

# REMOVAL OF HEAVY METALS BY IRON OXIDE NANOPARTICLES FROM GOLD MINING WASTEWATER

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## Abstract

*This study investigated the applicability of maghemite and magnetite nanoparticles (NPs) for the removal of heavy metals from mining wastewater. The maghemite and magnetite NPs of 122nm and 74nm were synthesized using a co precipitation method and characterized by Nanometer particle size analysis (NANOPHOX) and TEM, X-ray diffraction (XRD). Batch experiments were carried out for the removal of heavy metals from mining wastewater by maghemite and magnetite NPs. The adsorption process was found to be highly pH dependent. Maximum removal efficiency of As, W, U, Pb, Cu and Se were achieved 97.9%, 96.7, 99, 8, 61.5%, 30.4-78.3% and (63.2-68.4%) at pH 7, 11 in wastewater, respectively, (5g /L maghemite and magnetite NPs, 10minute) at room temperature.*

**Keywords:** iron oxide nanoparticles (NPs), heavy metal, gold mining wastewater, treatment

## Introduction

The term heavy metal refers to metallic elements with relatively high densities that are toxic at low concentrations. Heavy metals have atomic weights between 63.5 and 200.6, and a specific gravity higher than 5.0. Heavy metals are classified into three main groups as toxic metals (such as Hg, Cr, Pb, Zn, Cu, Ni, Cd, As, Co, Sn etc.), precious metals (such as Pd, Pt, Ag, Au, Ru etc.) and radionuclides (such as U, Th, Ra, Am etc.). Contamination of wastewaters by toxic metal ions is a worldwide environmental problem. The main sources of pollution are mining and electroplating industries discharging a variety of toxic metals such as Pb, Cu, Ni, Zn, As, and Cd ions into soils and water bodies. Gold mine wastewater generally contains heavy metal pollutants (such as Cu, As, Fe, Zn, Pb etc.) and cyanide at elevated concentrations. The toxicity of both metals and cyanide pollution is long lasting as these pollutants are non-biodegradable (Acheampong, 2013).

The excessive intake of copper by man leads to severe mucosal irritation, widespread capillary damage, hepatic and renal damage, central nervous problems followed by depression, gastrointestinal irritation and possible necrotic changes in the liver and kidney. On the other hand, arsenic dissolved in water is acutely toxic and leads to a number of health problems; including disturbances in the cardiovascular and nervous system functions and eventually death. Other heavy metals (such as Hg, Cd, Se, Pb, Ni, Zn, etc.) produce similar health effects when injected in significant quantities. Clearly, heavy metal pollution of the environment is of paramount concern due to their health risk to humans and threat to the ecosystem.

The conventional methods for removing heavy metal ions from wastewater include chemical precipitation, coagulation-flocculation, floatation, filtration, ion-exchange, reverse osmosis, membrane-filtration, evaporation recovery and electrochemical technologies. Although these treatment methods can be employed to remove heavy metals from contaminated wastewater, they have their inherent advantages and limitations in application (Acheampong, 2013).

The latest developments in nanotechnology, various types of magnetic NPs have been successfully synthesized and have received considerable attention to solve environmental problems, such as accelerating the coagulation of sewage, removing radionuclides, adsorption of organic dyes, and remediation of contaminated soils (Wang and Guo 2012).

Iron oxides exist in many forms in nature, with magnetite ( $\text{Fe}_3\text{O}_4$ ), hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ) and maghemite ( $\gamma\text{-Fe}_2\text{O}_3$ ), being most probably common and important technologically. It has been reported that surface effects have a strong influence on the magnetic properties of iron oxide NPs. The adsorption capacities of adsorbents rely largely on the available surface areas, and the increase of the surface area is normally obtained by the decrease of the particle size of adsorbents. As a result, there is a need to synthesize such adsorbents with proper particles sizes for the removal of heavy metals from wastewater (Qu and Pedro 2013).

In this study, maghemite and magnetite NPs has been synthesized using a co-precipitation method and applied for removal of heavy metals from mining wastewater. Maghemite and magnetite NPs as a novel adsorbent is expected to offer an attractive and inexpensive option for the removal of heavy metals by considering its simple synthesizing method, high surface area, and magnetic properties. Thus, the objectives of this study are: to synthesize adsorbents with proper particles sizes for the removal of heavy metals and to assess the performances of an iron oxide NPs for the heavy metals removal in mining wastewater.

