Eurasia Journal of Science and Technology
ISSN: 2663-1016
DOI: 10.61784/ejst3005

INVESTIGATION ON THE REMOVAL OF SE(IV) FROM AQUATIC SYSTEMS USING ORGANIC AND INORGANIC SORBENTS

CaiYu Liu[1], ZhongShan Zhao[1,*], Yue Sun[1]
[1]*College of Chemistry and Chemical Engineering, Qingdao University, Qingdao(266000), Shandong China*
**Corresponding Author: ZhongShan Zhao, Email: 1454320732@qq.com*

Abstract: Among various selenium (Se) species in water, Se(IV) poses a greater toxicity due to its unique structural characteristics. To address the contamination issue posed by Se(IV) more effectively, this study employed a hydrothermal synthesis method to create an inorganic metal material, specifically a Mg−Al layered double hydroxide (Mg−Al−CO_3 LDH). Meanwhile, the organic material, silk fibroin (SF), was synthesized via a lithium bromide approach. Scanning electron microscopy (SEM) was utilized to characterize the morphology and structure of the fabricated materials, confirming the successful preparation of both Mg-Al-CO_3 LDH and SF as adsorbents.Through adsorption experiments, their efficacy in removing Se(IV) was investigated, with results revealing that both Mg−Al−CO_3 LDH and SF demonstrate notable adsorption capacities for Se(IV). Specifically, the adsorption capacity of LDH towards Se(IV) was measured at 29 mg/g, while SF exhibited a capacity of 16 mg/g. Notably, the two adsorbents synthesized in this research offer significant advantages: they are environmentally friendly, low cost and their synthesis procedures are straightforward, thereby showcasing high potential for the remediation of Se(IV) in its anionic form from contaminated aqueous environments.

Keywords: Mg−Al−CO_3 LDH; Silk fibroin; Se(IV); Removal performance

1 INTRODUCTION

In recent years, the advancement of industrialization has led to frequent occurrences of Se overloads in industrial wastewaters, posing a severe threat to human health. Excessive exposure to Se not only inflicts damage to the respiratory system but also elevates cancer risks, leading to grave health consequences. Consequently, the hazardous nature of Se has garnered global attention. Classified as a metalloid element, Se shares similarities with sulfur and exists in four principal forms in aquatic environments, Among these, Se (IV) exhibits the most toxicity due to its unique molecular structure. Hence, developing an effective, economical, safe, eco-friendly, and efficient method for Se removal is of paramount importance. Various techniques have been explored for this purpose, including coprecipitation, ion exchange, coagulation, electrochemical methods, membrane separation, and adsorption, among which adsorption stands out due to its simplicity, technological maturity, energy efficiency, making it a pivotal technology in water purification. [1] Central to the adsorption process is the identification of a suitable adsorbent material. [2] An ideal adsorbent must not only demonstrate high adsorption efficiency but also be economically viable, sustainable, and environmentally benign.

In recent times, researchers have been incessantly exploring and fabricating diverse types of adsorbents to tackle the challenges presented by heavy metals and metalloid contaminants in water treatment. Adsorbent materials can broadly be categorized into two classes: organic and inorganic adsorbents. Organic adsorbents, SF standing out among them. Owing to its excellent properties, wide availability, low cost, good biocompatibility, and biodegradability, SF has emerged as a promising eco-friendly material, attracting substantial attention in recent years. The abundance of functional groups on the surface serves as efficacious adsorption sites, has great application potential its potential in water purification. Inorganic adsorbents such as LDH, it's a class of uniquely structured anionic clay materials. LDH boast simple synthesis procedures, high specific surface areas, ordered porous structures, good biocompatibility, strong anion exchange capabilities, and exceptional stability and regenerability, [3] positioning them as efficient,

environmentally friendly, and cost-effective adsorbents.[4]

In alignment with the aforementioned context, our research utilized readily available and inexpensive raw materials, adopting green and safe preparation methods to synthesize two distinct types of adsorbents, SF and Mg-Al-CO_3 LDH. SEM was employed to examine the microstructures of both materials, with images vividly illustrating the anticipated structural features, thereby validating the efficacy of our synthesis methodologies. Ultimately, the adsorptive performance of these two materials towards Se(IV) was evaluated.

2 EXPERIMENT SECTION

2.1 Materials and Equipment

Lithium bromide (LiBr, 99%, Shanghai Hushi Chemical Co., Ltd.,), sodium carbonate(Na_2CO_3, 99.5%, Shanghai Hushi Chemical Co., Ltd.,), sodium selenite (Na_2SeO_3, 99.5%, Shanghai Hushi Chemical Co., Ltd.,). Aluminum nitrate hexaahydrate ($AlCl_3·6H_2O$, 99.99%, Aladdin reagent Co., Ltd.,), magnesium chloride hexahydrate ($MgCl_2·6H_2O$, 98%, Aladdin reagent Co., Ltd.,). sodium hydroxide (NaOH, 96%, Aladdin reagent Co., Ltd.,). The concentration of Se(IV) in supernatant was determined by inductively coupled plasma emission spectrometry (ICP-OES, Avio 200). Sanning electron microscopy (SEM)images were taken on the Quanta 250 FEG (SEM).

