

Lead Removal from Agricultural Soil of Kurdistan Region by Fe₃O₄ Nanoparticles

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Abstract—Lead toxicity became a major concern worldwide and it is one of the most harmful pollutants in soil and groundwater. Hence, to remove lead from the soil, a high efficient technology with improved materials and system is required. This paper is a study shows removing of lead ions from soil samples, which have been taken from different sites in the Kurdistan Region, and investigated the adsorption of lead ions on high efficient adsorbent Fe₃O₄ nanoparticles. The magnetite nanoparticles of 27nm were synthesized by using a coprecipitation method and characterized by X-ray diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR) and scanning electron microscopy (SEM) equipped with energy dispersive X-ray spectroscopy (EDX). The adsorption experiments occurred at pH 8.0 under room temperature (25 °C) and the adsorption capacity was 22.8 mg/g which is 4 times higher than that of coarse particles. The correlation is measured between pH and absorbance, pH and concentration, electrical conductivity and concentration of lead ions in agricultural soil. These relationships indicate that the correlation coefficient values of ($r = -0.68, -0.70$ and $+0.83$) are statistically significant at ($\alpha = 0.05$). The limit of detection (LOD) and limit of quantification (LOQ) were found to be 0.73 mg/L and 2.44 mg/L, respectively.

Index Terms—Adsorption, adsorption capacity, chemical coprecipitation, correlation coefficient, Fe₃O₄ nanoparticles, lead removal, soil.

I. INTRODUCTION

The contamination of soil by lead ions has a serious effect on plants, animals, human being and living organism even at low concentration. It is known to be one of the heavy metals responsible to an environmental pollution by combination with other elements to form different minerals and it is widely used

in industries such as painting, newspaper, television tube, pigments, photographic materials, fuels, batteries.

The manufacturing process of these materials produces wastewaters, usually contain trace amount of lead, which accumulated in soils. The environmental pollution by lead ions causes severe damage to liver, kidney, brain cell, central nervous system in human (Southichak, et al., 2006; Gupta, et al., 1998). The standard concentrations of lead that occur naturally in surface agricultural soils in the range of 7 to 20 ppm with the average 10 parts per million (Holmgren, et al., 1993). Soils with lead levels above this range are primarily the result of lead contamination and according to the World Health Organization (WHO), the US Environmental Protection Agency (USEPA) and Indiana Department of Environmental Management (IDEM) have set standards for lead levels in garden soil or areas where children may come in contact with the soil, the maximum lead level is 400 parts per million (ppm) (Jason, et al., 2007). Due to serious threat mentioned above, research interest has been intensified on development of proper method for removing lead metal from agricultural soil.

The conventional technologies for the removal of heavy metal ions from aqueous solution include chemical precipitation, ion exchange, reverse osmosis, electrochemical treatment and adsorption (Elouear, et al., 2008). Among the different treatments described above, adsorption technology is attractive due to its merits of efficiency, economy and simple operation (Crini, 2005). Lead in soil and groundwater can be effectively removed by using a variety of conventional treatment processes. This paper looks at adsorption of lead on nano-sized magnetite. Fe₃O₄ nanoparticles have been also widely used for magnetic materials, pigments, ferrofluids and catalysts etc., (Cumbal, 2010). Synthesis of nano size iron oxide (Fe₃O₄) nanoparticles can be made by various methods such as; co-precipitation, microemulsion, hydrothermal method, and some novel methods; sonochemical synthesis, arc discharge method, microwave hydrothermal, and one-step hydrothermal process. But in this paper, Fe₃O₄ nanoparticles will synthesis via a Novel Ageing Process because of its simple procedure and pure Fe₃O₄ product (Dong, et al., 1998). The aim of the research is to removing Pb(II) ions from agricultural soil samples, which has been taken from different sites in the Kurdistan Region, by using magnetite

nanoparticles as a high efficient adsorbent through the adsorption process.

II. EXPERIMENT

A. Materials and methods

All the chemicals that used in this experiment were provided by Koya University in Kurdistan Region-Iraq. Ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) and Ferrous Sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) (Winsford industrial Estate, UK), Urea ($(\text{NH}_2)_2\text{CO}$, Scharlau chemicals, Spain), Lead nitrate ($\text{Pb}(\text{NO}_3)_2$) and Sodium hydroxide NaOH, GAINLAND CHEMICAL, UK), Nitric acid (HNO_3 , Biosolve chimie SARL, France), Hydrochloric acid (HCl), and Acetone (Sd fine-chem limited, Muumbai). All metal solutions were prepared from distilled water.

