



Chemical Studies on the Preparation of Magnetic Nanoparticles Coated with Glycine and its Application for Removal of Heavy Metals

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<http://dx.doi.org/10.13005/ojc/320324>

(Received: May 22, 2016; Accepted: June 30, 2016)

ABSTRACT

The aim of this study is the preparation of magnetic nanoparticles and coating with glycine to remove heavy metals such as Cu^{+2} . The magnetic nanoparticles were prepared by co-precipitation method using ferrous sulphate and potassium nitrate in presence of potassium hydroxide. Different instrumental analysis such as XRD, TEM, SEM and EDAX were used to study the magnetic nanoparticles which produced and comparing it after coated with glycine. The optimum conditions which reflect the high efficiency of removal are pH 10, concentration of the heavy metal 200 ppm, dosage 0.05 g and for 24 h duration time. Therefore we recommend using magnetic nanoparticles coated with glycine for removal of heavy metals.

Keyword: Magnetic nanoparticles, glycine, X-ray diffraction, Fe_3O_4 , co-precipitation, heavy metals.

INTRODUCTION

With the rapid development of nanotechnology, magnetic nanoparticles are currently studied widely. magnetic nanoparticles have attracted much attention because of their unique magnetic properties, small size, low toxicity, and widespread application, Iron oxide NPs are one of the most common NPs that could find their way into the water system because of their use in water and soil treatment¹.

Nanoparticles are good building blocks for developing high-capacity sorbents with modification

ability to enhance their affinity and selectivity for purification of contaminated waters. Application of nanoparticles (NPs) as novel adsorbents for removal of pollutants is gaining research interest².

Co-precipitation is the most conventional method and is also used by several commercial production plants for the synthesis of magnetic or black iron oxides. there is problem associated with particles in this size range is their intrinsic instability over longer periods of time. Such small particles tend to form agglomerates to reduce the energy associated with the high surface area to volume ratio of the nanosized particles³.

Moreover, naked metallic nanoparticles are chemically highly active, and are easily oxidized in air, resulting generally in loss of magnetism and dispersibility, coating helps not only in protecting the core shell but is also used in addition of functional groups for specific pollutant removal in water treatment⁴.

Generally, magnetic NPs are surface modified with carboxyl, hydroxyl and amino groups for their specific interactions⁵, The synthesis of magnetite nanoparticles has been intensively developed not only for its fundamental scientific interest but also for many technological applications, the use of magnetite nanoparticles as adsorbents in water treatment provides a convenient approach for separating and removing the contaminants by applying external magnetic fields. Bare magnetite nanoparticles are susceptible to air oxidation and are easily aggregated in aqueous systems⁶. Thus, for the application of these nanoparticles in various potential fields the stabilization of the iron oxide particles by surface modification is desirable. The magnetic structure of the surface layer, which is usually greatly different from that in the core of the nanoparticles, can have a notable effect on the magnetic properties of nanoparticles⁷.

EXPERIMENTAL

Chemicals and materials

Iron (II) sulphate heptahydrate, ferrous sulphate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), M.wt=278.01 g mol⁻¹ (98%), potassium nitrate (KNO_3) M.wt=101.1032 g mol⁻¹, potassium hydroxide (KOH) M.wt=56.11 g mol⁻¹, were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China), Glycine ($\text{NH}_2\text{CH}_2\text{COOH}$), sodium hydroxide (NaOH), hydrochloric acid (HCl), copper Sulphate (CuSO_4), were purchased from BDH Chemicals Ltd. (Poole, UK) and used without further purification. Cylindrical rod magnets (40 mm diameter x 40 mm thick) for settlement of magnetic nanoparticles was purchased from Magnet Expert Ltd. (Tuxford, UK). Distilled water was employed for preparing all the solutions and reagents.

Instrumentation

Magnetic stirrer and heater from Fisher Scintifi Co Ltd (Shanghai, China). Oven from Memmert (Nuremberg, Germany). PH meter from

Hanna Instruments (Cluj, Romania). Balance from Mettler Toledo Model JB1603c/FACT (Greifensee, Switzerland). Sonicator UltraSonic bath from wiseclean Model WUC-D10H (Wonju, Korea). UV-VIS Spectroscopy Thermo Fisher Scientific, GENESYS 10S VIS (Madison, USA). X-ray diffraction patterns (XRD) were obtained using Bruker diffractometer D8-advance $\text{CuK}_{\alpha 1}$ -radiation (Coventry, UK). The transmission electron microscopy (TEM) came from JEOL Ltd. (Welwyn Garden City, UK). Scanning Electron Microscope (SEM) with unit Energy Dispersive X ray (EDAX) analysis, JEOL JSM 6390 LA Analytical(Tokyo, Japan).