## Experiment

### 2.1. Preparation and Characterization of maghemite and magnetite NPs.

Maghemite and magnetite NPs were synthesized according to the co-precipitation method with some modifications (Jiang, W and Pelaez, M 2013). Maghemite and magnetite NPs **1** and **2** were synthesized the iron mixture and ammonium hydroxide solution. Magnetite NPs **2** were then encapsulated with the PEG-4000 polymers to endow the particles with dispersability and chemical stability (Shen et al., 2009). The resultant product of maghemite and magnetite NPs were obtained for subsequent characterization. A Nanometer particle size analysis (NANOPHOX Sympa TC, Germany) and transmission electron microscopy (TEM) were used to characterize the structure properties of the prepared materials. TEM images were performed on a (JEOL, JEM 2011). A typical sample for TEM was prepared by drying of a drop of the solution at room temperature on a carbon-coated copper grid. The crystallization phase analysis was executed by a powder X-ray diffraction (XRD) (EnrafNonius Delft).

### 2.2. Removal of Heavy Metals from mining wastewater.

The samples were collected from wastewater of mining in Bumbugur soum, Bayanhongor aimag, in May 2016. Batch adsorption studies were performed by mixing 0.5 g of maghemite and magnetite NPs with 50mL of sample in 100mL glass vials. The adsorption on maghemite and magnetite NPs were first studied at pH values of 2 to 11 to investigate the effects of pH values on heavy metals adsorption. 0.1M HCl and 0.1M NaOH solutions were used to adjust the pH values of water samples. The pH values of water samples were stable over the experiment period. All the adsorption experiments were carried out at a room temperature of  $22 \pm 2^\circ\text{C}$  and were performed in triplicate. (Cheng et al., 2012). The concentrations of heavy metals were measured by a plasma-atomic emission spectrometer ICP- before and after treatment in SGS IMME Mongolia LLC. The percent removal (%) of heavy metals was calculated. Three trails for each pH were conducted.

## Result and discussion

### 3.1. Synthesis and Characterization of iron oxide NPs.

The commonly used synthetic way of maghemite NPs is a co-precipitation method of the iron mixture ( $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  and  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ) using ammonium hydroxide solution (Jiang and Pelaez 2013). The size and structure of the maghemite NPs were confirmed Nanometer particle size analysis NANOPHOX Sympa TC, transmission electron microscopy (TEM) and X-ray diffraction (XRD). In **1**, the maghemite NPs have diameters around 122 nm. In **2**, the magnetite NPs are nanospheres have diameters around 74 nm and are well dispersed with no aggregation between the maghemite NPs in water. (Table 1 and Figure 1).

*Table 1. Nanophox particle size analysis of iron oxide NPs*

Name of iron oxide NPs	Size of NPs, nm	$S_v, \text{m}^2/\text{cm}^3$
maghemite	122	49.42
magnetite coated with PEG-4000	74	81.56

