rates of Cu^{2+} , Zn^{2+} , Cd^{2+} and Pb^{2+} can reach 79.00%, 76.00%, 72.00% and 70% of their maximum adsorption rates respectively. Although the increase in temperature can improve the adsorption effect of heavy metal ions, too high temperature is not conducive to the survival of aerobic microorganisms in the water body, and will affect the decomposition of other pollutants by the microorganisms in the water body. Combined with the actual situation of wastewater treatment, it is more appropriate to choose 50 °C.

4 Discussion

Because heavy metals have significant toxicity to humans, animals, plants and microorganisms and cannot be degraded by microorganisms, heavy metal wastewater has become a major global environmental problem (Tofighy M A .et al., 2011). Compared with other methods, the adsorption method has the characteristics of simple operation, high efficiency and low cost, and has been widely used in the treatment of heavy metal wastewater (Li L I .et al., 2012). The adsorbent is the core factor of the adsorption method, and its performance determines the quality of the separation effect and the level of separation efficiency. At present, adsorbents used for heavy metal treatment can be divided into natural adsorbents, biological adsorbents and synthetic adsorbents according to their source and chemical structure (Peng W .et al., 2017).

Loess-calcium binding is one of the natural adsorbents, and there are few studies on this adsorbent at present. However, some scholars have conducted research on the adsorption effect of other adsorbents on water heavy metals. The results show that pH, time, Adsorbent dosage, temperature and initial concentration of heavy metals are important factors affecting the adsorption effect of different adsorbents, which are consistent with our research results (Peng W .et al., 2017; D. Gu .et al., 2015; Zhang Z .et al., 2015; Wang YY .et al., 2018; Li L IY .et al., 2012; Liu J .et al., 2018; Hu H .et al., 2012). For example: Sheikhhosseini A et al. studied Competitive sorption of nickel, cadmium, zinc and copper on palygorskite and sepiolite silicate clay minerals (Sheikhhosseini A .et al., 2013). The research results show that palygorskite and sepiolite can effectively remove Cu from the solution regardless of the presence of other metals. Zou J et al. used corn stalks to prepare biochar, conducted experiments on the adsorption of

heavy metals Cd^{2+} and Pb^{2+} , and analyzed the adsorption capacity and adsorption efficiency of biochar to adsorb heavy metals (Zou J. et al., 2018). The results show that the optimal adsorption condition for Cd^{2+} is that the pH is 5 and the adsorption equilibrium is 120 min. The optimal adsorption condition for Pb^{2+} is that the pH is 1, and the adsorption equilibrium is 60 min. This is basically consistent with the results of the study on the effect of adsorption time on calcium binding and adsorption of heavy metal ions in this article. Li Li et al. studied the adsorption mechanism of corn stover biochar on Cd^{2+} (Li L. et al., 2012). The results showed that with the increase of pH, its adsorption rate continued to increase; our research also showed that with the increase of pH, its adsorption rate continued to increase. However, when reaching a certain value, the adsorption rate of different heavy metals will increase slowly or decrease. Peng W's research shows that the optimal solution pH for the adsorption of various heavy metal ions may be different due to their differences in the metal electronegativity, the standard reduction potential of the heavy metal ions and the first stability constant of the associated metal hydroxide (Peng W. et al., 2017). At the same time, As far as the amount of adsorbent is concerned, an appropriate amount of adsorbent can achieve the best adsorption effect, not as much as possible. In terms of time, as time increases, the adsorption effect increases, but the growth is slow after a period of time, just choose an appropriate adsorption time. In terms of temperature, as the temperature increases, the adsorption effect increases, but the most suitable temperature for different heavy metals is different. The above research conclusions are basically consistent with our research results.

5 Conclusion

Different adsorption conditions have different effects on the adsorption of heavy metal ions by calcium nodules. The particle size has a greater influence on the adsorption of Cu^{2+} , Zn^{2+} and Pb^{2+} by calcareous nodules. As the particle size increases, the adsorption rate gradually decreases, but it has no significant effect on the adsorption of Cd^{2+} . With the increase of the adsorption time and the amount of adsorbent, the adsorption rate of Cu^{2+} , Zn^{2+} , Cd^{2+} and Pb^{2+} increases first abruptly and then gradually increases, and the adsorption curves are similar. As the temperature rises, the adsorption rate first increases gently and then increases abruptly. With the increase of the initial concentration of heavy metal ions, the adsorption rate of Cu^{2+} , Zn^{2+} and Cd^{2+} gradually decreased, while the adsorption rate of Pb^{2+} increased first and then decreased. As the pH increases, the adsorption rate of Cd^{2+} increases first and then slowly increases, while the adsorption rate of Cu^{2+} , Zn^{2+} and Pb^{2+} first increases and then decreases.

The adsorption capacity of calcium nodules for 4 kinds of heavy metal ions is in the order of $\text{Pb}^{2+} > \text{Zn}^{2+} > \text{Cu}^{2+} > \text{Cd}^{2+}$. Calcareous nodules can achieve better adsorption of Pb^{2+} , Zn^{2+} , Cu^{2+} and Cd^{2+} when the particle size is 0.25 mm, the adsorption time is 120 min, and the dosage is 0.6 g. The adsorption rates are 63.33%, 42.00%, 31.00% and 22.67% respectively, respectively can reach 83.33%, 77.78%, 73.81% and 81.93% of its maximum adsorption rate. pH and temperature have a great influence on the adsorption of heavy metal ions by calcium nodules. The appropriate pH and temperature should be selected for different types of metal ions. Among them, the optimal adsorption pH of Pb^{2+} , Zn^{2+} , Cu^{2+} and Cd^{2+} are 7, 6, 5, 8, and the optimal temperature is 50 °C.

Declarations

Funding: The study is supported by the Fund Project of Shaanxi Key Laboratory of Land Consolidation (2019-ZD05).

Author contributions

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Figures

Figure 1

Scanning electron micrograph of calcareous nodules

Figure 2

The adsorption effect of different particle size calcium nodules on Cu²⁺, Zn²⁺, Cd²⁺ and Pb²⁺ in solution

Figure 3

The adsorption effect of adsorption time on Cu²⁺, Zn²⁺, Cd²⁺ and Pb²⁺ in solution

Figure 4

The adsorption effect of pH on Cu²⁺, Zn²⁺, Cd²⁺ and Pb²⁺ in solution

Figure 5

The adsorption effect of the amount of adsorbent on Cu²⁺, Zn²⁺, Cd²⁺ and Pb²⁺ in the solution

Figure 6

The adsorption effect of the initial concentration of heavy metal ions on Cu²⁺, Zn²⁺, Cd²⁺ and Pb²⁺ in the solution

Figure 7

Adsorption effect of temperature on Cu^{2+} , Zn^{2+} , Cd^{2+} and Pb^{2+} in solution