E3S Web of Conferences 165, 05032 (2020) https://doi.org/10.1051/e3sconf/202016505032
CAES 2020

Adsorption of molybdenum (VI) in contaminated water using Fe_3O_4/CTS magnetic nanoparticles

Lei Chao, Yao Wang*, Yu Cao, Yafeng Li

School of municipal and environmental engineering, Shenyang Jianzhu University, Shenyang, Liaoning Province, 110168, China

Abstract. To solve the problem of excess molybdenum, a new composite nanomaterial was prepared for adsorption and removal of Mo (VI). Chitosan-modified magnetic nanoparticles (Fe_3O_4/CTS) were prepared by the method of glutaraldehyde crosslinking. The morphology of the composite nanoparticles was characterized by a scanning electron microscope, and the magnetic properties of the nanoparticles were characterized by an external magnetic field. The content of Mo (VI) was determined by thiocyanate spectrophotometry. The relationship between adsorbent dosage, oscillation velocity, contact time and removal of Mo (VI) was studied. The results showed that when the dosage of Fe_3O_4/CTS magnetic nanoparticles was 0.4 g, the oscillation speed was 100 r min^{-1}, and the contact time was 10 min, 100 ml of Mo (VI) solution was treated under the condition of initial pH =4, and the removal effect of Fe_3O_4/CTS magnetic nanoparticles on Mo (VI) was the best. Treatment effluent can reach the comprehensive sewage discharge standard in Liaoning Province. At the same time, it is proved that Fe_3O_4/CTS magnetic nanoparticles are a kind of adsorbent which is easy to recover, easy to separate magnetically, and has the ability to remove Mo (VI) efficiently.

1 Introduction

Heavy metal molybdenum has the characteristics of high melting point, high density, high temperature resistance and high hardness[1]. It is widely used in electrical industry, iron and steel industry, chemical industry, fertilizer and so on[2]. China's molybdenum reserves are at the forefront of the world, and the Huludao region of Liaoning Province is an important molybdenum industry base in China. The increase of society's demand for molybdenum is accompanied by more mining of molybdenum ores. Molybdenum pollution in the water environment often results from the industrial wastewater produced in the process of mining molybdenum ore, such as mining wastewater, leaching water from molybdenum ore produced by rainfall, which enters rivers, lakes or reservoirs through soil and surface runoff, thus posing a threat to humans and animals and plants[4]. The body's maximum tolerance to molybdenum intake is 200-900μg/d. Excessive intake of molybdenum can lead to poisoning, resulting in weakness of limbs, gout, headache, kidney damage and other symptoms[5]. High molybdenum levels can also lead to deformities in some animals, and plant molybdenum poisoning can lead to chlorosis and yellowing[6]. There is no definite target for molybdenum emission in Integrated Wastewater Discharge Standards of China[7]. Because of the particularity of molybdenum pollution in Liaoning Province, Integrated Wastewater Discharge Standards of Liaoning Province stipulates that the molybdenum concentration allowed for direct discharge is 1.5 mg L^{-1}[8], but many molybdenum mining enterprises do not have a perfect discharge system to dispose of molybdenum wastewater, which leads to serious molybdenum pollution. Because the molybdenum content of mining wastewater from a molybdenum mining enterprise reaches 12-25 mg L^{-1}, attention should be paid to the problem of excess molybdenum emissions discharged by enterprises, and a method to remove molybdenum effectively should be found.

Nowadays, many methods have been applied to metal removal, including coprecipitation, ion exchange, membrane separation and adsorption[9], among which the adsorption of nano-materials has been considered as an efficient treatment method. But for now molybdenum removal studies are few, so it is urgent to prepare a kind of nano-adsorbed material to degrade excess molybdenum in water. Roxanne Brion-Robby[10] et al. used a green low-cost method to obtain chitosan and were able to remove molybdenum effectively. In this paper, Fe_3O_4 and chitosan (CTS) were synthesized by the method of glutaraldehyde crosslinking, and a magnetic nano-adsorption material was prepared. The adsorption of molybdenum by Fe_3O_4/CTS magnetic nanoparticles was studied by scanning electron microscopy. Discuss the relationship between the dosage of adsorbent, the oscillation speed, the contact time and Mo removal.