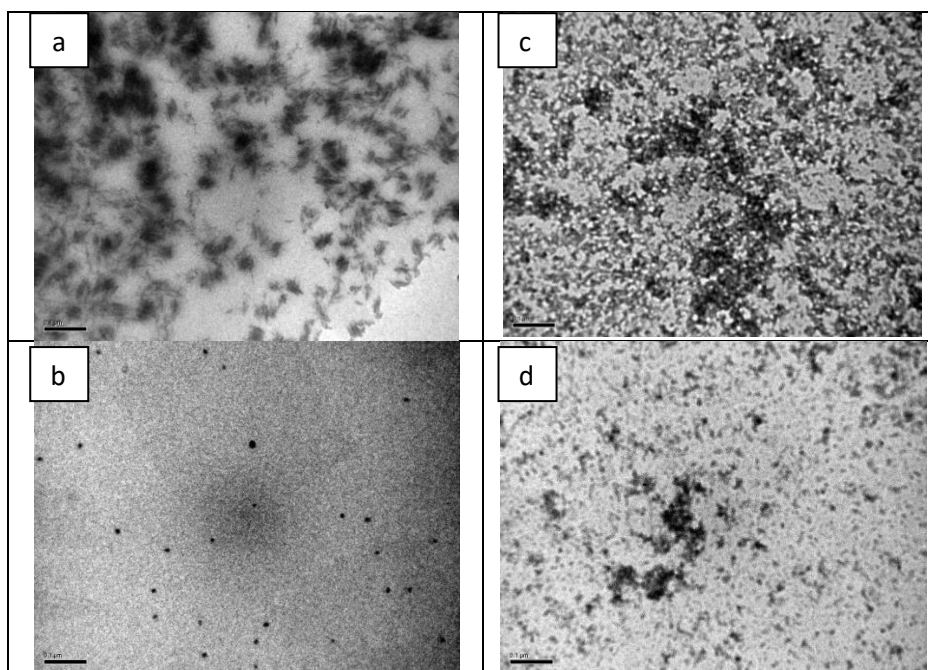


Fig. 1. TEM images of the maghemite 1 (a, b) and the maghemite 2 coated with PEG-4000 (c, d)

The structure identity and purity of the prepared maghemite NPs 1 were verified by XRD. Fig. 2 shows the spectrum of the XRD pattern included peaks at 8.35, 4.80, 2.96, 2.51, 1.60, and 1.47. XRD peaks of the nanocrystallite match well with standard  $\gamma\text{Fe}_2\text{O}_3$  and no other crystalline phases were detected (Aftabtalab and Sadabadi 2015).

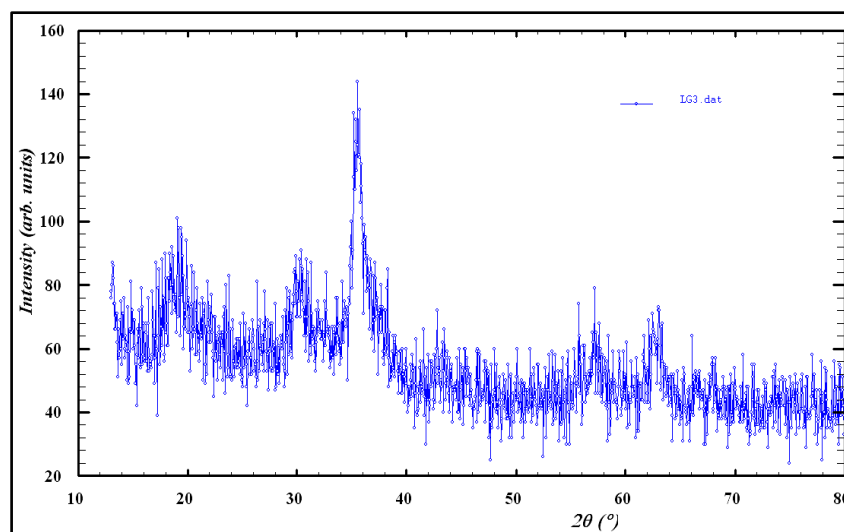


Fig 2.XRD patterns of maghemiteNPs 3.1.

### 3.2. Adsorption study

As one important application, the synthesized maghemite and magnetite NPs were used for treating the wastewater generated from the gold mining. Several factors can be affected to the adsorption process, such as solution pH, adsorbent dosage and contact time. In addition to these factors, the NPs type, size, shape and stabilizer also affect to the adsorption performance. Higher adsorption capacities can be obtained by optimizing above parameters. The effect some of these factors are discussed below.

#### 3.2.1. Effect of solution pH

The 57 heavy metals adsorption by iron oxide NPs was performed by comparison with  $\text{FeCl}_3$  in the sample at 5g /L, pH 2, and 10 minute. In this case, the 15 heavy metals were decreased corresponding to the increased size of

maghemite and magnetite NPs. (Fig 3). The pH of the solution is an important parameter which controls the adsorption process. It influences the ionization of the adsorptive molecule and hence the surface charges of the adsorbent. Therefore investigating the effect of pH on the adsorption is essential in adsorption experiments (Etale et al., 2014).

The experiments were carried out to find the optimum pH on the adsorption of heavy metals onto maghemite and magnetite NPs using different pH values of 2 to 11.

