Research Journal of Pharmaceutical, Biological and Chemical Sciences

Modified Starch Iron Oxide Nanocomposites as Low Cost Absorbents for Selective Removal of Some Heavy Metals From Aqueous Solutions.

Abdul-Raheim M Abdul-Raheim, Farag Reem K, El-Saeed Shimaa M, and Abdel-Raouf Manar E*.

Petroleum Application Department, Egyptian Petroleum Research Institute 1 Ahmed El-Zomor street, Nasr city, Cairo, Egypt.

ABSTRACT

In this work, the starch extracted from potato peels was modified with acrylic acid. Nanoparticles composed of modified starch polymer and Fe_3O_4 (modified potato starch-magnetic nanoparticles, MPS-MNPs) were synthesized. The prepared nanoadsorbents were used for selective removal of Cu^{2+}, Pb^{2+} and Ni^{2+} ions from water. They were characterized by TEM, FTIR and XRD. The adsorption of all studied metal ions onto MPS-MNPs was found to be dependent on pH, contact time, and temperature. Batch adsorption equilibrium was reached in 60 min and maximum uptakes for Cu^{2+}, Pb^{2+} and Ni^{2+} in non-competitive adsorption mode were 100, 70 and 100 mg g^{-1}, respectively at 35 °C. In competitive adsorption experiments, PS-MNPs preferentially adsorbed Ni^{2+} ions with an affinity order of $Ni^{2+}>Cu^{2+}>Pb^{2+}$. The effect of monomer and initiator concentrations on grafting process was studied. Furthermore, the recyclability of PS-MNPs was investigated.

Keywords: Removal, heavy metals, low cost, adsorbents, magnetic nanoparticles.

*Corresponding author

INTRODUCTION

Water contamination due to toxic heavy metals is a matter of great concern due to their detrimental effects on both the environment and human health. Heavy metal ions such as lead (Pb^{2+}), copper (Cu^{2+}), and nickel (Ni^{2+}) are toxic and carcinogenic at even very low concentrations, Table 1. Heavy metals are non-biodegradable and they can accumulate in living organisms.

They are generally discharged to the environment from various industrial activities such as smelting, electroplating, painting, mining, leather tanning, alloy and battery manufacturing, etc., posing a significant threat to the environment and public health [1]. Therefore, reliable methods are necessary for the removal of heavy metals from aquatic environment.

An extensive effort has been devoted to the effective removal of heavy metal ions from environment. There are various treatment techniques available for the removal of toxic metals such as adsorption, chemical precipitation, ion exchange, coagulation, reverse osmosis, electrolysis and membrane process, etc [2-4]. However, among all these methods, adsorption is considered an effective, efficient and economic method for the removal of different pollutants from wastewater. Moreover, adsorption is universal and fast in nature and applicable for the removal of organic and inorganic pollutants even at low concentration [5-8].

Development of new generation environmental friendly adsorbent based on natural nano materials is the current research interest [9].

In the removal of heavy metals from waste water, natural polymers, mainly polysaccharides such as chitosan, starch and its derivatives, cyclodextrins, have attracted particular attentions, due to their physico-chemical characteristics, low cost, availability and the presence of various reactive groups on the backbone [10, 11]. In spite of their importance, they have some disadvantages that limit their use, such as their low surface area and difficult separation from the solution. Magnetic sorbents on the other hand, have a relatively high surface area and are easy to separate and manipulate in complex multiphase systems with an external magnetic field [12].

Hybrid nanocomposites of increased stability can be obtained by incorporating a natural polymer in an inorganic material thus combining the advantages of both materials. Composites prepared from several polysaccharides represent a new category of environmentally safe materials for different biological and industrial applications. It was reported that magnetic nanomaterials functionalized with biopolymers such as chitosan [13], gum Arabic [14], cellulose [15] and chitosan [16, 17] have been used for the removal of toxic metals from aqueous solution.

Starch is a polysaccharide which consists of repeating D-glucopyranose units, linked together by α-1, 4 linkages, Figure 1. Starch products themselves are hardly suitable as sorbents, because they lack controllable particle size and certain wear resistance, hardness, and porosity; however it has been used for the removal of heavy metal ions in various modified forms [18-22]. This renewable and biodegradable compound has the ability to complex various metal ions this complexation ability can be improved by modifying starch with suitable functional groups through esterification, oxidation reactions and cross-linking of hydroxyls outside the interior cavity [23-28].