Preparation of magnetic nanoparticles MNPs

Magnetic nanoparticles were prepared as described else where by Abu Bakar *et al.*[2]. 1.67g of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, dissolved in 50 mL of distilled water, 1.01 g of KNO_3 dissolved in 10 mL of distilled water, and 2.5 M of KOH were prepared. Potassium nitrate solution was added to $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ solution and stirring was continued for 30 min. Then, 10 mL of KOH solution (2.5 M) was slowly added to the above solution. The reaction mixture was heated to 100°C and maintained at this temperature for 2 h. The mixture was cooled down to room temperature, and the black precipitate was repeatedly washed with distilled water, and allowed to dry at 50°C over night. The weight of the prepared MNPs using both techniques was measured.

Coating of MNPs with glycine

One gram of glycine was dissolved in 50 mL of distilled water. Then, 1 g of the prepared MNPs was added to the previous solution. The mixture was sonicated for 2 h. After that the magnetic nanoparticles coated with glycine was washed with distilled water and they were dried at room temperatures for 24 h.

Characterization of the prepared materials

Characterizations of the fabricated bare MNPs and MNPs-Gly were carried out using X-ray diffractometer (XRD) to determine the crystalline structure of the particles. The transmission electron microscopy (TEM) was used for size investigation, scanning electron microscopy (SEM) for surface morphology analysis, energy dispersive X-ray analysis (EDAX) to the compositional analysis.

Removal of heavy metals

The optimum condition for removal of heavy metal Cu^{+2} ions by the magnetic nanoparticles was investigated in aqueous solution at 25°C , chemical parameters were studied as the following

Effect of different pH of solution

We studied the effect of different pH (2, 4, 6, 8, 10), where the mixture was adjusted to certain pH with NaOH or HCl and mixed by ultrasonication several minutes. using 10 ml of solution that contain Cu^{+2} ions, its concentration 800 ppm, separately and with 0.001 g of MNP, on 700 rpm magnetic stirrer, for 1 h.

Effect of different concentrations of heavy metals

We studied the effect of different concentrations (200, 400, 600, 800, 1000 ppm), at optimum pH that we studied, using 0.001 g of MNP, for 1 h.

Effect of different dosages of MNPs and Gly-MNPs

We studied the effect of different dosages of magnetic nanoparticles (0.001, 0.002, 0.005, 0.01, 0.05 g), at optimum pH and concentration that we studied.

Effect of different contact time

We studied the effect of different contact time (30, 60, 120, 180 and 24 h), at optimum pH, concentration and dosage that we studied.

RESULTS AND DISCUSSION

Preparation of magnetic nanoparticles (MNPs)

The aim of this study was to fabricate

magnetic nanoparticles in order to use them for removal of heavy metals. The reasons for choosing this types of nanoparticles are because they are easy to separated from the solution by using external magnet, and easy to fabricated. In this study, two different methods were utilised to prepare MNPs, which will be discussed in the following see there

Figure 3.6 shows the prepared magnetic nanoparticles using second method in solution (A), and after separation using external magnet. Figure 3.6 (C) shows the dried magnetic nanoparticles. The prepared magnetic nanoparticles were characterized using different techniques which will be discussed in the following sections.



TEM analysis

TEM micrographs of the prepared Fe_3O_4 nanoparticles are shown in Figure 3.1. The TEM images reveal that Fe_3O_4 nanoparticles are similar in shape and appear to be uniformly dispersed and had cube shape. It clearly showed that they have distinctive outlines square.

SEM-EDAX analysis

Surface morphology of Fe_3O_4 was studied using SEM analysis, as can be seen in Figure 3.2. that shows cube shaped crystals structure of Fe_3O_4 . can find that most of the particles are roughly cube and aggregate together because of their high surface energy and adhesion.

Figure 3.3 show The EDAX spectrum that shows iron and oxygen. It reveals that the iron was from magnetic Fe_3O_4

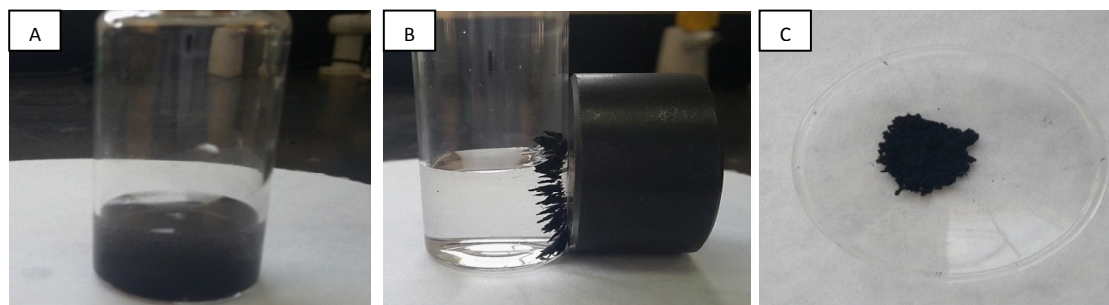


Fig. 1: Shows the prepared MNPs using second method in solution(A), after separation using external magnet, and (B) the formed dried MNPs (C)

The elements of Fe and O can be observed in the EDAX pattern, These results demonstrate the purity of the synthesis results.