Fig 3 shows the effects of pH on the adsorption of copper as compared to the wastewater sample. As observed in the graph, the removal efficiency of copper ions from water samples by the maghemite and magnetite NPs was clearly pH dependent and the highest adsorption efficiency was obtained at over pH 7. It indicated that a water sample with a higher pH value was favorable for the hydroxide anion of sorbent surface (Etale et al., 2014). Increased hydroxide anion could result in the increase of negatively charged sites, which enhanced the attractive forces between the sorbent surface and the cations with copper. Therefore, it will result in the increase in the adsorption capacity. On the other hand, in a water sample with lower pH, the positively charged sites dominate and this could enhance the repulsion forces existing between the sorbent surface and the cations with copper and therefore decrease the adsorption of cations with copper. Maximum removal efficiency of copper was achieved 78.3% at pH 7 and 73, 4% at pH 11, respectively, (5g /L maghemite NPs, 10minute) at room temperature. Maximum removal efficiency of copper was achieved 30.4% at pH 7 and 47,8% at pH 11, respectively, (5g /L magnetite NPs, 10minute) at room temperature. In copper case, maghemite NPs are higher efficiency than magnetite NPs.

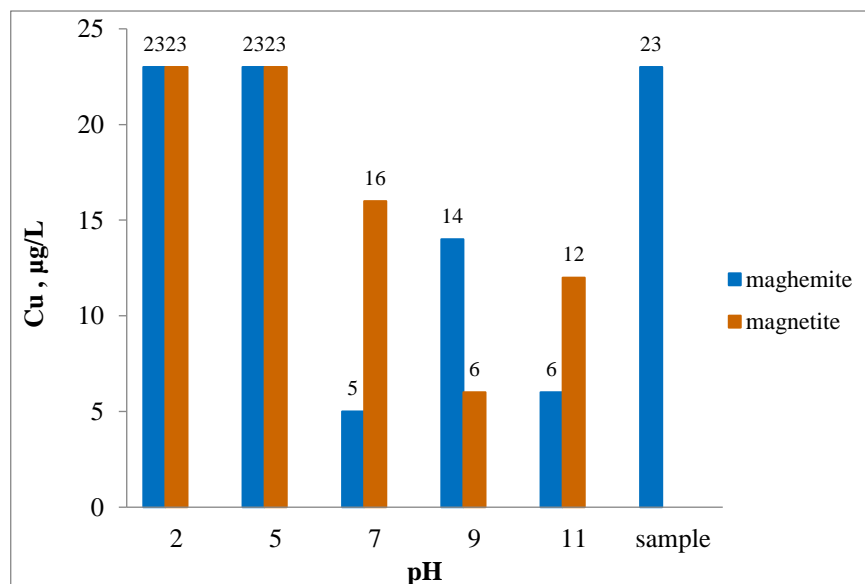


Fig.3 Effect of pH on Cu adsorption [iron oxide NPs] = 5 g/L, 10 minute

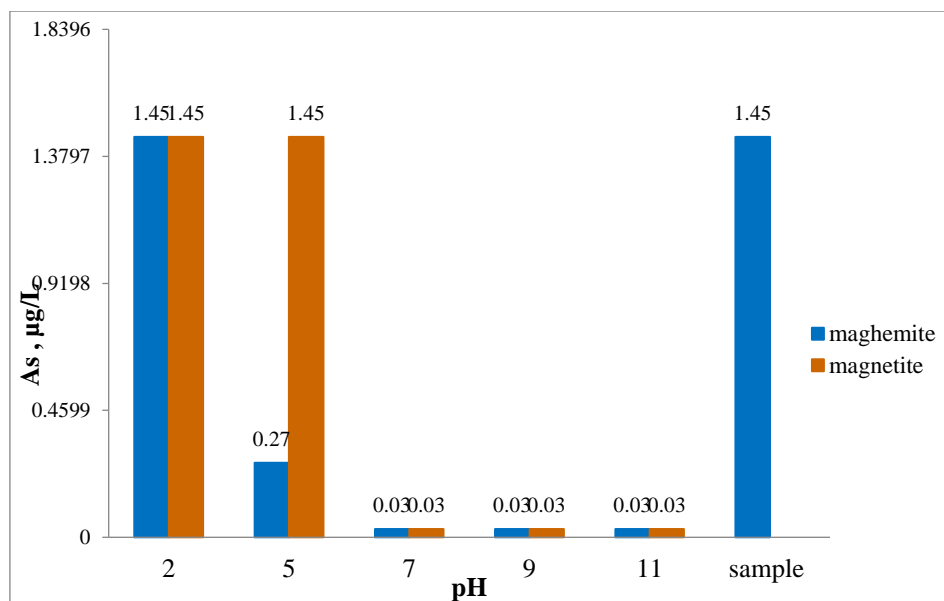


Fig.4 Effect of pH on As adsorption [iron oxide NPs] = 5 g/L, 10 minute