B. Synthesis of Magnetite Nanoparticles

The chemical reagents used in this preparation of magnetite nanoparticles were Urea: $(\text{NH}_2)_2\text{CO}$, Ferric chloride: $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, Sodium hydroxide: NaOH, Ferrous Sulfate: $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, and Acetone. A typical approach for this research work is as follow: 5.41 g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 3.6 g $(\text{NH}_2)_2\text{CO}$ were dissolved in 200ml distilled water in a container. After that, this solution was placed in a water bath at a constant temperature 90°C . Heating time was 3 hours. The solution turned into a kind of khaki slurry gradually and then it was cooled to room temperature. 1.99 g $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ was dissolved in the above mixture with mechanical stirring at a speed of 300 rpm for 30 min. Then, the NaOH solution (2 mol/L) was dropped into the reaction mixture until the $\text{pH} > 10$. Greenish precipitate can be observed at that time. The molar ratio of Fe (III) to Fe (II) in the observed system was nearly 2. When the pH reached greater than 10, the mixture was transferred into an ageing can with a cubage of 500 ml. Additional distilled water was added to make the ageing container full and then it was sealed by a capsule to prevent the air from entering. Finally, the container was aged at room temperature with ageing time such as 5 hr. The black magnetic precipitate was separated by filtration, followed by washing with distilled water of 500 ml and acetone of 100 ml in order. Then, the obtained powders were oven-dried at 50°C for 7 hr.

C. $\text{Pb}(\text{NO}_3)_2$ Stock solution

$\text{Pb}(\text{II})$ stock solution (50 ppm) was prepared by dissolving of lead nitrate $\text{Pb}(\text{NO}_3)_2$ in distilled water.

D. Soil Analyses

This includes;

Standard Soil Tests

To measure pH and electrical conductivity of soil samples was collected from different agricultural sites in Kurdistan Region. The analysis conducted in a soil/water mixture. By taking 2 gm of the agricultural soil of each sample which is mixed with 50ml of distilled water, allowed to be equilibrated for 5 hrs, and then pH and conductivity of the solution would be measured.

Measuring lead concentration in agricultural soil samples

This study was limited to the determination of Pb (II) levels in agricultural soil samples of selected cities located in the Kurdistan Region, namely: Site 1- Koya; Site 2- Darbandixan; Site 3- Bazian; Site 4- Shewashok (2011) and (2014); Site 5- Erbil; Site 6- Shaqlawa; Site 7- Chamchamal; Site 8- Xanaqin; Site 9- Dolly Jafayate; Site 10- Massif; Site 11- Kawer Gosk. Soil samples were collected from eleven sampling sites in each of the study areas. Samples from the selected sampling sites were obtained at a depth 0 to 50 cm from the road. A sample size of 2 gm is generally appropriate of each soil samples were collected from different agricultural sites in Kurdistan Region mixed with 5ml distilled water and 5ml concentrate HNO_3 in a conical flask. After mixing each conical flask which is covered by a watch glass placed concave up in order to reduce gas loss. By refluxing those for 10 min on a hot plate until the vapour condense on the bottom of watch glass and dripped back into the conical flask. Then soil samples were removed on the hot plate added another 5ml concentrated HNO_3 to each flask after cooled down and refluxed for 10 min. Lastly, the soil samples were mixed with 10 ml of distilled water and 5ml concentrate HCl, refluxed for another 15 min. After digesting all soil samples, the filtrate of each solution diluted up to 50 ml in volumetric flask. Then the concentration of the lead would be measured in soil samples by conducting double beam UV-Visible spectroscopy.

E. Lead Removal by Adsorption

The adsorption studies were carried out by mixing 0.05 gm of magnetite nanoparticles with lead solution extracted from soil samples, which was diluted to 50 ml. The pH of the mixture was set to the desired value by using 10M of NaOH. The content of the beaker was stirred uniformly with the help of magnetic stirrer by using magnetic bar for 20 min with 300 rpm at 25°C . The adsorbent was separated from a mixture by filtrations. Then, the amount of Pb (II) absorbed was determined by double beam UV-Visible spectroscopy. As shown by the flow chart in Fig. 1.

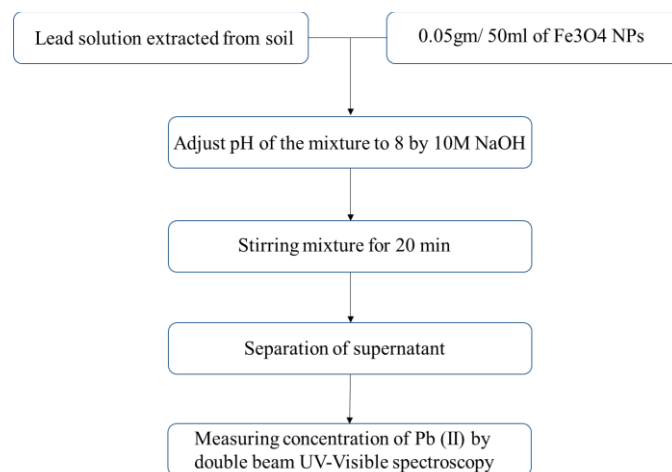


Fig. 1. Steps for removing lead from adsorption process.

