

## کاربرد نانوکامپوزیت مگنتیت، هماتیت، آهن سنتز شده به روش الکتروشیمیایی به عنوان یک جاذب جدید برای حذف یون‌های سرب از آب

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## Application of Electrochemically Synthesized Magnetite, Hematite, Iron Nanocomposite as a New Sorbent For The Removal of Lead Ions From Water

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### چکیده

آلودگی آب توسط یون‌های فلزات سنگین نظیر سرب به صورت جهانی در حال وقوع است. روش‌های معمولی حذف یون‌های فلزات سنگین از آب شامل روش‌های رسوبدهی شیمیایی و الکتروشیمیایی، مبادله یون، اسمز معکوس و جذب می‌باشد. بین روش‌های ذکر شده فوق، جذب سطحی یون‌های فلزات سنگین روی نانومواد جامد یکی از روش‌های جالب و توصیه شده می‌باشد. جذب سطحی به خاطر کارایی خوب، سهولت اجرا و ارزان قیمت بودن مورد توجه قرار گرفته است. در این مطالعه نانوکامپوزیت مگنتیت/هماتیت/آهن (MHINC) به روش تخلیه قوس الکتریکی کم ولتاژ در حضور میدان مغناطیسی خارجی با قدرت ۱/۲ تسلا سنتز شد. مطالعه تصاویر میکروسکوپ‌های الکترونی روبشی و عبوری نشان داد که نانوکامپوزیت سنتز شده شامل نانوذرات یکنواختی با قطر میانگین ۷ نانومتر می‌باشند. نانوکامپوزیت تهیه شده به عنوان جاذب جدید برای حذف یون‌های فلزات سنگین از آب‌های آلوده استفاده شد. داده‌های تجربی نشان می‌دهند که جذب یون‌های سرب بر روی MHINC به طور قابل قبولی با ایزوترم لانگمویر سازگار است. بر این اساس، ماکزیمم ظرفیت جذب یون سرب بر روی نانوکامپوزیت سنتز شده  $86 \text{ mg g}^{-1}$  به دست آمد. شرایط تجربی بهینه برای حذف یون‌های فلزات سنگین به ویژه یون سرب شامل  $\text{pH}=5$  حجم نمونه ۲۵ میلی لیتر، وزن جاذب ۲۵ میلی گرم، زمان مخلوط کردن ۲۵ دقیقه و دما برابر دمای اتاق می‌باشد. مطالعات واجذب یون سرب از روی نانوجاذب نشان داد که محلول اسیدی شامل اسید کلریدریک ۳ مولار و اسید نیتریک ۲ مولار می‌تواند به عنوان شوینده مناسب برای واجذب یون‌های سرب استفاده شود.

### واژه‌های کلیدی

نانوکامپوزیت مگنتیت، هماتیت، آهن؛ قوس الکتریکی؛ میدان مغناطیسی؛ حذف یون؛ یون‌های فلزات سنگین.

### Abstract

Water pollution by heavy metal ions such as Pb occur globally. The conventional methods for the heavy metal ions removal from the water include electrochemical and chemical precipitations, ion exchange, reverse osmosis and sorption. Among the above mentioned different methods, sorption of heavy metal ions on the surface of solid nanomaterials is one of the most recommended and interest methods. Sorption is attractive due to its merits of efficiency, cheap and simple operation. In this study, hematite/magnetite/iron nanocomposite (MHINC) is synthesized by the low voltage electrical arc method in the presence of 1.2 Tesla external magnetic fields. Scanning electron microscopy and transmission electron microscopy show that the synthesized MHINC includes uniform nanoparticles with 7 nm average diameters. The prepared MHINC is used as a new sorbent to remove heavy metal ions from polluted waters. Experimental data shows that the sorption of lead ions on the surface of MHINC is acceptably fitted to the Langmuir isotherm. Based on the experimental data, a maximum sorption capacity of  $86 \text{ mg g}^{-1}$  is achieved for the sorption of lead ions on the surface of MHINC. The experimental optimum conditions for the lead ion removal includes  $\text{pH}=5$ , 25 ml sample volume, 25 mg sorbet and 25 min mixing time in the room temperature. Desorption studies showed the adsorbed lead ions on MHINC surface can be done by using 1ml acidic solution containing 3 M HCl and 2 M  $\text{HNO}_3$ .

