

Magnetic Hydroxyapatite for Batch Adsorption of Heavy Metals

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Abstract. In this work, magnetic hydroxyapatite or hydroxyapatite-iron (III) oxide (HAp-Fe₃O₄) composite was used as the adsorbent of heavy metals and the performance was evaluated using the batch test. The presence of heavy metals in the effluent from wastewater discharge can be toxic to many organisms and can even lead to eye burns. Therefore, hydroxyapatite synthesized from the chemical precipitation of calcium nitrate tetrahydrate and diammonium hydrogen phosphate solutions is used to remove heavy metal in aqueous media. Magnetic properties of Fe₃O₄ can help prevent formation of secondary pollutants caused by the loss of adsorbent. The synthesized HAp-Fe₃O₄ can remove cadmium, zinc and lead effectively, which is up to 90% removal. Reusability study shows that the adsorbent could retain heavy metal ions even after four cycles. The percentage removal of heavy metals maintains at around 80% after four times of usage. The composite of HAp-Fe₃O₄ demonstrates good performance and stability which is beneficial for heavy metal removal in the future.

Keywords:- magnetic hydroxyapatite, adsorbent, heavy metals and batch test

1 Introduction

The environmental problems caused by globalization and rapid industrialization are increasingly harmful to humans. Lot of efficient methods is therefore necessary, especially for chemical activities. Heavy metals in wastewater within industrial effluent are a major concern for pollution of the environment. It is also sometimes quoted as a density of more than 5 g/cm³ which is a commonly used criterion for many articles. The untouched growth in urban areas has made it very difficult and expensive to plan and expand water and sewage systems. Statistics show that 90% of heavy metals uptakes in human body are caused by the consumption of vegetables grown in contaminated fields, and the remaining uptake sources are from air inhalation or direct skin contacts [1]. Lead, cadmium, copper, chromium, arsenic and zinc were heavy metals that are affected via grazing of animals in fields of the milk and dairy products which are the main source of diet for infants and adults [1]. In order to make up their routine needs, human being is exposed to heavy metals when using industrial products, such as batteries, paints, wires and pipes [1]. In most developed countries, emissions of heavy metals over the last 100 years have declined [2]. Meanwhile in some parts of the world such as less developed countries, exposure to heavy metals continues to increase although many adverse health effects by heavy metals have been long known.

Different treatment options can be used to remove heavy metals from industrial wastewater including unit operations such as chemical precipitation, coagulation, complexing, adsorption, ion exchange, solvent extraction, foam floatation, electrodeposition, cementation, and membrane operation. Hydroxyapatite (HAp) is a naturally occurring mineral form of calcium apatite with the formula Ca₁₀(PO₄)₆(OH)₂. Currently, hydroxyapatite is commonly the material of choice for various biomedical applications, such as replacement of bone defects, middle ear implants, tissue engineering system, and dental materials [3]. Apart from that, hydroxyapatite and its derivatives has also led to numerous non-medical industrial and technological applications, for example a catalyst for reactions such as methane oxidation, host material for lasers, ions conductors, as well as gas sensors [4]. Furthermore, it has been demonstrated that hydroxyapatite presents very good performance in water treatment process and remediation of heavy contaminated soils [4].

Hydroxyapatite which is naturally available form of calcium phosphate and a hard tissue component has been reported to be an efficient ion removal material from aqueous solutions for various heavy metals because of its excellent reactivity and low water solubility [5]. The efficiency of HAP in the removal of heavy metal ions depends heavily on the ion nature, load, diameter and concentration and the properties of the water such as pH

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and temperature during the treatment. It is important to know the capability of magnetic hydroxyapatite in order to adsorb the heavy metal from wastewater industry. Somehow, the developing a fast and low-cost method for removing metal ions from industrial wastewater is needed in terms of economic growth. Wang et al., (2010) reported that the synthesis of hydroxyapatite nanoparticles by wet chemical precipitation method under atmospheric pressure [6]. They found that the solvent systems, dispersant species and drying methods had influenced the particle size and dispersion in the solution. The hydroxyapatite (HAP) powders with various morphologies, such as sphere, rod, needle, wire, and bamboo-leaf-like were obtained by controlling the pH and temperature during the synthesis [6].

