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Removal of Cadmium Using Ferro Magnetic Gels

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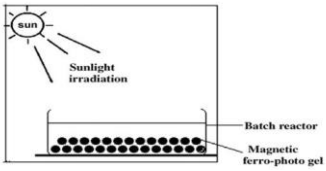
Graphical abstract



Abstract

The removal of cadmium (Cd) from aqueous solution of cadmium chloride using ferromagnetic photocatalyst gel was investigated. The experiments were performed under sunlight and also away from sunlight. Recycling experiments were also performed to determine the durability of the ferromagnetic photocatalyst gel. The results revealed that removal of cadmium was higher in the presence of sunlight irradiation compared to without sunlight. Apparently the treatment process for Cd involved both adsorption and photocatalytic process. The removal rate of Cd was faster when it was exposed to sunlight where almost 100% of Cd was removed within 4 hours. The presence of pores was observed from FESEM images and such morphology was considered helpful for mass transfer of Cd(II) to the photocatalyst active sites embedded in the PVA-alginate magnetic beads. The PVA-alginate magnetic beads produced were reused after treating with 25 ppm of Cd(II) solutions without washing them. The performance of each cycle was about the same as the previous cycle until it reached the seventh cycle where the ferro photo gels start to lose its removal efficiency.

Keywords: Photocatalyst; PVA-alginate magnetic beads; cadmium

1.0 INTRODUCTION

Nowadays, pollution by heavy metals is well acknowledged and can be harmful to living things like human and animals. Pollution can be defined as waste that is generated by human actions directly or indirectly which can cause environmental problems. Pollution can be divided into several categories such as; water, soil, air, thermal and solid waste pollution. Water pollution usually occurred when organic materials and inorganic materials are dissolved, and when other foreign materials especially toxic metal ions which are chemically dangerous are released from industries into the river and sea. There are many indicators that indicate that water is being polluted such as changes in color, turbidity, conductivity and temperature of the waste water.

Cadmium is an example of heavy metal that can be classified as hazardous material. Cadmium can cause health effects especially for human; for short term effect, cadmium can potentially cause nausea, vomiting, shock and renal failure when people are exposed to it at levels above the MCL (Maximum Contaminant Level). These MCL standards have been set by EPA (United States Environmental Protection Agency). Long term exposure to cadmium pollution can cause damage in the kidneys, liver and blood as a result of contact at levels above the MCL [1].

The increasing level of toxic metal ions in the environment, such as cadmium has become a major concern within the international community. Effluent from various agricultural practices and chemical industries, including metallurgical alloying, ceramics, textile industries, electroplating, plastic production, pigment manufacture, and polymerization processes contain cadmium [2].

The are several major causes for cadmium pollution: (i) cadmium rich phosphate based fertilizers, causes cadmium is introduced directly to the ground and from there to ground water resources in cultivated area, (ii) Ni/Cd battery production, which may deliver both Ni^{++} and Cd^{++} to ground water in untreated aqueous wastes or through uncontrolled disposal of used batteries, (iii) cadmium plating, which also introduces cyanide used as a strong complexing agent and (iv) non-ferrous metal mines release to the aquatic environment which contamination can arise from mine drainage water, wastewater from the processing of ores, overflow from the tailing pond, and rainwater run-off from the mine area. The major human source of cadmium release to the aquatic environment has been predictable from the smelting of non-ferrous metal ores [3].

Various methods have been urbanized for cadmium removal from wastewater such as biological treatment, ion exchange, liquid-liquid extraction, precipitation, reverse osmosis, and activated carbon adsorption [2]. However, these techniques often

utilize potentially hazardous or polluting materials and can only transform the pollutants from one phase to another [4]. More ever, most of these methods require a secondary removal process which involved cost. Unlike other methods, photocatalysis does not require any secondary removal and it can be reused back for many times before it loses its photocatalytic reduction property. Moreover, this method is very promising because it is capable of treating large amounts of wastewater in a short period [5]. Therefore, the photocatalyst technology has become an attractive and developing technology in wastewater treatment industry. This treatment method can be applied to the waste treatment pond.

Polyvinyl alcohol (PVA) ferromagnetic gel has been used as catalyst in photocatalytic reduction process to remove chromium in wastewater industry [6]. Polyvinyl alcohol (PVA) ferromagnetic gel has several advantages such as low cost, commercially available, easy to handle and it's accessible with different kinds of chemicals. Recently, it was revealed that the polyvinyl alcohol (PVA) ferromagnetic gel containing magnetic nanoparticles γ-Fe2O3 can behave as photocatalyst and can reduce Cr(VI) to Cr(III) in a short period of time and it doesn't require secondary treatment process [7]. To the best of our knowledge polyvinyl alcohol (PVA) ferromagnetic gel has not been used for the removal of Cd. Thus in this study the feasibility of treating Cd with polyvinyl alcohol (PVA) ferromagnetic gel is investigated. In addition the durability of gels was also evaluated by repeating the experiments.