### Keywords

Magnetite, Hematite, Iron Nanocomposite; Electrical Arc; Magnetic Field; Ion Removal; Heavy Metal Ions.

### 1. INTRODUCTION

Today, water pollution is a major problem. The

contaminants include heavy metals, radioactive compounds, organic and inorganic compounds.

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For non-disintegration of heavy metals and harmful physiological effects on organisms at low concentrations, are particularly important in environmental pollution. The bulk of their ultimate destination, especially in developing countries is groundwater and surface water resources, soil and ultimately human. There is a variety of methods for the removal and separation of heavy metal ions from aqueous solutions. The most important methods that can be used for this purpose are chemical precipitation [1], ion exchange [2], reverse osmosis [3], membrane processes [4], solvent extraction [5] and sorption methods [6]. Due to the electrical conductivity and magnetic properties of zero valent iron, hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ) and magnetite ( $\text{Fe}_3\text{O}_4$ ) nanoparticles, they have been used in various applications such as drug delivery [7-9], the removal of organic [10-12] and inorganic [13-15] pollutants from water and wastewater.

It is reasonable to expect a composite sorbent of magnetite, hematite and iron can be used as a more powerful sorbent in the removal of heavy metal ions than alone compounds. In this work, the MHINC with average diameters of 7 nm was electrochemically synthesized and used as solid a new potential sorbent for the removal of heavy metal ions from water.

## 2. EXPERIMENTAL

### 2.1. Materials

All materials including  $\text{HNO}_3$ ,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ,  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Fe}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$ ,  $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ ,  $\text{NiCl}_2$ ,  $\text{Pb}(\text{NO}_3)_2$ ,  $\text{NaNO}_3$ ,  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{AgNO}_3$ ,  $\text{NaOH}$  were purchased from Merck and used without any purification. Double-distilled water was used in all experiments.

### 2.2. Instrumentals

Two electrical power supply (Mps - 3010L-1, Taiwan made) are used to make an arc discharge. The morphology and the particles sizes of MHINC samples were studied by scanning electron microscopy (SEM: Sigma/VP model) and transmission electron microscope (TEM, Zeiss EM900). Flame Atomic Absorption (FAA, Sens AA model, GBC company) was applied for the determination of the metal ions concentrations. The pH values were controlled with a pH meter (Metrohm-827). Circulating device (PE 26 INF model, Grant Co., England) was used to adjust the solution temperature. The centrifuge (8.b - Pars Teb, Iran) and cellulose acetate membranes (0.46  $\mu$ , 47 mm, Empore Co.) were used to separate nanoparticle from solution. Fourier transform infrared spectroscopy (FT-IR, Vector 22, Bruker) is used to study the sorption mechanism of lead ions on the surface of

MHINC. The vacuum pump (DV-42N-2501, Platinum Co., USA) was used to flow the solution through the membrane in the separation of MHINC particles from lead ion solutions.

### 2.3. Procedures

#### 2.3.1. Preparation of sorbent

In order to synthesize MHINC samples, dc arc was discharged between two iron tip electrodes in distilled water under 80 V. The synthesized MHINC is characterized by SEM, TEM, XRD, VSM and DLS.

#### 2.3.2. Sorption experiments

To identify the best metal ion which can be removed by MHINC: 50 ml solution with pH=5 including 5 ppm from any of metal ions  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Ag}^+$ ,  $\text{Zn}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Mn}^{2+}$  and  $\text{Ni}^{2+}$  is separately mixed with 50 mg MHINC for 30 min at 650 rpm mixing rate. The residual concentration of metal ions was determined by the flame atomic absorption spectrophotometer.

The effects of sorption parameters including initial solution pH, sample volume, solution temperature, mixing time (contact time of MHINC with the solution of heavy metal ions), sample concentration and sorbent weight were investigated and optimized by the "one at a time" method. The adsorbed amount of metal ions onto the MHINC was calculated according to the following equation (Eq. 1):

$$\text{Removal efficiency (\%)} = \frac{C_i - C_f}{C_i} \times 100 \quad (1)$$

Where,  $C_i$  and  $C_f$  are the initial and final concentrations of the proposed ion in ppm, respectively. The equilibrium sorption capacity,  $q_e$  ( $\text{mgg}^{-1}$ ) of heavy metal ions was calculated using the mass balance equation (Eq. 2):

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

Where,  $C_i$  (ppm) and  $C_e$  (ppm) are initial concentration and the equilibrium concentration of metal ions, respectively; V (ml) is the sample volume, m (mg) is the MHINC amount.