Fig 4 shows the effects of pH on the adsorption of arsenic as compared to the wastewater sample. As observed in the graph, the removal efficiency of arsenic ions from water samples by the maghemite and magnetite NPs was clearly pH dependent and the highest adsorption efficiency was obtained at over pH 7. It indicated that a water sample with a higher pH value was favorable for the hydroxide anion of sorbent surface (Khodabakhshi et al., 2011). Increased hydroxide anion could result in the increase of negatively charged sites, which enhanced the attractive forces between the sorbent surface and the cations with arsenic. Therefore, it will result in the increase in the adsorption capacity. Maximum removal efficiency of arsenic was achieved 97.9% at pH 7, 9 and 11, respectively, (5g /L maghemite NPs, 10minute) at room temperature. Maximum removal efficiency of arsenic was achieved 97.9% at pH 7, 9 and 11, respectively, (5g /L magnetite NPs, 10minute) at room temperature. In arsenic case, maghemite and magnetite NPs are same efficiency.

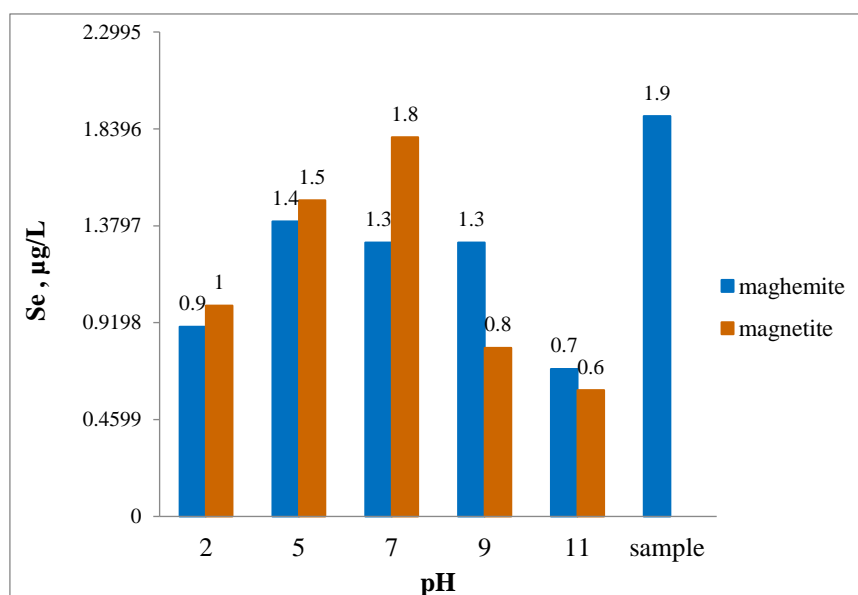


Fig.5 Effect of pH on Se adsorption [iron oxide NPs] = 5 g/L, 10 minute

Fig 5 shows the effects of pH on the adsorption of selenium as compared to the wastewater sample. As observed in the graph, the removal efficiency of selenium ions from water samples by the maghemite and magnetite NPs was clearly pH dependent and the highest adsorption efficiency was obtained at pH 11. Maximum removal efficiency of selenium was achieved 31.6% at pH 7, 63.2% at pH 11, respectively, (5g /L maghemite NPs, 10minute) at room temperature. Maximum removal efficiency of selenium was achieved

5.26% at pH 7 and 68.4% at pH 11, respectively, (5g /L magnetite NPs, 10minute) at room temperature. In a selenium case, magnetites NPs are higher efficiency than maghemite NPs at pH 11.

