DECONTAMINATION OF ARSENIC IN AQUEOUS SOLUTION BY MANGANESE FERRITES*

Cho Cho Thet[1], Aye Aye Hlaing[2] and Kobayashi Takaomi[3]

Abstract

Decontamination of pentavalent arsenic (As^{5+}) ions in aqueous solution by manganese ferrites ($MnFe_2O_4$) was presented in this paper. $MnFe_2O_4$ were prepared by sonochemical synthesis method and they were used as adsorbents for removal of arsenic. The essential parameters such as pH of the precursor and post annealing temperature based on the formation of spinel manganese ferrite were discussed. The structural properties of manganese ferrites including compound identification, the crystal structure and surface morphology were investigated by Fourier transform infrared (FT-IR), X-ray diffraction (XRD) and Scanning electron microscope (SEM). The adsorption behaviour of As^{5+} ions on the manganese ferrite has been performed by batch adsorption experiment. The concentration of arsenic adsorbed on manganese ferrite was determined by atomic absorption spectroscopy coupled with hydride vapour generation (HVG-AAS). The adsorption capacity was fitted with the *Langmuir* isotherm model. The decontamination efficiency and adsorption amount of As determined from *Langmuir* isotherm model were discussed.

Keywords: arsenic (As), adsorption, $MnFe_2O_4$, ferrite, HVG-AAS, sonochemical, spinel structure

Introduction

Most of the common materials for the decontamination of heavy metals ions include biomass-based materials, metal oxides, geopolymers, zeolites, silica, activated carbon, activated alumina and ferrites. Spinel ferrite nanoparticles have been focused on as adsorbents because their unique physicochemical properties are differ from their bulk. Besides, the shape and size as well as magnetic properties can be tuned. They also have surface versatility, high surface-to-volume ratio, long-lasting in water treatment and less aggregation. Manganese ferrite ($MnFe_2O_4$) has a face centered cubic (FCC) structure of either normal or inverse or mixed spinel-type as well as soft magnetic n-type semiconducting material. Ferrite particles have a wide variety of applications including heterogeneous catalysis (Zhang *et al*., 2019), adsorption (Durán *et al*., 2020), sensors (Vignesh *et al*., 2015) and magnetic technology (Chandunika *et al*., 2020).

Heavy metal ions in the waste water are removed by many techniques including reverse osmosis (Pires da Silva *et al*., 2016), precipitation (Alina Pohl 2020), solvent extraction (Silva *et al*., 2005), ion exchange (Hussain *et al*., 2021) and membrane filtration (Vo *et al*., 2020). Adsorption (Panda *et al*., 2020) is an alternative method by an adhesion of an adsorbate such as a fluid, liquid, or gas, by creating a thin layer on the surface of an adsorbent. Inorganic arsenic (As^{3+} and As^{5+}) elements are relatively scared to living organisms since they are toxic and carcinogenic elements. Symptoms of arsenic poisoning include vomiting, abdominal pain, encephalopathy and watery diarrhea. Long-term exposure to arsenic contaminated water could result in thickening of the skin, darker skin, abdominal pain, diarrhea, heart disease, numbness and cancer (Amighian *et al*., 2006). The permissible limit of total arsenic in drinking water is 0.01 ppm (10 ppb) by world health organization (WHO) (Agusu *et al*., 2019).

Therefore, the effective and efficient adsorbents only for selective removal of arsenic are urgently required. On the other hand, the development of new materials as well as technologies are becoming the challenges to the remediation of waste water treatment since improper separation

[1] Dr, Professor, Department of Physics, Dawei University
[2] Dr, Deputy Director, Department of Research and Innovation (DRI), Myanmar
[3] Dr, Professor, Department of Materials Science and Technology, Nagaoka University of Technology
[*] Best Paper Award Winning Paper in Physics (2021)

methods of heavy metals from aqueous solution can be spread to the living organisms and environment. In this work, the main aim is synthesis manganese ferrite by sonication method in order to use them as adsorbents for decontamination of arsenic heavy metal ions. The adsorption behavior of As by manganese ferrites was investigated by doing batch adsorption process.