III. RESULTS AND DISCUSSION

A. FTIR Analysis of Fe_3O_4 Nanoparticles

Fig. 2. Shows FT-IR spectrum of prepared Fe_3O_4 nanoparticles at room temperature. The spectrum was recorded in the range of $4000-800\text{ cm}^{-1}$. The FT-IR spectrum shows characteristic peaks. The significant absorption peaks observed at 578.12 cm^{-1} is attributed to the Fe-O bond vibration of Fe_3O_4 . The broad absorption peak observed at 3410.07 cm^{-1} reveals the stretching band of H-O-H caused by absorbing water molecules, while the absorption peak at 1618.84 cm^{-1} symbolized the bending band of adsorbed water and absorption peak at 1384.45 cm^{-1} is associated with the hydration water of Fe_3O_4 nanoparticles.

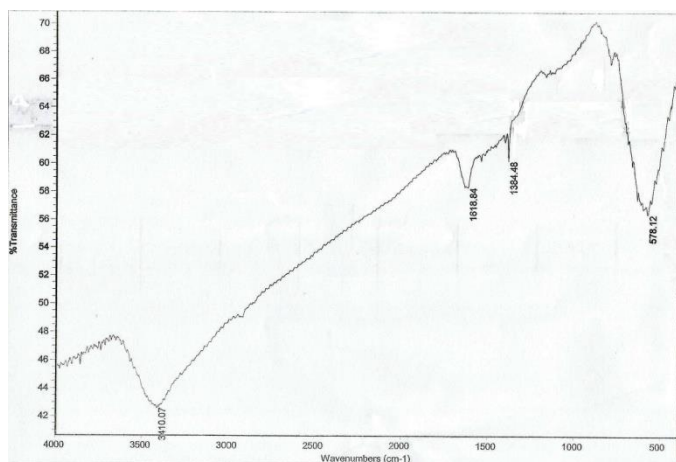


Fig. 2. FTIR spectra of Fe_3O_4 nanoparticles.

B. SEM Analysis of Fe_3O_4 Nanoparticles

The surface morphology of the synthesized magnetite Fe_3O_4 nanoparticles is studied by scanning electron micrograph. As shown in Fig. 3. The SEM images Fe_3O_4 nanoparticles with magnification of 5,000. The instrumental parameters, accelerating voltage, spot size, magnification, and working distances are indicated

SEM image exhibits the agglomeration occurred during the synthesis process. The particles are mostly circular and irregular in shape with a Nano sized range.

C. EDX Analysis of Fe_3O_4 Nanoparticles

The chemical composition of synthesized Fe_3O_4 nanoparticles was studied by using EDX analysis. Table I, shows the ratio of elements which contains weight% and atomic% for all elements and their total ratio equal to 100. Fig. 4. EDX results confirm that the presence of Fe and O in the sample.

TABLE I
CHEMICAL COMPOSITION OF IRON OXIDE NANOPARTICLES

Element	Weight%	Atomic%
O	30.57	59.18
Fe	69.43	40.82
Total	100.0	

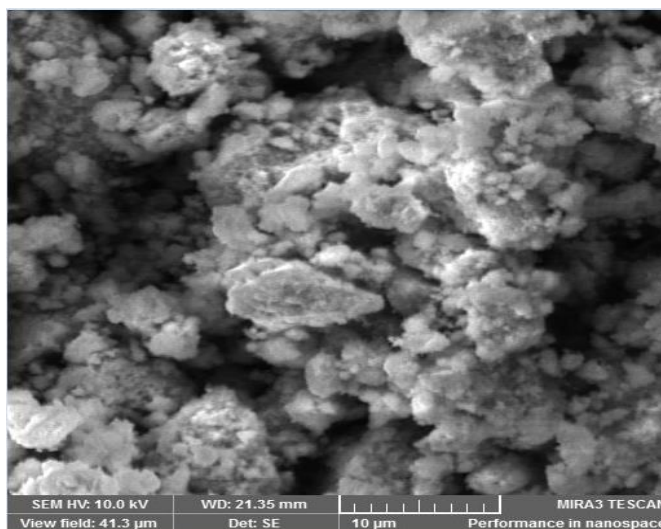


Fig. 3. SEM image of a prepared Fe_3O_4 nanoparticles.

