

SYNTHESIS OF CARBOXYL-MODIFIED $\text{Fe}_3\text{O}_4@\text{SiO}_2$ NANOPARTICLES AND THEIR UTILIZATION FOR THE REMEDIATION OF CADMIUM AND NICKEL FROM AQUEOUS SOLUTION

¹SAMINA GHAFoor, ²SADIA ATA

Institute of Chemistry, University of the Punjab, Lahore, Pakistan

Institute of Chemistry, University of the Punjab, Lahore, Pakistan

ABSTRACT

In the present study, general and versatile method for the functionalization of silica coated Fe_3O_4 nanoparticles by surface carboxylic group have been established. We have shown that malic acid functionalized magnetic nanoparticles (MA-MNPs) are an effective sorbent material for toxic metals such as cadmium and nickel. This magnetic sorbent was characterized by X-ray diffraction, scanning electron microscope and infra-red spectra. The adsorption of all studied metal ions onto Malic acid functionalized magnetic nanoparticles was found to be dependent on pH. Batch adsorption equilibrium was very fast under optimum conditions and maximum monolayer capacity, Q_m , obtained from Langmuir isotherm for Cd^{2+} and Ni^{2+} were 81.627 and 63.995 mgg^{-1} , respectively at 25 °C. Adsorption data were fitted well to Langmuir and Freundlich isotherm ($R^2 \approx 0.99$). The malic acid grafted on $\text{Fe}_3\text{O}_4@\text{SiO}_2$ enhanced the adsorption capacity because of the complexing abilities of the multiple hydroxyl and carboxyl groups with metal ions.

Keywords: Iron oxide nanoparticles, adsorption, heavy metals removal, co-precipitation method, malic acid.

1. INTRODUCTION

Poisoning of water resources by heavy metals pollutants is of huge environmental concern because of their toxic and non-biodegradable nature. They are lethal and toxic not only to humans, but also to plants, animals and microorganisms. Heavy metal ions such as cadmium (Cd^{2+}), and nickel (Ni^{2+}) are toxic and carcinogenic at even relatively low concentrations [1]. These toxic metal ions are mostly present in process waste streams from mining progressions, metal plating units, power production units, electronic device manufacturing units, and tanneries [2]. Because of economic and environmental factors, the eradication of heavy-metal ions from industrial wastewater have been a serious interest in most industrial branches. Many processes have been developed to decrease heavy metal pollution, such as chemical precipitation, electrophoretic deposition, solvent extraction, ion-exchange, activated carbon adsorption and biological methods [3]. Among these processes, adsorption has progressively received more consideration in recent years because it is simple, comparatively low-cost, and efficient in removing heavy metal ions from wastewaters [4].

In the last two decades immense research have been devoted to the progress of nano-technology and nano-materials. The main research interest is to design novel nano-materials [5]. Nanosized magnetic particles have multidiscipline applications in different fields and considered efficient adsorbents for heavy metals pollution in water because of their high surface area and the advantageous property of easy separation under external magnetic fields [6–9]. To further facilitate the adsorption affinity, surface modification, including physical coating and covalent functionalization, has often been explored to enable specific metal complexation [10–15]. For example, covalent bonding of carboxylic groups on the surface of magnetic nanoparticles (MNPs) was carried out by reacting MNPs with 11-undecanoic acid, and this material express marked ability in adsorbing $\text{Cd}(\text{II})$ [10]. The chitosan-coated Fe_3O_4 nanoparticles were found to be efficient adsorbent of $\text{Cu}(\text{II})$ ions [12]. Humic-acid functionalized Fe_3O_4 nanoparticles were reported as effective in sorbing $\text{Hg}(\text{II})$, $\text{Pb}(\text{II})$, $\text{Cd}(\text{II})$, and $\text{Cu}(\text{II})$ from water [13]. The dimercaptosuccinic acid-coated Fe_3O_4 nanoparticles have thiol group on their surface which also acted as binding ligands for Hg, Ag, Pb, Cd, and Tl metal ions [14]. Recently, a magnetic nanosorbent prepared by coating a maghemite core with chitosan and carboxylation with α -ketoglutaric acid, was used to remove $\text{Cu}(\text{II})$ ions from aqueous solution [15]. A natural biodegradable and renewable resin called shellac was coated on the surface of magnetic nanoparticles which prove to be an effective adsorbent for cadmium removal from aqueous solution [16]. The instability and leaching of magnetic nanoparticles in strongly acidic environment is the main limitation for its long life and reusability. This limitation can be overcome by coating magnetic nanoparticles with silica shells. It protect it from leaching and also prevents agglomeration of nanoparticles.