Experimental Details

Synthesis of Manganese Ferrite

All reagents were of analytical grade and they were used without further purification. Briefly, 2.7 g of ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$) and 0.845 g of manganese (II) sulfate, ($MnSO_4 \cdot H_2O$) were dissolved in 100 ml of deionized water so that the molar ratio of Mn to Fe in the solution is 1:2. The solution was then constantly stirred until completely dissolution. 9 M sodium hydroxide (NaOH) solution was used to adjust the pH of the precursor solution at 9. Then, the solution was transferred to high frequency ultrasonic bath. The sample was exposed by ultrasound irradiation at 500 kHz and 50 W for 1 h. The brownish precipitates were separated from the solution by centrifugation and washed with excess water to remove the impurities and followed by washing with acetone. Afterwards, the precipitates were dried at 50 °C for 24 h. The dry precipitates were grounded by agate motor to get the fine powders. Then, the powders were calcined at 500 °C for 6 h.

Batch Adsorption Experiment

The batch adsorption experiment were carried out by adding fixed amount 0.1 g of $MnFe_2O_4$ powders in 50 mL of As^{5+}aqueous solution having a concentration of 5 ppm. The process was continued by operating at 200 rpm for 1, 5, 10, 15, 20, 25, 30, 45, 60 and 120 min in a shaker at the room temperature (27 ºC). The solution was then filtered by using the Smith filter paper (125 mm) for the separation of the adsorbent particles from the aqueous solution and filtrate was measured by HVG-AAS. The values of initial concentration, C_i, were also varied from 0.1 to 400 ppm and measured equilibrium concentration (C_e) depending on C_i values.

Measurements and Characterization

The identification of functional group was investigated by FT-IR (IRPrestige-21 Shimadzu spectrophotometer). The crystal structure of the samples was measured by RIGAKU SmartLab XRD. Surface morphology of ferrite was revealed by JEOL-JSM 5300 LV scanning microscope. Concentrations of total As in the filtrate were determined by AAS (Shimadzu model AA-6300) coupled with a hydride generation system (HVG-1, Shimadzu). The spectrophotometer was operated at 193.78 nm with a slit width of 1.0 nm. The lamp current was 12 mA. The fuel acetylene (air-acetylene flame) flow rate was 2.0 liters per minute and the burner height of 7 mm. The flow rate of the argon carrier gas was 70 ml per minute at a pressure of 0.35 Mpa.

Results and Discussion

FT-IR spectroscopy is used to identify the functional groups of ferrites. From this investigation, it was found out that formation of spinel ferrite strongly depends on post annealing temperature. Only broad band around at 590 cm^{-1} was observed in as-synthesized ferrites. It implies that spinel structure was not obtained without treatment of post annealing. Thus, calcination is treated in order to enhance sufficient activation energy of the formation of ferrites. Complete spinel structures were formed at the band 587 cm^{-1} and 490 cm^{-1} at the annealing sample as shown in Fig. 1.

The characteristic peaks at 587 cm^{-1} and 490 cm^{-1} correspond to the metal-oxygen (M-O) bond stretching vibration at the tetrahedral sites and octahedral sites (Srinivasan *et al*., 2018). The difference between these absorption bands is due to the change in bond length (M-O) at the tetrahedral and octahedral site (Mounkachi *et al*., 2017). The other peaks at 3483 cm^{-1} corresponds to O-H bond stretching vibration revealing the presence of residual hydroxyl groups. Peak at 1122 cm^{-1} can be assigned to the vibration of groups OH. The strong peaks at 1636 cm^{-1} are corresponding to O–H bending vibrations in water.

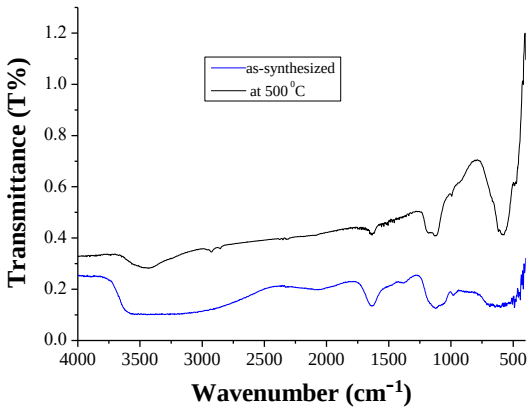

Figure 1 FT-IR spectra of (a) as-synthesized ferrite and (b) manganese ferrites calcined at 500 °C