Recently, some efforts have been made to the improvement of hydroxyapatite properties by combining hydroxyapatite with other materials [7]. Magnetic materials composed of hydroxyapatite and magnetite facilitate the separation of the composition adsorbent from the water and show good performance with respect to removal of the pollutants [7]. Magnetic iron oxide, Fe_3O_4 has the advantage for the usage as support material of composite adsorbent because it can be easily manipulated by an external magnetic field [8]. Magnetite is also known as black iron oxide, magnetic iron ore, loadstone, ferrous ferrite, or Hercules stone [9]. It exhibits the strongest magnetism of any transition metal oxide [9]. Thus, in this study, we employ a facile chemical precipitation method to synthesize magnetic hydroxyapatite (HAp- Fe_3O_4). Iron oxide will act as the supporting material for the hydroxyapatite. The performance of the magnetic hydroxyapatite will be tested on the removal of cadmium (Cd^{2+}), zinc (Zn^{2+}) and lead (Pb^{2+}) ions respectively. The resulting composite is proved to reduce time of treatment and increase the capability of magnetic hydroxyapatite.

2 Materials and methods

2.1. Materials hydroxyapatite

For this experiment, cadmium nitrate ($\text{Cd}(\text{NO}_3)_2$), zinc nitrate ($\text{Zn}(\text{NO}_3)_2$) and lead (II) nitrate ($\text{Pb}(\text{NO}_3)_2$) were purchased from Jatikhas Sdn Bhd. $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{FeCl}_3 \cdot 4\text{H}_2\text{O}$, ammonia (25%), $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{HPO}_4$ were all analytical grade. All metal solutions were prepared from their nitrate salts (AR) and distilled water.

2.2 Synthesis of magnetic hydroxyapatite

Magnetic hydroxyapatite was synthesized using the methodology reported by Feng (2010) with some modification [10]. Typically, about 25 ml amount of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (1.85 mmol) and 25 ml of $\text{FeCl}_3 \cdot 4\text{H}_2\text{O}$ (3.7 mmol) were dissolved on 30 ml of deoxygenated water under a nitrogen atmosphere at room temperature. Later, 10 ml of 25% NH_4OH solution was added to the resulting solution under vigorous mechanical stirring (300 rpm). A black precipitate was produced instantly. After 15

minutes, an amount 50 ml of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (33.7 mmol) and an amount of 50 ml of $(\text{NH}_4)_2\text{HPO}_4$ (20 mmol) solutions whose pH adjusted to 11 were dropwise added simultaneously to the obtained precipitate solution for 30 minutes. The resulting puce suspension was heated at 100°C for 2 hours and then the mixture was cooled to room temperature and aged for 12 to 24 hours without stirring. The obtained precipitate was separated by a magnet, then been washed repeatedly with deionized water until the pH was neutral. Following that, the obtained precipitate was dried in the drying oven at 100°C for about 3 hours. After cooling down to room temperature, the dried precipitate was grinded using mortar and pestle. The final products were the prepared magnetic hydroxyapatite adsorbents.

2.3 Characterization

The morphology of Fe_3O_4 -Hydroxyapatite (HAp- Fe_3O_4) samples was examined by using field emission scanning electron microscope (FE-SEM) (Ultra 55 Carl Zeiss, Germany). The energy dispersive X-ray (EDX) analysis was done by Zeiss Supra 55 VP. Fourier-transform Infrared Spectroscopy (FT-IR) analysis (Perkin Elmer Spectrum One, USA) was used to investigate the functional groups in the adsorbent recorded at the 4000 to 500 cm^{-1} regions. The crystallinity and phase of samples were analyzed by using X-ray diffractometer (XRD) spectroscopy using X'Pert3 Powder & Empyrean PANalytical with $\text{Cu K}\alpha$ irradiation ($\lambda = 1.54$), from 10° to 70° of diffraction angles (2θ), step size of 0.01° /step, and exposure time of 1s/step. The surface area and pore diameter of solid samples were identified using Micrometrics ASAP 2020 Plus surface area and porosimetry system. The samples were degassed at 200°C followed by N_2 adsorption-desorption isotherms measurements at -196°C . Magnetic properties of the sample were investigated using variable sample magnetometer (LakeShore 7404).

2.4 Batch adsorption of heavy metal ions

The setup for batch adsorption of heavy metal ions was shown in Fig. 1. below. Laboratory-scale anaerobic batch equipment was made of glass vessel with total volume of 3 litres and working volume of 2 litres was used in this experiment. The equipment was operated at ambient (room) temperature. The batch equipment temperature was controlled in mesophilic range by using the digital precise circulation water bath and with a hydraulic retention time of 24 hours. Samples of $\text{Cd}(\text{NO}_3)_2$, $\text{Zn}(\text{NO}_3)_2$, and $\text{Pb}(\text{NO}_3)_2$ were prepared at 500 ppm concentration respectively. After mixing them all in room temperature, the three heavy metal samples were stirred at a speed of 200 rpm until equilibrium was reached for about 30 minutes. The resulting solutions was collected for analysis. 0.1 g of magnetic hydroxyapatite was added to the beaker and the solutions were agitated again until the balance of solid solution was reached. 20 ml of the sample is collected after 1 hour, 3 hours, 5 hours, 7 hours and 24 hours at different time intervals or contact time.