This work is an effort to improve the metal complexing ability and selectivity with magnetic nanoparticles (MNPs) to create a novel dispersible sorbent that can be magnetically collected and has a high capacity and

selectivity for the heavy metals. Fe_3O_4 nanoparticles have been prepared by co-precipitation method and after coating with silica it was further functionalized with malic acid. Silicon oxide was chosen because of its great stability under acidic conditions and passiveness to redox reactions. Therefore it is examined as an ideal shell to protect the inner magnetic core [17]. The ligands on the surface were predominantly carboxyl groups, along with hydroxyl groups. This grafted magnetic nanoparticles were used as easily separable and highly efficient nanoadsorbent for the effective removal of metal ions, i.e. Cd^{2+} and Ni^{2+} ions from water. The objective of the present study is to appraise the performance of malic acid functionalize magnetic nanoparticles for the removal of heavy metal ions from water however this study can also be extended in future for the removal of other toxic metals from water.

2. EXPERIMENTAL SECTION

2.1. Materials

All the reagents used were of analytical grade. Stock solutions (1000mgL^{-1}) of Cd^{2+} , and Ni^{2+} were prepared by direct dissolution of proper amounts of $\text{Cd}(\text{NO}_3)_2$ and $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ in distilled water respectively. The standard solutions were diluted with distilled water to prepare the standard solutions. Ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), ferrous chloride ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$), citric acid (99%), sodium hydroxide (99.9%), tetraethoxysilane (TEOS 99.9%) and DL-malic acid (99%) were purchased from Merck. pH adjustments were performed with 0.01-1.0 molL^{-1} HCl and NaOH solutions.

2.2. Synthesis and functionalization

The magnetic Fe_3O_4 nanoparticles were synthesized by the chemical co-precipitation method, and the detailed procedure is described below. $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (2g) and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (5.2g) were dissolved into 25ml deoxygenated water followed by adding 0.85ml of concentrated hydrochloric acid. The resulting solution was dropped into 250ml of 1.5 M NaOH solution under vigorous stirring and N_2 protection at 353 K. The synthesized magnetic nanoparticles (MNPs) were separated from solution by a powerful magnet and washed with 200 ml deionized water three times.

The as-precipitated nanoparticles were used for the preparation of a stable aqueous suspension. A total of 10 mL of an aqueous solution of citric acid (0.5 g/mL) was added to the rigorously stirred suspension of washed nanoparticles. The pH value was set to 5.2 with a concentrated ammonia solution and heated to 80 °C. After 90 min, the pH value of the solution was elevated to 10.1. Lastly, the suspension was centrifuged for 5 min at 4000 rpm to remove any agglomerated nanoparticles.

Next, silica coat was fabricated on the surface of Fe_3O_4 MNPs through a sol-gel method. 100ml of ethanol containing 4ml TEOS was added in the above prepared stable aqueous suspension of Fe_3O_4 MNPs, followed by stirring at ambient temperature for 6 h. After rinsing with ethanol and water several times, the obtained $\text{Fe}_3\text{O}_4/\text{SiO}_2$ MNPs were dried at 60 °C.

The $\text{Fe}_3\text{O}_4/\text{SiO}_2$ magnetic nanoparticles were functionalized with malic acid. Briefly 2g of dried $\text{Fe}_3\text{O}_4/\text{SiO}_2$ MNPs was dispersed in 100mL of water,

followed by addition of 2 g of malic acid under vigorous stirring at 90°C for 90 min. the resulting functionalized nanoparticles were then washed with distilled water three times to remove any unreacted chemicals and dried in oven.

2.3. Adsorption of Heavy Metal Ions

The adsorption of the cadmium and nickel on the functionalized magnetic nanosorbent was studied by batch equilibrium technique. The effect of different factors such as sorbent dose, pH, contact time and initial metal ion concentration were studied according to the following procedure.

The effect of amount of nanosorbent on the metal uptake was studied by adding 10-80mg MNPs and MA-MNPs in 20ml of 50ppm of Cd(II) and Ni(II) solutions separately. After agitation in an orbital shaker for 30min the nanosorbent was separated by external magnetic field and the supernatant was collected for assay. The final concentrations of metals were measured using Atomic absorption Spectrometer.

The adsorption capacity (q_e , mgg^{-1}), the amount of metal ions adsorbed at equilibrium, was calculated according to the following equation:

$$q_e = \frac{V(C_o - C_e)}{m} \quad (1)$$

where C_o is the initial metal ion concentration in solution (mgL^{-1}), C_e is the equilibrium concentration (mgL^{-1}) after adsorption, V is the solution volume (L), m is the mass of NPs adsorbent (g).

The effect of pH on the metal uptake was studied by adding 40mg MA-MNPs in 20ml of 50ppm of Cd(II) and Ni(II) of pH range 1.0-7.0. pH of the solutions were adjusted by using 0.01-1.0 molL^{-1} HCl and NaOH solutions. Supernatant was collected with external magnetic field after agitation for 30min and final concentration of the solutions were measured by Atomic Absorption Spectrometer.