*Corresponding author's e-mail: 550897551@qq.com

2 Materials and methods

2.1. Preparation and characterization of Fe_3O_4/CTS magnetic nanoparticles

Using 2% acetic acid to dissolve chitosan, adding Fe_3O_4 magnetic nanoparticles, adding liquid paraffin, mixing evenly and adding sodium tripolyphosphate to make chitosan wrap Fe_3O_4 particles, finally adding glutaraldehyde and chitosan crosslinking. Repeatedly washed by petroleum ether, acetone and anhydrous ethanol. After vacuum drying, grind and set aside[11-12].

The morphology of Fe_3O_4/CTS magnetic nanoparticles was observed by SEM after preparation, and the magnetic properties of Fe_3O_4/CTS magnetic nanoparticles were determined by external magnetic field.

2.2. Instruments and materials

UV-6000 Visible Spectrophotometer for determination of molybdenum concentration. HZQ-X100 Incubator Shake for oscillating adsorption. PH-10 Type Acidity Meter for adjusting pH value of water sample. KQ-100E Ulirasonic Cleaner plays a dispersive role in preparing magnetic nanoparticles. VC20 Vacuum Drying Box for drying Fe_3O_4/CTS magnetic nanoparticles. Z366 Centrifuge for the solid-liquid separation of magnetic composites preparation.

All the reagents used in the experiment were analytical reagen. Chitosan, Na_2MoO_4, NH_4SCN, $(NH_4)_2Fe(SO_4)_2 \cdot 6H2O$, NaOH, $NaHCO_3$, CH_3COOH, H_2SO_4, HCl, $Na_5P_3O_{10} \cdot 6H_2O$, ethanol anhydrous, liquid paraffin, petroleum ether, glutaraldehyde, acetone. The experimental water is deionized.

Sodium molybdate was dissolved in water and 30 mg L^{-1} sodium molybdate standard solution was used for the adsorption of nanocomposites.

2.3. Adsorption experiment of Fe_3O_4/CTS magnetic nanoparticles

Molybdenum has different forms under different PH conditions, and mainly exists in water body in the form of MoO_4^{2-} under neutral and weak acidic conditions[13]. Adjusting pH to about 4 with 0.02 mol L^{-1} HCl and 0.02 mol L^{-1} NaOH.0.4 g Fe_3O_4/CTS magnetic nano-adsorbable material was mixed with 100 ml of 30 mg L^{-1} Mo (VI) in a conical bottle for a period of time with a certain oscillation rate.Separation of Mo(VI) solutions and adsorbents by magnetic separation of magnetite. Determination of molybdenum content by thiocyanate spectrophotometry[14].

3 Results and discussion

3.1. Characterization of materials

Figure 1 shows the SEM of the magnetic nanoparticles of Fe_3O_4/CTS, from which it can be observed that the nanocomposites are spherical and the particle size is about 100nm. Because of the small particle size, the surface viability of the Fe_3O_4/CTS magnetic nanoparticles is relatively large, resulting in the agglomeration between the particles.

In Figure 2 it can be observed that after the chitosan was added to iron trioxide, the composite has not only molybdenum removal properties, but also magnetic properties. The treated wastewater containing molybdenum can be separated by magnet or external magnetic field.

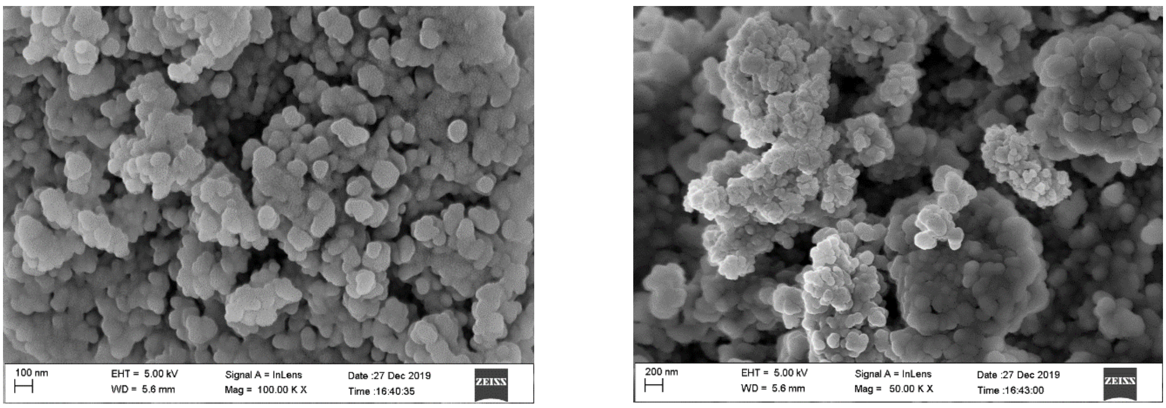

Figure 1. SEM images of Fe_3O_4/CTS magnetic nanoparticles.