■2.0 EXPERIMENTAL

2.1 Materials

Iron (II) chloride (FeCl2, 98%) and Iron (III) chloride solution (FeCl3, 45%) were purchased from Sigma Aldrich and Riedel-de Haen respectively. Hydrochloric acid (HCl, 37%), nitric acid (HNO3, 65%, v/v), acetone, cadmium chloride hemi (pentahydrate) CdCl2.2H2O and 1,5-diphenylcarbazide (DPC, 98%) were purchased from QReC and ammonia solution (NH3, 25%, w/v) was provided by Merck. Sodium alginate was obtained from Fluka. All the above materials were used without further purification. Distilled and deionised water was used throughout this research [7]. Cadmium solution was prepared by mixing cadmium chloride hemi (pentahydrate), CdCl2.2H2O with deionized water. 25 ppm of CdCl2.2H2O solutions at pH 6 was tested.

2.2 Synthesis of γ-Fe2O3 Nanoparticles

Maghemite nanoparticles (γ-Fe2O3) were synthesized by co-precipitation method [8-9]. The nanoparticles was synthesized by alkaline co-precipitation of a stoichiometric ferrous chloride (FeCl3) and ferric chloride (FeCl2) in ammonium hydroxide solutions (NH4OH). The black precipitate obtained called magnetite (Fe3O4) was acidified by nitric acid (HNO3) and oxidized at 100°C in a solution of ferric nitrate (Fe(NO3)3.9H2O) to γ-Fe2O3. The last step was to make the particles stable and can be used for further study. The particles was cautiously cleaned a few times to reduce the ionic strength of the acidic anionic ferrofluid (pH=2). This stability of the ferrofluid was caused by the existence of surface charges which induced screened electro-static repulsions between the particles.

2.3 XRD Analysis

XRD Siemens D5000 was used in this study to determine the elements present in the magnetic nanoparticles. Fine powder of magnetic nanoparticles which was used in the sample preparation was placed in a sample holder, and then the catalyst powder was pressed into the trough with a glass side to get an even distribution of the powder.

2.4 Preparation of PVA-Alginate Ferro Photo Gels

12% w/v PVA were conventionally heated for 5 hours, then heated in microwave for 4 minutes and finally mixed with 1% w/v sodium alginate and 8% w/v γ-Fe2O3. The solution mixture of PVA and γ-Fe2O3 was dropped into a mixed solution of calcium chloride and boric acid and stirred for 24 hours. The beads were then cleaned for three times and stored in deionized water for further use.

2.5 PVA-Alginate Magnetic Beads Characterization

FESEM-EDX was used to analyze the morphology and trace element contents in the PVA-alginate magnetic beads before and after the photocatalytic experiment. The wet PVA-alginate magnetic beads were dried using tissues and cut with surgical knife into halves. The bead was then placed on a stand and images of both the cross section and surface of the beads were taken. The composition of the trace elements on both the cross section and surface of the beads were also measured with FESEM-EDX JSM-6071F (Joel, USA Inc, USA).

2.6 Photocatalytic Experiments

Cadmium solution was prepared by dissolving $CdCl_2.2H_2O$ in deionized water. This solution was then used as a test contaminant for photocatalytic activity of the γ-Fe_2O_3 nanoparticles. The first set of photocatalytic experiments were performed under sunlight irradiation as shown in Figure 1 and the second set of experiments without sunlight irradiation for 4 hours. 100 ml of cadmium solution (25 mg/l) were contacted with 10.0 g of PVA-alginate magnetic beads in a conical flask at pH 6. 5 ml of sample were taken every 20 minutes for the first 2 hours and after that the samples are taken for every one hour. The samples collected were tested using atomic absorption spectrometer (AAS). The concentration of cadmium were determined using flame atomic absorption spectrometry (AAS, at λmax = 228 nm).

2.7 Recycle and Regeneration of the Beads

In order to determine the regeneration properties of PVA-alginate magnetic beads and the total times the beads can be used, regeneration experiments were performed [7]. The used PVA-alginate magnetic beads were recycled again and again until the removal efficiency decreased. All the experiments were done using the optimum dosage of γ-Fe_2O_3 and concentration of cadmium at 25 mg/l at pH 6. The experiments were repeated again and again until the beads lose the removal efficiency of photocatalytic reduction.