40mg of MA-MNPs was added in 20ml of 50ppm solution of cadmium and nickel ions at pH 6.0 to study the effect of contact time. These mixtures were shaken in an orbital shaker for selected time 10.0, 20.0, 30.0, 40.0, 50.0 and 60.0min. After that the supernatant was collected with the help of external magnetic field and final concentration of metal ions were analyzed by Atomic absorption Spectrometer.

An average of 40mg of dry functionalized magnetic nanoadsorbent was added to 20ml of Cd^{2+} and Ni^{2+} solution of various concentrations (from 30mgL^{-1} to 80mgL^{-1}) and shaken in an orbital shaker operated at 200rpm. The pH of the suspension was adjusted to 6.0 by adding either 0.1M NaOH or 0.1M HNO_3 . After equilibrium was reached magnetic nanosorbents were removed using a permanent magnet and supernatant was collected for analysis. The final concentrations of Cd^{2+} and Ni^{2+} ions were measured using Atomic Absorption Spectrometer. Adsorption equilibrium isotherms were applied to evaluate the effect of metal ion concentration on removal.

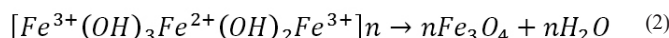
2.4. Characterization of Material

Scanning electron microscopy was used to observe the surface morphology of the MA-MNPs using a JSM-6400 machine (JOEL, Tokyo, Japan) and crystallite phase of the synthesized nanoparticles was examined by powder X-ray diffraction (PXRD, PANalytical X'Pert PRO, PW3040/60). To examine the functional groups, Fourier transform infrared spectroscopy of the materials was recorded over the range of $500\text{--}4000\text{ cm}^{-1}$ on a Agilent Technologies spectrophotometer (Model Cary 630) with ATR.

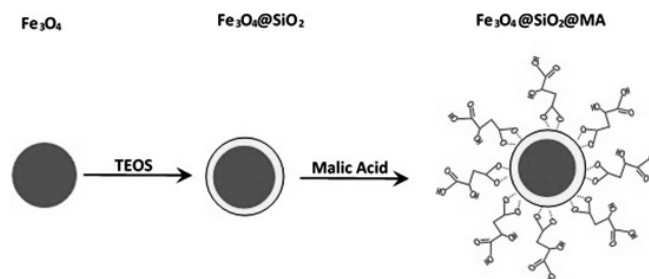
3. RESULTS AND DISCUSSION

3.1. Synthesis and Characterization

Magnetic nanoparticles were prepared by chemical co-precipitation method. Salts solutions of Fe(II) and Fe(III) reacted in basic media to produce precipitates of hydroxides which simultaneously converted to Fe_3O_4 with the loss of water molecules according to the following equation [18].



These magnetic nanoparticles can be collected from the solution with the help of external magnetic field. The next step as shown in scheme.1 was to wrap the surface of nanoparticles with a shielding layer of nano silica which was achieved by reaction of aqueous stable suspension of nanoparticles with TEOS in basic media. The last synthetic step was to functionalize the silica coated magnetic nanoparticles with malic acid to introduce hydroxyl and carboxylic acid groups on the surface of nanoparticles so that they have strong interaction with metal cations and thus facilitate their removal.



Scheme 1. Schematic presentation of malic acid functionalizing on $\text{Fe}_3\text{O}_4@SiO_2$ nanoparticles

The corresponding compositions and crystalline phases of the as-synthesized MA-MNPs was first studied using XRD. As shown in Figure 1 all of the relatively strong peaks, such as the peaks at $2\theta=30.0^\circ$, 35.6° , 43.9° , 58.0° , 63.5° could be assigned to the face-centered cubic phase of the Fe_3O_4 crystals (JCPDS card number: 89-4319). The XRD pattern of the as-prepared product exhibited rough peaks with weak intensities, indicating low crystallization which might be due to silica coating on the surface of magnetic nanoparticles.