#### 2.3.3. Effect of mixing time

The effect of mixing time on the lead ion removal was studied in different time intervals ranging from 3 min to 40 min with the initial metal ion concentration of 5 ppm. After completing of the reaction, MHINC particles were separated from solution phase and the residual concentration of lead ions adsorbed was measured.

#### 2.3.4. The effect of initial lead ions concentration

Sorption isotherms were obtained by equilibrating nano-sorbent with lead ion solutions of different

initial concentrations 5-40 ppm. After separation, the final concentrations of metal ions in the solutions were calculated.

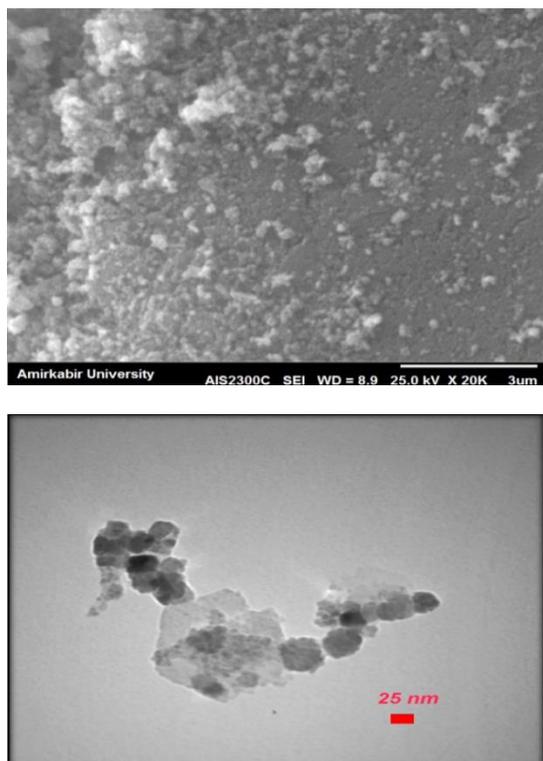
### 2.3.5. The effect of pH

Sorption amounts of lead ions for the same initial concentrations and same equilibrium times were studied as a function of pH. The initial pH values were adjusted from 2 to 6, using 0.1M HNO<sub>3</sub> and NaOH solution. After mixing for a constant time and constant stirring rate, the nanoparticles were separated and the residual concentrations of lead ions were measured.

## 3. RESULT AND DISCUSSION

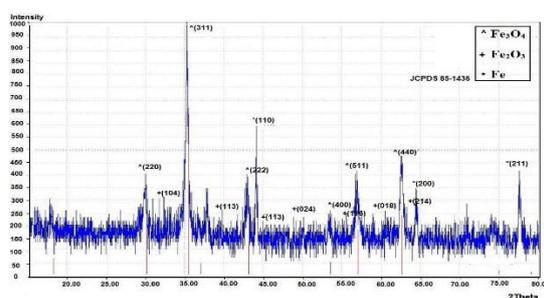
### 3.1. Properties of the prepared MHINC

The morphology and particle size of the MHINC were characterized by SEM and TEM (Fig. 1). According to the SEM image observed samples containing uniform spherical particles with average diameter about 7 nm. TEM image shows that the sample consisting the regular spherical nanoparticles.