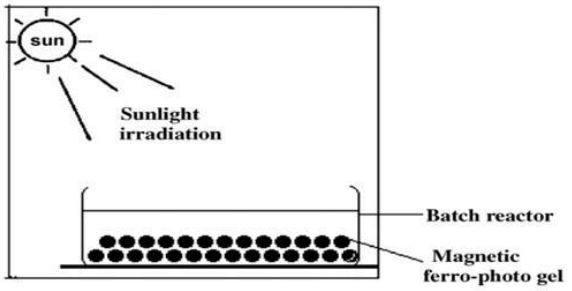


Figure 1 Experiment set-up for the photocatalyst reduction of cadmium [7]

3.0 RESULTS AND DISCUSSION

3.1 Characterization of Maghemite Nanoparticles γ-Fe2O3

Figure 2 illustrates the x-ray diffraction (XRD) of maghemite nanoparticles where the XRD peaks of the nanoparticles are similar to the standard γ-Fe_2O_3 with no other crystalline phase's recognized [7].

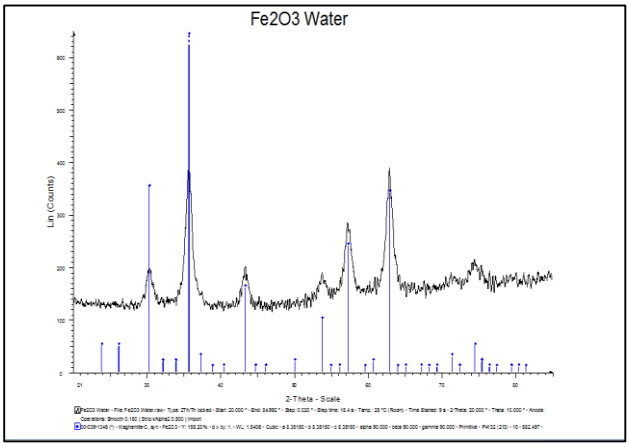


Figure 2 XRD patterns of maghemite nanoparticles

3.2 Photocatalytic Experiments

3.2.1 Presence of Sunlight Irradiation and Without Sunlight Irradiation

Figure 3 depicts the rate of cadmium removal when using the PVA-alginate ferromagnetic beads under sunlight and without sunlight irradiation. The experiments were done at initial cadmium concentration of 25 mg/l at pH 6 and 10.0 g of photocatalyst dosage. Under presence of sunlight, the rate of removal is 97.8% after 2 hours irradiation time. However, when placed away from sunlight, the rate of removal is 81.6%. These results proved that light energy is an important parameter in cadmium reduction. Therefore, light energy can improve the removal of cadmium.

In the absence of sunlight irradiation only 91.7% cadmium can be achieved after 4 hours. The rate of cadmium removal in the presence of sunlight irradiation for 4 hours is 99.4% which is faster than the rate of cadmium removal without sunlight irradiation. The result shows that cadmium can also be removed without sunlight irradiation but it is a slow process. Hence, only 91.7% of cadmium is removed after 4 hours without sunlight irradiation which proved that, only absorption process has taken place.

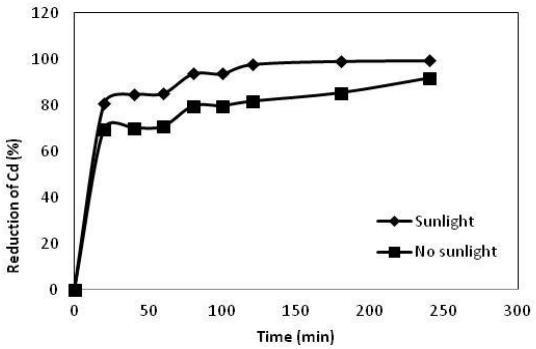


Figure 3 Rate of cadmium removal when using the PVA-alginate ferromagnetic beads under sunlight and without sunlight irradiation with concentration 25 mg/l; catalyst dosage 8% (v/v); pH 6

3.3 Recycle and Regeneration of the Beads

Recyclability is one of the most primary issues to be considered when dealing with photocatalyst beads. The beads must have the ability to be regenerated and reused again in order to make the beads more attractive to be used in industrial scale. Moreover, the beads must retain almost its original properties for successful recycle.