Table 3.4 shows the composition components of the formed Fe_3O_4 where the percentage of mass

of O is 40.64%, and Fe is 59.36%, while the atom percentage of O is 70.50%, and Fe is 29.50%.

XRD analysis

Figure 3.4 shows the XRD spectrum of the prepared magnetic nanoparticles using second method, XRD pattern of the prepared Fe_3O_4 using

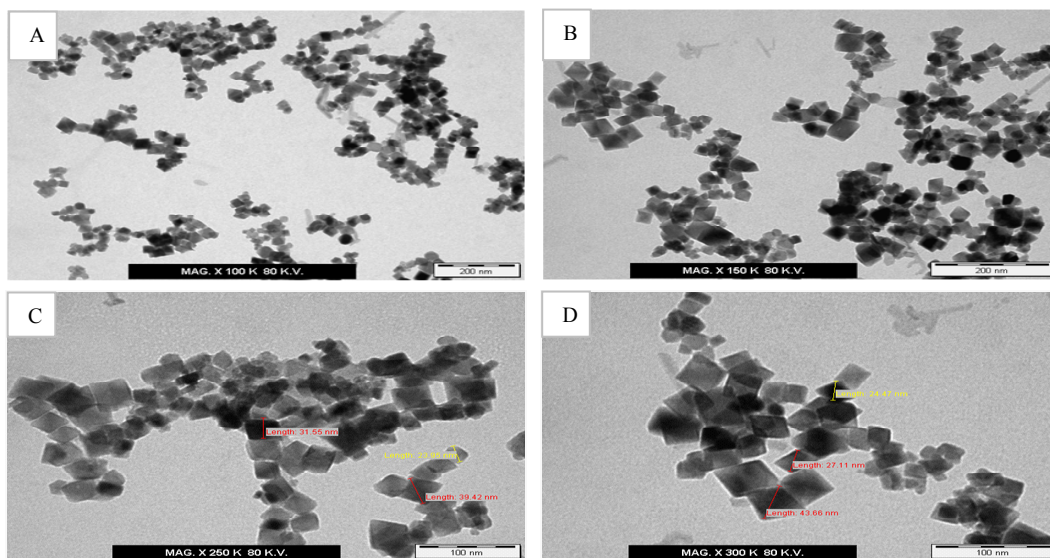


Fig. 2: TEM images of Fe_3O_4 magnetic nanoparticles at different magnifications

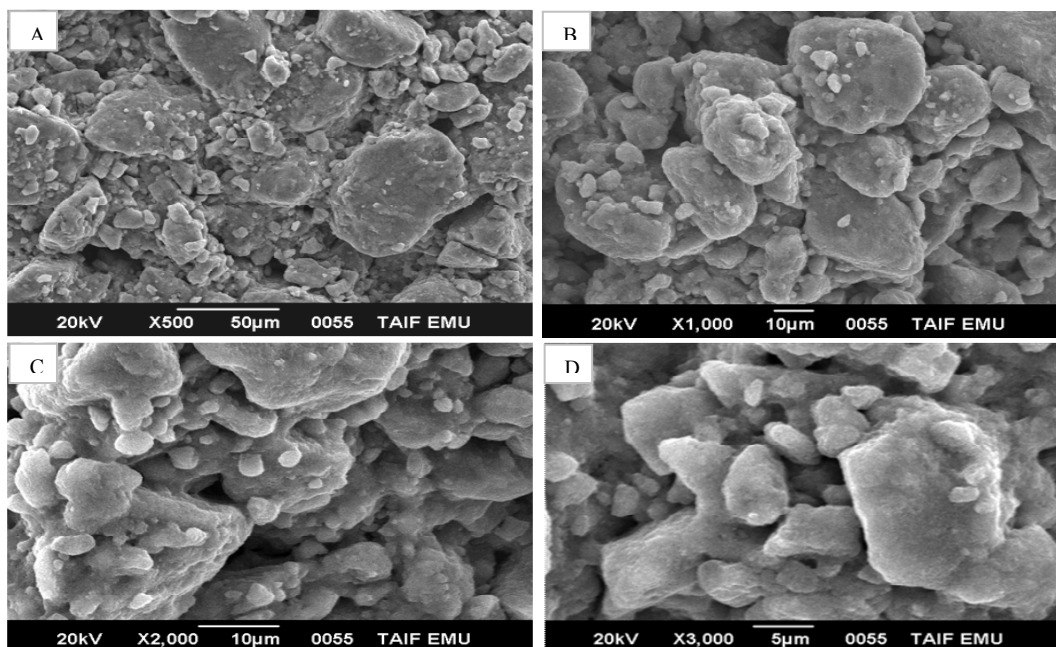


Fig. 3: SEM analysis of Fe_3O_4 magnetic nanoparticle at different magnifications