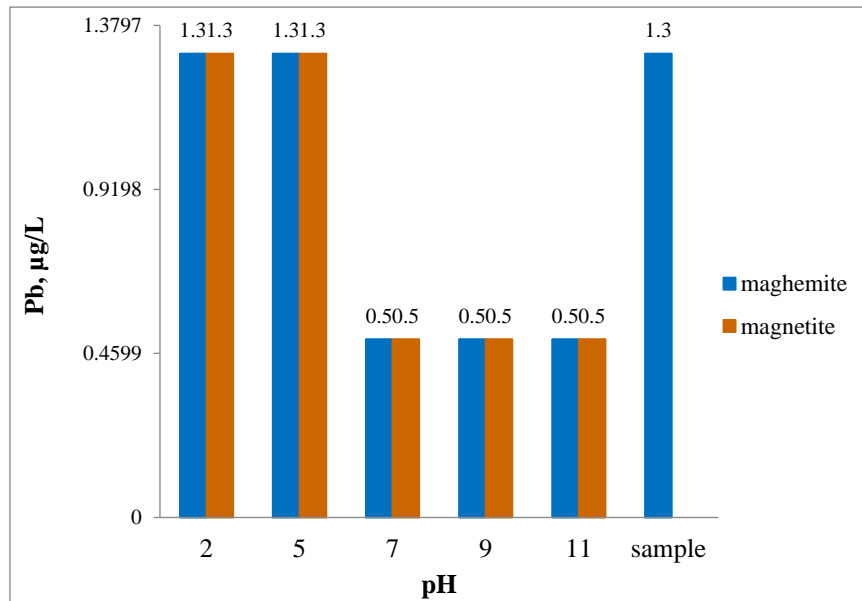


Fig.6 Effect of pH on Pb adsorption [iron oxide NPs] = 5 g/L, 10 minute

Fig 6 shows the effects of pH on the adsorption of Pb as compared to the wastewater sample. As observed in the graph, the removal efficiency of Pb ions from water samples by the maghemite and magnetite NPs was clearly pH dependent and the highest adsorption efficiency was obtained at pH 7,9 and 11 (Cheng et al., 2012).

Maximum removal efficiency of Pb was achieved 61.5% at pH 7,9 and 11, respectively, (5g /L maghemite NPs, 10minute) at room temperature. Maximum removal efficiency of Pb was achieved 61.5% at pH 7, 9 and 11, respectively, (5g /L magnetite NPs, 10minute) at room temperature. In a Pb case, maghemite and magnetite NPs are same efficiency at pH 7, 9 and 11.

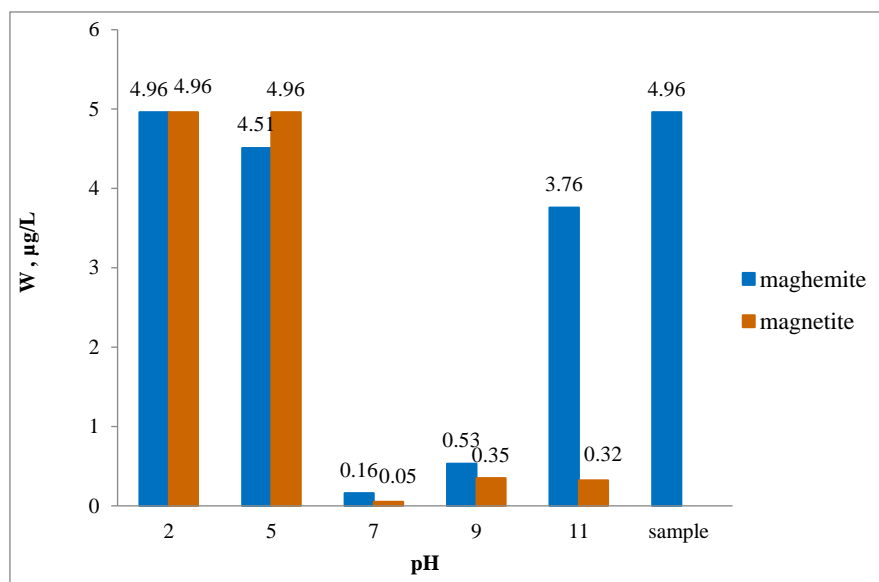


Fig.7 Effect of pH on W adsorption [iron oxide NPs] = 5 g/L, 10 minute

Fig 7 shows the effects of pH on the adsorption of W as compared to the wastewater sample. As observed in the graph, the removal efficiency of W ions from water samples by the maghemite and magnetite NPs was clearly pH dependent and the highest adsorption efficiency was obtained at pH 7.

Maximum removal efficiency of W was achieved 96.7% at pH 7, and 24.2% at pH 11, respectively, (5g /L maghemite NPs, 10minute) at room temperature. Maximum removal efficiency of W was achieved 98.9% at pH

7, and 93.5% at pH 11, respectively, (5g /L magnetite NPs, 10minute) at room temperature. In a W case, magnetites NPs are higher efficiency than maghemite NPs at pH 7, 11.

