Evaluation of removal efficiency of Fe(III) and Al(III) ions in acid sulfate water using agarose-based magnesium oxide composite

Ngoc Xuan Dat Mai^{1, 2}, Tan Le-Hoang Doan^{1, 2}, Le Nguyen Bao Thu^{2, 3}, Bach Thang Phan^{1, 2*}

¹Center for Innovative Materials and Architectures (INOMAR), Vietnam National University, Ho Chi Minh city ²Vietnam National University, Ho Chi Minh city

³Department of Mathematics and Physics, University of Information Technology, Vietnam National University, Ho Chi Minh city

Received 1 April 2020; accepted 30 June 2020

Abstract:

Agarose/MgO composite adsorbents were developed through interspersing MgO nanoparticles with agarose to create an absorbent. The elimination capacity of the composite towards iron (Fe), aluminium (Al), and arsenate (As) in acid sulfate water was evaluated by means of batch method at room temperature. The constituents of the composite were characterized by thermal gravimetric analysis (TGA). The removal efficiency was determined through inductively coupled plasma (ICP) mass spectrometry. The composite adsorbent exhibited an excellent adsorption capacity towards three types of ions and heavy metals that are found in acid sulfate water. After treating with agarose/MgO, the concentrations of Fe and Al decreased from 60.28 and 604.84 μ g/l, respectively, to under 3.42 and 1.78 μ g/l, respectively. These exceptional results reveal the potential uses of agarose/MgO composites as adsorbents in the treatment of acid sulfate water.

Keywords: acid sulfate water, agarose composite, MgO adsorption, treatment.

Classification number: 2.3

Introduction

Over 40 percent of the soils in the Mekong river delta are acid sulfate soils affected by acidity [1]. Groundwater and surface water from these areas are primary contaminated by iron, aluminium, and other heavy metals. These contaminants affect agriculture and daily life. Besides, industrial development in the area has resulted in significant environmental pollution that has large impacts on human health as the accumulation of heavy metals in the human body causes serious diseases [2]. Thus, it is necessary to remove these toxic elements from water. There exists various conventional techniques for the elimination of ions and heavy metals in water such as ion-exchange [3, 4], chemical precipitation [5, 6], membrane filtration [7, 8], coagulation [9], reverse osmosis [10, 11], electrochemical processes [12, 13], and adsorption [14-17], which is an effective method owing to its simple technique, excellent removal performance, and cost effectiveness [18-20]. Due to their high

specific surface area, metal oxide nanoparticles have a considerable adsorption capacity and thus have attracted the attention of researchers for heavy metal removal applications. Mahdavi, et al. (2013) [21] investigated the removal of some heavy metals from aqueous solutions using metal oxide nanoparticles such as titanium dioxide (TiO_2) , magnesium oxide (MgO), and alumina (Al_2O_2) . Among these sorbents, MgO nanoparticles hold great removal efficiency compared to others, especially in pHindependent adsorption. Furthermore, MgO is non-toxic, noncorrosive, thermally stable, and environmentally friendly [22-24]. Being useful in practical application, small MgO nanoparticles should be immobilized into rigid supports for easy recovery after treatment. Also an environmentally-friendly material, agarose is a biopolymer comprised of D-galactose with 3,6-anhydro-L-galactopyranose that can be formed into a hydrogel of any desired shape [25-27]. Hence, agarose is an excellent matrix to trap nanoparticles for practical applications and the porous feature of agarose has positive influences on

^{*}Corresponding author: Email: pbthang@inomar.edu.vn

contaminated fluid diffusion.

In this study, we advance the ideas from our previous work [28] to fabricate agarose-based absorbents that eliminate ions from contaminated solutions. MgO nanoparticles performed as the main sorbents, which are entrapped in the porous agarose structure. We further investigate the composition of the agarose/MgO composite by thermal gravimetric analysis (TGA). In addition, we evaluate the adsorption efficiency towards various ions and heavy metals like iron (Fe), aluminium (Al), and arsenate (As), which are found in acid sulfate water collected from the Mekong delta.

Materials and methods

The details of the agarose/MgO synthesis procedure can be found in the previous work [28]. Briefly, MgO nanoparticles (0.1, 0.2, and 0.25 g) were first slowly added into distilled water (28.5 g) following by sonication for 15 min at room temperature. Then, agarose powder (1.5 g) was slowly added. After 15 min of sonication, the homogeneous solution was heated to 100°C and was kept at that temperature for 1 h until transparent. The obtained gel mixture, at room temperature, was placed in a glass petri dish and then cut to cylindrical units (5×3 mm) (Fig. 1).

For further characterization from the previous work [28], thermal gravimetric analysis (TGA) using a TA Instruments Q-500 instrument, was carried out under airflow at temperatures ranging from room temperature to 800°C.