The recycle results are shown in Figure 4 where almost all the Cd(II) removal was still achievable after 7 cycles within 4 hours. The beads can be reused up to 7 cycles and the removal efficiency reduces after every successive cycle. Fresh beads are capable of removing 99.2% Cd(II) in 4 hours. Then, the removal rate decreases to 96.7%, 96.1%, 94.9%, 92.7%, 92.5%, 91.2% and 84.4% for the first, second, third, fourth, fifth, sixth and seventh cycle respectively. Although, the removal rate is high but it cannot remove Cd(II) to 100% within 4 hours contact time.

In this study, PVA-alginate ferro photo gels were reused after treating with 25 ppm of cadmium solutions without washing them. The performance of each cycle was almost the same as the previous cycle but the rate of removal was decreased until it reached the seventh cycle when the beads start to lose its removal efficiency as shown in Figure 3. The results revealed that the PVA alginate ferromagnetic gel possessed excellent reusability properties although the removal efficiency of Cd is not 100%. This hypothesis was proven by the EDX results (see Table 1) which depicts that there was Cd inside the cross section of the beads.

3.4 FESEM-EDX Analysis

Figure 5 and 6 show the surface and cross section morphology and structure of the PVA-alginate magnetic beads respectively before and after photocatalytic reactions at magnification of 500X. Jeon *et al*., (2002) studied that the pores that was observed from FESEM images was considered helpful for mass transfer of Cr(IV) to the photocatalyst sites embedded in the PVA-alginate [10]. Figure 5(b) shows that, some small pore areas are slightly covered mainly because of the adsorption of Cd(II). FESEM images in Figure 6 shows that, PVA-alginate ferro photo gels have a porous structure with the active sites embedded throughout its structure. Thus, the porous structure of PVA-alginate allows

Cd(II) to be absorbed through it and permits better accessibility to the photocatalyst active sites.

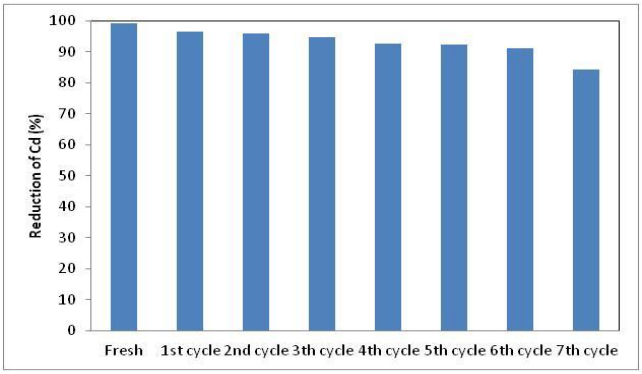


Figure 4 Regeneration of PVA-alginate ferro photo gels on Cd (II) reduction. [initial Cd(II) concentration; 25 mg/l, pH 6]

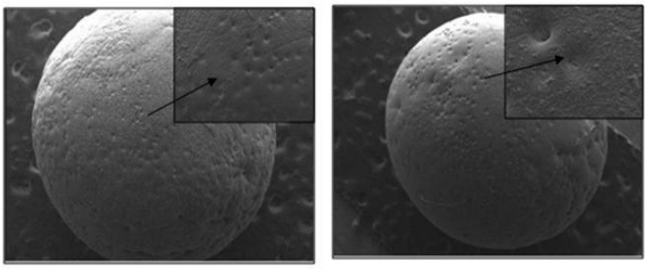


Figure 5 FESEM images of surface of PVA-alginate ferro photo gel (a) before photo reduction (b) after photo reduction

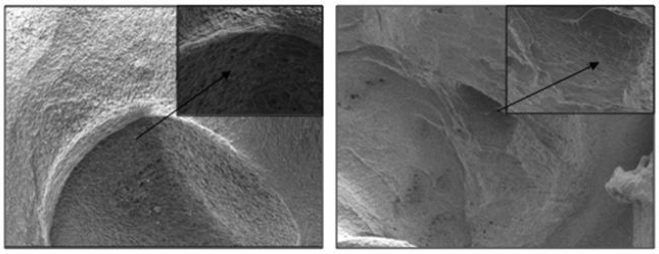


Figure 6 FESEM images of cross section of PVA-alginate ferro photo gel (a) before photo reduction (b) after photo reduction

EDX analysis was done in combination with FESEM analysis to verify the elemental composition on the bead cross section on chosen spots. Table 1 shows the EDX analysis of the various elements on the cross section of PVA-alginate magnetic beads before and after photocatalytic activity under sunlight irradiation. It was observed that, there are 4 components present in the beads. The result in Table 1 shows that, there was an increase in Cd concentration after photo reduction which is 16.22%. This could be credited to the porous structure of the PVA-alginate ferro photo gel which allows Cd(II) to diffuse through the beads into interior of the beads thus resulting in higher concentration of Cd observed in the cross section of the beads.

