

**Short Communication**

# Selective Removal of Lead (II) Ion from Wastewater Using Superparamagnetic Monodispersed Iron Oxide ( $\text{Fe}_3\text{O}_4$ ) Nanoparticles as a Effective Adsorbent

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***Abstract:***

*This study investigated the applicability of polyethylene glycol (PEG-4000) coated  $\text{Fe}_3\text{O}_4$  magnetic nanoparticles for the selective removal of toxic pb (II) ion from wastewater. The  $\text{Fe}_3\text{O}_4$  magnetic nanoparticles of 24 nm were synthesized using a coprecipitation method and characterized by Scanning electron microscopy (SEM), vibrating-sample magnetometer (VSM), and X-ray diffraction (XRD). SEM images show that the dimension of particles is about 24 nm. VSM patterns indicate superparamagnetic properties of  $\text{Fe}_3\text{O}_4$  magnetic nanoadsorbent. XRD indicated the sole existence of inverse cubic spinel phase of  $\text{Fe}_3\text{O}_4$  magnetic nanoadsorbent. The influence of different parameters, such as pH, contact time and type of eluent on the amount of  $\text{Pb}^{2+}$  removed were investigated. The adsorption process was found to be highly pH dependent, which made the nanoparticles selectively adsorb this metal from wastewater. The optimum pH required for maximum adsorption was found to be 6 for lead. The maximum contact time for the equilibrium condition is 10 min. The modified  $\text{Fe}_3\text{O}_4$  magnetic nanoparticles thus regenerated could be used again to remove the  $\text{Pb}^{2+}$  ions.*

**Keywords:** Polyethylene Glycol (PEG-4000), Coated  $\text{Fe}_3\text{O}_4$  Magnetic Nanoparticles, Pb (II) Ion, Superparamagnetic, Co-precipitation, Wastewater.

## 1. INTRODUCTION

The environment and all the life forms on earth face a very serious threat from the heavy metal pollution due to their toxicity and strong tendency to concentrate in environment. At recent years heavy metal are classified as toxic and half of these are emitted into the environment in quantities that pose risk to human health [1].

These toxic metals can cause accumulative poisoning, cancer, and brain damage when found above the tolerance levels [2].

Lead (II) is one of the most toxic heavy metals

causing health problem when present in high amounts in water. The presence of lead in drinking water above the permissible limit (5 ng/ml) may cause adverse health effects such as anaemia, encephalopathy, hepatitis, nephritic syndrome [2,3]. Water is essential to all forms of life. It is also a vital resource for agriculture, manufacturing and other human activities. Therefore, the development accurate, rapid and selective determination method for removal pb(II) from polluted water due to extreme toxicity pb(II) is necessary and indispensable. Removal of metals from wastewater principally achieved by the application of several processes such

as adsorption, precipitation, electroplating, chemical coagulation, ion-exchange, membrane separation, and electrokinetics. Each method has been found to be limited for cost, complexity and efficiency, as well as secondary waste [4,5].

Recently, it was reported that using superparamagnetic monodispersed iron oxide ( $\text{Fe}_3\text{O}_4$ ) nanoparticles as an effective adsorbent for heavy metals removal from water, may result in development of a new and efficient technology in industrial wastewater treatment. The major advantages of this technology are its effectiveness in reducing the concentration of heavy metal ions such as Pb(II), avoid the generation of secondary waste, produced no contaminants, has the capability of treating large amount of wastewater within a short time, good selectivity and the adsorption materials employed in this method can be recycled and used easily on an industrial scale.

Because traditional adsorbents show poor recovery of the target metal ions from large volumes of solution due to low binding capacity, diffusion limitations and the lack of active surface sites. The search for new adsorbents is important in recent years. Nanometer-sized materials have attracted substantial interest in scientific community because of their special properties.  $\text{Fe}_3\text{O}_4$  magnetic nanoparticles, as a new kind of nanometer-sized materials are attractive because they can exhibit an array of novel and specified properties such as large surface area, potential for self assembly, high specificity, high reactivity, catalytic potential, and absence of internal diffusion resistance, which are promising to develop new or improve existing technologies in wastewater treatment. These particles are superparamagnetic, which means that they are attracted to a magnetic field, but retain no residual magnetism after the field is removed. Therefore, suspended superparamagnetic particles adhered to the target can be removed very quickly from a matrix using a magnetic field, but they do not agglomerate after removal of the field [1,6,7].

In this study, the  $\text{Fe}_3\text{O}_4$  magnetic nanoparticles were first modified by the surface modification, polyethylene glycol (PEG-4000). Then, the polyethylene glycol-coated magnetic nanoparticles were then used for the selective separation of Lead (II) from water. The effect of different parameters,

for example pH, adsorption time, type of eluent and desorption have been studied.