After that, the sample was observed using inductively coupled plasma mass spectrometer (Perkin Elmer ELAN 6100, USA). The adsorbent with the best contact time was utilized for the next experiment.



Fig. 1. Batch equipment setup for adsorption analysis

2.4 Reusability of magnetic hydroxyapatite analysis

Reusability of magnetic hydroxyapatite was checked. 30 ppm of heavy metals sample was used for this part. Adsorbent with the optimum contact time from the previous experiment was used. The sample was observed using inductively coupled plasma mass spectrometer (Perkin Elmer ELAN 6100, USA). The adsorbent was recollected with a magnet bar and washed with distilled water. The adsorbent was repeatedly used to analyse its reusability within the optimal contact time. The experiment was repeated for 4 times.

3 Results and discussions

3.1. Morphology and element analysis.

Fig. 2. shows the morphology and colour of the HAp-Fe₃O₄ sample. It can be observed that the addition of iron oxide onto hydroxyapatite gives the hydroxyapatite a brownish colour. According to the Field Emission Scanning Electron Microscope (FESEM) analysis at magnification of x 50.0K, the composite HAp-Fe₃O₄ displays a rod-like morphology. The size of the composite clearly shows a mixture of hydroxyapatite (in rod shape) and iron oxide (in spherical shape). The synthesized HAp-Fe₃O₄ experiences agglomeration due to the intermolecular forces and magnetic forces between the iron oxide and hydroxyapatite [11].

Fig. 3. shows the EDX analysis for the HAp-Fe₃O₄ sample. The EDX analysis clearly shows that when Fe₃O₄ is added into hydroxyapatite (HAp), aside from the calcium and phosphate elements contained in HAp, it shows an increase in Fe intensity which is 1.35%, indicating the existence of the Fe₃O₄ inside the HAp-Fe₃O₄ composite.

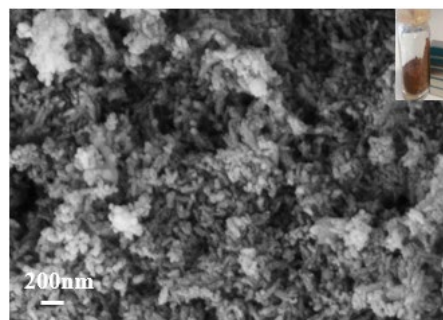


Fig. 2. Morphology of HAp-Fe₃O₄ at magnification of x 50.0K

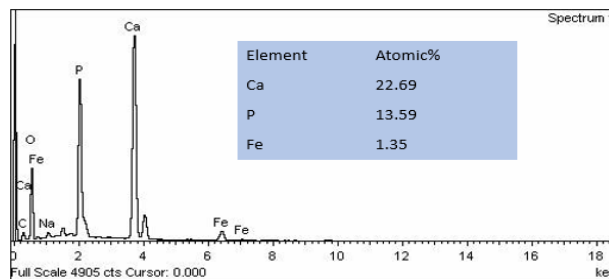


Fig. 3. EDX analysis of HAp-Fe₃O₄

3.2. Functional groups analysis

Fig. 4. shows the FTIR spectrum of HAp-Fe₃O₄. FTIR spectrum confirms the presence of hydroxyapatite. Wide peaks at 3446 cm⁻¹ give the hydroxyl (O-H) stretch [12]. Characteristic bands for PO₄³⁻ appear at around 446 cm⁻¹ [13]. The absorption bands appeared at 567 cm⁻¹ is attributed to the *n*4 bending mode of (PO₄³⁻) functional group, while the peaks at 872 cm⁻¹ can be attributed to the *n*3 vibrations of (PO₄³⁻) [14]. The bands at 1047 and 1098 cm⁻¹ represent the *v*3 vibrations of PO₄³⁻ groups [15]. The hydroxyapatite functional groups in the range of 1047 cm⁻¹ can be found to merge with the functional group of Fe-O [16]. While the CO₃²⁻ intensive peaks can be found at 1400 cm⁻¹ [13].