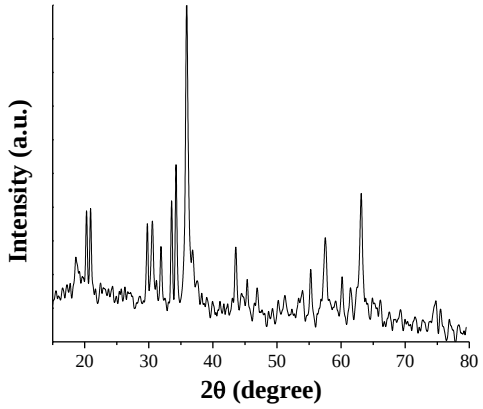

Figure 2 FT-IR spectra of manganese ferrites calcined at 500 °C

XRD measurement was performed in order to additionally confirm the formation of ferrite structure. The diffraction peaks [(220), (311), (222) (400), (422), (511), (440), (533)] in XRD pattern in Figure 2 was corresponding to the characteristic crystallographic planes of the spinel structure of ferrites (Mary Jacintha *et al*., 2017). These Miller indices indicated the single-phase $MnFe_2O_4$ with face centered cubic (FCC) crystal structure. The better crystallinity of spinel ferrite structure was observed at 500 °C by XRD result.

The SEM micrograph in Fig.3 shows that the porous structure providing the greater surface area which is an advantage for the adsorption. To evaluate the porosity, nitrogen adsorption was conducted at 25 °C. The surface area of manganese ferrite 3.6572 m^2/g was obtained according to Brunauer– Emmett–Teller (BET) method. Figure 4 showed amounts of adsorbed N_2 in the ferrite at different relative N_2 pressures.

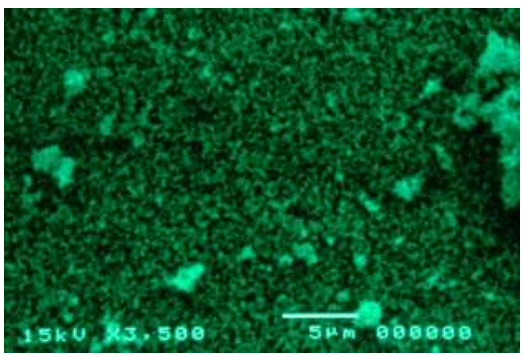

Figure 3 SEM micrograph of manganese ferrite

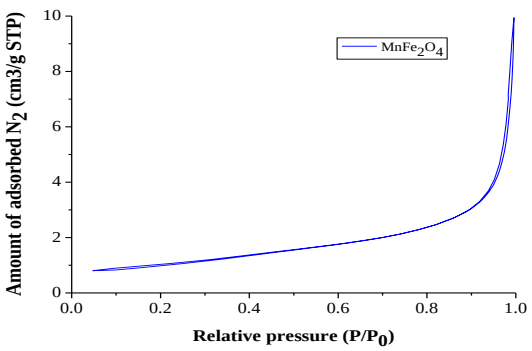

Figure 4 N_2 isotherms of manganese ferrite

To identify the possible rapidness of removal process As by Mn-ferrite, time dependence adsorption test was performed. The removal percent was calculated by the following formula:

$$\text{removal}(\%) = \frac{C_i - C_e}{C_i} \times 100 \qquad (1)$$

The adsorption amount (q_e) of As ion generally is calculated by following formula:

$$q_e = \frac{(C_i - C_e)V}{m} \qquad (2)$$

Where, q_e = equilibrium adsorption amount (mg/g)

C_i = initial concentration (mg/L or ppm)

C_e= equilibrium concentration (mg/L or ppm)

V = volume of the aqueous solution (mL)

m = mass of adsorbent (mg)

The maximum removal percent and equilibrium adsorption amount (q_e) are found out to be 57 % and 1.4256 mg/g at the shaking 25 min until to 2 h as shown in plot 5 (a) and (b).