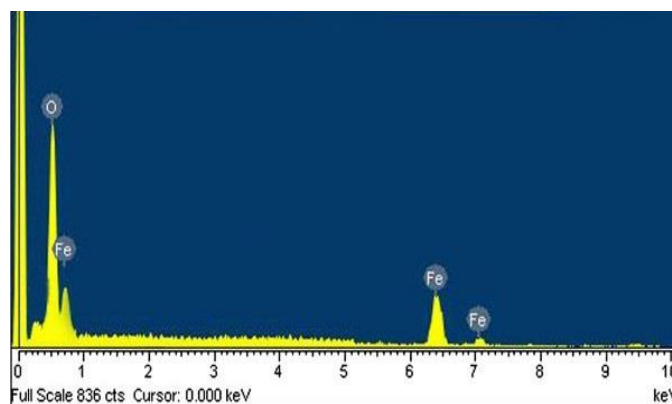


Fig. 4. Energy Dispersive X-ray indicating the chemical composition of prepared Fe_3O_4 nanoparticles.

D. XRD Analysis of Fe_3O_4 Nanoparticles

The ultrafine Fe_3O_4 powders obtained from novel ageing process were characterized by using X-ray diffraction (XRD). XRD was collected by using a Rigaku Mini with $Cu\ K\alpha$ radiation ($\lambda = 0.1541\text{ nm}$). The diffractograms were recorded in range of $10-80^\circ$. Fig. 5. Shows X-ray diffraction study of magnetite nanoparticles synthesized by chemical Co-precipitation method. From the XRD pattern, it is clear that Fe_3O_4 nanoparticles synthesized purely crystalline in nature.

All the peaks found to be the broadened and indicating the formation of small crystallites. The average particle sizes of synthesized Fe_3O_4 nanoparticles were calculated by using the Debye-Scherrer formula.

$$D = \frac{K\lambda}{\beta \cos\theta} \quad (1)$$

Where 'D' is the mean diameter particle size, 'K' is the shape factor, ' λ ' is the X-ray wavelength (0.1541nm), ' θ ' is the Bragg's angle in radians and ' β ' the full width at half

maximum in radians. The mean diameter particle size is calculated by using the above formula is 27 nm.

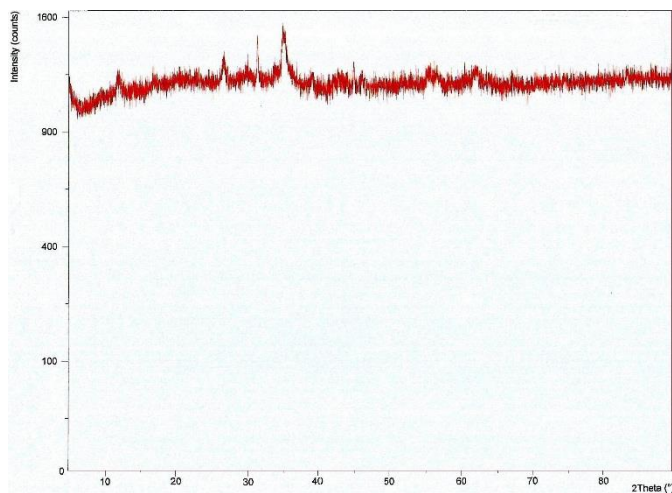


Fig. 5. XRD pattern of prepared Fe₃O₄ nanoparticles

E. Physical analysis of agricultural soil samples

Table II shows the physical properties of the soil. Soil pH was measured in a soil-water 2:50 (w/v) ratio of soil to distilled water by using pH meter according to Davey and Conyers (Davey and Conyers, 1988) while electrical conductivity was determined by the method of Chopro and Kanzar (Chopro and Kanzar, 1988).

TABLE II
PHYSICAL PROPERTIES OF AGRICULTURAL SOIL SAMPLES

Sites	pH	Ec μ s/cm
1	8.14	132
2	8.01	199
3	8.56	121
4	8.06	187
5	8.2	141
6	8.18	134
7	8.25	143
8	7.91	378
9	7.86	380
10	7.83	383
11	7.80	397

The mean pH values of all the soil samples analyzed indicate that the heavy metal-polluted soil samples had low pH values 7.80 – 7.91 relative to the pH values 8.01 – 8.56. It shows that the addition of these metals at these concentrations have lowered the pH of the soil sample. Soil pH is an important soil property, having great effects on solute concentration and adsorption in soil. High soil acidity creates

chemical and biological conditions which may be harmful to plants and soil microorganisms. That the heavy metals from automobile service centers decreased soil pH, thus increasing the soil acidity.

Soil electrical conductivity (EC) also is one of the important soil physical properties, which have a good relationship with the other soil characteristics. Measurement of apparent soil electrical conductivity is the best way of obtaining useful information about soil pollution condition because heavy metals increased soil acidity and electrical conductivity.