Table 1: The composition components of the formed Fe_3O_4 using EDAX analysis

Element	Mass%	Atom%
O K	40.64	70.50
Fe K	59.36	29.50
Total	100.00	100.00

second method shows six characteristic peaks at 30° , 35° , 43° , 53° , 57° , and 62° were corresponding to the (220), (311), (400), (422), (511), and (440) crystal planes of a pure Fe_3O_4 with a spinel structure. The peaks indicating that Fe_3O_4 with a spinel structure and no characteristic peak of impurities are detected in the XRD pattern[8]. The XRD results also confirmed the purity of the products via the absence

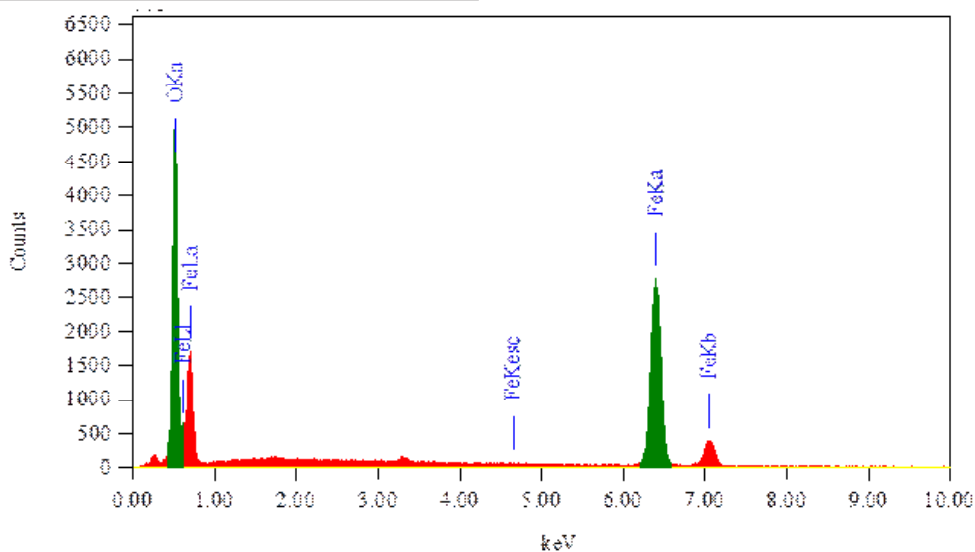


Fig. 4: Energy dispersive analysis