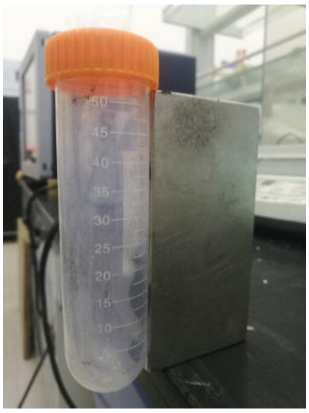

Figure 2. Magnetic performance of Fe_3O_4/CTS magnetic nanoparticles.

3.2. Effect of adsorbent dosage

In order to study the effect of adsorbent dosage, the initial pH value of 4 was adjusted at room temperature, adding 100ml of molybdenum standard solution to each conical bottle. Fe_3O_4/CTS magnetic nanoparticles with different qualities: 0.05g, 0.1g, 0.2g, 0.3g, 0.4g, 0.5g, 0.6g, oscillating adsorption at a speed of 200 r min^{-1} for 30 min, magnetic separation of magnet solid solution was used to study the relationship between the dosage of adsorbent and Mo(VI) removal. The experimental results are shown in figure 3.

The results show that the removal rate of molybdenum by Fe_3O_4/CTS magnetic nanoparticles has been increasing with the addition of adsorbent. This can be attributed to the large specific surface area of the nanoadsorbed materials. With the increasing addition of the Fe_3O_4/CTS magnetic nanoparticles, the specific surface area of the adsorbed materials in contact with molybdenum is also increasing, but also implies more adsorption sites[15]. At first, the adsorption efficiency of Fe_3O_4/CTS magnetic nanoparticles to Mo (VI) is very high until the dosage reaches 0.4 g, and the removal efficiency of Mo (VI) tends to be gentle, the removal rate of molybdenum can reach more than 90% at this time. This can be explained that when the dosage of Fe_3O_4/CTS magnetic nanoparticles is very small, the adsorbent is easier to obtain Mo (VI), and the removal rate of Mo (VI) by adsorbent per unit mass is very high. With the increase of the amount of adsorbent, the inter-nanoparticle interaction leads to the phenomenon of aggregation between ions, the decrease of total surface area and the increase of diffusion path length, which are the main reasons for the gradual decrease of the removal rate curve[16-17].

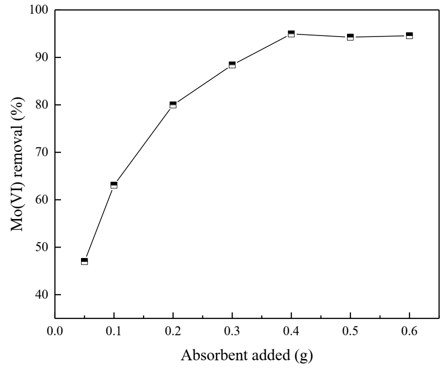

Figure 3. Effect of adsorbent dosage of adsorbent on Mo(VI) adsorption at T 298 K. Conditions: solution volume 100 mL, Mo(VI) initial concentration 30 mg L-1, pH 4, oscillation speed 200 r min-1, apsorption time 30min.

3.3. Effect of oscillation speed

The effect of Fe_3O_4/CTS magnetic nanoparticles on molybdenum at different oscillating velocities was investigated. Several groups of composite adsorption materials with a mass of 0.4 g and 100 ml of 30 mg L^{-1} molybdenum-containing wastewater were taken into the conical bottle. After adsorption for 30 min at different oscillating speeds, the solid liquid was magnetically separated, and the Mo(VI) concentration was measured by thiocyanate spectrophotometry and the removal rate was calculated. The results are shown in figure 4.

In the process of oscillating adsorption, if the oscillation speed is too low, the magnetic nanoparticles of Fe_3O_4/CTS may not be in full contact with Mo(VI). It can be observed that the removal rate of Mo(VI) reaches a maximum of 97.1% when the oscillation speed reaches 100 r min^{-1}, and the molybdenum concentration is 0.857 mg L^{-1}. The residual concentration of molybdenum in the range of 100 r min^{-1}–200 r min^{-1} can be controlled below the comprehensive discharge limit of sewage in Liaoning Province, when the oscillation speed is higher than this range, the removal rate of molybdenum is gradually reduced. This may be the oscillations are so intense that the magnetic nanoparticles of Fe_3O_4/CTS have an understanding of Mo(VI) desorption[18].

