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Synthesis of MgLaFe MMO Composites and Their Adsorption Properties for Co-removal of Fluoride and Arsenic from Water

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Abstract: Fluorine and arsenic co-contamination in groundwater is a common phenomenon in Northwest China, leading to serious health problems when consumed as drinking water due to high levels of both contaminants. It is important to note that the region's highly fluoridated and arsenic groundwater is widely distributed. Achieving efficient adsorption and co-removal of these pollutants is particularly challenging due to their co-pollution and strict drinking water standards. The study achieved the preparation of Mg-La-Fe mixed metal oxide composites through a green and stable synthesis pathway. The composites consist of magnesium and lanthanum hydroxides with a strong affinity for fluoride ions and iron, which can form stable compounds for arsenate and arsenite, enabling efficient co-removal of fluoride and arsenic ions. The material can adsorb up to 30.26 $mg \cdot g^{-1}$, 36.96 $mg \cdot g^{-1}$, and 133.65 $mg \cdot g^{-1}$ of As(III), As(V), and F^-, respectively, in solution. Even after four cycles, the adsorption of As(III), As(V), and F^- remains at 81.11%, 81.36%, and 80.87%, respectively. This study obtained an efficient adsorption material for the co-removal of fluorine and arsenic, providing a theoretical basis and technical support for ensuring the safety of drinking water in remote areas of Northwest China.

Keywords: Adsorption, Fluorine, Arsenic, Mixed metal oxides.

1. Introduction

Groundwater quality is influenced by various factors such as meteorology, hydrology, lithology, underground water supply and drainage, tectonics, and geomorphology. Some groundwater may contain harmful substances like arsenic and fluorine due to the influence of parent rock[1-2]. It is important to note that the presence of these toxic substances can pose a risk to human health. In the northwest region of China, both the closed flow area and the inner river area have high levels of groundwater mineralization, exceptionally high levels of fluorine and arsenic. These substances can harm the human body if consumed as drinking water. According to China's drinking water quality standards, the fluorine content should not exceed 1mg/L, and the arsenic content should not exceed 0.01mg/L. In northwestern China's agricultural and pastoral areas, residents live in dispersed communities where water treatment capacity is insufficient. As a result, the drinking water quality is generally poor, with high levels of fluoride and arsenic. Long-term consumption of such water can lead to health problems such as dental fluorosis, fluorosis, skin keratosis, and neurasthenia[3-6].

The leading technologies used for removing fluoride and arsenic from drinking water are membrane separation, coagulation and precipitation, and adsorption[7, 8]. Adsorption has unique advantages for co-removing fluorine and arsenic from groundwater in agricultural and pastoral areas of Northwest China due to its high ion removal efficiency, ease of operation, lack of secondary pollution, and absence of wastewater. The method primarily utilizes the adsorbent's high specific surface area, developed pore structure, and wealthy functional groups to adsorb fluorine and arsenic ions[9, 10].

Modified materials, composites, and nanomaterials are a new type of adsorbent material that is increasingly of interest to scholars worldwide due to their large adsorption capacity and efficient adsorption effect on various ions[11, 12]. However, it is essential to note that these materials may have limitations in their ability to co-exclude specific ions or molecules. Due to the synthesis of multiple components, the ion co-adsorption process is complex, making it challenging to achieve high efficiency. Additionally, poor recycling effects limit the applicability of adsorbent materials in drinking water treatment. Therefore, their application is limited to narrow scenarios.

This study prepared magnesium, lanthanum, and iron using the simple urea method to obtain a composite hydroxide. The composite material was then calcined to obtain the MgLaFe mixed metal oxides(MMO) composite material. This was achieved by using the mechanism that oxides of magnesium and lanthanum can form strong bonds with fluoride ions through the mechanism of inner-sphere complexation[13-14] and the mechanism that arsenate and arsenite can easily combine with iron oxides to form inner-sphere double-dentate compounds[15]. The study demonstrated that the composite adsorbent material possesses several advantages, including a large adsorption capacity, fast adsorption rate, simple and rapid solid-liquid separation, and a straightforward synthesis method. The material has a high recycling rate, making it a promising green fluorine-arsenic co-removal adsorbent material.