2.2 Preparation of Organic Material

The process of synthesis of SF aqueous solution is shown in Figure 1. Firstly, the chopped silkworm cocoons was boiled in 0.5wt% Na_2CO_3 solution for degumming, during which time it was constantly stirred for 30 minutes and repeated twice. The cooked silk was then rinsed several times in a beaker filled with deionized water to remove sericin and residual ions. After the degumming, the SF were pulled loose and dried at 50°C to get the degumming silk.

After the above operation, the degumming silk was dissolved by lithium bromide, and 0.5g deglumed silk was put into a centrifuge tube, and 9.3 M lithium bromide solution was added, and then heated and stirred in a water bath at 60°C for 4h to obtain a transparent and viscous SF solution. The obtained SF solution was centrifuged at low speed, and the insoluble matter and bubbles in the solution were removed and put into a dialysis bag for dialysis with ultra-pure water for three to four days. The supernatant was centrifuged and freeze-dried to obtain the regenerated SF.

Figure 1 Diagram for preparation process of SF aqueous solution

2.3 Preparation of Inorganic Materials

The synthesis of the Mg−Al−CO_3 LDH adsorbent was carried out via a widely-employed and straightforward hydrothermal method. A series of Mg−Al−CO_3 LDH nanomaterials with varying molar ratios of Mg^{2+}/Al^{3+} ranging from 1 to 5 were fabricated in the experiment. Initially, quantified amounts of $MgCl_2·6H_2O$ and $AlCl_3·6H_2O$ were mixed in deionized water at molar ratios of 1.0, 2.0, 3.0, 4.0, and 5.0 to form a mixed metal salt solution. Under vigorous magnetic stirring at room temperature, a combined solution of Na_2CO_3 and NaOH was gradually added to the above mixture until the pH of the reaction mixture was maintained above 10. Subsequently, after continuous stirring for two hours at room temperature, the mixture was transferred to a reaction kettle and heated at 170°C for 17 hours. Upon cooling to room temperature, the resultant white precipitate was collected by centrifugation, washed several times with deionized water and ethanol, and finally dried in an oven at 50°C.

2.4 Microstructure of SF

The microscopic morphology of SF was analyzed by SEM, and the observation results were shown in Figure 2. The SEM image clearly reveals the fine structure inside the SF material. SF is composed of numerous interwoven and connected filament fibers, which presents a complex winding state. In particular, some areas showed that SF had been successfully stripped to form SF nanofibers, indicating that degumming and subsequent treatment effectively exposed the nanoscale structure of fibroin. However, a certain degree of heterogeneity in the length of SF nanofibers was also observed, suggesting that there may be some randomness or control challenges in the process of fiber dissociation or preparation.

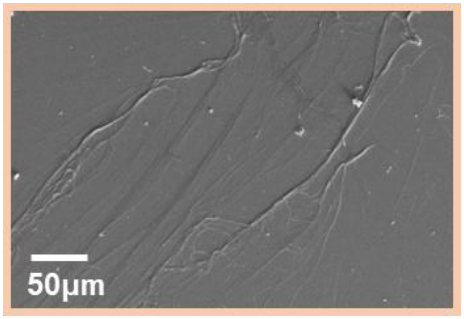

Figure 2 SEM images of SF

2.5 Microstructure of Mg-Al-CO3 LDH

The microstructure and structure of Mg-Al-CO_3 LDH with $Mg2^{+}/Al^{3+}$ ratio of 3 were investigated by scanning electron microscopy (SEM), and the observed results were shown in Figure 3. It can be clearly seen in the figure that the prepared LDH material presents a typical hexagonal sheet structure with regular edges and intact structure, which directly confirms the success of LDH material synthesis. Each layer structure is evenly distributed, showing good crystallinity and order, which is crucial for understanding the interaction mechanism of LDH materials and its application properties in adsorption, catalysis and other fields.

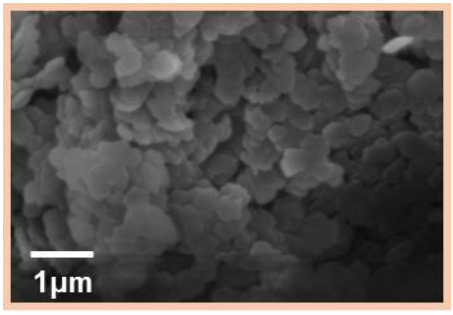

Figure 3 SEM mages of Mg−Al−CO3 LDH

2.6 Se(IV) Concentration Determination

The concentration of Se(IV) in water was quantitatively analyzed using ICP-OES to establish an accurate standard curve, with standard solutions prepared over a concentration range of 0-80.00 mg/L. As illustrated in Figure 4, the tested standard curve was obtained with a correlation coefficient reaching 0.999, indicating excellent linearity.