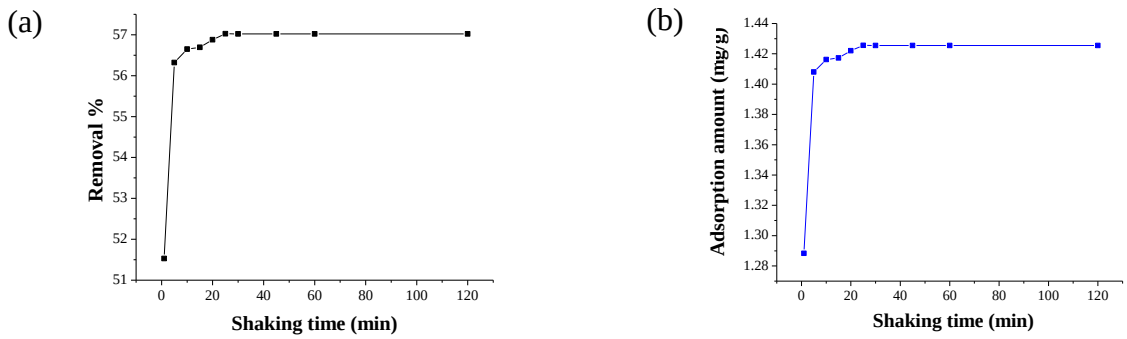

Figure 5 Time course curve of (a) removal % and (b) adsorption amounts of As ions on manganese ferrite (C_i = 5ppm)

Figure 6 (a) illustrates the graphical representation of isotherm which was subjected to sorption isotherm of *Langmuir*. Figure 7(b) represents the adsorption isotherm of As ion on manganese ferrite. The adsorption amount for each equilibrium concentrations can be observed in this plot. The adsorption amount (q_e) is gradually increased until the value of C_e is 46 ppm. Then, the q_e becomes constant beyond this concentration and it implies that adsorption amount of As has been saturated at C_e 46 ppm.

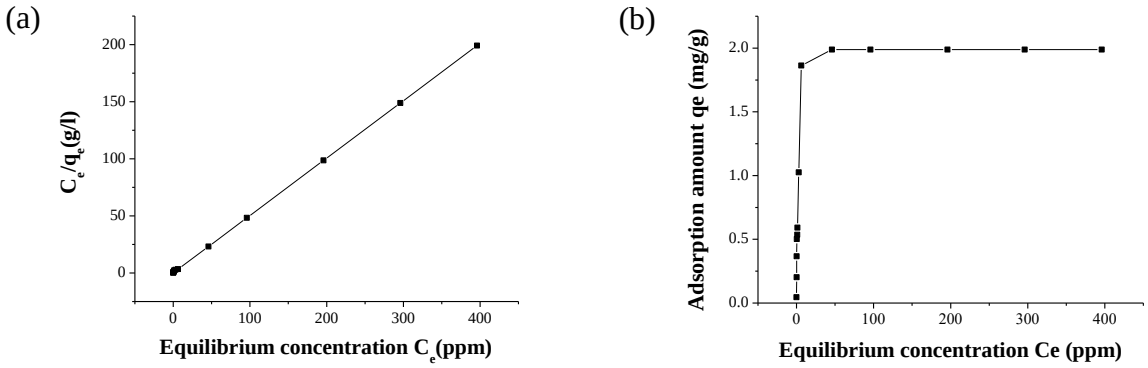

Figure 6 (a) *Langmuir* adsorption isotherm plots of As on manganese ferrite and (b) adsorption isotherm of As^{5+} ion on manganese ferrite

Conclusions

Manganese ferrites ($MnFe_2O_4$) synthesized by high frequency (500 kHz, 50 W) ultrasound method have been applied to decontaminate the arsenic (As) from aqueous solution. Annealing temperature 500 ºC plays the essential parameter in the present sonochemical synthesis system to obtain the manganese ferrite particles. The formation of cation at the tetrahedral and octahedral site in FT-IR spectrum revealed that $MnFe_2O_4$ is spinel ferrite crystal system. XRD study additionally confirmed that the final product is manganese spinel crystal phase. According to the batch adsorption experiment and measurement results by AAS, the removal efficiency of As was found out to be 92 % from the 100 ppb concentration of As^{5+} aqueous solution. Thus, the manganese ferrite synthesized at pH 9 and annealing at 500 ºC could effectively decontaminate to trace level concentration of arsenic from aqueous solution.

Acknowledgements

We would like to acknowledge to Prof Dr Theingi Shwe, Rector, Dawei University, for her encouragement and allowing us to participate in this event. We are especially thanks you to Prof Dr Cho Cho Myint, Pro-rector, Dawei University, for her kind permission to contribute this work. Our special thanks go to Dr Ye Chan, Professor and Head of Universities' Research Centre (URC) for the supporting of research facilities and excellent discussion.

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