**Fig. 1.** Electron microscope images of MHINC, a) SEM image of MHINC with enlarged 20000 times. b) TEM image of MHINC.

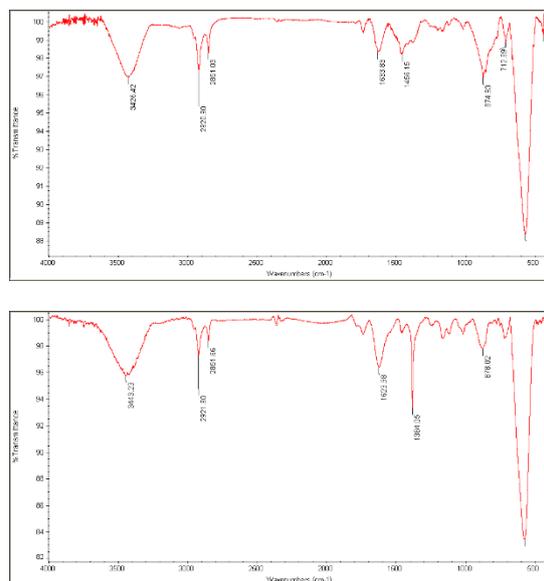
The phase composition of the synthesized sample was examined by XRD patterns (Fig. 2). The XRD patterns showed the sample consisting 56 %wt Magnetite, 30 %wt Hematite and 14 %wt zero-valent Fe.



**Fig. 2.** XRD patterns of MHINC sample synthesized in the presence of 1.2 T magnetic field.

The magnetization properties of the sample were determined by VSM. The VSM results showed that the sample shows 93 emu g<sup>-1</sup> magnetization saturation.

As an additionally study, the infrared spectroscopy was used to determine the vibrational frequency changes of MHINC functional groups. Fig. 3 shows the IR spectrums of the MHINC sample before and after contact with lead ion solution. In comparing the two spectrums, the greatest difference is the peak corresponding to the stretching vibration of functional group *O-H* that Dative bond between non-bonding electron pairs of oxygen and Pb<sup>2+</sup> ion alters the *O-H* bond energy and consequently displacement of the vibration of functional group *O-H* and another strong stretching vibration is related to *Fe-O* due to pairing with lead ions were transported.



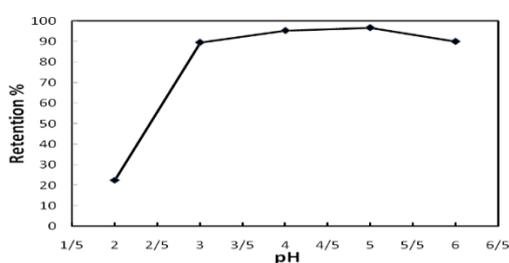
**Fig. 3.** IR spectrum, (a) Iron oxide nanoparticles, (b) Iron oxide with lead ions adsorbed on it.

### 3.2. Sorption studies

#### 3.2.1. The effect of pH

To investigate the effect of initial solution pH on the sorption of lead ions was studied in the pH

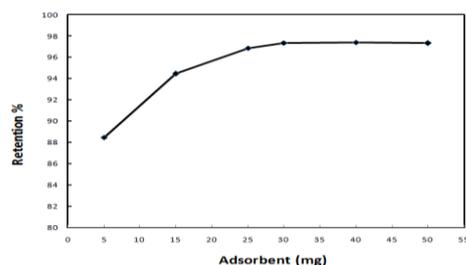
range of 2-6. The relationship between the initial pH values and the lead ions removal efficiency was presented in Fig. 4. In maximum sorption by the nanoparticles takes place at pH= 5. The results presented in Fig. 4 show that at low pH because of the high abundance of protons ( $H^+$ ) ions compared to  $Pb^{2+}$ , the amount of lead ions sorption by MHINC is decreased. In other words, some adsorption sites on the surface of MHINC is occupied by  $H^+$  ions. By increasing the pH to more than 5, the percentage of lead ion removal decreases that it is probably due to the formation of sediment of cations like  $Pb(OH)^+$  which is less likely to be attracted to the surface of the nanoparticles [17-18].



**Fig. 4.** Effect of initial solution pH on the lead ion retention.

### 3.2.2. The effect of sorbent amount

To study the effects of sorbent values on the lead ion sorption with keeping constant other factors, preconcentration were carried out with different sorbent weights at range of 5 to 50 mg. Fig. 5 shows the effect of sorbent values on the lead ion removal efficiency. As it can be seen in Fig. 5, with the increasing amount of sorbent, the percentage of retention gradually increases up to the point of 25 mg reaches to maximum amount and then remains constant. In the small amounts of sorbent, due to the saturation of the sorption sites by  $Pb^{2+}$  ions, the ion removal is not completed [16].

