Study of Pb Ions Removal from Aqueous Solutions by a Novel Sodium Formate-Coated Magnetite Nanoparticles

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Abstract. One of the problems that continuously happen from the past ages till the present time is the contamination of the water sources with heavy metal ions; as a continuation of the many studies have been done so far to solve this problem. Novel magnetite nanoparticles (NPs) coated with sodium formate (SF-Ni$_{0.31}$Mg$_{0.15}$Ag$_{0.04}$Fe$_{2.5}$O$_4$) have been prepared using co-precipitation method. Characterization of the prepared SF-magnetite NPs was done by using spectroscopic devices (XRD), (SEM), (EDX), (FT-IR), and (AAS). From the XRD spectrum it was found that the crystal structure of the prepared SF-magnetite NPs is a cubic inverse spinel structure, which has average crystallite size, the lattice constant, and X-ray density of 28.57 nm, 8.33 Å, 5.29 g/cm$^3$, respectively. SEM images have shown that the prepared NPs have a sphere-like shape with a measured average crystallite size of 25.93 nm. By EDX spectrum the presence of the constituent elements was confirmed by giving their energy peaks (O: K$\alpha$=0.525), (Fe: K$\alpha$=6.4, L$\alpha$=0.705), (Ni: K$\alpha$=7.84, L$\alpha$=0.85), (Mg: K$\alpha$=1.25), and (Ag: L$\alpha$=2.98, L$\beta$=3.35). The attachment of the SF molecules to the magnetite NPs was proven by the FT-IR spectrum through appearing the absorption peaks in the SF-magnetite NPs spectrum at 1600 cm$^{-1}$ and 3400 cm$^{-1}$ return to the bonds (C=O) and (C-H stretch) in SF. By ASS results, adsorption of Pb ions was clearly influenced by SF coating giving removal rate (93%) at equilibrium time (10 min) in the prepared solution of Pb(NO$_3$)$_2$ salt, while for the wastewater samples the removal rate was (55%)- (100%).

Keywords: Magnetite NPs, Sodium Formate, Adsorption, Coating, Pb Ions.

1. Introduction

Pollution with heavy metals such as lead, zinc, cadmium and, others is causing serious health and environmental problems. Water contamination with Pb ions is caused by different processes as mining, manufacturing, and smelting, which result in multi-effects that negatively influence human health. The important thing for considering is that metals are resistant to degradation, which end up in living organisms. The existence of the ions of heavy metals represents a big problem because of their toxicity for many lives [1].

Various contaminants removal from wastewater was studied by utilizing different processes [2-4]. The major methods used to purify wastewater from metal ions are adsorption, ion exchange, membrane filtration, flotation, chemical precipitation, and electrolytic [5-8]. Different advantages and
functional operation parameters are presented by different nanomaterials for heavy metal removal due to the high volume surface area, surface chemistry, and a huge amount of particles, surface interactions, and magnetic separation. Their special capability of adsorbing, which are both assistants to the heavy metal ions removal, participates in these characteristics. In the present time, many studies concerned with nanomaterials have been carried out to examine, their capacity to clean wastewater from heavy metal ions and have shown very good potentiality for adsorbing metal ions from polluted water [9-12]. Adsorption is a simple, relatively low-cost and, effective method, utilized to adsorb the metal ions from wastewater. Thus, water treatment by adsorption techniques has become more efficient than by other techniques [13,14].

During the past decades, tremendous studies concentrated on magnetite nanoparticles due to their adsorption strength, high magnetization, special electrical characteristics, and low toxicity to eliminate wastewater contaminants. Magnetic nanoparticles are suitable for heavy metals adsorption from the wastewater. There is a strong magnetic moment in the iron atom due to the existence of unpaired electrons in the orbital (3d) [15]. In magnetic nanoparticles, there is a great ability for aggregation. So, surface modulation functional groups is necessary to improve the magnetite nanoparticle’s stability [13,14], to enhance their physicochemical features, and to accomplish different kinds of applications [16].