2. Materials and Methods

2.1. Materials

Magnesium nitrate ($Mg(NO_3)_2 \cdot 6H_2O$); Lanthanum nitrate

($La(NO_3)_3·6H_2O$); Iron nitrate ($Fe(NO_3)_3·9H_2O$); Sodium fluoride; Sodium hydroxide (NaOH); Urea, etc. All the chemical reagents are of analytical grade and can be used without further purification. All solutions were prepared with ultrapure water (18.2 MΩ-cm).

2.2. Adsorbent characterization and measurement techniques

Scanning electron microscope (TESCAN MIRA field emission scanning electron microscope), atomic fluorescence photometer (AFS-8220 Beijing Jitian Instrument Co., Ltd.), ion chromatograph (Aptar 940, Switzerland).

2.3. Synthesis of MgLaFe MMO

A reaction mixture was prepared with 0.2 M of the relevant salt solution in the amount of $Mg(NO_3)_2·6H_2O$ (20 mL), $La(NO_3)_3·6H_2O$ (1.66 mL) and $Fe(NO_3)_3·9H_2O$ (8.33 mL). The reaction mixture was heated at 90 ℃ for 24 h, the precipitate was washed with distilled water to pH neutral, dried at 105 ℃ for 12 h, and later calcined at 650 ℃ for 5 h to obtain the MgLaFe MMO composite.

2.4. Adsorption experiments

As(III) and As(V) solutions (100 $mg·L^{-1}$) were prepared by dissolving $NaAsO_2$ and $Na_2HAsO_4·7H_2O$ in deionised water, and F^- solution (5000 $mg·L^{-1}$) was prepared by dissolving NaF in deionised water. Different concentrations of arsenic and fluorine solutions were prepared by diluting the stock solutions for adsorption experiments. The adsorption kinetics of As(III), As(V) and F^- on the prepared materials was studied by mixing 100 mg of adsorbent with 200 mL of solutions of As(III) (5 $mg·L^{-1}$), As(V) (5 $mg·L^{-1}$) and F^- (100 $mg·L^{-1}$) at concentrations. The solutions were kept at pH 7.0 ± 0.1 and shaken at 120 rpm for adsorption kinetics experiments. Samples were collected at specific time intervals from 5 min to 360 min for ion concentration analysis. The initial As(III) concentrations for adsorption isotherm experiments ranged from 5 to 100 $mg·L^{-1}$, As(V) concentrations ranged from 5 to 100 $mg·L^{-1}$, and F- concentrations ranged from 10 to 500 $mg·L^{-1}$. Desorption and reusability were carried out using 1M NaOH, and the MgLaFe MMO composites were first proceeded the adsorption experiments above, and then separated and immersed in NaOH solution for another 24 h. All experiments were repeated at 25℃.

2.5. Kinetics of adsorption study

The kinetic experimental data were fitted and analysed by pseudo-first-order and pseudo-second-order with the following model equations, respectively:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (1)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (2)$$

Where Q_t (mg/g) is the sorption amount at time t; Q_e (mg/g) is the sorption capacity of F^-, As(Ⅲ) and As(V) at equilibrium; k_1 (min^{-1}) and k_2 (min^{-1}) are the rate constants of the pseudo-first-order kinetics and pseudo-second-order kinetics models, respectively.

2.6. Adsorption isotherms study

Adsorption experiments for fluoride-arsenic were conducted using MgLaFe MMO composites. The adsorption isotherms were used to study the maximum adsorption capacity of the composite material for As(III), As(V), and F^-. The initial F^-/As concentration was varied using As(III) (5 $mg·L^{-1}$), As(V) (5 $mg·L^{-1}$), and F^- (100 $mg·L^{-1}$). The experimental results were fitted to the Langmuir and Freundlich models using the following equations, respectively:

$$q_e = \frac{q_m b c_e}{1 + b c_e} \quad (3)$$

$$q_e = K_F C_e^{-n} \quad (4)$$

Where Q_e (mg/g) and C_e (mg/L) are defined as above; Q_m (mg/g) was the theoretical maximum sorption amount; K_L (L/mg) is the Langmuir sorption constant (L/mg); K_F $(mg/g)·(L/mg)^{1/n}$ is the constant associated with the relative sorption amount; and n was the sorption intensity.