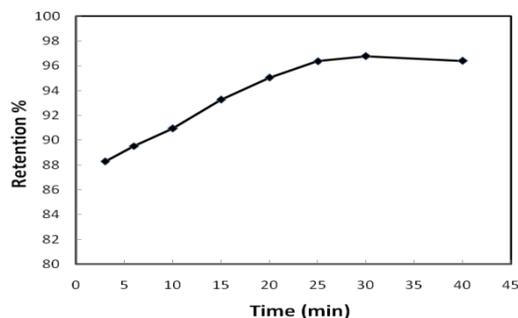


**Fig. 5.** Effect of MHINC sorbent on the lead ion removal.

### 3.2.3. The effect of contact time

The results of sorption studies as a function of contact time (mixing of lead ion solution with

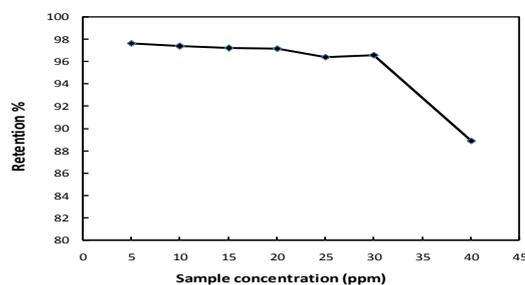
MHINC particles is shown in Fig. 6. According to the Fig. 6 the lead ion removal is completed before 30 minutes. Comparing of this results with those of the previous reports [19-21] shows that MHINC can acts as a fast removal agent for the lead ions.



**Fig. 6.** Effect of mixing time on the lead ion retention.

### 3.2.4. Sorption isotherms

Lead ions removal performance of MHINC was investigated as a function of the initial lead ion concentration (from 5 ppm to 40 ppm) in room temperature. In this study, the sorption time was fixed at 30 min. Fig. 7 shows the effect of initial ion concentration on the removal efficiency.



**Fig. 7.** Effect of initial sample concentration on the lead ion retention.

As it can be observed in Fig. 7, by increasing the initial concentration of the sample, the sorption of lead ions is decreased. The drop in the removal efficiency indicates that sorption sites on the sorbent surface become saturated [22]. The maximum sorption capacities of the MHINC for lead ions were evaluated using the sorption isotherms such as Langmuir, Freundlich and Temkin. In the Langmuir model, it is assumed that is a homogeneous surface, the sorption energy is constant and equal in all places. Sorption on the surface to be performed in certain sites, each site can only accommodate a single ion, and also monolayer sorption takes place and none of adsorbed molecules are interactive with each other [23]. Langmuir and Temkin isotherms equations are presented as follows:

$$q_e = \frac{q_m b C_e}{1 + b C_e} \quad (3)$$

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m} \quad (4)$$

Where,  $q_e$  is the equilibrium sorption capacity of the sorbent for metal ions in  $\text{mg g}^{-1}$ ,  $C_e$  is the equilibrium concentration of metal ions in ppm,  $q_m$  is the maximum amount of metal ions adsorbed in  $\text{mg g}^{-1}$  and  $b$  is the constant that refers to the bonding energy of sorption process in  $\text{L mg}^{-1}$ . The constants  $b$  and  $q_m$  can be determined from the intercept and slope of the linear plot  $C_e/q_e$  versus  $C_e$ . On the contrary, the Freundlich model is based on a reversible heterogeneous sorption. In the Freundlich model, it is assumed that the level of energy distribution is non-uniform, different pieces of the same level are not impact together [23]. Freundlich isotherm equation is presented as follows:

$$q_e = k_f C_e^{1/n} \quad (5)$$

The linear form of Freundlich equation is as follows:

$$\log q_e = \log k_f + \frac{1}{n} \log C_e \quad (6)$$

Where  $q_e$  is the equilibrium sorption capacity of the sorbent in  $\text{mg g}^{-1}$ ,  $C_e$  is the equilibrium concentration of heavy metal ions in ppm,  $K_f$  is the constant related to the sorption capacity of the sorbent in ppm, and  $n$  is the constant related to the sorption intensity. The constants  $n$  and  $K_f$  can be determined from the slope and intercept of the linear plot  $\log q_e$  versus  $\log C_e$ . The Temkin model contains a factor that interactions between the sorbent particles and adsorbed ions clearly show. Temkin isotherm can be presented as following equation:

$$q_e = \frac{RT}{b} \ln(AC_e) \quad (7)$$

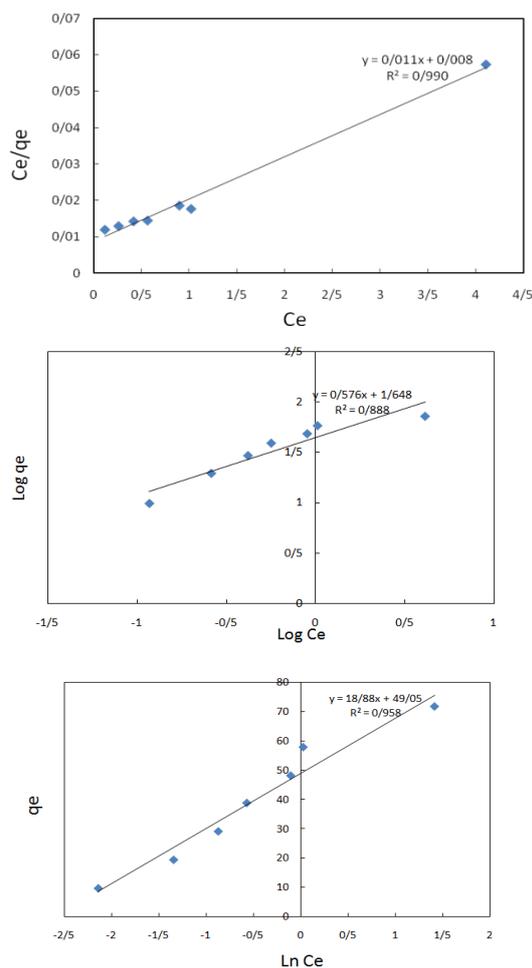
In this equation,  $\frac{RT}{b} = B$  the linear form of the Temkin isotherm equation is as follows:

$$q_e = B \ln A + B \ln C \quad (8)$$

Where  $q_e$  is the equilibrium sorption capacity of the sorbent in  $\text{mg g}^{-1}$ ,  $C_e$  is the equilibrium concentration of heavy metal ions in ppm.  $A$  is the binding constant related to the maximum binding energy in  $\text{L mg}^{-1}$ .  $B$  is the constant proportional to the heat of sorption.  $b$  is the constant in  $\text{J mol}^{-1}$ . The quantitative relationship between initial  $\text{pb}^{2+}$  ion concentration and the sorption capacity was analyzed with three different isotherm models which were shown in Fig. 8.

The calculated parameters ( $b$ ,  $q_m$ ,  $n$ ,  $K_f$ ,  $B$ ,  $b$  and  $A$ ) and linear regression coefficient ( $R^2$ ) values for Langmuir, Freundlich and Temkin models are summarized in Table 1. The Langmuir isotherm was better fitted to the experimental data. The result showed that the value of correlation coefficient ( $R$ ) for the sorption of  $\text{pb}^{2+}$  onto

MHINC was 0.99 which demonstrated the good fitting of experimental data by the Langmuir model. Based on the Langmuir model, maximum sorption capacity of  $\text{pb}^{2+}$  by MHINC was calculated  $86 \text{ mg g}^{-1}$ .



**Fig. 8.** Sorption isotherms of  $\text{pb}^{2+}$  ions by hematite/magnetite nanosorbent (a) Langmuir isotherm (b) Freundlich isotherm (c) Temkin isotherm.

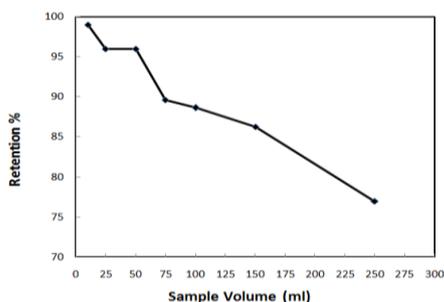
**Table 1.** The calculated parameters of Langmuir, Freundlich and Temkin isotherms.