Fawzia et al. [17] have prepared magnetite NPs of (Fe3O4) by co-precipitation method, stabilized by non-ionic and cationic surfactants. The cubic crystalline structure of the prepared magnetite was confirmed by XRD. Uniform dispersity was ensured by TEM images. The adsorption efficiency of the prepared NPs for Pb, Zn, and Cd was examined by ASS by changing several factors as pH of the metal ion solution and the doses of the adsorbent. The adsorption equilibrium was achieved within (4) hr., and was highly affected by the pH of the solution and the dose of the adsorbent. Khai et al. [18] have used sludge as an adsorbent from an iron-ore area to remove Mn, Cd, Zn, Pb, and as from aqueous solutions. The capacity of adsorption of the adsorbent was examined in a set of experiments including the use of single and mixed metal solutions. It was found that the adsorption capacity of the heavy metals is ordered as Pb > As > Cd > Zn > Mn. Moreover, in the single-metal solution, the minimum adsorption capacity is (0.7-1.13) mg/g; while in the mixed-metal solution, it is ranged (0.370-1.059) mg/g. iron-ore sludge has been proved that it is an efficient adsorbent for plenty of metal ions and its promising adsorbent for toxic metal pollutants from water. Jin et al. [19] studied (Fe3O4) magnetite NPs adsorption properties for Cr(VI) and Cu(II) that are coexisted in the mixed solution. They investigated different factors, adsorbent dose; metal ions initial concentration, pH, and temperature. The results revealed that pH influenced the adsorption of the two metal ions and the optimal pH was 4.0. The increment of adsorbent dose increased the adsorption efficiency. It was found that temperature had no clear effect under the practical design. The maximum adsorption capacity of 2.0g/dm³ of Fe3O4 was found to be 18.61mg/g and 8.67mg for Cu(II) and Cr(VI), respectively in 80mg/dm³ mixed solution for both metal ions. Fe3O4 nanoparticles performed as a good adsorber and are separated easily and recovered once a magnetic field is applied to it.

Sodium formate (SF), HCOONa, is the sodium salt of formic acid, HCOOH. It’s an environmentally friendly salt and it has multiple uses as in fabric dyeing and printing processes. It is also used as a buffering agent for strong mineral acids to increase their pH, as a food additive (E237), and as a de-icing agent [20, 21].

SF has never been used in the field of heavy metal ions removal from aqueous solutions but could have a positive effect on the adsorption process due to its chemical nature; so this study was aimed toward discovering the effect of sodium formate on the adsorption capacity of the prepared magnetite NPs for Pb ions removal from different aqueous solution.

2. Materials and Methods

2.1 Materials
Ni0.31Mg0.15Ag0.04Fe2O4 Magnetite NPs were prepared by using metal sulfates, these sulfates included ferrous sulfate (FeSO4.7H2O, 99.0%), nickel sulfate -6-hydrate pure (NiSO4.6H2O, 99.0%), magnesium sulfate heptahydrate AR (MgSO4.7H2O, 99.5%), silver sulfate (Ag2SO4, 99.0%), potassium nitrate (KNO3, 99.9%), potassium hydroxide (KOH, 99.5%), and sodium formate (HCOONa, 98.0%).
2.2 Preparation

Ni$_{0.31}$Mg$_{0.15}$Ag$_{0.04}$Fe$_{2.5}$O$_4$ magnetite NPs were prepared by the co-precipitation method as used by Jawaher et al. [22]. 0.12M of the following sulfates (FeSO$_4$.7H$_2$O), (MgSO$_4$.7H$_2$O), (NiSO$_4$.6H$_2$O), and (Ag$_2$SO$_4$) were dissolved in deionized water (50ml). KNO$_3$ (1.01g) was dissolved in deionized water (10ml) and was added to the former solution, then stirring the solution for 30min. After that, a solution of KOH (1.402g was dissolved in 10 ml of deionized water) was slowly added to the last solution. The final mixture was heated until the mixture temperature reached 100°C then the reaction mixture remained at this temperature for 2h; the precipitate was cooled down to room temperature and then washed with deionized water several times and dried at 50°C overnight. Finally, the prepared magnetite NPs were sintered at 600°C for 2h.