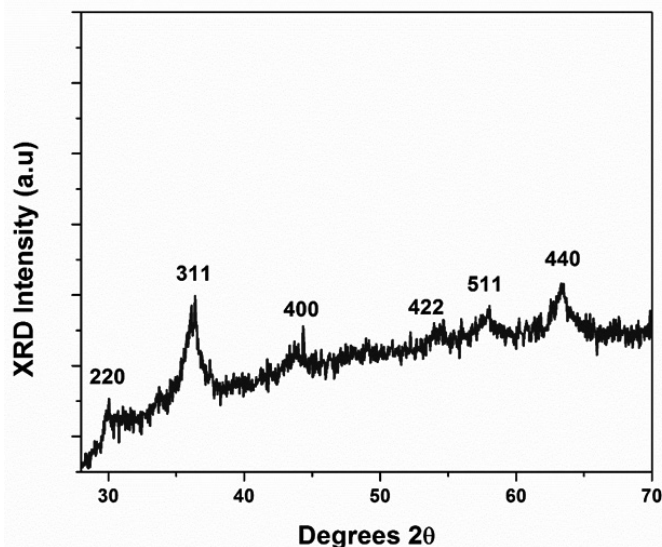


Figure 1. The XRD pattern of functionalized magnetic nanoparticles.

The surface and textural morphology of the as-synthesized MA-MNPs was observed by scanning electron microscopy. Figure 2 shows typical images of iron oxide nanoparticles coated with silica and malic acid. Figures show that the iron oxide nanoparticles had a spherical shape with average diameter of 70nm, and were transformed into an agglomerated structure.

The functionalization of Malic acid on silica coated magnetic nanoparticles was confirmed by FTIR spectroscopy. Figure 3 (a) shows the FTIR spectra of magnetic nanoparticles, (b) silica coated magnetic nanoparticles and (c) functionalized silica coated magnetic nanoparticles in the $4000\text{--}500\text{ cm}^{-1}$ wavenumber range. The characteristic absorption band of magnetic nanoparticles is 568cm^{-1} which is due to Fe-O bonds and common among three spectras. The absorption band at 1083cm^{-1} can be ascribed to the stretching and deformation vibrations of SiO_2 , reflecting the coating of silica on the nanoparticles surface. Successful carboxylic acid functionalization of silica layer on $\text{Fe}_3\text{O}_4@SiO_2$ was also confirmed by the absorption at 1388cm^{-1} and 1700cm^{-1} , attributed to the stretching and bending vibration of carboxyl group ($-\text{COOH}$). The results verified the formation of a silica shell on the Fe_3O_4 surface and the carboxyl-functionalization of the silica shell. The absorption band at almost 3400cm^{-1} is mainly due to the intramolecular hydrogen bonding in all nano-materials [19].

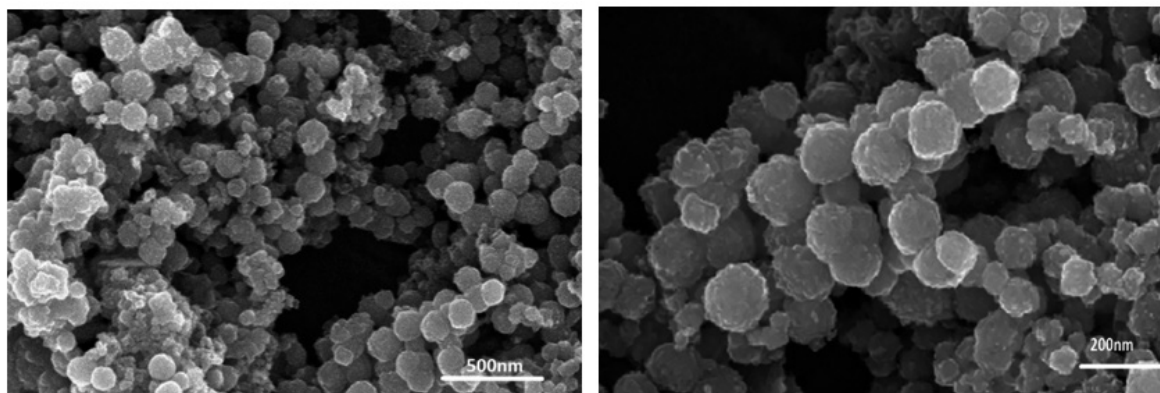


Figure 2. SEM images of functionalized magnetic nanoparticle at different resolution

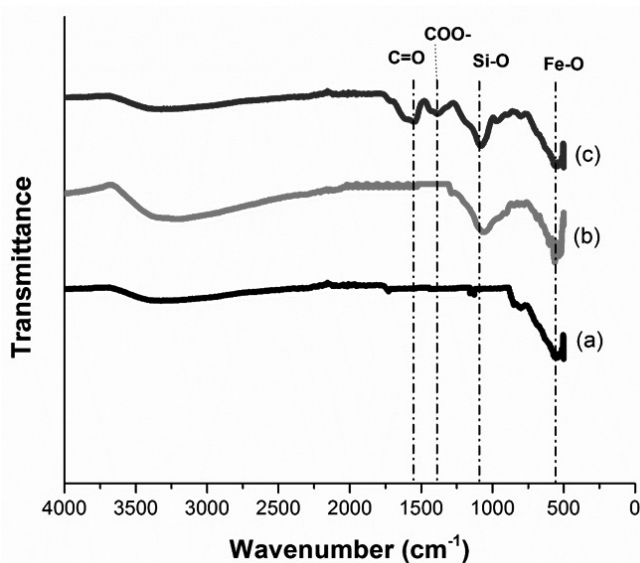


Figure 3. FTIR spectra for (a) uncoated MNPs (b) silica coated MNPs (c) functionalized silica coated MNPs