Isotherm	Constants	$R^2$
Langmuir	$q_m = 86 \text{ mg/g}$ $K = 1.02 \times 10^{-4}$	0.99
Freundlich	$K_f = 44.49$ $bf = 0.58$	0.89
Temkin	$A = 13.42$ $B = 18.88$ $b = 131.19$	0.96

### 3.2.5. Effect of sample volume

The effect of sample solution volume on the  $\text{pb}^{2+}$  ions removal efficiency was studied by used different volumes (10- 250 ml) of aqueous solution with 25 mg MHINC sorbent. Fig. 9 shows the results of these studies. As it can be

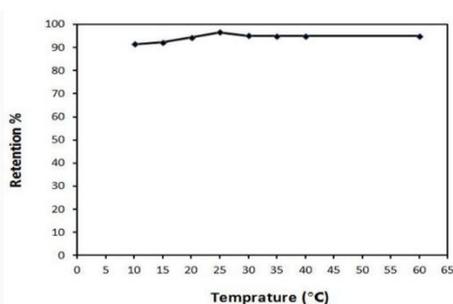
seen in Fig. 9, when the sample volume is 50 ml (the concentration of lead ions 5ppm), the removal efficiency is high.



**Fig. 9.** Effect of initial sample volume on the lead ion retention.

### 3.2.6. Effect of temperature on the $Pb^{2+}$ ions removal

To investigate the temperature dependency of  $Pb^{2+}$  ion removal, sorption studies were carried out at wide temperature range of 0 to 60 °C. The obtained results are summarized in Fig. 10. According to the presented data in Fig. 10, the ion removal efficiency is increased as the temperature is increased from 0 to 25 °C. At higher temperatures, lead ion removal does not depend on the solution temperature. The observed results show that the sorption kinetics depends on solution temperature. The kinetics rate constant of the lead ion sorption is increased by increasing the temperature. The rate constant in 25 °C is large enough to be able to remove all lead ions in the duration of 30 minutes. Applying the higher temperatures can still increase the sorption rate and causes to decrease the sorption time.

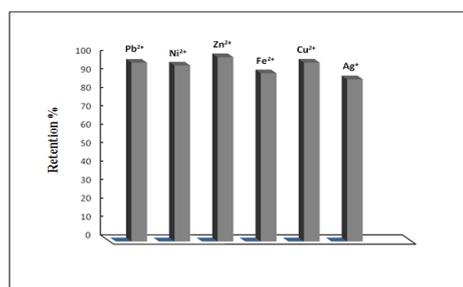


**Fig. 10.** Effect of temperature on the lead ion retention.

### 3.2.7. Application of MHINC for the removal of other ions

To investigate the ability of MHINC in the removal of other ions such as  $Cu^{2+}$ ,  $Ag^+$ ,  $Zn^{2+}$ ,  $Fe^{2+}$  and  $Ni^{2+}$ , 25 ml of 5 ppm solution of each ion at pH=5 was mixed with 25 mg of the MHINC and stirred for 30 min and then, each one was centrifuged and the residual concentration of each ion was determined (Fig. 11). Based on the

presented data in Fig. 11, all the mentioned cations can be removed with high efficiencies.



**Fig. 11.** Retention percentage of some heavy Metal ion by MHINC on the optimized conditions.

### 3.2.8. The effects of other metal ions on the sorption of lead ions by MHINC

To investigate the effect of other ions on the sorption of  $Pb^{2+}$  ions on MHINC, the removal efficiency of lead ion in the mixed solution was examined. The obtained results are shown in Table 2. The results show that the lead ions can be completely removed from water in the presence of other ions. As an additional study, the effects of  $Na^+$  and  $Mg^{2+}$  on the removal of lead and zinc ions were investigated. The obtained results showed that the presence  $Na^+$  upto 200 ppm does not any interfering effect on the removal efficiency of lead and zinc ions. The presence of  $Mg^{2+}$  in 200 ppm can only decreases the removal efficiencies of lead and zinc ions from 100% to 87% and 83%, respectively.

**Table 2.** The removal efficiency of lead ions in the presence of some metal ions with different concentrations.

Ion Concentration	$Cu^{2+}$	$Ag^+$	$Zn^{2+}$	$Fe^{2+}$	$Ni^{2+}$
5	%100	%100	%100	%97	%96
50	%80	%100	%100	-	-
150	-	-	%100	-	-

The ability of MHINC in the simultaneous removal of some metal ions ( $Pb^{2+}$ ,  $Cu^{2+}$ ,  $Ag^+$ ,  $Fe^{2+}$ ,  $Zn^{2+}$  and  $Ni^{2+}$  with initial concentrations of 5 ppm in pH=5) in the mixed solution was evaluated. The removal efficiencies for all ions were shown in Table 3.