The adsorption experiments were followed similar to our previous work [28]. Agarose/MgO (5 g) was added into a conical flask of ion solution (100 ml, 100 ppm), which was diluted from a stock solution (1000 ppm). The flask was continuously shaken (250 rpm) using a shaker (Lab Companion, IST-3075R). At certain intervals, 1 ml of aqueous solution was sampled for concentration measurements. Inductively coupled plasma-optical emission spectrometry (ICP-OES) was used to measure the ion concentration. The following equation was used to calculate removal efficiency:

Removal efficiency (%) = $(C_0 - C_t)/C_0 \times 100\%$

where C_0 and C_t are the original concentration and sampling time concentration, respectively.

The same experiment was also conducted using acid sulfate water (100 ml) with the above procedure.

Results and discussion

Cylindrical agarose/MgO composite units and bare agarose units were created with 3×5 mm shape. The transparent bare agarose unit changed to an opalescent colour due to the presence of white MgO nanoparticles (Fig. 1).



Fig. 1. Photograph of agarose and cylindrical agarose/MgO units.



Fig. 2. Thermal gravimetric analysis of agarose/MgO compared with the agarose unit.

The composition of the composite adsorbent was investigated. As can be seen from the TGA result shown in Fig. 2, both samples present two weight loss stages. The first stage occurred around 100°C, which may result from the loss of water in the porous structures. The weight decrement in the agarose sample is approximately 15%, which is higher than that of the composite sample, which was approximately 5%. The second stage of weight loss happened at the range of 200-400°C that corresponds to the evaporation of glycerol, which is the result of charring agarose [29, 30]. The difference between the two samples is the mass of analysis residues. There is no residue for the bare agarose sample while that of the composite sample is approximately 12.6%, which corresponds to MgO nanoparticles entrapped in the agarose matrix. From our previous work [28], the agarose/MgO composite showed high adsorption capacity towards Fe(III), Al(III) and As(V) in both single-component solutions as well as multi-component solutions (Table 1). In the single-component solution, the capacity varied depending on the ion types: the highest capacity was with Fe(III) and the lowest capacity was with As(V). In contrast, agarose/MgO showed the highest elimination efficiency towards As(V) in the multi-component aqueous solution.

Table 1. Removal efficiency of agarose/MgO composite towards some ions and heavy metal in single- and multi-component solution.

	Removal efficiency (%)		
	Fe	Al	As
Single-component solution	90.69	54.90	14.66
Multi-component solution	50.70	50.05	61.14

We further evaluated the efficiency toward these ions and heavy metals in an acid sulfate water sample with the agarose/MgO composite. The acid sulfate water sample was collected in the An Cu hamlet, Tan Hoa commune, Tieu Can town, Tra Vinh province (Fig. 3) of Vietnam. The adsorption capacities of the bare agarose and agarose/ MgO samples with different MgO concentrations were evaluated by the batch method.

Table 2. Concentration of ions in the acid sulfate water and after treatment with various agarose/MgO composites.

	Fe (µg/l)	Al (µg/l)	As (µg/l)
Initial water	60.28	604.84	N/A
Treated with agarose	11.54	387.84	N/A
Treated with agarose/MgO-0.1	0.342	0.033	N/A
Treated with agarose/MgO-0.2	3.42	1.78	N/A
Treated with agarose/MgO-0.25	1.046	0.113	N/A

The results are presented in Table 2 and Fig. 4. The initial concentration of iron in the acid sulfate water was lower than that of the solution prepared in the laboratory in the previous work, however, the concentration of aluminium was significantly higher. All the agarose/MgO samples showed a significantly high adsorption capacity. After 24 h of contact time, the concentrations of Fe and Al decreased from 60.28 and 604.84 µg/l to under 3.42 and 1.78 μ g/l, respectively, when the agarose/ MgO composites were used. It is clear that the removal efficiency towards the Al ion was much higher than that of the Fe ion. This could be due to the competitive adsorption between various components in the aqueous solution, although the activity towards the Fe and Al ions was similar to the laboratory's multi-component solution. In this case, without the presence of the As ion, the composite material removed Al more completely. The near-complete removal activity indicates that the addition of MgO nanoparticles is beneficial. The concentration of MgO influenced the adsorption behaviour insignificantly due to low ion concentration of the aqueous solution. These results demonstrate that the agarose/MgO composite is effective for acid sulfate water.



Fig. 3. Photographs of (A) acid sulfate water sample and (B) experimental batches after treatment with agarose and agarose/MgO units.



Fig. 4. Adsorption capacity of bare agarose and agarose/ MgO units toward Fe and AI ions in the acid sulfate water sample.