Table 1 EDX analysis of various elements on the cross section of PVA-alginate ferro photo gels before and after photoreduction with sunlight

Component	Mass Percentage (%)	
	Cross section of PVA-alginate	
	Before photo reduction	After photo reduction
Carbon (C)	53.87	59.98
Oxygen (O)	22.28	7.09
Iron (Fe)	23.84	16.71
Cadmium (Cd)	0.00	16.22

PVA is a synthetic functional polymer (-CH2CHOH-)n. PVA-alginate beads are formed by crosslinking of the alcohol groups on adjacent chains with borate ions B(OH)4− [11]. As a result, it will formed uniform beads matrix which allowed accessibility of metal ions into the beads. This is proven by porous structure (exhibited under FESEM) which allows Cd(II) to diffuse into the beads. Due to the abundant active sites present in the beads, it allows the beads to be used to the fullest. Therefore, the beads can be reused back without cleaning the beads.

4.0 CONCLUSION

As a conclusion, it is proven that PVA-alginate ferromagnetic beads can remove Cd by photocatalytic reduction under sunlight irradiation. The study discovered that Cd can be removed by both photocatalytic reduction and adsorption process. The rate of removal of Cd was faster when it is exposed to the sunlight irradiation where almost 100% of Cd can be removed within 4 hours of treatment time. The treatment was performed under pH 6, 10 g of photocatalyst dosage and at 25 ppm initial concentration of cadmium to achieve optimum removal. In terms of recyclability, the PVA-alginate ferromagnetic beads can be recycled up to 7 times with higher percentage of removal of Cd without losing their initial properties. Moreover, no washing and regeneration for the beads was required after each cycle. Therefore, due to excellent photocatalytic performance exhibited, the use of PVA-alginate ferro magnetic gels are commercially feasible for the removal of Cd(II) from wastewater.

Acknowledgement

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References

[1] Barakat, M. A. 2010. New Trends in Removing Heavy Metals from Industrial Wastewater. *Arabian Journal of Chemistry*. 4(4): 361–377.
[2] Patterson, J. W. 1985. *Industrial Wastewater Treatment*. 2nd ed. Boston-London-Sydney-Wellington-Durban-Toronto: Butterworth Publisher.
[3] Nosier, S. A. 2003. Removal of Cadmium Ions from Industrial Wastewater by Cementation, *Chemical and. Biochemical Engineering Quarterly.* 17(3): 219–224
[4] Litter, M. I. 1999. Review: Heterogeneous Photocatalysis—transition Metal Ions in Photocatalytic Systems. *Applied Catalysis B: Environmental*. 23: 89–114.

[5] Rocher, V., J. M. Siaugue, B. Cabuil, and A. Bee. 2008. Removal of Organic Dyes by Magnetic Alginate Beads. *Water Research*. 42: 1290–1298.
[6] Idris, A., N. Hassan, N. Mohd Ismail, E. Misran, N. Yusuf, A. F. Ngomsik, and A. Bee. 2010. Photocatalytic Magnetic Separable Beads for Chromium (VI) Reduction. *Water Research*. 44(6): 1683–1688.
[7]Idris, A., N. Hassan, R. Rashid, and A.F. Ngomsik. 2011. Kinetic and Regeneration Studies of Photocatalytic Magnetic Separable Beads for Chromium (VI) Reduction under Sunlight. *Journal of Hazardous Materials*. 186(1): 629–635.
[8] Massart, R. 1981. Preparation of a Aqueous Magnetic Liquids in Alkaline and Acidic Media. *IEEE Transaction on Magnetics*. 17: 1247–1248.
[9] Bee, A., R. Massart, S. Neveu. 1995. Synthesisn of Very Fine Maghemite Particles. *Journal of Magnetism and Magnetic Materials*. 149(1–2): 6–9.
[10] Jeon, C., J. Y. Park, and Y. J. Yoo. 2002. Novel Immobilization of Alginic Acid for Heavy Metal Removal. *Journal of Biochemical Engineering*. 11: 159–166.
[11] Idris, A., N.A. Mohd Zain, and M.S. Suhaimi. 2008. Immobilization of Baker's Yeast Invertase in PVA-alginate Matrix Using Innovative Immobilisation Technique. *Process Biochemistry*. 43: 331–338.