Vietnam Journal of Catalysis and Adsorption
Tạp chí xúc tác và hấp phụ Việt Nam

Application of adsorbents based on LaFe$_{1-x}$Mn$_x$O$_3$ perovskites to treat As, Pb in contaminated groundwater in the craft village

Vu The Ninh[1*], Nguyen Viet Dung[1], Lưu Minh Đại[1], Nguyen Thanh Anh[2]

[1]Institute of Materials Science, Vietnam Academy of Science and Technology
[2]Thang Long High School for the Gifted, Da Lat, Lam Dong, Viet Nam
*Email: ninhvt@ims.vast.ac.vn

ARTICLE INFO

ABSTRACT

The nanoparticle crystals of perovskite LaFe$_{1-x}$Mn$_x$O$_3$ were prepared by the PVA (polyvinyl alcohol) gel combustion method to determine the adsorption capacity of As(V), Pb^{2+} from solution was investigated. Single-phase crystalline perovskite of LaFe$_{1-x}$Mn$_x$O$_3$ is formed by solid solution formation which completely replaces LaFeO$_3$ perovskite and LaMnO$_3$ perovskite. In LaFe$_{1-x}$Mn$_x$O$_3$ perovskites, the x substitution composition, or the rate of participation to form the substitution solid solution between the two components LaFeO$_3$ and LaMnO$_3$ will determine the type of original structure, the interaction between the Fe and Mn in in the crystal lattice. Thereby determining the characteristics and adsorption activity of perovskite LaFe$_{1-x}$Mn$_x$O$_3$. Perovskite LaFe$_{1-x}$Mn$_x$O$_3$ with the formula LaFe$_{0.3}$Mn$_{0.7}$O$_3$ gave the best As(V) adsorption efficiency on the x components, while the LaFe$_{0.7}$Mn$_{0.3}$O$_3$ formula gave the best As(V) adsorption efficiency on the x components. The LaFe$_{1-x}$Mn$_x$O$_3$ perovskite-based adsorbent pelletized with the composition LaFe$_{0.3}$Mn$_{0.7}$O$_3$-LaFe$_{0.7}$Mn$_{0.3}$O$_3$-bentonite has practical potential to remove arsenic, lead in contaminated water.

Introduction

Heavy metal pollution from wastewater is a worldwide concern, as the release of heavy metals into water and soil environments can affect human health and ecosystems. Heavy metals are considered the main pollutants in water sources.

Because of their non-biodegradable nature, they tend to accumulate over time. Heavy metal poisoning can lead to contamination of drinking water, increased concentrations in the air near the emission source, or ingestion through the food chain. The increase in heavy metal use in industry is the main cause of the increase in heavy metal content in natural water sources [1-4].

In Vietnam, industrial processes have brought about a significant change in the quality of people's lives. However, the use of many materials, raw materials and chemicals in the production process also has the potential to cause environmental pollution, or release toxic substances that pollute water sources such as heavy metals, toxic organic substances, etc [3].

In fact, there have appeared craft village areas, where the population lives, with a high rate of death from cancer, which is mainly due to the use of contaminated water.

When analyzing water samples taken from rivers, streams, wells... that people are using in craft villages, a list of 10 craft villages has been listed with water samples with pollution levels exceeding the standards for allowed many times, in the criteria of cyanide, benzene, bentazone, phenol, cadmium, lead, arsenic, manganese. Therefore, the development of treatment technologies to remove water pollutants is necessary and urgent [4].

Methods widely used to remove heavy metals from water and wastewater include ion exchange, chemical precipitation, and adsorption. Each method has certain advantages and limitations. In particular, the adsorption method is now recognized as an effective and economical method in the treatment of heavy metal contaminated water. The adsorption process offers flexibility in design, operation and in many cases the adsorbent is renewable and easy to store. Studies have tested the optimal adsorbent materials for heavy metals, from common substances such as: activated carbon, clay, chitosan, agricultural waste, fly ash. metal oxide. Nano-adsorbents have emerged with great application potential due to their strong activity with high capacity.[5-12]

In previous study, $LaFe_{1-x}Mn_xO_3$ perovskite was fabricated and evaluated the adsorption efficiency of Arsenic, lead, and cadmium. In this paper, the research results related to determination of adsorption capacity, calculation and installation of equipment containing $LaFe_{1-x}Mn_xO_3$ perovskites to treat groundwater contaminated with arsenic and lead will be presented [13,14].