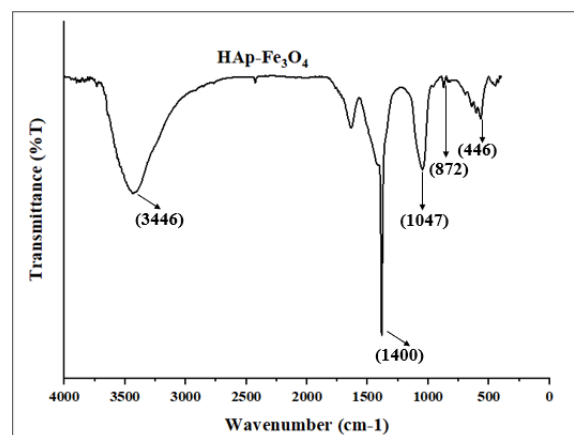


Fig. 4. FTIR spectrum of HAp-Fe₃O₄

3.3. Crystallinity

Fig. 5. shows the XRD spectrum of the synthesized HAp-Fe₃O₄. The synthesized hydroxyapatite shows peaks

belong to hydroxyapatite at diffraction angles of 26°, 31.5°, 40°, 47° and 50° which are attributed to planes (102), (211), (310), (222) and (213) respectively based on JCDPS card number 09-0432 [17]. The appearance of Fe₃O₄ can be clearly seen in hydroxyapatite composite through the peaks at diffraction angles of 23.94°, 30.22°, 35.7°, 43.25°, 54°, 57.3°, and 63° which are attributed to (012) of Fe [18], (220), (311), (440), (422), (511), and (440), respectively, which belong to Fe₃O₄ [18].

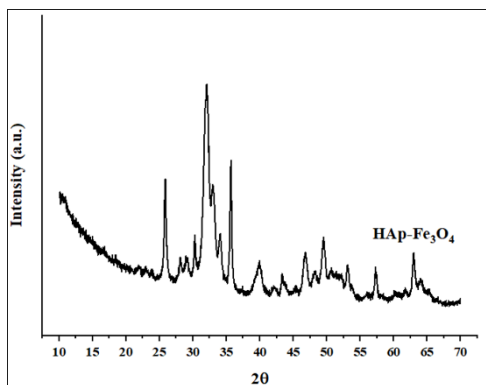


Fig. 5. XRD pattern of HAp-Fe₃O₄

3.4. Surface area, porosity and pore size

Table 1 shows the surface area, porosity and pore diameter of HAp-Fe₃O₄ sample. High surface area will contribute to greater adsorption capacity of the composite [19, 20]. Fig. 6. illustrates the adsorption isotherm of the synthesized HAp-Fe₃O₄. Type IV isotherm is shown by the sample, indicating that HAp-Fe₃O₄ is mesoporous.

Table 1. Surface area, porosity and pore diameter of HAp-Fe₃O₄

Sample	Surface area (m ² /g)	Pore volume (cm ³ /g)	Pore diameter (nm)
HAp-Fe ₃ O ₄	75.202	0.610	32.454

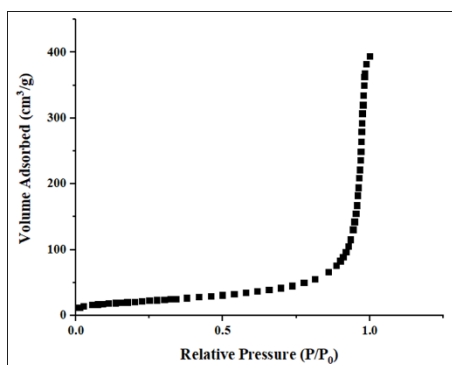


Fig. 6. N₂ Adsorption isotherm for HAp-Fe₃O₄

3.5. Magnetic properties

VSM studies were done to analyse the hysteresis behaviour of HAp-Fe₃O₄. It is observed that the synthesized HAp-Fe₃O₄ show ferromagnetic behaviour,

whereby the Ms value is measured to be 7.863 emu/g as shown in the Fig. 7.