3. Results and Discussion

3.1. Morphology of the adsorbents

Table 1 shows the sample synthesis ratios and physicochemical properties of the synthesized MgLaFe MMO composites. The BET surface area for ML was 20.01 $m^2·g^{-1}$, and for MF, it was 61.01 $m^2·g^{-1}$. The BET surface area of the MgLaFe MMO composites increased from 50.16 $m^2·g^{-1}$ for MLF-1 to 203.46 $m^2·g^{-1}$ for MLF-3 with the increase in Fe content. This increase is attributed to the fact that Fe acts as a dispersant and increases the specific surface area of the nanocomposites compared to sample ML. With an increase in Fe content, the BET-specific surface area of the material decreased. This may be due to the formation of nanocomposite aggregation and an increase in the particle size of the nanocomposites.

Table 1. Preparation conditions and names of MgLaFe MMO composites samples

Raw materials	Molar ratio	Urea (g)	Sample abbreviation	BET surface area ($m^2·g^{-1}$)
$Mg(NO_3)_2$/ $La(NO_3)_3$	2:1	10	ML	20.01
$Mg(NO_3)_2$/ $Fe(NO_3)_3$	2:1	10	MF	61.01
$Mg(NO_3)_2$/ $La(NO_3)_3$/$Fe(NO_3)_3$	4:1:1	10	MLF-1	50.16
$Mg(NO_3)_2$/ $La(NO_3)_3$/$Fe(NO_3)_3$	8:1:3	10	MLF-2	70.67
$Mg(NO_3)_2$/ $La(NO_3)_3$/$Fe(NO_3)_3$	12:1:5	10	MLF-3	203.46
$Mg(NO_3)_2$/ $La(NO_3)_3$/$Fe(NO_3)_3$	16:1:7	10	MLF-4	132.58
$Mg(NO_3)_2$/ $La(NO_3)_3$/$Fe(NO_3)_3$	20:1:9	10	MLF-5	32.46

Figure 1 displays scanning electron micrographs of the MgLaFe MMO samples with varying ratios in Table 1. The SEM results indicate that the ML MMO material exhibits agglomerated granular spherical shapes, the MF MMO material displays smooth multilayered lumps, and the composite of magnesium-lanthanum-iron ternary presents lumps surrounded by amorphous particles.

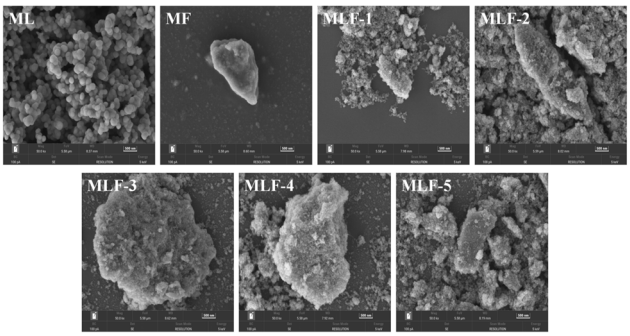

Figure 1. SEM images of MgLaFe MMO composites at different molar ratio

3.2. Evaluation of adsorption performance

Figure 2 displayed the adsorption amount of MgLaFe MMO after 360 minutes in the fluoride-arsenic co-adsorption experiment. This experiment simulates the maximum concentration of fluoride and arsenic in actual groundwater, with both trivalent and pentavalent arsenic concentrations at 5 mg·L^{-1} and fluoride ion concentrations at 100 mg·L^{-1}. The proportion of iron in MgLaFe MMO positively correlates with the adsorption of trivalent arsenic, pentavalent arsenic, and fluoride ions. This enhancement continues until the maximum adsorption in LDHs is reached at MLF-3.