## 2. EXPERIMENTAL

### 2.1. Materials

All chemicals were of analytical grade. A stock solution of  $\text{Pb}^{2+}$  was prepared by direct dissolution of  $\text{Pb}(\text{NO}_3)_2$  salt from Merck in deionized water. The working solution of lead was obtained by dilution of the stock solution. Oleic acid and polyethylene glycol (PEG-4000) were purchased from Merck. Other reagents including Ferric chloride hexahydrate ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ), ferrous chloride tetrahydrate ( $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ ) and ammonium hydroxide ( $\text{NH}_4\text{OH}$ ) purchased from Merck. For pH adjustment throughout the experiment, hydrochloric acid (0.1 M) and/or sodium hydroxide (0.1 M) solutions were used as necessary. All acids used were of the highest purity available and were obtained from Merck.

### 2.2. Instrumentation

A graphite furnace atomic absorption spectroscopy (GF-AAS, Shimadzu model AA-670G) was used for the determination of trace element in the samples. The size of the particles were characterized by X-ray diffraction (XRD, Philips model Expert) with Ni-filtered  $\text{Cu K}\alpha$  radiation ( $\text{CuK}\alpha_1 = 0.154 \text{ nm}$ ) and Scanning electron microscopy (SEM, Philips model XL30), respectively. Magnetic properties of the particles were assessed with a vibrating-sample magnetometer (VSM, Homade 2 tesla). A magnet ( $\Phi 17.5 \times 20 \text{ mm}$ , 5500 Oe) was utilized for the collection of magnetic particles.

### 2.3. Preparation of the polyethylene glycol-coated iron oxide nanoparticles (PCMNPs)

The magnetic nanoparticles (MNPs) were prepared according to Ref. [8]. Briefly, ferrous chloride tetrahydrate ( $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ ) and ferric chloride hexahydrate ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ) were dissolved in deionized water as the solvent. The solution of  $\text{FeCl}_3$  and  $\text{FeCl}_2$  was mixed with molar ratio of  $\text{Fe}^{3+}/\text{Fe}^{2+}=2$ . Co-precipitation occurs with the addition of ammonium hydroxide ( $\text{NH}_4\text{OH}$ ) as precipitating

agent to the solution under nitrogen atmosphere with vigorous stirring. The color of solution changed to black immediately. The black magnetic precipitate obtained was washed twice with deionized water. For coating magnetic mixture of water and  $\text{Fe}_3\text{O}_4$  nanoparticles was stirred and heated at  $70^\circ\text{C}$  for 30 min under a nitrogen atmosphere, and then a solution of 25 ml oleic acid was added to the mixture with slow agitation. The suspension was then slowly cooled down to  $45^\circ\text{C}$  with constant stirring.

The polyethylene glycol (PEG-4000) solution was then added to the suspension. Then, mixture was kept at  $45^\circ\text{C}$  under vigorous stirring and a nitrogen atmosphere for 1 h. Then, it was cooled down to room temperature. The above solution was slowly added into deionized water for 2 days to allow the formation of hydrophilic nanoparticles and to remove organic solvents. The repulsive force between hydrophobic surfactant molecules coated on single particles can prevent them from agglomeration. Then, polyethylene glycol (PEG-4000) coated nanoparticles were collected by magnetic field separation with a permanent magnet and were dried at room temperature in air atmosphere to form polyethylene glycol-coated  $\text{Fe}_3\text{O}_4$  nanoparticles powders.

#### 2.4. General procedure

The procedure details for the removal of lead (II) ion from wastewater using magnetic ( $\text{Fe}_3\text{O}_4$ ) nanoparticles is demonstrated in follows: a portion of sample solution containing 100 mg  $\text{Pb}^{2+}$  ion was transferred to a 200 mL beaker, the pH value was adjusted to 6 with  $0.1\text{molL}^{-1}$  HCl and  $0.1\text{molL}^{-1}$  NaOH, and the final volume was diluted to 200 mL. Then 10 mg of PCMNPs were added, and the solution was mixed for 10min to facilitate adsorption of the metal ion onto the nanoparticles.

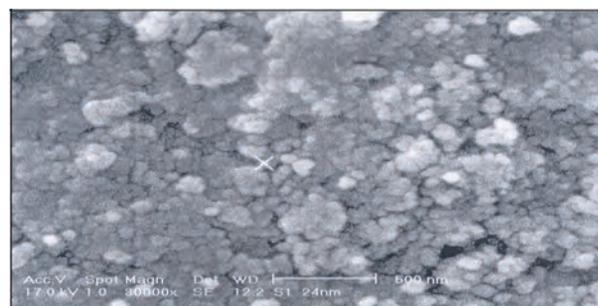
Then the magnetic adsorbent was separated easily and quickly using a magnet and the supernatants were decanted directly. The magnet was removed, and a solution containing  $0.1\text{molL}^{-1}$   $\text{HNO}_3$  was added as eluent and mixed again for 5 min. Finally, the magnet was used again to aggregate the magnetic nanoparticles, and eluate was injected to GF-AAS for subsequent analysis.