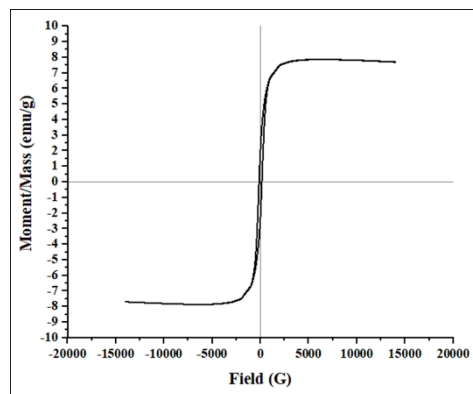


Fig. 7. VSM studies for HAp-Fe₃O₄

3.6. Effect of contact time on batch adsorption of heavy metals

Fig. 8. shows the effect of contact time for the removal of heavy metals by using HAp-Fe₃O₄. The removal of heavy metals sample by adsorption using magnetic hydroxyapatite was found to be rapid at the initial period of contact time which is after 1 hour and then become slower with the increase of contact time. This might be due to the strong attractive forces between the heavy metal molecules and the adsorbent. As contact time increased, initially percentage removal also increased, but after some time it gradually approached almost constant value after equilibrium was reached. It was suggested by Feng (2010), that the removal of heavy metals by the magnetic hydroxyapatite adsorbents took place in two distinct steps which is a relatively quick phase that is on first two hours, followed by a slow increase until equilibrium was reached [10]. Feng also stated that the necessary time to reach the equilibrium was about 24 hours [10]. Though there was a slight increase in adsorption quantity after 24 hours, it did not bring any remarkable effect, so a contact time until 24 hours was chosen in this experiment. A longer contact time of adsorption resulting in bigger collision between particle of adsorbent and adsorbate. The changes in the rate of removal with time might be due to the increment of adsorption sites during the adsorption process. More heavy metal ions or adsorbates are attached to the increasing number of active sites in the adsorbent [21]. After about 60 minutes or 1 hour of contact time, it started to reach a constant heavy metals removal. Thus, this sample is taken as the optimum contact time for the next adsorption experiment. Iron (III) oxide in magnetic hydroxyapatite has higher strength in adsorbing heavy metals due to the strong magnetic moment in iron atom which is its four unpaired electrons in its 3d orbitals [22, 23]. When crystals are formed from iron atoms, different magnetic states can arise. When adsorption reached equilibrium, magnetic hydroxyapatite could be completely separated from the aqueous solution.

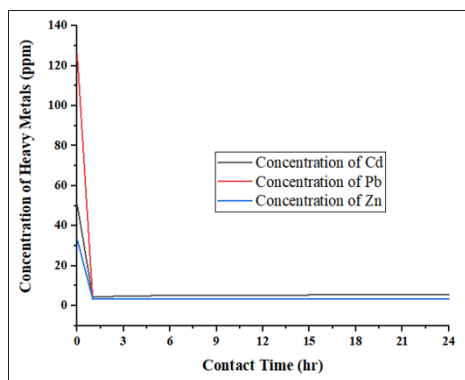


Fig. 8. Effect of contact time on the removal of heavy metal using HAp-Fe₃O₄

3.7. Reusability of magnetic hydroxyapatite

To prove that the material is a cost-effective material for wastewater treatment process, the magnetic hydroxyapatite was tested for its reusability. This is to analyse how many times it can be used for the adsorption of 0.5 ppm of lead, 1.0 ppm of cadmium, and 0.5 ppm of zinc which is later those three heavy metals been mixed together into a solution that contained 1 litre of distilled water. Fig. 9. shows the graph of frequency vs percentage removal of heavy metals.

Based on the result, it is shown that the percentage removal of heavy metals reduces from 89.0% to 80.0% at the four runs of the experiment. The reduction in adsorption efficiency is due to the reduction in active sites in the adsorbent after recycling [24]. The synthesized adsorbent is proved to be an excellent renewable adsorbent as it maintains at 80% percentage removal after four cycles of usage. The experiment is run for four times because it shows a constant performance for the last two runs.

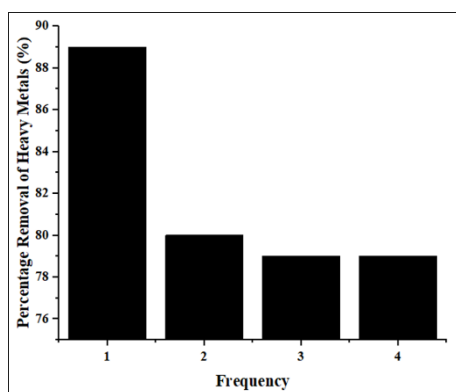


Fig. 9. Graph of percentage removal of heavy metals vs frequency

4 Conclusion

In conclusion, magnetic hydroxyapatite was synthesized with chemical precipitation and its adsorption behaviour was investigated on heavy metal. The experimental results show that this adsorbent can be used to remove heavy

metal of lead, zinc, and cadmium from heavy metals sample solution. The experiment investigated the effect of contact time, the initial concentration of heavy metals (cadmium, zinc, and lead) and the amount of adsorbent magnetic hydroxyapatite. In terms of contact time, the percentage of removal increase and the concentration of heavy metals sample decrease to a constant value due to the achievement of balance. The best adsorbent is after 1 hour of contact. Apart from that, this reusability shows that even after four cycles of usage, the adsorbent maintains at a percentage removal of 80%, indicating that it is an excellent renewable adsorbent.

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