Conclusions

In summary, we evaluated the removal efficiency of a composite created by trapping MgO nanoparticles in a porous agarose matrix. The presence of MgO nanoparticles in the composite was demonstrated by TGA analysis. The adsorption capacity towards Fe(III), Al(III), and As(V) was found to have different behaviours depending on the aqueous solution, either single-or multi-component. Especially noteworthy is the activity of the agarose/MgO composite showed excellent ion removal efficiency in acid sulfate water, which was collected from the Mekong delta region. Although the ion concentrations were extremely high in the practical solution, the material still showed the great removal efficiency especially towards the Al ion. The results indicate that the agarose/MgO composite shows potential as a great adsorbent for the elimination of harmful ions and heavy metals from acid sulfate water, especially in water from the Mekong delta region.

ACKNOWLEDGEMENTS

The work was supported by grants from Vietnam National University, Ho Chi Minh city grant number C2018-50-01. The authors would like to thank Lab of Multifunctional Material and Central Analysis Laboratory, University of Science, Vietnam National University, Ho Chi Minh city for freeze-drying our samples and ICP-OES measurements.

COMPETING INTERESTS

The authors declare that there is no conflict of interest regarding the publication of this article.

REFERENCES

[1] T. Hashimoto (2001), Environmental issues and recent infrastructure development in the Mekong delta: review, analysis and recommendations with particular reference to large-scale water control projects and the development of coastal areas/Takehito 'Riko' Hashimoto, Australian Mekong Resource Centre: Sydney.

[2] F. Lu, D. Astruc (2018), "Nanomaterials for removal of toxic elements from water", *Coordination Chemistry Reviews*, **356**, pp.147-164.

[3] A. Keränen, T. Leiviskä, B. Y. Gao, O. Hormi, J. Tanskanen (2013), "Preparation of novel anion exchangers from pine sawdust and bark, spruce bark, birch bark and peat for the removal of nitrate", *Chemical Engineering Science*, **98**, pp.59-68.

[4] Y.X. Zhang, Y. Jia (2018), "Fluoride adsorption on manganese carbonate: ion-exchange based on the surface carbonate-like groups and hydroxyl groups", *Journal of Colloid and Interface Science*, **510**, pp.407-417.

[5] C.K. Mbamba, D.J. Batstone, X. Flores-Alsina, S. Tait (2015), "A generalised chemical precipitation modelling approach in wastewater treatment applied to calcite", *Water Research*, **68**, pp.342-353.

[6] L.K. Wang, D.A. Vaccari, Y. Li, N.K. Shammas (2005), "Chemical precipitation", *Physicochemical Treatment Processes*, pp.141-197.

[7] Y.K. Ong, F.Y. Li, S. P. Sun, B. W. Zhao, C. Z. Liang, T. S. Chung (2014), "Nanofiltration hollow fiber membranes for textile wastewater treatment: lab-scale and pilot-scale studies", *Chemical Engineering Science*, **114**, pp.51-57.

[8] M.E. Ersahin, H. Ozgun, R.K. Dereli, I. Ozturk, K. Roest, J.B. van Lier (2012), "A review on dynamic membrane filtration: materials, applications and future perspectives", *Bioresource Technology*, **122**, pp.196-206.

[9] Meenakshi, R.C. Maheshwari (2006), "Fluoride in drinking water and its removal", *Journal of Hazardous Materials*, **137(1)**, pp.456-463.

[10] S. A. Schmidt, E. Gukelberger, M. Hermann, F. Fiedler, B. Großmann, J. Hoinkis, A. Ghosh, D. Chatterjee, J. Bundschuh (2016), "Pilot study on arsenic removal from groundwater using a small-scale reverse osmosis system-towards sustainable drinking water production", *Journal of Hazardous Materials*, **318**, pp.671-678.

[11] A. Bódalo-Santoyo, J.L. Gómez-Carrasco, E. Gómez-Gómez, F. Máximo-Martín, A.M. Hidalgo-Montesinos (2003), "Application of reverse osmosis to reduce pollutants present in industrial wastewater", *Desalination*, **155(2)**, pp.101-108.

[12] K. Fominykh, J.M. Feckl, J. Sicklinger, M. Döblinger, S. Böcklein, J. Ziegler, L. Peter, J. Rathousky, E.-W. Scheidt, T. Bein, D. Fattakhova-Rohlfing (2014), "Water splitting: ultrasmall dispersible crystalline nickel oxide nanoparticles as high-performance catalysts for electrochemical water splitting", *Advanced Functional Materials*, **24(21)**, pp.3123-3129.