### 3. RESULTS AND DISCUSSION

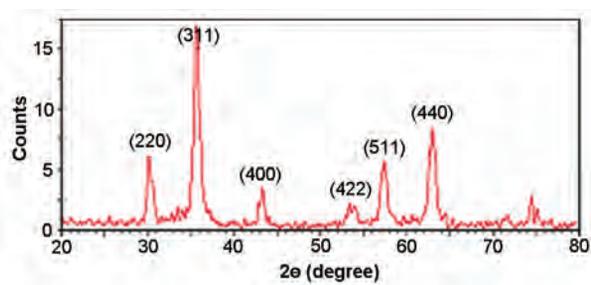
#### 3.1. Characterization of adsorbent

The Scanning electron microscopy (SEM) image (Figure 1) of the sample revealed that the magnetic  $\text{Fe}_3\text{O}_4$  nanoparticles synthesized in this study were monodispersed with an average diameter of around 24 nm. Figure 2(a) shows the X-ray diffraction (XRD) pattern of the  $\text{Fe}_3\text{O}_4$  nanoparticles. Six typical peaks for  $\text{Fe}_3\text{O}_4$ ,  $2\theta = 30.29^\circ$ ,  $35.69^\circ$ ,  $43.30^\circ$ ,  $53.69^\circ$ ,  $57.38^\circ$ , and  $62.98^\circ$ , which corresponds to (220), (311), (400), (422), (511), and (440) Bragg reflection, respectively, in Figure 2(a) agree with standard magnetite ( $\text{Fe}_3\text{O}_4$ ) XRD patterns, identify that the  $\text{Fe}_3\text{O}_4$  nanoparticles are cubic spinel structure. also X-ray diffraction (XRD) was used for structural phase identification (Figure 2(b)).

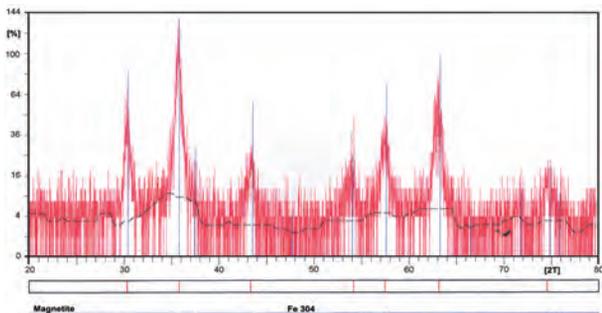
The XRD measurements indicated that magnetite ( $\text{Fe}_3\text{O}_4$ ) was the dominant phase for the sample. The magnetic property of MNPs was measured by vibrating-sample magnetometer (VSM). The hysteresis loop of the nanoparticles, which was measured in the powder state, is shown in Figure 3 which provided evidence that all the MNPs were superparamagnetic at room temperature, with no hysteresis. This superparamagnetic property of the magnetic nanoparticles makes them very susceptible to magnetic field and, therefore, the nanoparticles separate easily from solution. Without the external field, the nanoscale magnetic will not show any magnetic properties toward outside.



**Figure 1:** SEM image of the synthesized polyethylene glycol-coated  $\text{Fe}_3\text{O}_4$  magnetic nanoparticles

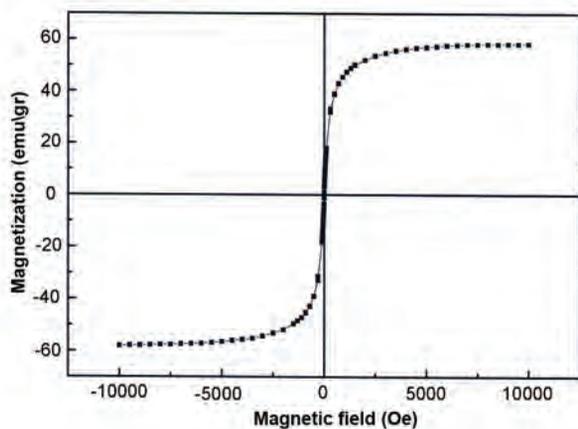


(a)



(b)