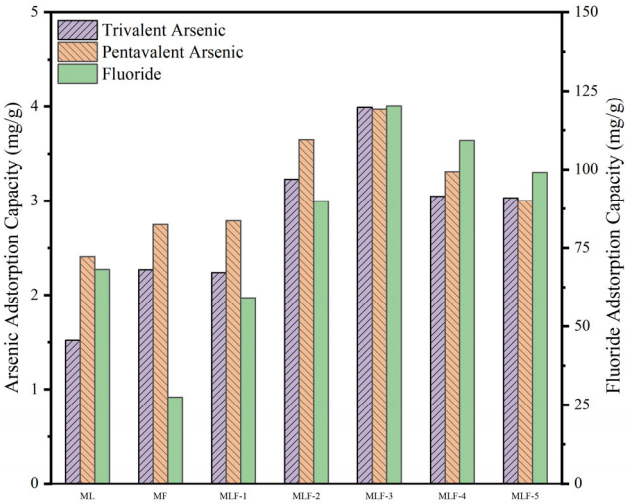

Figure 2. Adsorption performancet of fluoride and arsenic with MgLaFe MMO composites

The adsorption of As(III), As(V), and F increased with increasing concentration, as shown in Figure 3, Figure 4, and Table 2. The experimental data for the adsorption of F^- was better fitted by the Langmuir isotherm model (r^2 >0.99) than the Freundlich isotherm model (r^2 >0.75). Meanwhile, the adsorption properties of As(III) and As(V) were consistently better fitted by the Langmuir isotherm models (r^2 >0.984 and 0.989) than the Freundlich isotherm models (r^2 >0.91 and 0.94). Furthermore, the MgLaFe MMO composites demonstrated significantly improved maximum adsorption capacities of 30.26 mg/g for $H_2AsO_3^-$, 36.96 mg/g for AsO_4^{3-}, and 133.65 mg/g for F^- in simultaneous adsorption. The Langmuir constant K_L and Freundlich constant 0< n< 1 in the fluoride-arsenic co-adsorption system also suggested the excellent adsorption performance of the composites in this system.

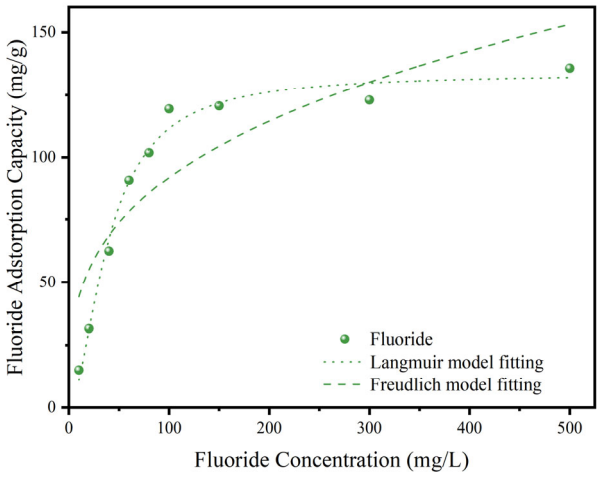

Figure 3. Sorption isotherms and fitting figures with the Langmuir and Freundlich models with simultaneous sorption of F-on MgLaFe MMO composites

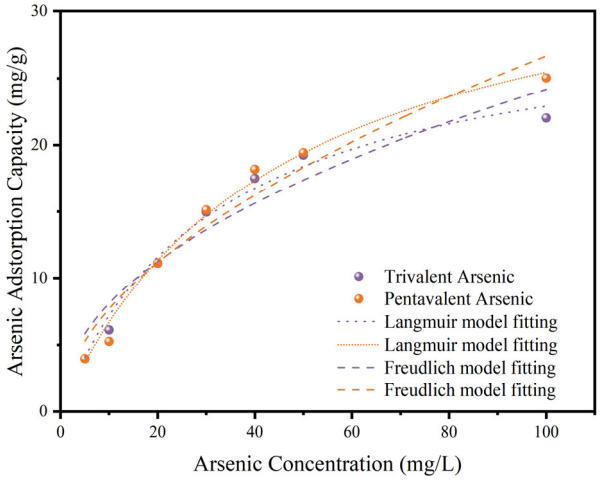

Figure 4. Sorption isotherms and fitting figures with the Langmuir and Freundlich models with simultaneous sorption of As(III) and As(V) on MgLaFe MMO composites

Table 2. Parameters related to the Langmuir and Freundlich equations for fluorine and arsenic adsorption on MgLaFe MMO composites