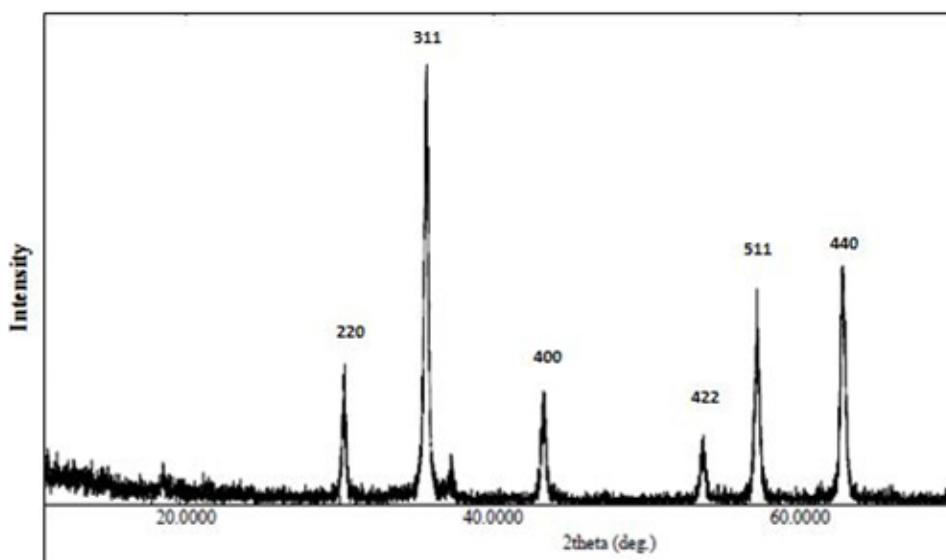


Fig. 5: X-ray diffraction patterns of Fe_3O_4 magnetic nanoparticles

Table 2: The composition components of the formed Fe_3O_4

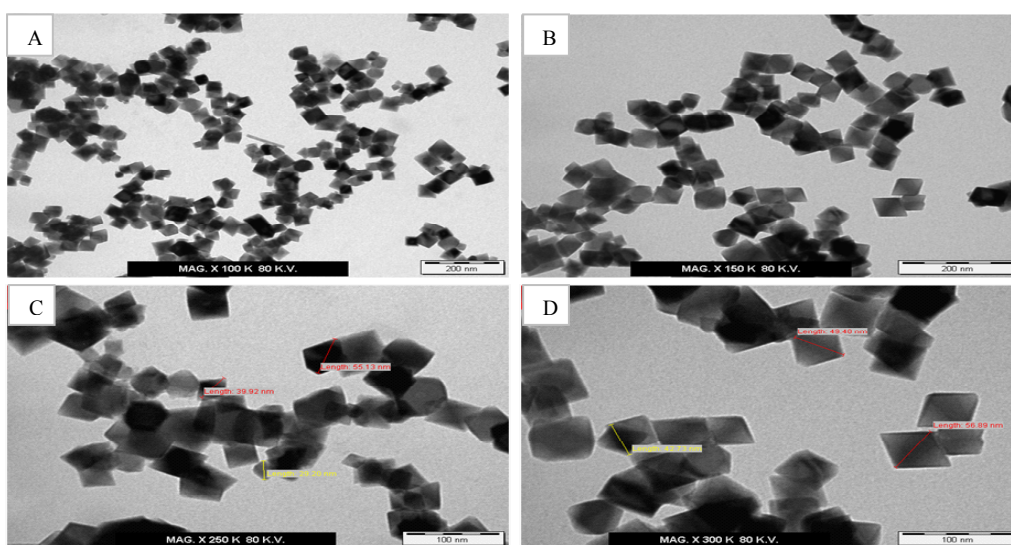
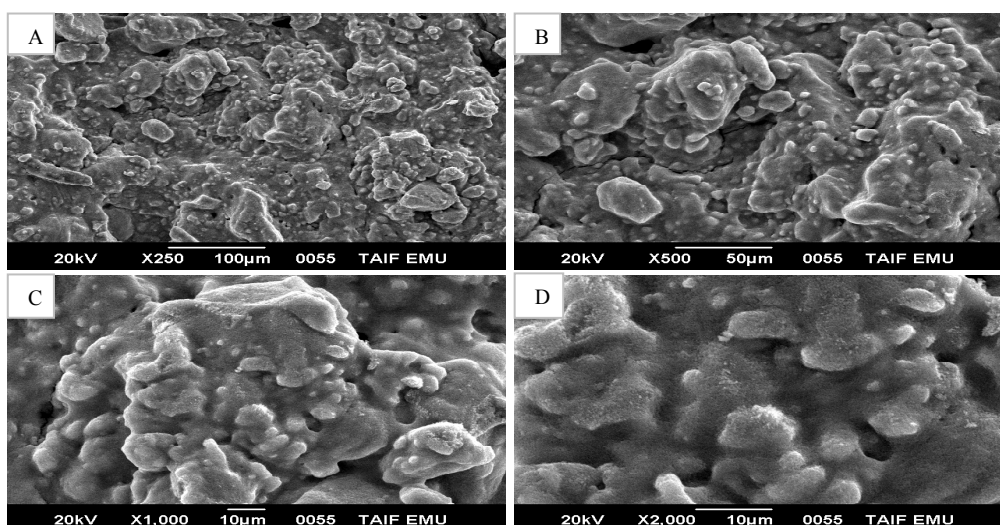
Element	Mass(%)	Atom(%)
C K	17.63	33.91
O K	31.06	44.86
Fe K	51.31	21.23
Total	100.00	100.00

of other phases of iron oxide such as maghemite or hematite in sample

Coating of magnetic nanoparticles MNPs with glycine

Surface modification of magnetic nanoparticles is a challenged key for different applications and can be accomplished by physical/chemical adsorption of organic compounds[9].

