

COBALT FERRITE ADSORBENTS FOR THE EFFECTIVE AND EFFICIENT REMOVAL OF ARSENIC

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Abstract

The effective and efficient adsorbent for the removal of pentavalent arsenic (As^{5+}) ions was presented in this paper. Cobalt ferrites, CoFe_2O_4 , adsorbents were prepared by sonochemical synthesis method. The synthesis parameters including pH of the precursor solution and post annealing temperature, based on the formation of spinel cobalt ferrite were discussed. The compound identification, the crystal structure and surface morphology of cobalt ferrite were studied by Fourier transform infrared (FT-IR), X-ray diffraction (XRD) and Scanning electron microscope (SEM) analysis. The adsorption behaviour of As^{5+} ions on the cobalt ferrite has been investigated by batch adsorption method. The amount of As concentration adsorbed on cobalt ferrite is measured by atomic absorption spectroscopy coupled with hydride vapour generation (HVG-AAS). The adsorption capacity was fitted with the *Langmuir* isotherm model. The removal efficiency and adsorption amount of As determined from *Langmuir* isotherm model were discussed.

Keywords: arsenic (As), adsorption, CoFe_2O_4 ferrite, HVG-AAS, sonochemical, spinel structure.

Introduction

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 may 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 [Ratnaike *et al.*, 2003]. The permissible limit of total arsenic in drinking water is 0.01 ppm (10 ppb) by world health organization (WHO) [WHO (2011)]. Thus, the effective and efficient adsorbents only for selective removal of heavy metal ions (as As) 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 methods of heavy metals from aqueous solution can be spread to the living organisms and environment.

Heavy metal ions in the waste water are removed by many techniques including reverse osmosis [Mohsen-Nia *et al.*, 2007], precipitation [Byambaa *et al.*, 2018], solvent extraction [de los Ríos *et al.*, 2007], ion exchange [Budak *et al.*, 2013] and membrane filtration [Maximous *et al.*, 2010]. Adsorption [Kang *et al.*, 2015] 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.

Most of the common materials using for the removal of heavy metals ions are including biomass-based materials, metal oxides, geopolymers, zeolites, silica and 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. The shape and size as well as magnetic properties can be tuned. They also have surface versatility, high surface-to-

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volume ratio, long-lasting in water treatment and less aggregation. CoFe_2O_4 has a face centered cubic (FCC) structure of normal spinel-type and soft magnetic n-type semiconducting material. Ferrite particles have a wide variety of applications including heterogeneous catalysis, adsorption, sensors and magnetic technology [Sanasi *et al.*, 2104; Kirankumar *et al.*, 2017; Leroux *et al.*, 2014; Ponce *et al.*, 2013].

The conventional synthesis methods of cobalt ferrites include ball milling, sol-gel autocombustion, coprecipitation, reverse micelles, hydrothermal, microemulsions, laser ablation, a polyol method, sonochemical approaches and aerosol method. Among these methods, sonochemical synthesis is a relatively new technique for the ferrite, in which they are synthesized using ultrasonic irradiation of the reaction mixture. This route has many advantages over any other methods such as short reaction time, cost efficiency, uncomplicated, compact, on-site treatment and higher purity of the final product. In the present work, the main aim is synthesis of cobalt ferrite by sonication method in order to use them as adsorbents for decontamination of arsenic heavy metal ions. The adsorption behavior of As by cobalt ferrites was investigated by doing batch adsorption process.

Materials and Method

Synthesis of Cobalt Ferrite

Briefly, 6.88 g of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and 2.48 g of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were dissolved in 100 mL of distilled water so that the molar ratio of Co:Fe in the solution is 1:2. The solution was constantly stirred at the room temperature. pH 9 of the synthesis solution was adjusted by using 9 M NaOH aqueous solution. The reaction was then continued for 15 min. After that, the solution was transferred to high frequency ultrasonic bath. The sample was exposed at 500 kHz and 50W for 1h at room temperature. The transient motion of cavitation bubbles due to vibrational energy of transducer results in the formation of high-intensity shock waves. The metal oxide particles get drifted in these waves at very high velocities and collide with each other. The energy released during collision can induce reaction between the metal oxide precursors leading to the formation of mixed metal oxide product. The brownish precipitates were separated by centrifugation and washed with excess of distilled water (DW) to remove the impurities followed by washing with acetone. Afterwards, the precipitates were dried at 50 °C for 24 h. The dry precipitates were grinded by agate motor to get the fine particles. Finally, they were annealed at 600 °C for 4 h.