Experimental

Chemicals

All reagents were analytical grade and used as received without further purifi cation. $La(NO_3)_3.6H_2O$, $Fe(NO_3)_3.9H_2O$, $Mn(NO_3)_2.4H_2O$, NH_4OH, HNO_3, Na_3AsO_4, $Pb(NO_3)_2$, Polyvinyl alcohol (PVA) were purchased from Sigma-Aldrich and Merck. Bentonite trade (Viet Nam), Deionized water was used for all experiments.

Fabrication of adsorbent materials

Fabrication of $LaFe_{1-x}Mn_xO_3$ perovskites by PVA gel combustion, the factors affecting the formation of $LaFe_{1-x}Mn_xO_3$ perovskite have been identified in previous studies [13,14].

Fabrication of 02 samples of $LaFe_{1-x}Mn_xO_3$ perovskite, in which $LaFe_{0.7}Mn_{0.3}O_3$ perovskite is optimal for Pb^{2+} adsorption and $LaFe_{0.3}Mn_{0.7}O_3$ perovskite is optimal for As(V) adsorption. The fabrication process is carried out as follows: drop by drop a solution of mixed nitrate salt $La^{3+}+Fe^{3+}+Mn^{2+}$ (molar ratio $La^{3+}/Fe^{3+}/Mn^{2+}$ has values of 10/7/3 and 10/3/7 corresponding to the formation of 2 different perovskites) into 5% PVA solution to form a mixture of metal salt solution-PVA with molar ratio of metal/PVA = 1/1. Then, the metal-PVA solution mixture was mixed continuously at 80^oC until a gel was obtained, continued to heat the gel sample until combustion occurred, and the product of combustion was calcibed at 600^oC for 2 hours to form the single-phase crystalline perovskite.

Fabrication of adsorbent materials based on $LaFe_{1-x}Mn_xO_3$ perovskite for use in the adsorption equipment is carried out as follows: mix well 03 components $LaFe_{0.7}Mn_{0.3}O_3$ perovskite, $LaFe_{0.7}Mn_{0.3}O_3$ perovskite, bentonite in mass ratio 2/2/1, along with an adequate amount of water. The paste was made into mechanical pellets approximately 2 mm in diameter, then dried and calcined at 400^oC for 2 h to obtain the adsorbent based on perovskite $LaFe_{1-x}Mn_xO_3$-bentonite (called LFMB material).

Methods to evaluate the adsorption capacity of materials

Determine the maximum adsorption capacity of the material

The saturated adsorption capacity (Q_{bh}, $mg.g^{-1}$) of As(V) and Pb^{2+} of the material was determined by conducting an adsorption experiment between 100 ml of solution with different initial concentrations of As(V), Pb^{2+} (C_i, $mg.L^{-1}$) with 0.05 g of $LaFe_{1-x}Mn_xO_3$ perovskites. When the adsorption equilibrium, collect the solution to determine the remaining concentration of As(V), Pb^{2+} (C_f, $mg.L^{-1}$). The saturated adsorption capacity was calculated by the formula: $Q_{bh} = 2*(C_i-C_f)$ [15].
The maximum adsorption capacity of the $LaFe_{1-x}Mn_xO_3$ perovskites (Q_{max}, $mg.g^{-1}$) for As(V), Pb^{2+} was determined according to Langmuir isotherm adsorption model. Represent the experimental points (Q_{bh}, C_f) determined on the graph showing the dependence of Q_{bh} on C_f and regress those experimental values by using specialized calculation software Table Curve. 2D 5.01 to obtain the maximum adsorption capacity of the $LaFe_{1-x}Mn_xO_3$ perovskites for As(V), Pb^{2+} [15].

Determine the adsorption capacity on the column of the material

The model for evaluating the adsorption capacity on the column of the material is shown in Figure 1. The adsorption column is a glass tube with a diameter of 1.5 cm containing 15 g (10.7 ml) of adsorbent material based on $LaFe_{1-x}Mn_xO_3$ perovskites-bentonite. The upper end connects to the As(V) or Pb^{2+} solution tank to be treated, the lower end connects to a valve that can adjust the flow rate of the solution flowing through the column. The upper end of the column is connected to the As(V) or Pb^{2+} solution tank with with a concentration of 5 mg.L^{-1}, the lower end of the column has a lock that can adjust the solution flow rate through the column. Retention time is calculated by the formula τ (minute) = $V/\overset{\circ}{V}$, where V (ml) is the volume of adsorbent, $\overset{\circ}{V}$ (ml.min^{-1}) is the flow rate.[15]
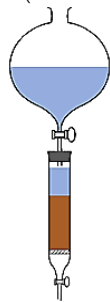

Figure 1: Model of adsorption column to remove As(V), Pb^{2+} from solution

The retention time of the adsorption column was determined by gradually increasing the column flow rate until the appearance of As(V), Pb^{2+} at the column outlet. The column safe adsorption capacity of the column is determined by running a stream of solution containing fixed concentrations of As(V), Pb^{2+} continuously through the column until the contents of As(V), Pb^{2+} are at the outlet of the column. below allowable standards [16].