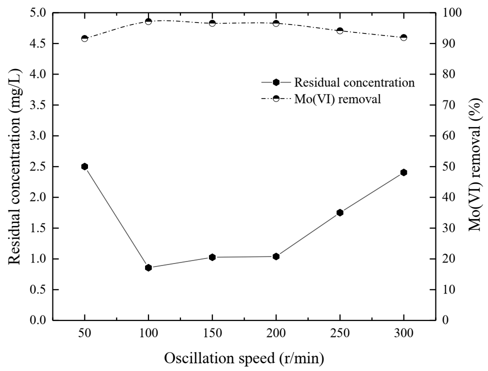

Figure 4. Effect of oscillation speed of adsorbent on Mo(VI) adsorption at T 298 K. Conditions: solution volume 100 mL, pH =4, Fe_3O_4/CTS magnetic nanoparticles 0.4 g,Mo(VI) initial concentration 30 mg L^{-1}, apsorption time 30min.

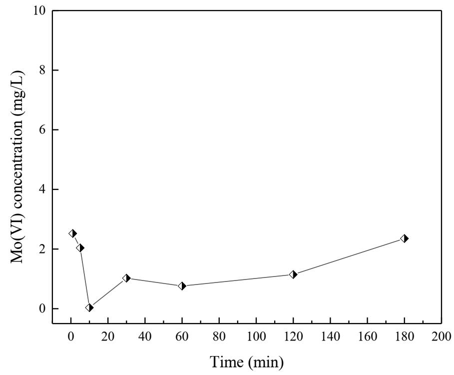

Figure 5. Effect of apsorption time of adsorbent on Mo(VI) adsorption at T 298 K. Conditions: Fe_3O_4/CTS magnetic nanoparticles 0.4 g, solution volume 100 mL, Mo(VI) initial concentration 30 mg L^{-1}, pH=4, oscillation speed 100r min^{-1}.

3.4. Effect of opsorption time

The contact time in the adsorption process is an important parameter to judge the high efficiency of the adsorbed material. For water samples with initial Mo (VI) concentration of 30 mg L^{-1}, the relationship between contact time and Mo (VI) removal was studied under the condition of initial PH =4 and oscillation velocity of 100 r min^{-1}. The experimental results are shown in Figure 5.

The adsorption efficiency of Fe_3O_4/CTS magnetic nanoparticles to Mo (VI) is very high in the initial stage of adsorption, and the maximum adsorption capacity of the adsorbent is reached in the contact time of about 10 min. The residual Mo (VI) concentration is 0.033 mg L^{-1}, and the removal rate is 99%, which indicates that Fe_3O_4/CTS magnetic nanoparticles are adsorption materials with high adsorption efficiency. The reason for the high initial adsorption efficiency may be that there is a strong interaction between Mo (VI) and Fe_3O_4/CTS magnetic nanoparticles which have positive electrical properties[19]. As the contact time increases, that is, the removal rate of Mo (VI) is the highest after the adsorption time is 10 min, and the adsorption vacancies on the adsorbed materials tend to saturate. When the oscillation time exceeds 1 h, the residual concentration of Mo (VI) has an increasing tendency, which may be that the magnetic nanoparticles of Fe_3O_4/CTS have an understanding of Mo (VI)[20].

4 Conclusion

Removal of Mo (VI) in solution by Fe_3O_4/CTS magnetic nanoparticles prepared by glutaraldehyde crosslinking method is rapid and effective. Fe_3O_4/CTS magnetic nanoparticles are spherical adsorption materials with small particle size, large surface area and good magnetic properties. The optimum experimental conditions for molybdenum removal were obtained by studying the dosage of magnetic nano-adsorbed materials, the oscillation speed and contact time of the adsorption process under the condition of initial PH 4 treating with 100ml Mo(VI) wastewater. When the dosage of Fe_3O_4/CTS magnetic nanoparticles is 0.4 g, the removal effect of Mo (VI) is the best, which can reach more than 90%. When the oscillation rate is 100r min^{-1}–200r min^{-1}, the residual concentration of molybdenum in water is the lowest and the removal rate is 97.1%. The oscillatory adsorption time is 10 min, and the removal rate can reach 99% as the optimal contact time. The magnetic properties of Fe_3O_4/CTS magnetic nanoparticles can be quickly separated from the solution by external magnetic field, which is easy to recycle, and its adsorption and removal of Mo (VI) is fast and efficient, which has great potential in the treatment of Mo(VI) solution.