Batch Adsorption

The batch adsorption were carried out by adding fixed amount 0.1 g of CoFe_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 °C). 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.

Characterization Tools

UV/VIS/NIR JASCO-V570 spectrophotometer within the wavelength range of 190-1100 nm was utilized to measure the absorbance of the samples. The identification of functional group was investigated by FT-IR (IRPrestige-21 Shimadzu spectrophotometer). The crystal

structure of the samples was measured by RIGAKU Smart Lab 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

The UV-Visible absorption spectrum of as-synthesized cobalt ferrite is shown in Fig.1. It displays a characteristic band at the wavelength 297 nm, which developed particularly according to the dispersion and absorption phenomenon of CoFe_2O_4 particles [Mushtaq *et al.*, 2016].

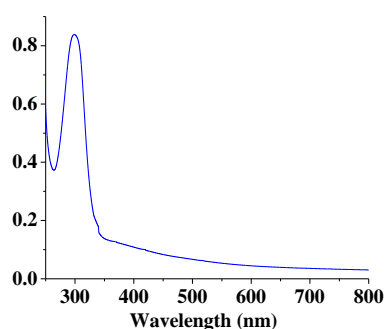


Figure 1(a) UV-Vis absorption spectrum of as-synthesized cobalt ferrite.

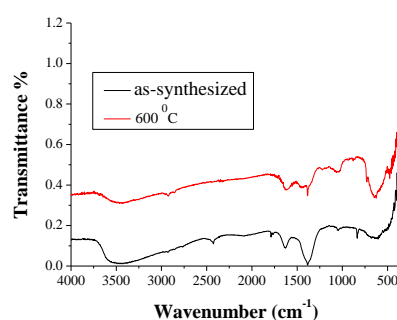


Figure 2 FT-IR spectra of as-synthesized and annealing at 600 °C of cobalt ferrite.

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 620 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 624 and 476 cm^{-1} at the annealing sample as shown in Fig. 2.

The characteristic peaks at 624 cm^{-1} and 476 cm^{-1} correspond to the metal-oxygen (M-O) bond stretching vibration at the tetrahedral sites and octahedral sites [Rumale *et al.*, 2013]. The difference between these absorption bands is due to the change in bond length (M-O) at the tetrahedral and octahedral site [Rajasekhar *et al.*, 2017]. The other peaks at 3440 cm^{-1} corresponds to O-H bond stretching vibration revealing the presence of residual hydroxyl groups. The antisymmetric stretching, symmetric stretching, out of plane bending, peaks of the cobalt metals are observed at 1636 , 1384 , 880 cm^{-1} , respectively [Allaedini *et al.*, 2015].

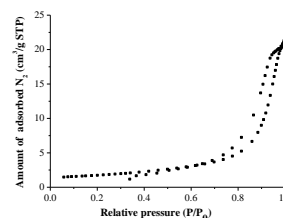
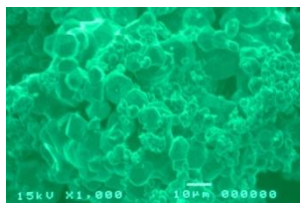
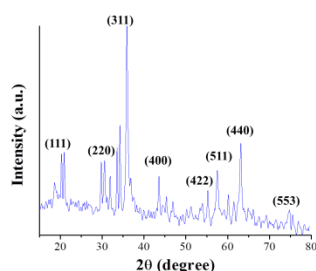


Figure 3 XRD spectrum of spinel cobalt ferrite

Figure 4 SEM micrograph of spinel cobalt ferrite

Figure 5 N₂ isotherms of Co-ferrite

XRD measurement was carried out in order to confirm the crystal structure of synthesized material. The diffraction peaks around 2θ at 18, 30, 35, 37, 43, 54, 58, 63, and 74 degrees, marked by their corresponding indices (111), (220), (222), (311), (400), (422), (511), (440) and (553), in Fig. 3 are corresponding to the characteristic crystallographic planes of the spinel structure of cobalt ferrites [Allaiedini *et al.*, 2015].

The SEM micrograph in Fig.4 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 cobalt ferrite measured by Brunauer–Emmett–Teller (BET) method is obtained 6.0063 m²/g. Figure 5 shows amounts of adsorbed N₂ in the ferrite at different relative N₂ pressures.

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

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

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

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

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 92 % and 1.7402 mg/g at the shaking 30 min until to 2 h as shown in plot 6 (a) and (b).