During the adsorption process, Na_2SeO_3 powder was dissolved in deionized water to prepare a stock solution of 1000 mg/L Se(IV). Thereafter, this stock solution was utilized for conducting adsorption experiments to attain an initial Se(IV)

concentration of 50 mg/L. Upon completion of each experiment, samples of the supernatant were taken for determining the residual Se(IV) concentration.

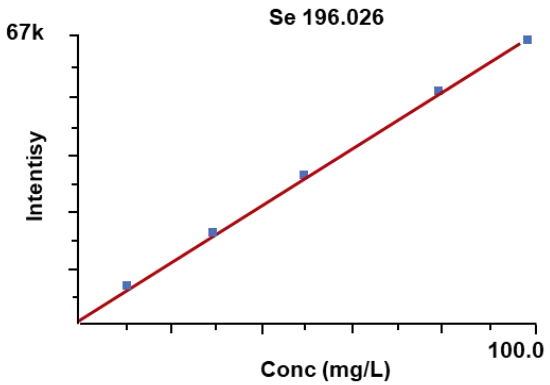

Figure 4 Standard curve of Se(IV) concentration

2.7 Adsorption Experiment

It was discovered that pure SF exhibited an adsorption capacity of 16 mg/g for Se(IV).As depicted in Figure 5, the influence of varying Mg^{2+}/Al^{3+} molar ratios on the adsorption performance of Se(IV) was investigated. The findings revealed that as the molar ratio of Mg^{2+}/Al^{3+} increased from 1.0 to 5.0, there was a corresponding ascending trend in the adsorption capacity, followed by a decline as the ratio continued to increase beyond 3. Notably, when the Mg^{2+}/Al^{3+} molar ratio was precisely 3, the highest adsorption capacity of 29 mg/g was observed. This observed trend is potentially attributed to the fact that with an increment in the molar ratio, the formation of a more orderly structured LDH leads to an increased exposure of adsorption sites, thus enhancing the overall adsorption capacity.

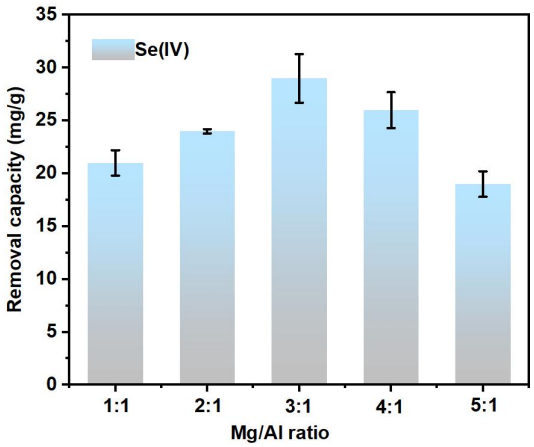

Figure 5 Influence of Varied Mg/Al ratios on the adsorption performance of Se(IV)

3 CONCLUSION

This study successfully developed two adsorbent materials, SF and Mg-Al-CO_3 LDH, for the removal of Se(IV) from aqueous solutions. SF exhibited an adsorption capacity of 16 mg/g for Se(IV), while the Mg-Al-CO_3 LDH demonstrated a higher capacity of 29 mg/g when the molar ratio of $Mg^{2+/}Al^{3+}$ was set at 3. The inherent nature and structural characteristics of SF contribute to its favorable adsorption performance. Meanwhile, the unique layered structure of Mg-Al-CO_3 LDH facilitates the effective adsorption of Se(IV). Both synthesis processes are characterized by simplicity, environmental friendliness, and economic viability, thereby presenting novel strategies for the mitigation of Se(IV) contamination.

Through comprehensive experimental evaluations and meticulous analyses, the adsorption efficiency of these materials was validated, establishing their potential application in water treatment. Future research endeavors can delve deeper into the adsorption mechanisms, refine operational conditions, and facilitate the practical application of these materials, thereby addressing the challenge of selenium pollution in the environment.

COMPETING INTERESTS

The authors have no relevant financial or non-financial interests to disclose.

REFERENCES

[1] Taka A L, Klink M J, Mbianda X Y, et al. Chitosan nanocomposites for water treatment by fixed-bed continuous flow column adsorption: A review. Carbohydrate Polymers, 2021, 255: 117398.

[2] Keshvardoostchokami M, Majidi M, Zamani A, et al. A review on the use of chitosan and chitosan derivatives as the bio-adsorbents for the water treatment: Removal of nitrogen-containing pollutants. Carbohydrate polymers, 2021, 273: 118625.

[3] Goh K H, Lim T T, Dong Z. Application of layered double hydroxides for removal of oxyanions: a review. Water research, 2008, 42(6-7): 1343-1368.

[4] Guan X, Yuan X, Zhao Y, et al. Application of functionalized layered double hydroxides for heavy metal removal: A review. Science of The Total Environment, 2022, 838: 155693.