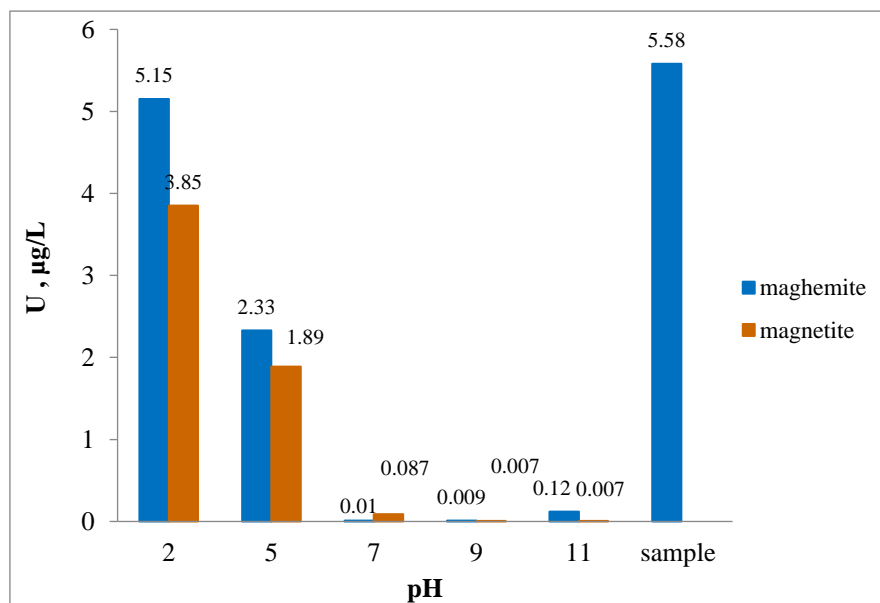


Fig.8 Effect of pH on U adsorption [iron oxide NPs] = 5 g/L, 10 minute

Fig 6 shows the effects of pH on the adsorption of U as compared to the wastewater sample. As observed in the graph, the removal efficiency of U ions from water samples by the maghemite and magnetite NPs was clearly pH dependent and the highest adsorption efficiency was obtained at pH 7,9 and 11 (Etale et al.,2014).

Maximum removal efficiency of U was achieved 99.8% at pH 7, 9 and 97.8% at pH 11, respectively, (5g /L maghemite NPs, 10minute) at room temperature. Maximum removal efficiency of U was achieved 99.8% at pH 7, 9 and 11, respectively, (5g /L magnetite NPs, 10minute) at room temperature. In a U case, maghemite and magnetite NPs are same efficiency at pH 7, 9 and 11.

Table 2. Effect of pH on the adsorption of heavy metals in mining wastewater [Iron oxide NPs] = 5 g/L, 10 minute

N	Heavy metals	Maghemite NPs		Magnetite NPs	
		Efficiency %		Efficiency %	
		pH 7	pH 11	pH 7	pH 11
1	Cu	78.3	73.4	30.4	47.8
2	As	97.9	97.9	97.9	97.9
3	Se	31.6	63.3	5.26	68.4
4	Pb	61.5	61.5	61.5	61.5
5	W	96.7	99.8	99.8	99.8
6	U	99.8	99.8	99.8	99.8

As shown in Table 2, most interestingly, our present investigations indicate that, maximum removal efficiency of As, W, U, Pb by using maghemite and magnetite NPs were achieved 97.9%, 96.7, 99, 8 and 61.5% at pH 7, 11 in wastewater, respectively. And removal efficiency of Cu, maghemite NPs are higher than magnetite NPs at pH 7,11. Also removal efficiency of Se , maghemite and magnetite NPs were achieved (63.2-68.4%) at pH 11.

Therefore, this two novel magnetic separation technology will be perspective used as the separation and purification of heavy metal ions in mining wastewater.

## Conclusion

Magnetic maghemite and magnetite NPs were synthesized by a coprecipitation method characterized and employed for heavy metals removal in mining wastewater.

Maximum removal efficiency of As, W, U, Pb, Cu and Se by using maghemite and magnetite NPs were achieved 97.9%, 96.7, 99.8, 61.5%, 30.4-78.3% and (63.2-68.4%) at pH 7, 11 in wastewater, respectively, (5g /L maghemite and magnetite NPs, 10minute) at room temperature.

Therefore, this two novel magnetic separation technology will be perspective used as the separation and purification of heavy metal ions in mining wastewater.

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