3.2. Adsorption Studies

3.2.1. Effects of adsorbent dosage

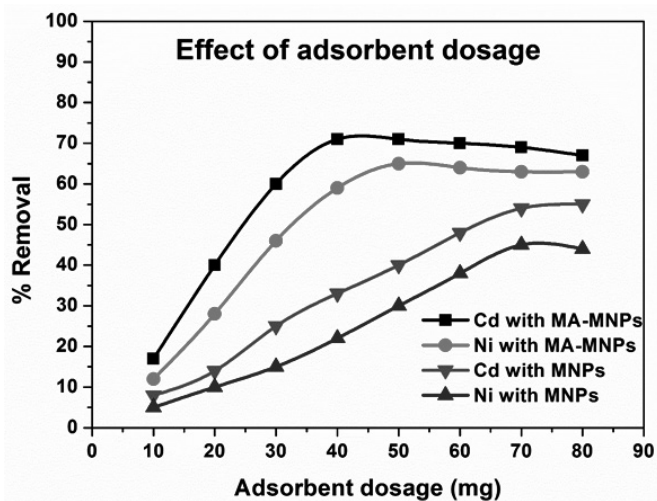


Figure 4. Effect of adsorbent dose of MNPs and MA-MNPs on cadmium and nickel removal

The effect of sorbent dose on the metal removal was evaluated and found to be an important controlling factor and the results are shown in Figure 4. A comparative study was performed for functionalized (MA-MNPs) and non-functionalized (MNPs) nanoparticles for the removal of metal ions. Apparently, the percentage removal of metal ions increased by increasing the amount of nanosorbent due to the greater availability of the active sites which can attach more cations. The maximum removal of cadmium ions was 71% by 40mg and 65% of nickel ions by 50mg of MA-MNPs. However the maximum removal of cadmium ions was 55% by 80mg and 44% of nickel ions by 70mg of MNPs. This clearly shows how effectively the removal efficiency has enhanced by functionalization on the surface of magnetic nanoparticles. As shown in the figure after equilibrium further increase of sorbent dose cause slight decrease in the removal because more concentration of nanoparticles cause the agglomeration and result in the decrease of active sites.

3.2.2. Effects of pH

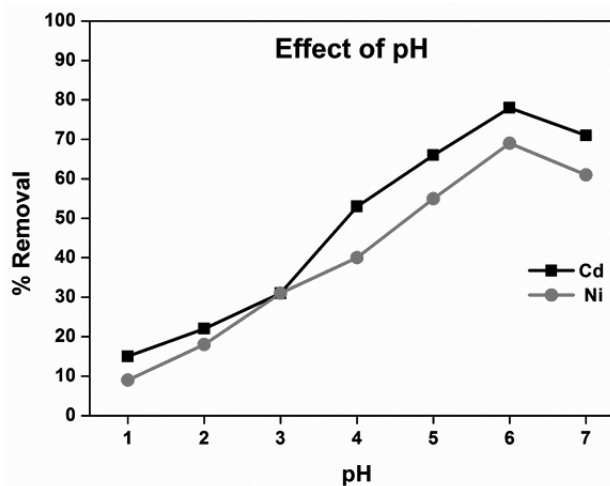


Figure 5. Effect of pH on metals removal

The solution pH plays a significant role in the adsorption process and particularly on the adsorption efficiency of affinity. The effect of initial solution pH on Cd^{2+} and Ni^{2+} adsorption onto MA-MNPs was investigated at pH 1–7, 25°C, and an initial M^{2+} ion concentration of 50 mgL^{-1} . Experiments were not conducted at initial pH above 7 as the precipitation of metal hydroxide, $\text{M}(\text{OH})_2$, is likely to occur [20], introducing uncertainty into the results. From Figure 5, it is observed that the metal uptake capacity increases with an increase in pH from 1 to 6. All studied metal ions exhibit maximum adsorption capacity at pH 6. Below pH 6, the dominant species of all metals are M^{2+} and $\text{M}(\text{OH})^+$ [21]. At greater pH the negatively charged carboxylate ions (COO^-) have strong coordinative affinity towards positively charged metal ions. The electrostatic of attraction allow the carboxylate ions to capture the M^{2+} through surface complexation, forming chelate complexes [22]. The degree of surface complexation increases with increasing pH. Hence, maximum

adsorption capacity occurs at pH 6. At low pH there is a net positive charge on the MA-MNPs. This enhances the repulsive forces that exist between the positively charged metal ions and the sorbent adsorption sites, therefore decreasing the adsorption. In addition, the presence of a large amount of H⁺ ions at low pH causes the H⁺ ions to compete effectively with M²⁺ ions for MA-MNPs adsorption sites through ion exchange mechanism, decreasing the metal uptake capacity [22].