2.3 Coating

The coating procedure was done as mentioned in ref. [22], but the ratio of magnetite NPs to the coating material was 1:6 due to the experiment. 6g of sodium formate (SA) were dissolved in 200ml of deionized water, and then 1g of magnetite NPs was added to the sodium formate solution. The last solution was mixed for 1h. The mixing process, magnetite NPs were washed with deionized water several times and left to be dry at room temperature.

3. Characterization

The crystallographic structure of synthesized magnetite NPs was examined by XRD (x-ray powder diffraction) by the instrument (XRD-6000 Shimadzu) with a Cu target, $\lambda=1.54$ Å, and angle 20=20-80 degree. The surface characteristics of the NPs were observed utilizing a scanning electron microscope (SEM TESCAN MIRA3) equipped with energy-dispersive X-ray spectroscopy (EDX). Magnetite NPs were also characterized by Fourier transform infrared (FTIR) spectrophotometer (IRPrestige-21 Shimadzu). Pb ions concentrations were measured by the atomic absorption spectrophotometer (AA-7000 Shimadzu).

4. Adsorption Process

Two aqueous solutions have been used in this process, the first one is a prepared solution of Pb (NO$_3$)$_2$ prepared to have (25ppm) of Pb ions in a bottom flask of 50ml for each sample. The second solution represents two samples of the wastewater of a battery factory located at Al-Waziria, Baghdad, Iraq; the first one is contaminated with Pb ions, sample (C), and the second one is filtered by the factory staff, sample (P). The adsorption process was done at 30°C in a water bath shaker at (100 rpm). The dosage of magnetite NPs understudy was (0.1g) for different contact times (5, 10, 15, 20, & 25) min. Magnetite NPs were removed from the solution by a magnet after the adsorption process was done. This solution was tested by atomic absorption spectrometer (AA-7000, Shimadzu) for detecting Pb ions concentrations remained after the completion of the adsorption process. The adsorption amount (qt) and the removal rate (A%) were calculated using the relation (1) and (2), respectively [18, 23].

$$q_t=(c_0-c_t)\times\frac{V}{m}$$  

$$A(\%)=\frac{c_0-c_t}{c_0}\times 100$$

Where $C_0$ is Initial Pb ion concentration in (mg/L) at time t=0, $C_t$ denotes Pb ion concentration in (mg/g) at time t, V represents Volume of water in (ml), and m= Weight of the magnetite NPs in (g).

5. Results and Discussion

XRD pattern of the synthesized magnetite NPs is illustrated in Fig. 1. The structural properties were studied in the range of (20°-80°). This diffraction pattern clearly coincides with the standard pattern of the cubic spinel magnetite phase JCPDS no. (19-0629) [24]. The remarkable peaks of the synthesized magnetite NPs were indexed to the crystal planes of the cubic inverse spinel iron oxide (Fe$_3$O$_4$), which
are found to be (220), (311), (400), (422), (511), and (440); corresponding to the diffraction angles 30.22°, 35.68°, 43.38°, 54.10°, 57.16°, and 62.56° respectively. Also, there is an appearance of extra peaks than (Fe$_3$O$_4$) peaks return to other phases of iron oxide (cubic $\gamma$-Fe$_2$O$_3$ and tetragonal $\gamma$-Fe$_2$O$_3$ (incomplete)); these phases appear as a result of the sintering process, where cubic $\gamma$-Fe$_2$O$_3$ appears at 200°C, while tetragonal $\gamma$-Fe$_2$O$_3$ appears at 600°C [25]. The average crystallite size of the synthesized magnetite NPs was calculated using Scherrer’s formula [26, 27], its value was found to be 28.57 nm.

$$D = \frac{0.9 \lambda}{\beta \cos \theta}$$  \hspace{1cm} (3)

Where $\lambda$ is the wavelength of the X-ray and $\beta$ denotes FWHM in radians.