Coating of magnetic nanoparticles can decrease the toxicity of MNPs through decreases the

**Fig. 6: TEM images of Fe_3O_4 magnetic nanoparticles coating with glycine****Fig. 7: SEM analysis of Fe_3O_4 magnetic nanoparticle coating with glycine**

saturation magnetization and increases the particle volume. It is important to consider that smallest particles present highest adsorption capabilities and high magnetizations optimize the magnetic

separation. To avoid these constraints, an alternative to polymer coatings is the chemical modification of the magnetic nanoparticle surface by small functional molecules. In this way, easily adsorbed onto the iron

Table 3: Effect of different pH on the removal of Cu⁺² using Gly-MNPs

PH	%Up take of MNPs	%Up take of Gly- MNPs
2	41.25	50
4	63	65
6	75.1	85
8	80	97.5
10	89	98

Table 4: Effect of different concentrations on the removal of Cu⁺² using Gly-MNPs

Conc. (ppm)	%Up take of MNPs	%Up take of Gly- MNPs
200	88	100
400	82.5	100
600	78	100
800	65	100
1000	63	87

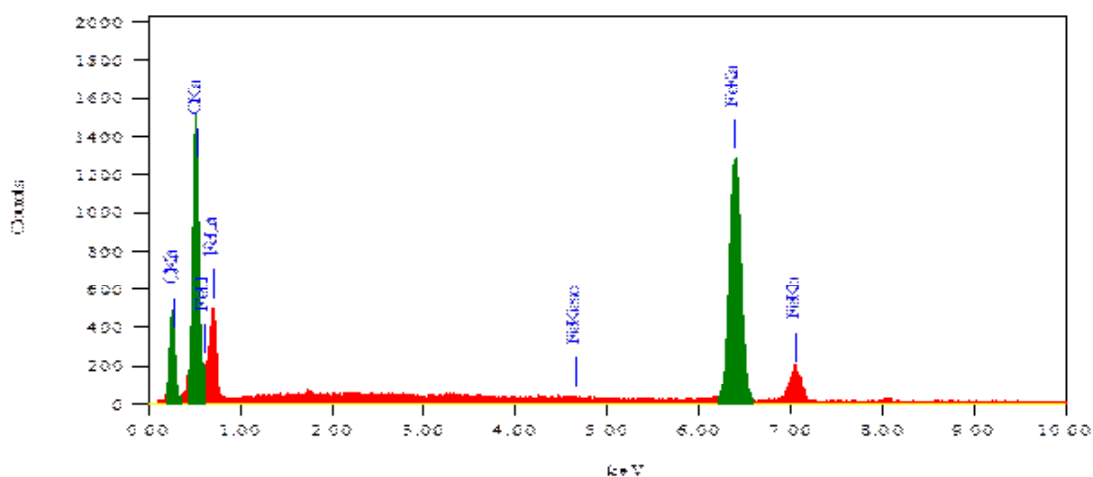


Fig. 8: Energy dispersive analysis of X-ray spectrum (EDAX) of Gly-MNPs

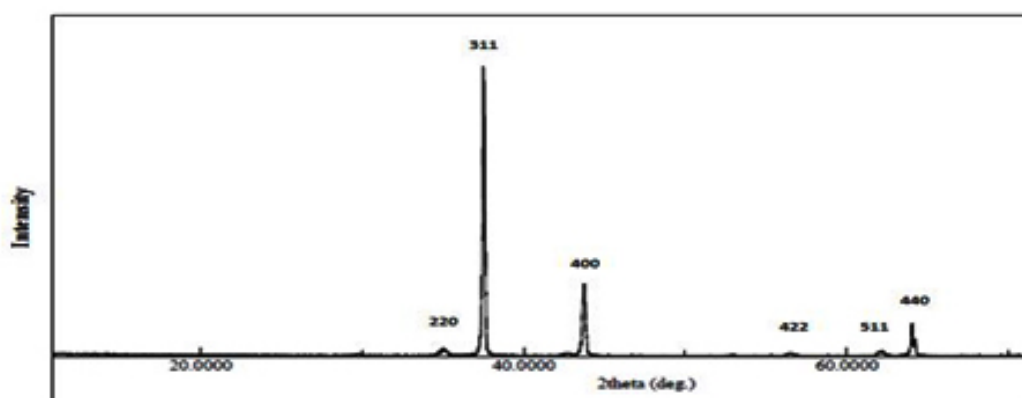


Fig. 9: X-ray diffraction patterns of coated magnetic nanoparticles

Table 5: Effect of different dosages on the removal of Cu²⁺ using Gly-MNPs

Dose (g)	%Up take of MNPs	%Up take of Gly- MNPs
0.001	46.66	62.4
0.002	54.6	77.9
0.005	64	86.8
0.01	71.7	93
0.05	88	100

oxide surface, and NH₂ groups at surface that could interact with the bio-environment. In fact, the potential of amine functionalized magnetic nanoparticles was already evidenced for magnetic removal of organic contaminants and heavy metals in water treatment¹⁰.