MgLaFe MMO	Langmuir model			Freundich model		
	Q_m(mg/g)	K_L(L/mg)	r^2	K_F	n	r^2
As(III)	30.26	0.03	0.98	2.70	0.48	0.91
As(V)	36.96	0.02	0.99	2.21	0.54	0.94
F-	133.65	0.01	0.99	21.25	0.32	0.75

Figure 5, 6 and Table 3 presented the kinetic parameters. The results indicated that the pseudo-first-order kinetic correlation coefficients (r^2) for both As(V) and F^- adsorption were the highest (>0.97). The theoretical adsorption values (mg/g) calculated using the pseudo-first-order kinetic model are almost equal to the experimental adsorption values. This suggested that the pseudo-first-order kinetic model was better suited to describe the adsorption of As(V) and F^- on the MgLaFe MMO composites. For the adsorption of As(III), the pseudo-first-order and pseudo-second-order kinetic correlation coefficients (r^2 > 0.99) were closer, indicating that the MgLaFe MMO composites have better adsorption capabilities. This suggested that electrostatic and chemical adsorption of As(III) might be occurred on the MgLaFe MMO

composites.

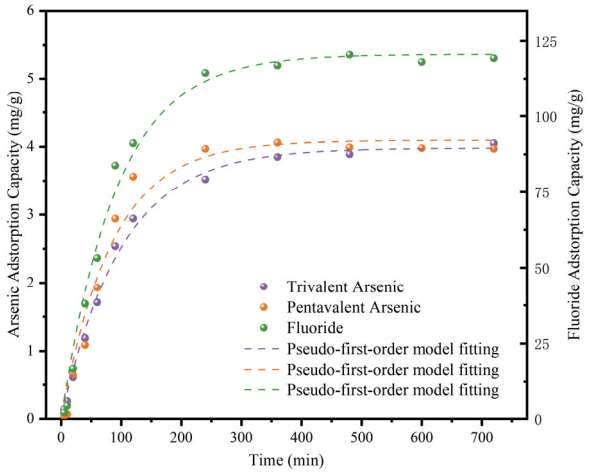

Figure 5. Pseudo-first-order model fitting with simultaneous sorption of F-, As(III) and As(V) on MgLaFe MMO composites

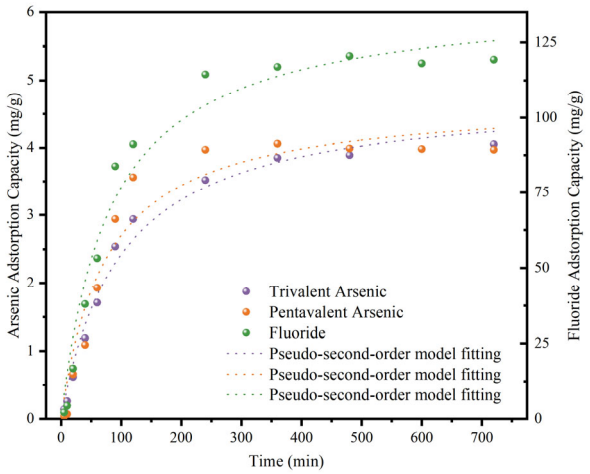

Figure 6. Pseudo-second-order model fitting with simultaneous sorption of F-, As(III) and As(V) on MgLaFe MMO composites

Table 3. Parameters related to the Pseudo-first-order model and Pseudo-second-order model for fluorine and arsenic adsorption on MgLaFe MMO composites

MgLaFe MMO	Pseudo-first-order model			Pseudo-second-order model		
	Q_e (mg /g)	k_1 (min^{-1})	r^2	Q_e (mg /g)	k_2 (g/mg·min^{-1})	r^2
As(III)	4.98	0.01	0.99	4.82	0.0021	0.99
As(V)	4.09	0.01	0.97	4.73	0.0028	0.95
F-	120.75	0.01	0.99	130.94	0.0001	0.97

3.3. Effect of solution pH

Figure 7 illustrated the adsorption of As (III), As (V), and F^- as a function of solution pH. The pH was maintained within the range of 3 to 11, with initial concentrations of 5 $mg·L^{-1}$ for As (III), 5 $mg·L^{-1}$ for As (V), and 100 $mg·L^{-1}$ for F^-, a contact time of 360 min, and an adsorbent dosage of 500 $mg·L^{-1}$. The results indicated that As (V) uptake was highest within the pH range of 6-7, while As (III) uptake exhibited a similar trend. Furthermore, F^- was efficiently adsorbed within the pH range of 6-7. Lower pH values caused the conversion of F^- to hydrofluoric acid, which made adsorption difficult. Conversely, higher pH values resulted in an abundance of hydroxides accumulating on the surface of the adsorbent material, occupying the adsorption sites that contain deprotonated As (III), As (V), and F^-. This led to a significant decrease in the adsorption capacity.