It is worth saying that only magnetite particles having a particle size less than 30 nm exhibit super paramagnetic properties and have a large surface area that make them prone to magnetic fields and without an external magnetic field to support them; they do not become permanently magnetized. These properties are highly useful in the novel separation process development [28].

The lattice constant was calculated using Rietveld refinement and it was found to be 8.33Å. In addition, the x-ray density was calculated using the formula (4) and has a value of 5.29 g/cm$^3$ [29].

$$\rho = \frac{8M_w}{N_A a^3}$$  \hspace{1cm} (4)

Where ($M_w$) is the molecule weight, ($N_A$) is Avogadro’s number, and (a) is lattice constant.

![Figure 1. XRD pattern of the (Ni$_{0.31}$Mg$_{0.15}$Ag$_{0.04}$Fe$_{2.5}$O$_4$) magnetite NPs.](image)

Scanning Electron microscope (SEM) image of the synthesized (Ni$_{0.31}$Mg$_{0.15}$Ag$_{0.04}$Fe$_{2.5}$O$_4$) magnetite NPs at magnification of 200 nm is shown in Figure 2a. It can be noticed from this figure the homogeneity and uniformity of the synthesized NPs, they have sphere-like shape and are distributed regularly. Figure 2a also proves that the synthesized NPs are in the nanometer range have an average crystallite size of 25.93nm which is so close to that has been calculated by Debye Scherrer’s formula. The high porosity of the synthesized NPs is remarkable and that increases the capacity of ion adsorption on the nanomaterial surface. As seen from Figure 2a there are some agglomerations of nanoparticles; this is due to sintering processes. As well as the nanoparticles possess high surface energies, so they tend to agglomerate and grow to larger assemblies [30].

Figure 2b shows EDX peaks of the synthesized magnetite nanoparticles. The observed peaks appear the existence of some elements as O, Fe, Ni, Mg, and Ag. These elements have the energies spectra in keV as it follows: (O: $K\alpha=0.525$), (Fe: $K\alpha=6.4$, $L\alpha=0.705$), (Ni: $K\alpha=7.84$, $L\alpha=0.85$), (Mg:
Kα=1.25), and (Ag: Lα=2.98, Lβ=3.35. There is no Kα for Ag in the figure since it appears at 22.16 keV and the devices limited to 10 keV). There are other spectra than the spectra of the constituent elements identified at the energies (2.3 and 3.3) keV. These are false peaks the appeared in the EDX spectra because of the automatic peak identification process. This process is sensitive to noise in the X-ray continuum that forms the spectral background because random groupings of background counts can mimic a characteristic peak [31].

Figure 2. (a- SEM image, b-EDX spectra) of the prepared magnetite NPs.

Figure 3 demonstrates the FT-IR absorption bands for the prepared magnetite NPs. In figure 3a for bare magnetite NPs there are strong characteristics, bands, at around 600 cm\(^{-1}\) due to (Fe-O) bond; this proves that the main phase of the synthesized NPs is the magnetite (Fe\(_3\)O\(_4\)) of spinel-type structure [16]. These characteristic peaks can be attributed to the lattice absorption of iron oxide [32]. There is also a small absorption band at 2360 cm\(^{-1}\) can be attributed to the CO\(_2\) vibration. The broad absorption band at 3433 cm\(^{-1}\) indicated the existence of surface hydroxyl groups (O-H stretch) [16].

Figure 3b represents the FT-IR spectrum of (SF). Two characteristic absorption bands have been noticed. The first band is broad (1400-2000) cm\(^{-1}\) and may attribute to the bond (C=O) stretch. The other band is medium and sharp at around (3000 cm\(^{-1}\)) may attribute to the bond (C-H) stretch. Figure 3c represents the FT-IR spectrum of SF-coated magnetite NPs. A band has been appeared at around (1600 cm\(^{-1}\)) may concern to the (C=O) functional groups present in SF. In addition there is a band at around (3400 cm\(^{-1}\)) which is a boarder and more intense than those of the bare magnetite NPs (Figure 3a), can be attributed to (C-H) bond stretch in SF which, proves that prepared magnetite NPs were successfully coated with SF.
Figure 3. FT-IR spectra for a- bare magnetite NPs, b- SF, c- SF-coated magnetite NP