TEM analysis

TEM measurements showed that synthesis yields nearly cubic Gly-MNPs and regular in shape, and close in size dramatically. Moreover, there is

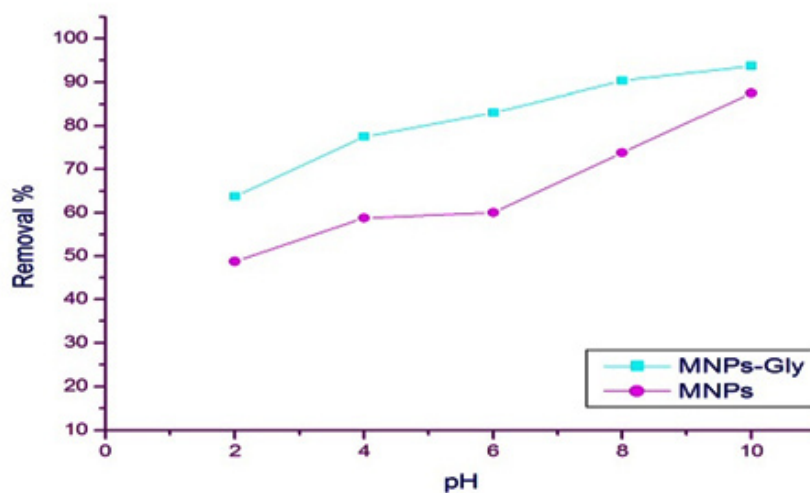
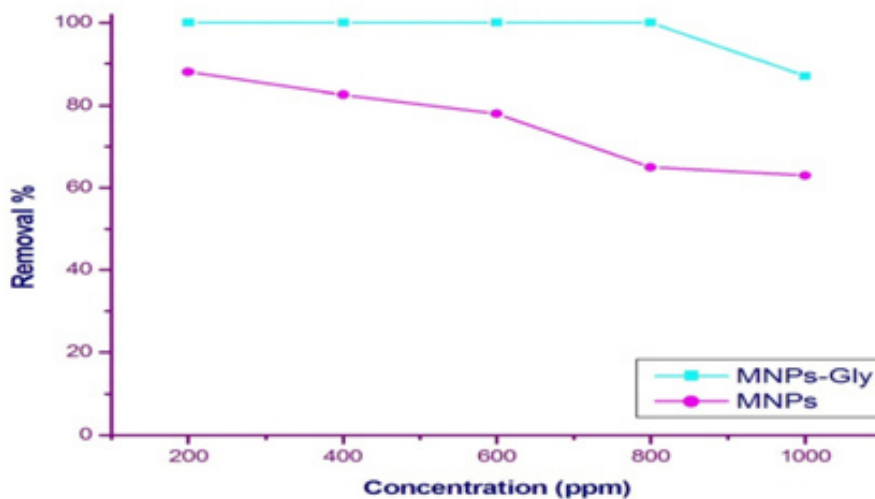
**Fig. 10: Effect of different pH on the removal of Cu²⁺using Gly-MNPs****Fig. 11: Effect of different concentrations on the removal of Cu²⁺using Gly-MNPs**

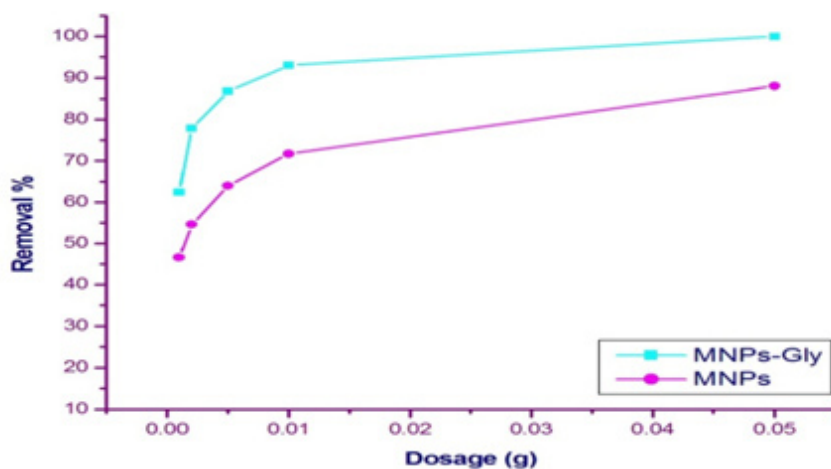
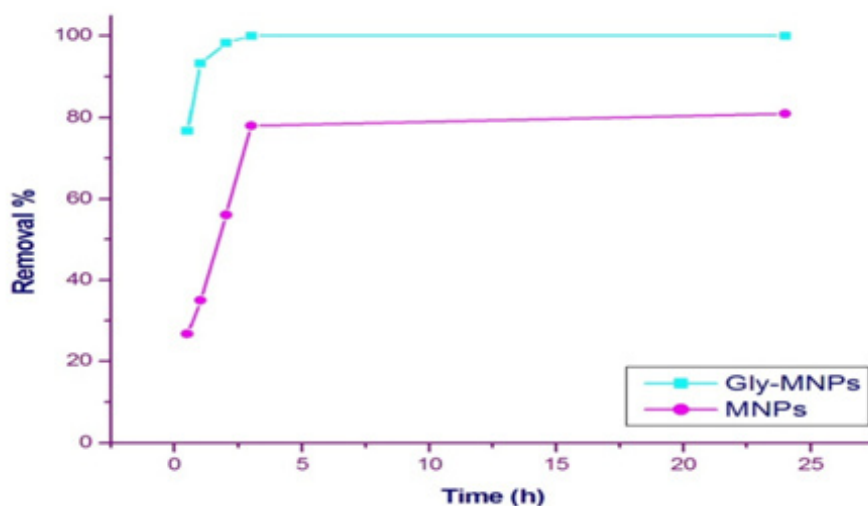
Table 6: Effect of contact time on the removal of Cu⁺² using Gly-MNPs