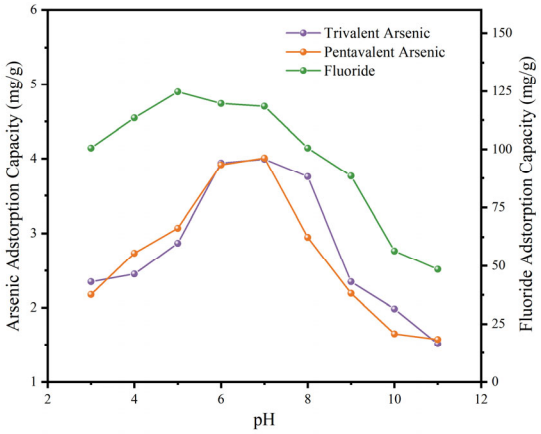

Figure 7. Effect of pH on As(Ⅲ), As(V), and F^- adsorption by MgLaFe MMO composites

3.4. Regeneration and recyclability

Figure 8 displayed the results of cyclic adsorption experiments of MgLaFe MMO composites. After adsorption, the MgLaFe MMO underwent impregnation with 1M sodium hydroxide solution. Following the repetition of the calcination step in the preparation process, it underwent five fluoride-arsenic co-sorption experiments. After 4 cycles, the adsorbed amount of As (III), As (V), and F^- remained at 81.11%, 81.36%, and 80.87%, respectively. These results indicated that the material has high recycling value and low material cost.

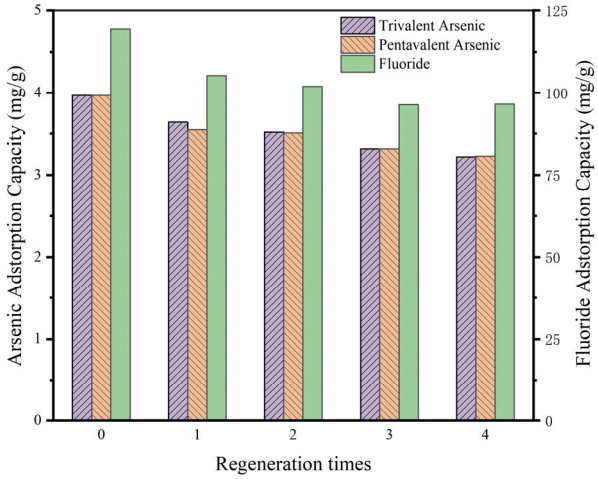

Figure 8. Regeneration cycle of MgLaFe MMO adsorbent material (initial pH 7; The temperature is 25℃; Adsorption time 6h)

4. Conclusion

By studying the adsorption performance of MgLaFe MMO composite adsorbent materials on As(III), As(V), and F- in water, the following conclusions can be drawn from the analysis results:

(1) The isothermal adsorption model of MgLaFe MMO

composites adsorbent on As(III), As(V), and F^- in water is consistent with the Langmuir adsorption isothermal model. The adsorption capacity for As(III), As(V), and F^- in solution is excellent, reaching 30.26 $mg \cdot g^{-1}$, 36.96 $mg \cdot g^{-1}$, and 133.65 $mg \cdot g^{-1}$, respectively.

(2) Equilibrium for the adsorption reaction is reached in approximately 360 minutes. The pseudo-first-order kinetic model is more effective in describing the adsorption process of MgLaFe MMO composites on As(V) and F^-. Both electrostatic and chemical adsorption processes occur for As(III).

(3)After 4 cycles, the adsorption rates for As(III), As(V), and fluoride ions remained at 81.11%, 81.36%, and 80.87%, respectively. The MgLaFe MMO composite adsorbent material has a high recycling value.

Acknowledgment

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