F. UV-Visible spectroscopy method

The UV-Visible method for the estimation of lead ions in aqueous solution was validated. Fig. 6 shows the strongest absorption peak of the prepared (50 ppm) Pb(II) stock solution at 305 nm.

The proposed method of determination of lead ions showed molar absorptivity of 1.8×10^4 l/mol/cm and exhibits its maximum absorption at 305 nm. Under the experimental conditions, the calibration graphs of the absorbance versus concentration was found to be linear in the range of 10-50 mg/L for the proposed method. The absorbance (Abs) of the prepared standard solution (10-50 mg/L) was determined at 305 nm. The mean absorbance was found to be 0.2 – 0.9. The absorbance plotted versus concentration as shown in Fig. 7. The linear regression of absorbance on concentration gave equation $y = 0.01997x - 0.0003226$ with a correlation of 0.9997.

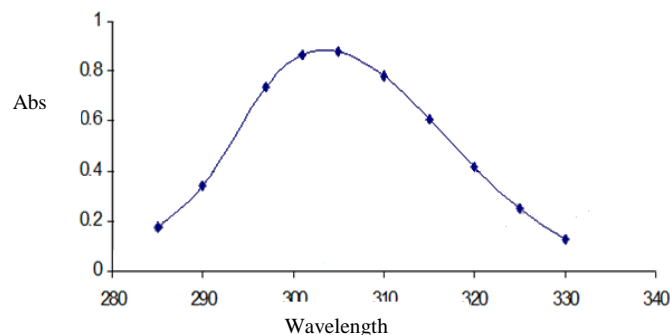


Fig. 6. Determination λ_{max} of Pb(II) ions in stock solution.

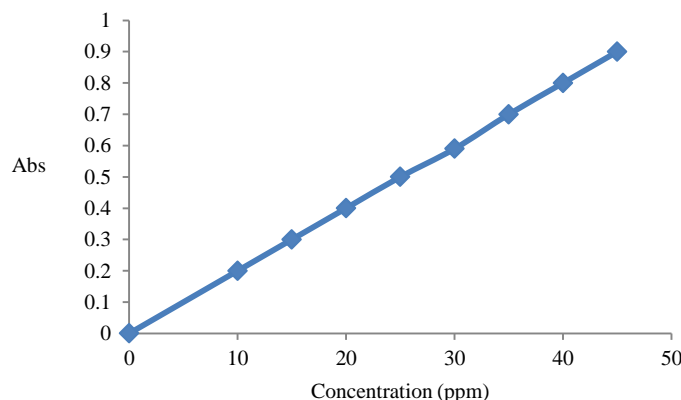


Fig. 7. Calibration curve of Pb(II) in aqueous solution at 305 nm.

G. Limit of Detection and quantification

The limit of detection (LOD) is the lowest amount of analyte in a sample, which can be detected but not necessarily quantified. The limit of quantification (LOQ) is the lowest amount of analyte in a sample. The limit of quantification and the limit of detection were determined based on equations (2) and (3) (Poonan, et al., 2011).

$$\text{LOD} = 3.3\sigma/S \quad (2)$$

$$\text{LOQ} = 10\sigma/S \quad (3)$$

Where, σ is the standard deviation of the intercept of the calibration plot and S is the slope of the calibration curve.

The limit of detection (LOD) and limit of quantification (LOQ) was found to be 0.73 mg/L and 2.44 mg/L respectively as shown in Table III.

TABLE III
VALIDATION PARAMETER FOR STANDARD SOLUTION OF LEAD

Parameter	Values
λ_{max} (nm)	305 nm
Linearity range (mg/L)	10 – 50
Molar absorptivity (l/mol/cm)	1.8×10^4
Intercept (a)	-0.0003225
Slope (b)	0.0199677
Correlation coefficient (r)	0.9997
Regression equation	$y = 0.01997x - 0.0003226$
Limit of detection (LOD)	0.73 mg/L
Limit of quantification (LOQ)	2.44 mg/L

H. UV-Visible Analysis of Pb (II) ions

Study of Pb (II) level in soil samples

The lead concentration in soil samples is collected from different agricultural sites in the Kurdistan Region. It has been measured by double beam UV-Visible spectroscopy as shown in Fig. 8. It can be observed that the lead concentration level in most of sites are in normal range except site 9, 10 and 11; also it shows that the lead concentration in site 4; (2011) was increased compare to (2014), therefore, the preconscious steps should be taken into consideration to prevent increasing the lead level in the Kurdistan Region's agricultural soil because of with the passing time, the lead level will be increases due to industrial sources, their waste products and acid rain which are threaten Kurdish health and their environmental in the future.