Table 1 lists the concentration (Cₜ) mg/ml, amount (qₜ) mg/g, and removal rate (A%) values of Pb ions of the prepared SF-magnetite NPs. As shown by Figure 4, qt firstly increased then settled at approximately (11 mg/g) in (10 min) which represents the equilibrium time. The removal rate (A%) as has been seen by Table 1 and Figure 4 is high (93%), indicating the high efficiency of these NPs. This performance can be attributed to the ionic bond in SF that is easily broken in the solution emptying Na ions site. So the molecule of SF became a seeker for other cations in the solution and picks Pb ion rather than Na ion because Pb ion radius is bigger than Na ion radius so the selectivity for adsorbing Pb ions from the solution is higher than for other cations in the solution [33].

Table 1. Concentration, amount of Pb ions, and removal rate of the prepared SF-magnetite NPs.

| Time (min) | Cₜ (mg/ml) | qₜ (mg/g) | A%   |
|-----------|------------|-----------|------|
| 5         | 0.0039     | 10.4542   | 84.4172 |
| 10        | 0.0016     | 11.5906   | 93.5936 |
| 15        | 0.0017     | 11.5220   | 93.0397 |
| 20        | 0.0015     | 11.6164   | 93.8015 |
| 25        | 0.0016     | 11.5725   | 93.4475 |

The adsorption of Pb ions from the wastewater samples (C and P) was done at the same conditions used before, but the time has been used is (10 min.). Table 2 lists the concentration of Pb ions (mg/ml), adsorption amount (mg/g), and removal rate of Pb ions from wastewater. The SF-magnetite
NPs showed an excellent removal rate with both samples giving (55%) for (C) and (100%) for (P). The contaminated wastewater sample (C) could have other particles that affect the removal of Pb ions since the prepared NPs have already shown a great capacity to adsorb Pb ions from a solution contains 25 ppm of Pb ions as has been proved in the above paragraph giving removal rate (93%). So the prepared SF-magnetite NPs could be a possible good adsorbent for other heavy metals in special and pollutants in general.

Table 2. Concentration, adsorption amount, and removal rate of Pb ions from wastewater of the prepared SF-magnetite NPs.

| Wastewater sample | C₀ (mg/ml) | Cₜ (mg/ml) | qₜ (mg/g) | A%  |
|-------------------|------------|------------|-----------|-----|
| C                 | 2.6127     | 0.0012     | 0.7198    | 55.100 |
| P                 | 0.2185     | 0           | 0.0011    | 100  |

6. Conclusion

SF-coated magnetite NPs (SF-Ni₀.₃₁Mgo.₁₅Ag₀.₀₄Fe₂.₅O₄) have been prepared by the co-precipitation method. The crystal structure of the prepared NPs was confirmed by XRD and, it was matched with the standard pattern of the inverse spinel cubic iron oxide (Fe₃O₄) and have average crystallite size of 28.57 nm, the lattice constant of 8.32582 Å, and x-ray density of 5.2890 g/cm³. The size of the prepared NPs was in the nanometer range as clarified by the SEM images and has an average crystallite size of 25.93 nm. By EDX spectra, the presence of the constituent elements was confirmed. The attachment of the SF molecules to the nanoparticle surface was proven by FT-IR spectra analysis. For adsorption of Pb ions from the prepared Pb (NO₃)₂ solution, a great adsorption capacity was shown by the prepared SF-magnetite NPs. That giving an adsorption amount (11.60 mg/g) that corresponds to the removal rate (93%) at equilibrium time (10 min); while for adsorption of Pb ions from the wastewater samples (C and P). The prepared NPs showed an excellent removal rate for adsorbing Pb ion equals to (55% for C) and (100% for P). It was concluded that the crystal structure of SF has played an important role in the process of adsorption giving more sites to be filled by Pb ions; making the prepared NPs surface a possible adsorbent for other pollutants.
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