**Figure 2:** X-ray diffraction patterns for the polyethylene glycol-coated  $Fe_3O_4$  magnetic nanoparticles

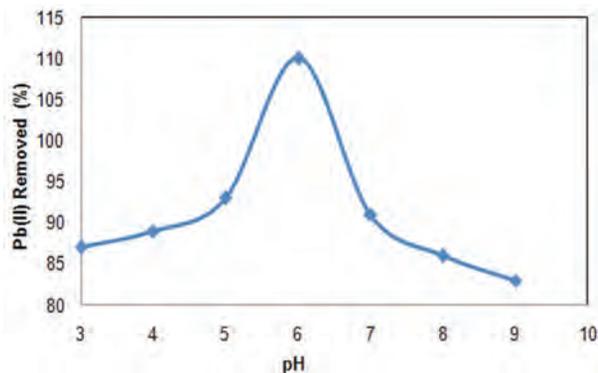


**Figure 3:** VSM measurements for polyethylene glycol-coated  $Fe_3O_4$  magnetic nanoparticles

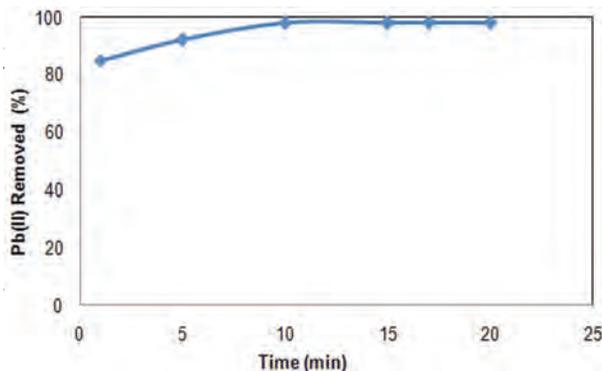
### 3.2. Influence of pH

In order to determine the optimal pH, it is important to study the effect of pH in a wider range. Therefore, the influences of pH were investigated at the pH ranges 3–9 with model solutions keeping the other

parameters constant. Figure 4 shows the effects of pH on the adsorption of  $Pb^{2+}$ . As observed in the graph, the removal efficiency of  $Pb^{2+}$  ions from water samples by the magnetic  $Fe_3O_4$  nanoparticles was clearly pH dependent and Maximum adsorption efficiency was obtained at pH 6 at room temperature. The decrease in signal at  $pH < 6$  may be due to competition of hydronium ion toward complexation with poly ethylene glycol (PEG), In an acidic solution the protonation of PEG occurs and there is a weak tendency for reaction between  $Pb(II)$  and PEG, which leads to the decrease in the extraction yield. but at higher pHs ( $pH > 6$ )  $Pb(II)$  precipitation is formed as lead hydroxide  $Pb(OH)_2$ .



**Figure 4:** Effect of pH on  $Pb^{2+}$  adsorption onto  $Fe_3O_4$  magnetic nanoadsorbents, Initial  $Pb^{2+}$  concentration: 100 mg/L.



**Figure 5:** Effect of adsorption time on the removal of  $Pb(II)$  ions.  $C_0 = 100$  mg/L

### 3.3. Effect of eluent on removed of lead

Some preliminary experiments were carried out

in order to choose a proper eluent for desorption  $Pb^{2+}$  ions after extraction from polyethylene glycol coated  $Fe_3O_4$  magnetic nanoparticles. The lead was stripped with different acids ( $HNO_3$ ,  $CH_3COOH$ ,  $HCl$  and  $H_2SO_4$ ). Results showed that among four different acid solutions used,  $1.0\text{ molL}^{-1}$  nitric acid can accomplish the quantitative elution of lead, while other acids used are ineffective for the complete elution of these ions. Nitric acid can penetrate into the PEG coated  $Fe_3O_4$  magnetic nanoparticles and react with the PEG (by protonation of oxygen atoms and reducing its complex stability) and formation of free PEG coated  $Fe_3O_4$  magnetic nanoparticles that can easily used again.

#### 4. CONCLUSIONS

In the present study, the superparamagnetic polyethylene glycol coated iron oxide nanoparticles ( $Fe_3O_4$ ) with cubic spinel structure and an average particle size of 24 nm were successfully synthesized by the co-precipitation method and could be used as an alternate to the conventional adsorbents for the removal of metal ions from wastewater with high removal efficiency within a very short time. The removal of  $Pb^{2+}$ , as a typical metal ion commonly present in wastewater, by adsorption onto  $Fe_3O_4$  magnetic nanoparticles was successfully accomplished.

Adsorption was very rapid and equilibrium was achieved within 10min. It also showed that adsorption was highly dependent on the concentration of  $Pb^{2+}$  and pH value. Maximum removal efficiency was achieved at pH 6 at room temperature. Therefore, the method is accurate, and economical and  $Fe_3O_4$  magnetic nanoparticles were recommended as fast,

effective, and inexpensive nanoadsorbents for rapid removal and recovery of high concentration of  $Pb^{2+}$  ions from such wastewaters.

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