Methods of elemental analysis

Determination of ionic content of elements Pb, As, La, Fe, Mn and other elements in solution by atomic absorption method (AAS) on instrument 200 Series AA (Agilent, USA).

Results and discussion

Characterization of $LaFe_{1-x}Mn_xO_3$

When determining some characteristics of $LaFe_{1-x}Mn_xO_3$ perovskite, it was found that the substituted composition x affects the original structure characteristics, phase crystal size, surface area and zero of point charge. In particular, the differences in the characteristics of the $LaFe_{1-x}Mn_xO_3$ perovskites according to the x composition led to a change in the adsorption efficiency of As(V), Pb. In which, As(V) adsorption efficiency was highest on $LaFe_{0.3}Mn_{0.7}O_3$ perovskite and Pb^{2+} adsorption efficiency was highest on $LaFe_{0.7}Mn_{0.3}O_3$ perovskite. Table 1 presents some characteristics of 2 samples perovskite $LaFe_{0.7}Mn_{0.3}O_3$ and $LaFe_{0.3}Mn_{0.7}O_3$.

Table 1: Characterization of $LaFe_{1-x}Mn_xO_3$

Perovskit $LaFe_{0.7}Mn_{0.3}O_3$ (LaFeO$_3$ phase)		
D, nm	S_{BET}, $m^2.g^{-1}$	pH$_{ZPC}$
27	28	6.35
Perovskit $LaFe_{0.3}Mn_{0.7}O_3$ (LaMnO$_3$ phase)		
D, nm	S_{BET}, $m^2.g^{-1}$	pH$_{ZPC}$
14	24	5.95

Maximum adsorption capacity of As(V), Pb^{2+} on perovskite $LaFe_{1-x}Mn_xO_3$

The results of investigating the influence of the initial concentration of As(V), Pb^{2+} solution on the saturation adsorption capacity on $LaFe_{1-x}Mn_xO_3$ perovskites are shown in Table 2.

The results recorded in Figure 2a show that the As(V) adsorption process is described quite well by the Langmuir isotherm adsorption model with the regression coefficient R^2 = 99.5%. The maximum adsorption capacity of As(V) on $LaFe_{0.3}Mn_{0.7}O_3$ perovskite calculated according to this model reached 166.88 mg.g^{-1}. Similarly, figure 2b also shows that the maximum adsorption capacity of Pb^{2+} on $LaFe_{0.7}Mn_{0.3}O_3$ perovskite calculated according to Langmuir adsorption isotherm model reached 180 mg.g^{-1} (regression coefficient R^2 = 0.97).

The adsorption process of As(V), Pb^{2+} of LFMB materials on the column

In water treatment technology, filter columns combined with granular materials have been and are being applied most commonly in water purification, ion exchange and adsorption. When the column is in operation, the contaminant treatment process occurs continuously, over time the contaminant-saturated

material area at the column inlet will move to the column outlet, which is called the mass transfer zone. The column run should be stopped when the mass transfer zone reaches a certain limit, then the column output will appear contaminant.

In order to completely remove the pollutant on the adsorption column, it is necessary to keep the pollutant on the column for a sufficiently long time $\geq \tau_{min}$ ($\tau_{minimum}$ corresponding to the pollutant appearance at the allowable standard concentration) . Table 3 presents the results of determining As(V), Pb^{2+} content at the output of the column when increasing the flow rate gradually. Calculation results in Table 3 show that,

for the complete adsorption of As(V), Pb^{2+} on the adsorption column, the flow rate is maintained at 6 ml.min^{-1} corresponding to the retention time of 1.72 minutes.

Run the adsorption column at a flow rate of 6 ml.min^{-1}, determine the concentration of As(V), Pb^{2+} at the outlet of the adsorption column, while continuously running the solution containing As(V), Pb^{2+} through column. Table 3 presents the results of determination of As(V), Pb concentration and calculation shows that the safe adsorption capacity on the column of LFMB material reached 7.3 mgAs(V).g^{-1} and 7.9 mgPb^{2+}.g^{-1}.