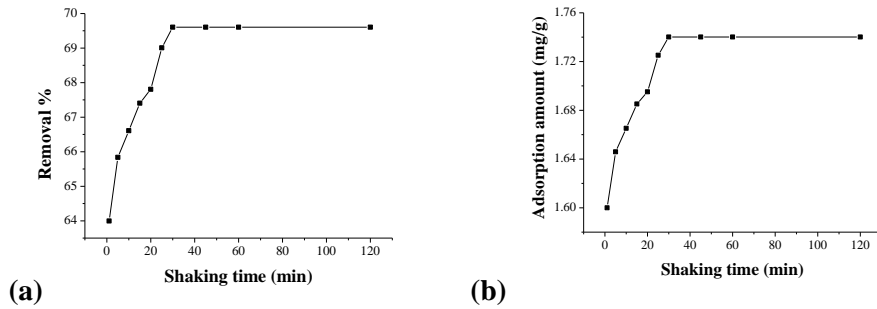


Figure 6 Time course curve of (a) removal % and (b) adsorption amounts of As ions on cobalt ferrite ($C_i=5\text{ppm}$)

Figure 7 (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 Co-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 44 ppm. Then, the q_e becomes constant beyond this concentration and it implies that adsorption amount of As has been saturated at $C_e 44$ ppm.

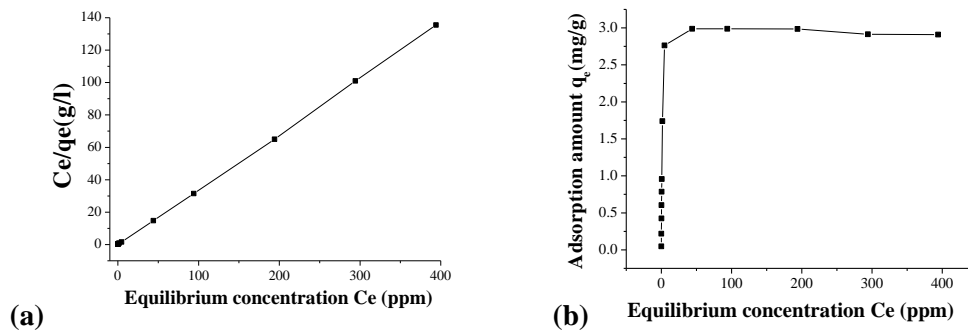


Figure 7 (a) *Langmuir* adsorption isotherm plots of As on cobalt ferrite and (b) adsorption isotherm of As^{5+} ion on Coferrite

The graph shown in Fig. 8 illustrates the removal percent of As at different C_i . Ferrite can effectively remove As at the trace level of initial concentrations (0.1 ppm, 100 ppb). In contrast, removal % is gradually decreased with increasing of C_i . Therefore, by using the amount of adsorbent 0.1 g and shaking time 30 min, maximum removal percent is found out 92 %, which is an excellent for the elimination of trace level As concentration. Therefore, cobalt ferrites will be very effective to eliminate the As ions which is usually contained especially in drinking water as a trace level.

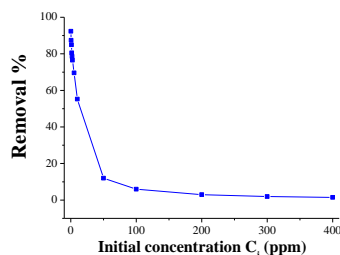


Figure 8 Graph showing the removal % as the function of C_i of As aqueous solution

Conclusions

In this study, CoFe_2O_4 spinel ferrites have been synthesized by high frequency (500 kHz, 50 W) ultrasound method. The annealing temperature $600\text{ }^\circ\text{C}$ was systematically investigated to get the novel formation of spinel cobalt ferrite structure and found out that annealing temperature plays the essential parameter in the sonochemical synthesis of cobalt ferrite particles. UV-Vis result informs that the synthesized particle was CoFe_2O_4 . FT-IR revealed that the cation formation at the tetrahedral and octahedral site in spinel ferrite crystal system. XRD study additionally confirmed that sonochemical synthesis is a good method to form single spinel crystal phase. According to the measurement and calculation results of concentration of arsenic (As) 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 cobalt ferrite synthesized at pH 9 and annealing at $600\text{ }^\circ\text{C}$ could be effectively removed to trace level concentration of arsenic from drinking water.

Acknowledgements

We would like to acknowledge to Prof Dr Ni Ni Oo, Rector in charge, Myeik University, for her encouragement and allowing us the chance to participate in this event. We are especially thank you to Prof Dr Win Win Than, Pro-rector, Myeik University, for her permission to contribute of this work. We sincerely thank to Prof Dr Yin Yin Myint, Head of Department of Physics, Myeik University, for her encouragement of 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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