Time (h)	%Up take of MNPs	%Up take of Gly- MNPs
0.5	26.66	76.66
1	35	93.3
2	56	98.3
3	78	100
24	81	100

no significant difference in shape of functionalized nanoparticles and non-functionalized ones, as showed in Figure 3.9.

SEM-EDAX analysis

Figure 3.10. image scanning electron microscope clearly shows a layer of glycine encapsulate nanoparticles compared to the previous image in Figure 3.6. where completely covered show and this proves the success of the coating of magnetic nanoparticles.

**Fig. 12: Effect of different dosages on the removal of Cu⁺² using Gly-MNPs****Fig. 13: Effect of contact time on the removal of Cu⁺² using Gly-MNPs**

The EDAX spectrum of Gly-MNPs sample is shown in Figure 3.11, and it clearly shows the evidence of Fe, O and C. This result presented solid proof of the proposed structure of Gly-MNPs.

XRD analysis

Fig.3.12. shows XRD pattern of Fe₃O₄ MNPs coated with glycine.

The presence of six characteristic sharp and intense peaks confirmed the formation of highly crystalline nanoparticles. And was found there on difference with XRD result of second method.

The impact of various factors on adsorption of heavy metal ion

$$\text{Removal efficiency (\%)} = \frac{C_0 - C}{C_0} \times 100$$

Where: C₀ and C are the initial and residual concentrations of the heavy metal in the solution (ppm), respectively.

To obtain the optimum condition for removal of heavy metal different chemical parameters were studied as the following:

1. Effect of different pH of solution.
2. Effect of different concentration of heavy metals.
3. Effect of different dosage of MNPs and Gly-MNPs
4. Effect of different contact time.

Effect of different pH of solution

As shown in tables no.3.3. and Figures 3.10. it can be concluded that heavy metal adsorbed on the Gly-MNPs increased with pH value where the %up take was 100% at pH 10.

This observation may be due to electrostatic attraction between the negatively charged, Gly-MNPs surface and the positively charged heavy metals Cu⁺²¹¹.

Effect of the concentrations of heavy metals

According to Table no. 3.4. and Figure no. 3.11. we can be note that the percentage for removal heavy metal decreases from 100% to 87% with

increasing concentration of heavy metal for (200-1000 ppm).

At equilibrium unit adsorption increased from (200 to 600 ppm), and after that the %up take decreased, this is because the mass transfer driving force would become larger as the initial concentration increased. Hence, it results in higher heavy metals adsorption¹².

Effect of the dosages of MNPs and Gly-MNPs

Table no. 3.5 and Figure no. 3.12 represent that the highest percent of removal of Cu⁺² increased from (62.4 to 100 %) as the adsorbed dosage increased. Where as the adsorbent dosage increases the surface area of the adsorbent will be increased. Hence, more adsorption sites are available to adsorb heavy metals from aqueous solution¹³.

Effect of the contact time

From Table no. 3.6, and Figure no. 3.13 the trend of the plots show the system with take longer contact time to achieve adsorption equilibrium.

The Gly-MNPs first has to reach the boundary layer and them diffuses into the tiny pores of the adsorbent during the adsorption process. This phenomenon takes relatively longer contact time¹⁴.

CONCLUSIONS

Advances in nanoscale science and engineering are providing new opportunities to develop technology. The experimental results showed that MNPs were prepared by co-precipitation methods and different chemical analysis indicating that the MNPs coated with glycine. This study had shown that the difference between of Gly-MNPs for removal of heavy metals compared with naked MNPs. The obtain Gly-MNPs was used as adsorbents for removal of heavy metals. where magnetic nanoparticles contain high surface area and large pore size for heavy metal to be adsorbed on the surface of Gly-MNPs.

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