**Table 3.** The removal efficiencies of some metal ions by MHINC in the mixed solution.

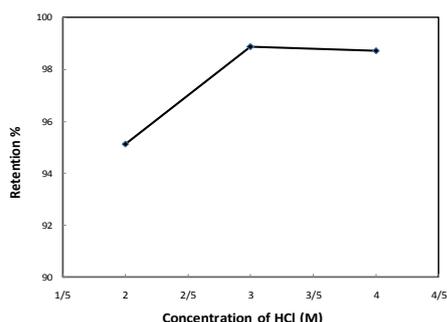
Cation	%Inhibition
$Pb^{2+}$	95.2
$Ni^{2+}$	90.34
$Zn^{2+}$	100
$Fe^{2+}$	87.78
$Cu^{2+}$	97.12
$Ag^+$	88.02

As it can be seen in Table 3, all cations can be removed from mixed solution by MHINC with acceptable efficiencies.

### 3.2.9. The desorption studies

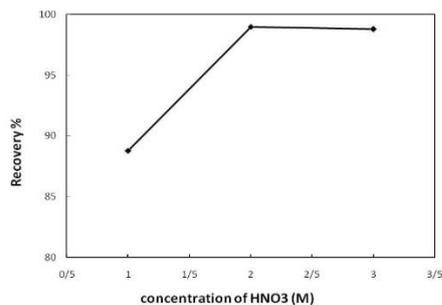
In desorption step, adsorbed ions on the surface of MHINC are eluted with a little volume of a suitable solvent. In this study, the elution of the adsorped ions was examined by hydrochlorid acid, nitric acid and mixed acid solutions. The experimental data showed that the mixed solution of hydrochloric acid aand nitric acid (2:3) can be used for the reliable desorption of lead ions.

To optimize the desorption process, the concentrations of both hydrochloric acid and nitric acid and also their volume were changed. Fig. 12 shows the effect of hydrochloric acid concentration on the extraction efficiency of lead ions. Based on the presented data in Fig. 12, hydrochloric acid with concentration of 3 M in the presence of 2 M nitric acid can be used as an efficient eluent to desorp the lead ions from MHINC surface.



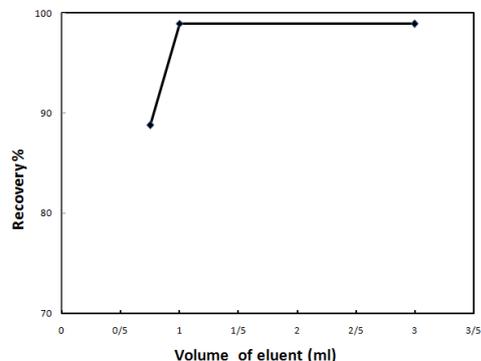
**Fig. 12.** Effect of HCl concentration on the lead ion recovery.

In the next steo, the nitric acid concentration was varied while the hydrochloric acid concentration was constant (3 M). Fig. 13 shows that the 2 M nitric acid in the presence of 3 M hydrochloric acid can be used to reliable desorb the lead ions. In the final step, some experiments were done to determine the minimum volume of the eluent for the efficient desorption of lead ions.



**Fig. 13.** Effect of HNO<sub>3</sub> concentration on the lead ion recovery.

Fig. 14 shows the obtained results. Based on the presented data in Fig. 14, 1 ml mixed solution (3 M hydrochloric acid and 2 M nitric acid) can efficiently desorb the lead ions from MHINC surface.



**Fig. 14.** Effect of eluent volume on the lead ion recovery.

## 4. CONCLUSIONS

Low voltage arc discharge in water can be used as a power full technique to synthesize Magnetite/Hematite/Iron nanocomposite (MHINC). The experimental results shows that MHINC can be acts as an efficient nano- sorbent to remove the heavy metal ions such as Pb<sup>2+</sup>, Cu<sup>2+</sup>, Ag<sup>+</sup>, Fe<sup>2+</sup>, Zn<sup>2+</sup> and Ni<sup>2+</sup>. The Langmuir isothermal model can explain the sorption mechanism of lead ions on the MHINC surface. The adsorbed ions can recover by using a small volume of HCl/HNO<sub>3</sub> mixed solution.

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