3.2.3. Effect of contact time

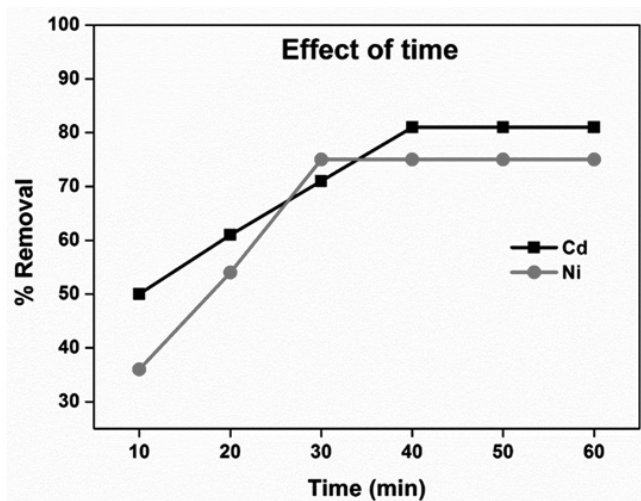


Figure 6. Effect of time on metals removal.

The importance of contact time of sorption can be evaluated for the possible rapidness of binding and removal of the targeted metal ions by the nanosorbent. The sorption equilibrium time of cadmium and nickel ions as shown in Figure 6 was achieved after 40 and 30min of contact time respectively. These results shows that sorption equilibrium achieved rapidly. The maximum removal was estimated as 80 and 75% of cadmium and nickel ions respectively.

3.2.4. Adsorption Isotherms

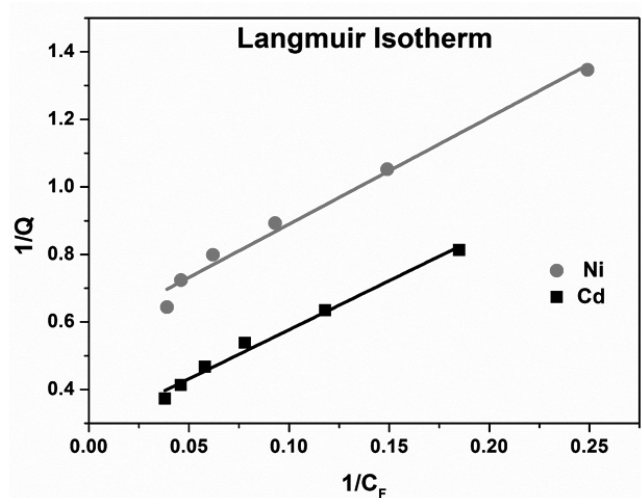


Figure 7. Langmuir adsorption isotherm for nickel and cadmium

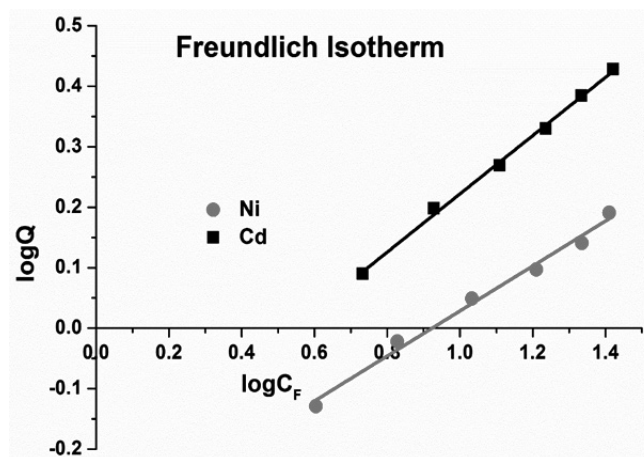


Figure 8. Freundlich adsorption isotherm for nickel and cadmium

Table 1. Adsorption isotherm parameters of Ni²⁺ and Cd²⁺ onto MA-MNPs

Isotherm models	Parameters	Ni ²⁺	Cd ²⁺
Langmuir	Q _m (mgg ⁻¹)	63.995	81.627
	b (Lmg ⁻¹)	0.316	0.344
	R ²	0.989	0.999
Freundlich	N	2.688	2.083
	K _f (Lg ⁻¹)	4.640	0.779
	R ²	0.980	0.996

The equilibrium data of Cd²⁺ and Ni²⁺ are fitted well by Langmuir and Freundlich adsorption isotherm models. Langmuir and Freundlich adsorption isotherms are widely used to describe the relationship between the amount of adsorbate adsorbed on adsorbent and its equilibrium concentration in aqueous solution. The Langmuir equation [23] given in Eq. (3) was applied to the data to provide an insight into the mechanism of the adsorption.