Study adsorption of Pb(II) ions in soil samples

Under the optimized conditions, i.e., pH 8.0 and $T = 25^\circ\text{C}$, 0.05 gm of the synthesized Fe_3O_4 nanoparticles with 27nm particle size were used for removing extracted lead ions in agricultural soil samples by stirring it with extracted lead ions from soil samples for 20 min. Then the filtrated was analyzed for remaining Pb(II) concentration in soil samples after the adsorption process as shown in Fig. 9.

The adsorption rate and available capacity of magnetite nanoparticles (adsorbent) are decreased by the diffusion limitation within the particles on a combination of organic

matter which present in agricultural soil and inorganic Fe_3O_4 particle at the Nano-sized level for its high specific area. The observed pH confirmed that the agricultural soil samples are rich with organic matter.

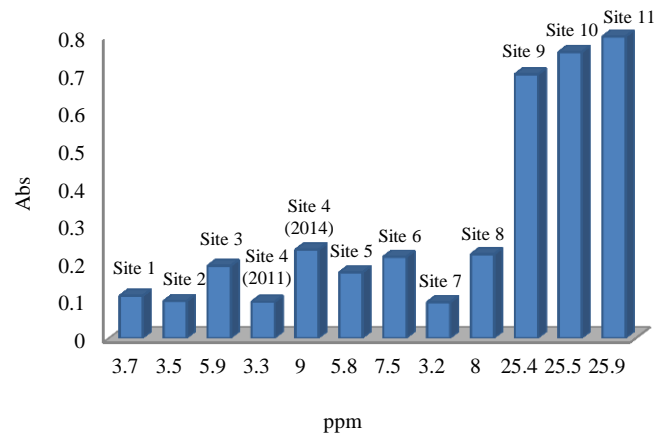


Fig. 8. Lead concentration in different sites of agricultural soil samples.

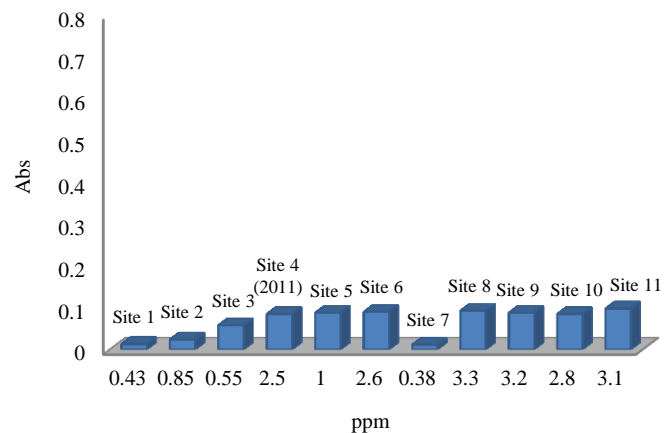


Fig. 9. Lead concentration in agricultural soil samples after adsorption process.

The adsorption rate and available capacity of magnetite nanoparticles (adsorbent) are decreased by the diffusion limitation within the particles on a combination of organic matter which present in agricultural soil and inorganic Fe_3O_4 particle at the Nano-sized level for its high specific area. The observed pH confirmed that the agricultural soil samples are rich with organic matter.

Study of Lead Removal in soil samples

Fig. 10. Shows the percent removal of Pb(II) in soil samples by magnetite nanoparticles adsorbent, and the %Removal of lead was calculated by the following equation:

$$\% \text{Removal of Pb(II)} = \frac{C_{\text{initial}} - C_{\text{final}}}{C_{\text{initial}}} \times 100 \quad (4)$$

Where; $C_{initial}$ is a concentration of Pb(II) ion (mg/L) before adsorption, and C_{final} is a concentration of Pb(II) ion (mg/L) after an adsorption process.

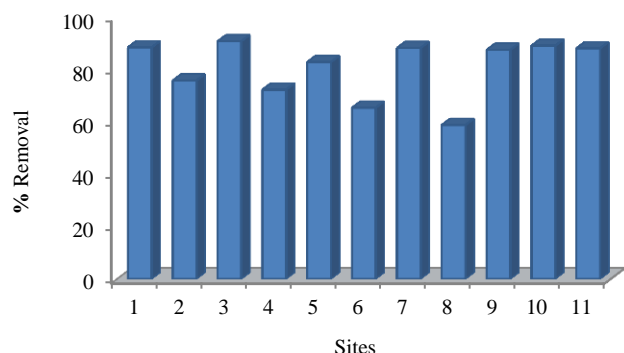


Fig. 10. Lead removal from different sites of agricultural soil in Kurdistan Region.