Table 3: Results of determination of As(V), Pb^{2+} concentration at column output according to flow rate

For As(V)			For Pb^{2+}		
$\overset{\text{v}}{V}$, ml.min^{-1}	C_f, mg.L^{-1}	τ, minute	$\overset{\text{v}}{V}$, ml.min^{-1}	C_f, mg.L^{-1}	τ, minute
1.2	Nd	8.92	1.2	Nd	8.92
2.5	Nd	4.28	2.5	Nd	4.28
3.5	Nd	3.04	3.5	Nd	3.04
5.0	Nd	2.12	5.0	Nd	2.12
6.2	Nd	1.73	6.2	Nd	1.73
7.5	0.005	1.43	7.5	0,03	1.43

Table 4: Results of determination of As(V), Pb^{2+} concentration of column output according to filter volume

For As(V)			For Pb^{2+}		
No.	V_{column}, ml	C_f, mg.L^{-1}	No.	V_{column}, ml	C_f , mg.L^{-1}
1	21.000	Nd	1	24.000	Nd
2	500	0.005	2	200	0.02
3	500	0.005	3	200	0.06
4	500	0.005	4	200	0.15
5	500	0.005	5	200	0.25
6	500	0.010	6	200	0.75
7	500	0.010	7	200	1.22
8	500	0.010	8	200	1.45
Q_{safe} = 7.3 mgAs(V).g^{-1}			Q_{safe} = 7.9 mgPb^{2+}.g^{-1}		
9	500	0,015	8	200	1,74

Installation of adsorption equipment in craft villages

Aluminum recycling craft village in Man Xa village, Van Mon commune, Yen Phong district, Bac Ninh province is evaluated as one of the craft villages with serious pollution status. After receiving recommendations from the authorities, people here have exploited the deep underground water source ($\geq$ 120m) and combined the design of the filter tank using a combination of materials such as quartz sand, activated carbon. … to obtain better quality water for domestic use. However, from the results of analysis of domestic water samples of households here, a large amount of arsenic and lead may have leaked from aluminum recycling wastewater into the groundwater.
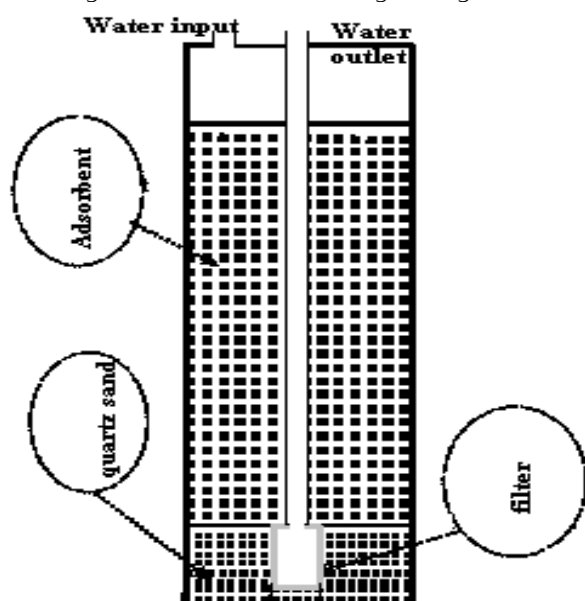
In order to completely remove arsenic and lead pollution from domestic water sources, a filter device containing LFMB adsorbent material was calculated and tested to be installed right after the family's filter tank with a design capacity of $\geq$250 liters.hour^{-1}. Figure 3(a,b) shows the schematic diagram of the device and the commercial water purifier (composite 817 with 5-way valve) was selected to install LFMB material into the device. The volume of LFMB material installed on each unit is 1.8 kg (1.8 kg mixes with quartz sand to make 8 liters of material, along with 2 liters of quartz sand for the bottom). From the results of determining the required retention time for As(V), Pb^{2+} on the column in Table 3, it shows that the effective treatment

speed of As(V), Pb^{2+} of the adsorbent can reach 280 liters.hour^{-1}.

Table 5: Analysis results of water samples before and after equipment installation

targets	Input Water	Outlet water	
	concentrate, mg.L^{-1}	250 liters.h^{-1}	300 liters.h^{-1}
As	0.0120	Nd	0.0022
Pb	0.0128	Nd	0.0028
Cd	Nd	-	-
TDS	224	220	221

The results of analysis of domestic water samples in the craft village area show that, although the groundwater has been treated through a filter tank, there are still significant toxic pollutants such as arsenic and lead. After filtering through the adsorbent at the rate of 250 liters.hour, the presence of arsenic and lead was not detected; when the filtration rate of the device reaches 300 liters.hrs, arsenic and lead appear in traces. The analysis results also showed that the total dissolved solids in water after filtration decreased. Calculating from the results of the safe column adsorption capacity, pollutant content, under stable operating conditions, the operating capacity of the device to completely remove arsenic and lead contamination can be up to over 500 m^3.