Acknowledgments

This research was funded by the China National Critical Project for Science and Technology on Water Pollution Prevention and Control (2018ZX07601002), to which the authors express their thanks.

References

1. Lian J. Study on molybdenum removal mechanism and efficiency of constructed wetland substrates [D]. Dalian University of Technology,2012.(In Chinese)

2. Zhao H, Ning Y, et al. Experimental study on adsorption of molybdenum by D314 resin [J]. Mining and Metallurgical Engineering, 2018, 38(01): 81-83+87. (In Chinese)
3. Lou Z, Wang J, Jin X, et al. Brown algae based new sorption material for fractional recovery of molybdenum and rhenium from wastewater[J]. Chemical Engineering Journal, 2015, 273: 231-239.
4. W. Salomons. Environmental impact of metals derived from mining activities: Processes, predictions, prevention [J]. Journal of Geochemi cal Ex ploration, 1995, 52(1): 5-23.
5. Zhu Y. Adsorption of Mo (VI) by mesoporous silica nanospheres and its application in DGT technology [D]. BOHAI University, 2019. (In Chinese)
6. Jia T, Jia Y, et al. Contamination of molybdenum and heavy metals in farmland around a molybdenum mine in mindong [J]. Environmental Monitoring in China, 2015, 31(01): 45-49. (In Chinese)
7. GB8978-1996. Integrated Wastewater Discharge Standards of China[S]. Beijing: Department of Environmental Protection of the People's Republic of China, 1996.
8. DB21/1627-2008. Integrated Wastewater Discharge Standards of Liaoning Province[S]. Shenyang: Department of Environmental Protection of Liaoning Province, 2008.
9. Lian J, Zhou F, Chen B, et al. Enhanced adsorption of molybdenum (VI) onto drinking water treatment residues modified by thermal treatment and acid activation[J]. Journal of Cleaner Production, 2020, 244: 118719.
10. Brion-Roby R, Gagnon J, Nosrati S, et al. Adsorption and desorption of molybdenum(VI) in contaminated water using a chitosan sorbent[J]. Journal of Water Process Engineering, 2018, 23: 13-19.
11. Gao Q. Preparation of magnetic chitosan composite microspheres and their adsorption on ibuprofen[D]. East China Normal University, 2019. (In Chinese)
12. Pu S, Zhang Y, et al. Preparation and application of magnetic nanosorbent in water treatment [J]. Industrial Water Treatment, 2019, 39(10): 1-6+13.
13. Guibal E, Milot, Céline, Tobin J M. Metal-Anion Sorption by Chitosan Beads: Equilibrium and Kinetic Studies[J]. Industrial & Engineering Chemistry Research, 1998, 37(4): 1454-1463.
14. Bai Y, Shao H, et al. Determination of Molybdate in Industrial Circular Cooling Water [J]. Industrial Water Treatment, 2012, 32(07): 84-86. (In Chinese)
15. Afkhami A, Aghajani S, Mohseni M, et al. Effectiveness of $Ni_{0.5}Zn_{0.5}Fe_2O_4$for the removal and preconcentration of Cr(VI), Mo(VI), V(V) and W(VI) oxyanions from water and wastewater samples[J]. Journal of the Iranian Chemical Society, 2015, 12(11): 2007-2013.
16. Fungaro D A, Bruno M, Grosche L C. Adsorption and kinetic studies of methylene blue on zeolite synthesized from fly ash[J]. Desalination and Water Treatment, 2009, 2(1-3)231-239.
17. Harikumar P S, TK H. Application of CuNi bimetallic nanoparticle as an adsorbent for the removal of heavy metals from aqueous solution[J]. International Journal of Environmental Analytical Chemistry, 2019: 1-15.
18. Li K. Adsorption of dye wastewater based on modified zeolite adsorbent [D]. North China Electric Power University, 2016. (In Chinese)
19. Allwar Allwar, Ade Setiawan, et al.Removal of Cu(II) ions from aqueous solution by activated carbon produced from banana fruit bunch (Musa paradisiaca)[J]. Desalination and Water Treatment. 172 (2019) 139–147.
20. Jiang D, Yang Y, Huang C, et al. Removal of the heavy metal ion nickel (II) via an adsorption method using flower globular magnesium hydroxide[J]. Journal of hazardous materials, 2019, 373: 131-140.