Study adsorption capacity of adsorbent nanoparticles for removing Pb(II) ions in soil samples

The adsorption experiments were performed in extract lead solution from soil samples at pH 8 and 25°C. The adsorption capacity (Q_e) was calculated by following equation:

$$\text{Adsorption Capacity } (Q_e) = \frac{(C_o - C_e)V}{W} \quad (5)$$

Where, C_o is the initial concentration of Pb(II) ion (mg/L), C_e is the concentration of Pb(II) ion (mg/L) at equilibrium, V is the volume of Pb(II) ion solution (L) and W is the weight of magnetite nanoparticles used. It was observed the efficiency of Fe_3O_4 nanoparticles as an adsorbent to remove the Pb(II) ions in soil samples was around 22.8 mg/g.

Study effect of pH on adsorption

The charge density of metal oxide surface is a main factor affecting the adsorption of analytes and it varies strongly with pH. Thus, pH is a very important parameter and it plays a major role for the adsorption of target compounds.

The Fe_3O_4 nanoparticles do not exhibit obvious adsorption of lead when the pH value was lower than 8.0. With increasing pH, the adsorption efficiency, increased dramatically and reached maximum when the pH was between 8.0 and 9.0. This is mainly due to the fact that negative charges were favorable for the adsorption of cationic surfactants. When pH value was around Fe_3O_4 nanoparticles isoelectric point (about 7.0) the charge density of Fe_3O_4 nanoparticles surface was very low (Zhao, et al., 2008). When the pH value was above their isoelectric point, the Fe_3O_4 nanoparticles surface became negatively charged which gave rise to the strong electrostatic attraction between the Fe_3O_4 nanoparticles surface and lead ions. But, at pH higher than 9.0, lead can precipitate as hydroxide form. Therefore the pH between 8.0 and 9.0 is favorable for the adsorption lead on adsorbent nanoparticles. Under this condition the pH of 8.0 was selected for this study.

Correlation between lead concentration and physical properties of agricultural soil.

The correlation analysis is one of the most widely statistical methods used in scientific research. In this research correlation coefficient used to determine the relationship between two different variables such as pH and electrical conductivity with absorbance and concentration. Soil pH significantly correlated with absorbance and concentrations of lead in agricultural soil. The negative correlation coefficient of ($r = - 0.68$ and $- 0.70$) is shown in Fig. 11 and Fig. 12. They indicate an inverse relationship between pH and absorbance, pH and concentration of lead in soil samples as pH increases, absorbance and concentration will decrease.

The positive correlation coefficient of ($r = + 0.83$) is observed between electrical conductivity of the soil solutions and the concentration of lead in soil samples as shown in Fig. 13. It indicates a direct relationship between electrical conductivity of soil solutions and the concentration of lead in soil samples. As the concentration of lead in soil samples increases, the electrical conductivity of soil solutions will increase.

The coefficient of determination (r^2) which is calculated for the relationship between pH and absorbance is ($r^2 = 0.46$), in percentage form indicates that only 46% of the total variation of pH could be accounted for by variation of absorbance.

The coefficient of determination which is calculated for relationship between pH and concentration is ($r^2 = 0.49$), in percentage form indicates that only 49% of the total variation of pH could be accounted for by variation of concentration.

The coefficient of determination which is calculated for the relationship between EC and concentration is ($r^2 = 0.68$), in percentage form indicates that only 68% of the total variation of EC could be accounted for by variation of concentration.

The correlation coefficient of ($r = - 0.68$, $- 0.70$ and $+ 0.83$) indicate a statistical significant linear relationship at ($\alpha = 0.05$) which exist between these variables.

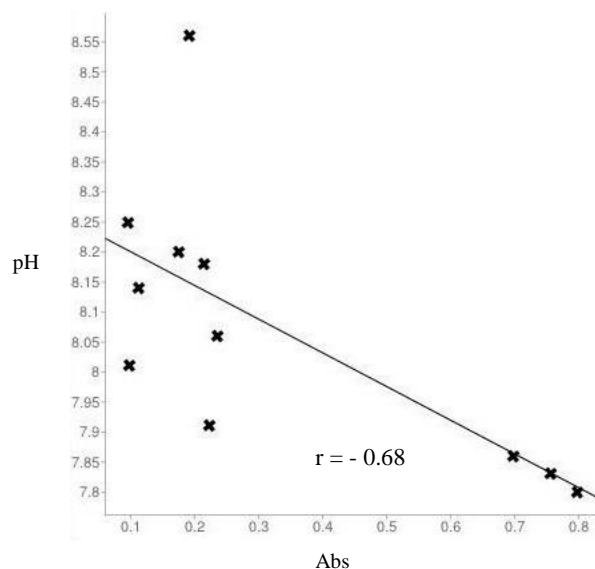


Fig. 11. Correlation between pH and (Abs) Absorbance.