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

where Q_m and b are Langmuir constants related to the maximum adsorption capacity and energy of adsorption respectively. Likewise, the Freundlich equation [24] given in Eq. (4) was also applied in the form

$$\log q_e = \log K_f + \frac{\log C_e}{n} \quad (4)$$

where K_f is a Freundlich constant (index of adsorption capacity), n is Freundlich constant (index of adsorption intensity or surface heterogeneity).

The values of Q_m and b are determined from the slope and intercept of the linear plots of C_e/q_e versus C_e and the values of K_f and n are determined from the slope and intercept of the linear plot of ln q_e versus ln C_e (as shown in figure 7 and 8). The isotherm parameters and related correlation coefficients (R²) are shown in Table 1. The adsorption isotherm data of two metal ions on this adsorbent are best fitted to Langmuir isotherm model and Freundlich model. Based on Langmuir isotherms, the maximum uptake for Ni²⁺ and Cd²⁺ ions using functionalized magnetic particles were 63.995 and 81.627mg g⁻¹, respectively which are higher than those using uncoated magnetic nanoparticles as reported by Nassar (2010, 2011). These results indicate that the modification of magnetite surface by Malic acid could enhance the adsorption capabilities of MNPs. The multiple oxygen containing groups (mainly carboxyl and hydroxyl groups) present in MA functionalized silica coated MNPs can form complexes with Cd²⁺ and Ni²⁺ ions. Furthermore, the values of b for the Langmuir isotherm were between 0 and 1, and all the Freundlich adsorption intensity variables (n values)

were >2, which supports the favorable adsorption of metal ions with this adsorbent. However, the considerable difference among the values of Q_m should be attributed to the different complexation capacity of the oxygen containing groups on surface with the metal ions.

4. CONCLUSIONS

Superparamagnetic magnetite (Fe_3O_4) nanoparticles coated with silica and functionalized with malic acid were synthesized, which were found to be an efficient adsorbent for the removal of heavy metal ions such as cadmium and nickel from wastewater. The adsorption capacities of Fe_3O_4 nanoparticles were enhanced upon the surface modification with malic acid which provides numerous surface carboxyl and hydroxyl groups, and hence, possesses the strong affinity for metal ions. The solution pH affected the adsorption of metal ions onto malic acid functionalize MNPs. Adsorption reaches equilibrium within 30min. The maximum uptake capacities for Cd^{2+} and Ni^{2+} were 81.62 and 63.995 $mg\ g^{-1}$, respectively at 25°C and the equilibrium data are fitted well by the Langmuir and Freundlich model. Adsorption of Cd^{2+} ions was preferential to that of Ni^{2+} ions. In the future this material can also be applied for the removal of other toxic metals from water or wastewater.