(a): Schematic diagram of the adsorption device
(b): The adsorbent is installed in the household
Figure 3(a,b): Diagram of the principle and adsorption to remove arsenic and lead pollution in households

Conclusion

The maximum adsorption capacity of As(V), Pb^{2+} on LaFe$_{1-x}$Mn$_x$O$_3$ perovskite nanomaterials has been determined, the maximum As(V) adsorption capacity on LaFe$_{0.3}$Mn$_{0.7}$O$_3$ perovskite is 166.88 mg.g^{-1}, the maximum adsorption capacity of Pb^{2+} on LaFe$_{0.7}$Mn$_{0.3}$O$_3$ perovskite reached 180 mg.g^{-1}. Determined the dynamic adsorption process on the column for As(V), Pb^{2+} of perovskite substrate LaFe$_{1-x}$Mn$_x$O$_3$ granulated with bentonite binder (mass ratio LaFe$_{0.7}$Mn$_{0.3}$O$_3$/LaFe$_{0.3}$Mn$_{0.7}$O$_3$/bentonite = 2/2/1). The safe column adsorption capacity for As(V), Pb^{2+} on LFMB material reached 7.3 mg.g^{-1}, 7.9 mg.g^{-1} respectively. From the results of the adsorption process on the column for As(V), Pb^{2+} of LFMB materials, an adsorption device to treat actual domestic water pollution has been established in the aluminum recycling craft village. Experiments show that a family-sized adsorption device with a filtration capacity of 250 liters.h^{-1} after installation can completely remove arsenic and lead pollution from water sources.

Acknowledgments

References

1. M. Branislava, L. Vesna, N. Đorđe, V. Ljubinka, J. Serb. Chem. Soc., 76(10) (2011) 1437-1452. https://10.2298/JSC101029122J

2. World Health Organization. Guidelines for Drinking-water Quality, WHO Press, Third Edition Incorporating The First And Second Addenda, (2008).
https://10.1016/j.jmmm.2007.08.010.

3. A. Khan, S. Rasul, A. Munir, M. Habibuddowla, M. Alauddin, S. Newaz, A. Hussan, J. Environ. Sci. Health, 35(7) (2000) 1021-1041. https://10.2320/MATERTRANS.MD201703.

4. WHO/UNICEFF. Meeting the fundamental need for water, sanitation and hygiene services in health care facilities, Global meeting held Madrid (2015).

5. L. Rajaković, Faculty of Technology and Metallurgy, PhD Thesis, University of Belgrade, Belgrade, (1986).

6. K. Chakresh, A. Imran, Water Reseach 34(17) (2000) 4304-4312.
https://10.1016/s0043-1354(00)00182-2.

7. D. Wolfgang, S. Reiner, J. Martin, Water Research, 29(1) (1995) 297-305.
https://10.1016/0043-1354(94)e0089-o.

8. J. Giménez, M. Martínez, J. dePablo, M. Rovira, L. Duro, Journal of Hazardous Materials 141 (2007) 575-580.
https://10.2109/jcersj2.16056.

9. Moore J.N., Walker J.R., Hayes T.H., Reaction scheme for the oxidation of As (III) to arsenic (V) by birnessite, Clays Clay Miner 38 (1990) 549-555.

10. S. Tokunaga, S. Wasay, S. Park, Water Science Technology, 35(7) (1997) 71-78.
https://10.1016/s0273-1223(97)00116-9.

11. Luu Minh Dai, Nguyen Thi To Loan, Dao Ngoc Nhiem, Vu The Ninh, Vietnam Journal of Chemistry, 46(2A) (2008) 43-49.

12. J. Lai, K. Shafi, V. Kurikka, A. Ulman, The Journal of Physical Chemistry B, 108(39) (2004) 14876–14883.
https://10.1021/jp049913w.

13. Vu The Ninh, Dao Ngoc Nhiem. Vietnam Journal of Chemistry, 56(6E1) (2018) 217-222.

14. Vu The Ninh, Pham Ngoc Chuc, Luu Minh Dai. Vietnam Journal of Catalytic Adsorption, 8(2) (2019) 92-97.

15. Nguyen Huu Phu. Textbook of Physical Chemistry, Hanoi Science and Technology Publishing House, (2000).