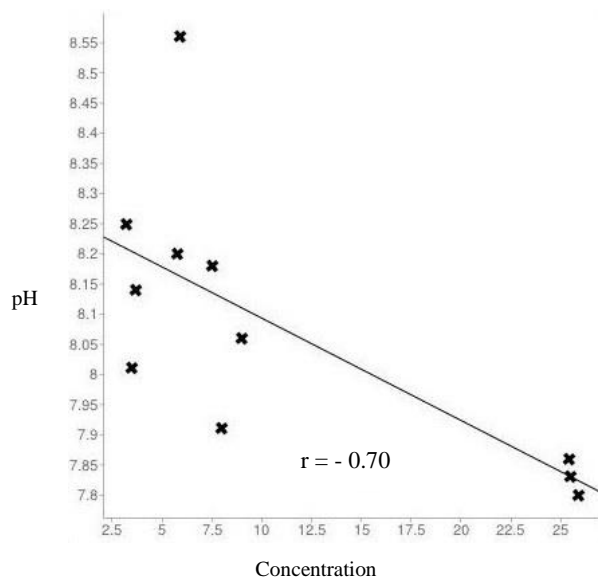


Fig. 12. Correlation between pH and concentration (ppm).

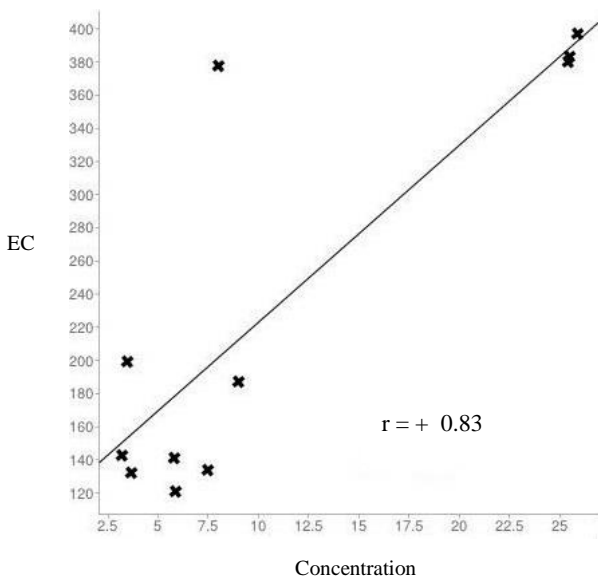


Fig. 13. Correlation between EC and concentration (ppm).

IV. CONCLUSION

Novel Fe_3O_4 nanoparticles have been synthesized successfully through the chemical co-precipitate method. FT-IR, SEM-EDX and XRD characterization techniques confirm the results. UV-Visible spectroscopy method was validated in a term linearity range. The limit of detection (LOD) and limit of quantification (LOQ) were found to be 0.73 mg/L and 2.44 mg/L, respectively. Therefore, it was used for determining the lead concentration before and after adsorption processes.

Fe_3O_4 nanoparticles were applied as an adsorbent for removal of Pb(II) ions from an extracted solution of agricultural soil samples, which was collected from different sites in Kurdistan Region at pH 8 and 25 °C temperature. The Pb(II) ions adsorbate adsorbed on the Nano-adsorbent is

relatively rapid and reaches equilibrium within 20 min stirring. The present results suggest that the adsorption capacity of Fe_3O_4 nanoparticles strongly depends on the surface area of adsorbent, pH and organic matter in agricultural soil.

The adsorption mechanism mainly depends on the electrostatic attraction under the room temperature (25°C) and pH 8. The Fe_3O_4 nanoparticles with the particle size 27 nm can be effectively used to absorb Pb (II) ions in the agricultural soil. The adsorption capacity of Fe_3O_4 nanoparticles reached to 22.8 mg/g, nearly 4 times higher than that of the coarse particles. The percentage removal of toxic Pb(II) ions is, 88.37 mg/L in Site 1, 75.71mg/L in site 2, 90.69 mg/L in site 3, 72.22 mg/L in site 4 (2014), 82.75 mg/L in site 5, 65.33 mg/L in site 6, 88.12 mg/L in site 7, 58.72 mg/L in site 8, 87.40 mg/L in site 9, 89.01 mg/L in site 10, 88.03in mg/L in site 11. Therefore, it is expected that the Fe_3O_4 nanoparticles with the fine range will be used as one of the effective, convenient and low-costing method for removal Pb(II) ions from agricultural soil. The correlation coefficient between pH with absorbance and concentration, showed strong negative linear ship and electrical conductivity with concentration of lead ions in agricultural soil, showed strong positive linear ship which was indicated as a statistical significant which existed between variables.

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