5. REFERENCES

- 1.- Badruddoza, A. Z. M., Shawon, Z. B. Z., Tay, W. J. D., Hidajat, K., & Uddin, M. S. (2013). Fe 3 O 4/cyclodextrin polymer nanocomposites for selective heavy metals removal from industrial wastewater. *Carbohydrate polymers*, 91(1), 322-332.
- 2.- Ozay, O., Ekici, S., Baran, Y., Aktas, N., & Sahiner, N. (2009). Removal of toxic metal ions with magnetic hydrogels. *Water Research*, 43(17), 4403-4411.
- 3.- Adeli, M., Yamini, Y., & Faraji, M. (2012). Removal of copper, nickel and zinc by sodium dodecyl sulphate coated magnetite nanoparticles from water and wastewater samples. *Arabian Journal of Chemistry*.
- 4.- Stafiej, A., & Pyrzynska, K. (2007). Adsorption of heavy metal ions with carbon nanotubes. *Separation and Purification Technology*, 58(1), 49-52.
- 5.- Jian, X., Wu, B., Wei, Y., Dou, S. X., Wang, X., He, W., & Mahmood, N. (2016). Facile Synthesis of Fe₃O₄/GCs Composites and Their Enhanced Microwave Absorption Properties. *ACS applied materials & interfaces*, 8(9), 6101-6109.
- 6.- Oliveira, L. C., Petkowicz, D. I., Smaniotto, A., & Pergher, S. B. (2004). Magnetic zeolites: a new adsorbent for removal of metallic contaminants from water. *Water Research*, 38(17), 3699-3704.
- 7.- Hu, J., Lo, I., & Chen, G. (2004). Removal of Cr (VI) by magnetite. *Water Science & Technology*, 50(12), 139-146.
- 8.- Hu, J., Chen, G., & Lo, I. M. (2005). Removal and recovery of Cr (VI) from wastewater by maghemite nanoparticles. *Water Research*, 39(18), 4528-4536.
- 9.- Yavuz, C. T., Mayo, J. T., William, W. Y., Prakash, A., Falkner, J. C., Yean, S., ... & Colvin, V. L. (2006). Low-field magnetic separation of monodisperse Fe₃O₄ nanocrystals. *Science*, 314(5801), 964-967.
- 10.- Hai, B., Wu, J., Chen, X., Protasiewicz, J. D., & Scherson, D. A. (2005). Metal-ion adsorption on carboxyl-bearing self-assembled monolayers covalently bound to magnetic nanoparticles. *Langmuir*, 21(7), 3104-3105.
- 11.- Hu, J., Lo, I. M., & Chen, G. (2007). Comparative study of various magnetic nanoparticles for Cr (VI) removal. *Separation and Purification Technology*, 56(3), 249-256.
- 12.- Chang, Y. C., & Chen, D. H. (2005). Preparation and adsorption properties of monodisperse chitosan-bound Fe 3 O 4 magnetic nanoparticles for removal of Cu (II) ions. *Journal of Colloid and Interface Science*, 283(2), 446-451.
- 13.- Liu, J. F., Zhao, Z. S., & Jiang, G. B. (2008). Coating Fe₃O₄ magnetic nanoparticles with humic acid for high efficient removal of heavy metals in water. *Environmental science & technology*, 42(18), 6949-6954.
- 14.- Yantasee, W., Warner, C. L., Sangvanich, T., Addleman, R. S., Carter, T. G., Wiacek, R. J., ... & Warner, M. G. (2007). Removal of heavy metals from aqueous systems with thiol functionalized superparamagnetic nanoparticles. *Environmental science & technology*, 41(14), 5114-5119.
- 15.- Zhou, Y. T., Nie, H. L., Branford-White, C., He, Z. Y., & Zhu, L. M. (2009). Removal of Cu 2+ from aqueous solution by chitosan-coated magnetic nanoparticles modified with α -ketoglutaric acid. *Journal of colloid and interface science*, 330(1), 29-37.
- 16.- Gong, J., Chen, L., Zeng, G., Long, F., Deng, J., Niu, Q., & He, X. (2012). Shellac-coated iron oxide nanoparticles for removal of cadmium (II) ions from aqueous solution. *Journal of Environmental Sciences*, 24(7), 1165-1173.
- 17.- Wang, J., Zheng, S., Shao, Y., Liu, J., Xu, Z., & Zhu, D. (2010). Amino-functionalized Fe 3 O 4@ SiO 2 core-shell magnetic nanomaterial as a novel adsorbent for aqueous heavy metals removal. *Journal of Colloid and Interface Science*, 349(1), 293-299.
- 18.- Mahmoud, M. E., Abdelwahab, M. S., & Fathallah, E. M. (2013). Design of novel nano-sorbents based on nano-magnetic iron oxide-bound-nano-silicon oxide-immobilized-triethylenetetramine for implementation in water treatment of heavy metals. *Chemical Engineering Journal*, 223, 318-327.
- 19.- Li, Y. S., Church, J. S., & Woodhead, A. L. (2012). Infrared and Raman spectroscopic studies on iron oxide magnetic nano-particles and their surface modifications. *Journal of Magnetism and Magnetic Materials*, 324(8), 1543-1550.
- 20.- Naiya, T. K., Bhattacharya, A. K., & Das, S. K. (2009). Adsorption of Cd(II) and Pb(II) from aqueous solutions on activated alumina. *Journal of Colloid and Interface Science*, 333, 14-26.
- 21.- Nassar, N. N. (2011). Kinetics, equilibrium and thermodynamic studies on the adsorptive removal of nickel, cadmium and cobalt from wastewater by superparamagnetic iron oxide nanoadsorbents. *Canadian Journal of Chemical Engineering*, 9999, 1-8.
- 22.- Singh, S., Barick, K., & Bahadur, D. (2011). Surface engineered magnetic nanoparticles for removal of toxic metal ions and bacterial pathogens. *Journal of Hazardous Material*, 192, 1539-1547.
- 23.- Langmuir, I. (1918). The adsorption of gases on plane surfaces of glass, mica and platinum. *Journal of American Chemical Society*, 40, 1361-1403
- 24.- Ng, C., Losso, J. N., Marshall, W. E., & Rao, R. M. (2002). Freundlich adsorption isotherms of agricultural by-product-based powdered activated carbons in a geosmin-water system. *Bioresource technology*, 85(2), 131-135