[13] F.C. Walsh, G.W. Reade (1994), "Electrochemical techniques for the treatment of dilute metal-ion solutions", *Studies in*

PHYSICAL SCIENCES | ENGINEERING

Environmental Science, 59, pp.3-44.

[14] M. Visa (2016), "Synthesis and characterization of new zeolite materials obtained from fly ash for heavy metals removal in advanced wastewater treatment", *Powder Technology*, **294**, pp.338-347.

[15] S.P. Suriyaraj, R. Selvakumar (2016), "Advances in nanomaterial based approaches for enhanced fluoride and nitrate removal from contaminated water", *RSC Advances*, **6(13)**, pp.10565-10583.

[16] V. Srivastava, C.H. Weng, V.K. Singh, Y.C. Sharma (2011), "Adsorption of nickel ions from aqueous solutions by nano alumina: kinetic, mass transfer, and equilibrium studies", *Journal of Chemical & Engineering Data*, **56(4)**, pp.1414-1422.

[17] D. Zamboulis, E.N. Peleka, N.K. Lazaridis, K.A. Matis (2011), "Metal ion separation and recovery from environmental sources using various flotation and sorption techniques", *Journal of Chemical Technology and Biotechnology*, **86(3)**, pp.335-344.

[18] A.I.A. Sherlala, A.A.A. Raman, M.M. Bello, A. Asghar (2018), "A review of the applications of organo-functionalized magnetic graphene oxide nanocomposites for heavy metal adsorption", *Chemosphere*, **193**, pp.1004-1017.

[19] Y. Cai, C. Li, D. Wu, W. Wang, F. Tan, X. Wang, P.K. Wong, X. Qiao (2017), "Highly active MgO nanoparticles for simultaneous bacterial inactivation and heavy metal removal from aqueous solution", *Chemical Engineering Journal*, **312**, pp.158-166.

[20] K.Y. Kumar, H.B. Muralidhara, Y.A. Nayaka, J. Balasubramanyam, H. Hanumanthappa (2013), "Low-cost synthesis of metal oxide nanoparticles and their application in adsorption of commercial dye and heavy metal ion in aqueous solution", *Powder Technology*, **246**, pp.125-136.

[21] S. Mahdavi, M. Jalali, A. Afkhami (2013), "Heavy metals removal from aqueous solutions using TiO₂, MgO, and Al₂O₃ nanoparticles", *Chemical Engineering Communications*, **200(3)**, pp.448-470.

[22] J. Wu, H. Yan, X. Zhang, L. Wei, X. Liu, B. Xu (2008), "Magnesium hydroxide nanoparticles synthesized in water-in-oil microemulsions", *Journal of Colloid and Interface Science*, **324(1-2)**, pp.167-171.

[23] M.A. Alavi, A. Morsali (2014), "Syntheses and characterization of Mg(OH)₂MgO nanostructures by ultrasonic method", *Ultrasonics Sonochemistry*, **17**(2), pp.441-446.

[24] Y. An, K. Zhang, F. Wang, L. Lin, H. Guo (2011), "Removal of organic matters and bacteria by nano-MgO/GAC system", *Desalination*, **281**, pp.30-34.

[25] J. Hur, K. Im, S.W. Kim, J. Kim, D.-Y. Chung, T.-H. Kim, K.H. Jo, J.H. Hahn, Z. Bao, S. Hwang, N. Park (2014), "Polypyrrole/ agarose-based electronically conductive and reversibly restorable hydrogel", *ACS Nano*, **8(10)**, pp.10066-10076.

[26] D.Y. Lewitus, J. Landers, J. Branch, K.L. Smith, G. Callegari, J. Kohn, A.V. Neimark (2011), "Biohybrid carbon nanotube/agarose fibers for neural tissue engineering", *Adv. Funct. Mater.*, **21(14)**, pp.2624-2632.

[27] G.L. Drisko, X. Wang, R.A. Caruso (2011), "Strong silica monoliths with large mesopores prepared using agarose gel templates", *Langmuir*, **27(6)**, pp.2124-2127.

[28] N.X.D. Mai, T.A.C. Le, T.L.-H. Doan, S. Park, K.H. Park, B.T. Phan (2020), "Agarose@MgO composite tablet for heavy metal removal from acid sulfate water", *Journal of Electronic Materials*, **49(3)**, pp.1857-1863.

[29] Q. Cao, Y. Zhang, W. Chen, X. Meng, B. Liu (2018), "Hydrophobicity and physicochemical properties of agarose film as affected by chitosan addition", *International Journal of Biological Macromolecules*, **106**, pp.1307-1313.

[30] A. Awadhiya, D. Kumar, V. Verma (2016), "Crosslinking of agarose bioplastic using citric acid", *Carbohydrate Polymers*, **151**, pp.60-67.