In order to crosslink polymers containing hydroxyl groups on the backbones , such as starches, the crosslinkers must have a capability to react with at least two hydroxyl groups in a single polymer molecule or in adjacent molecules. For starch crosslinking, bifunctional and multifunctional reagents are normally used to form ether, ester or other linkages with the hydroxyl groups in starch molecules [29]. By varying crosslinker dosages, starch concentration, pH, and temperatures, the extent of crosslinking could be controlled. In addition, the crosslinking of starch can also be achieved by irradiation without any additives, which is normally used in grafting processes [30].

Compared to native starches, crosslinked starches have superior properties in aspects of mechanical, thermal and chemical resistance, such as an improved viscosity, better textural properties, and a higher resistance to high temperature, low pH, and high shear force [31]. Therefore, crosslinked starch hydrogels have many applications, in food, oilfield, pharmaceutical, water treatment and other industries [32].

The aim of the present work is to prepare modified starch nanocomposite by reaction with acrylic acid and application of the modified starch as absorbent for heavy metals from aqueous media under different conditions. Furthermore, the influences of process parameters such as monomer and initiator concentrations on the graft polymerization of acrylic acid to potato starch were investigated.
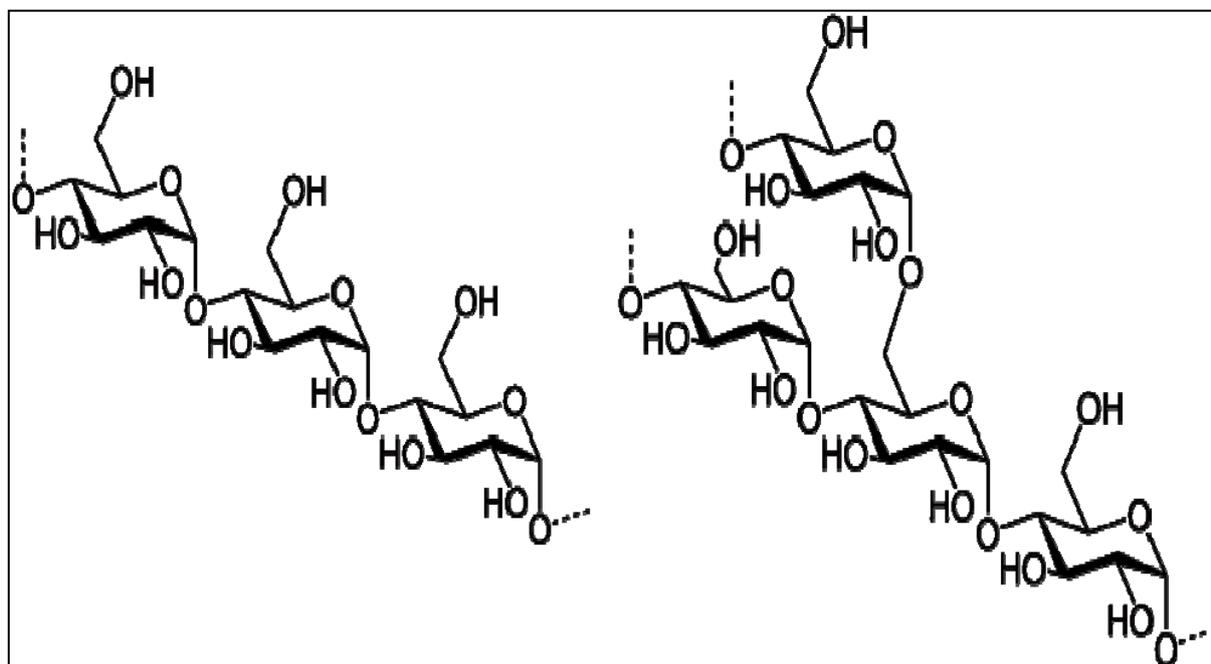

Figure 1: Molecular structures of starch (left: amylose; right: amylopectin).

Heavy metal	Toxicities	MCL(mg/L)
Arsenic	Skin manifestations, visceral cancers, vascular disease	0.050
Cadmium	Kidney damage, renal disorder, human carcinogen	0.01
Chromium	Headache, diarrhea, nausea, vomiting, carcinogenic	0.05
Copper	Liver damage, Wilson disease, insomnia	0.25
Nickel	Dermatitis, nausea, chronic asthma, coughing, human carcinogen	0.20
Zinc	Depression, lethargy, neurological signs and increased thirst	0.80
Lead	Damage the fetal brain, diseases of the kidneys, circulatory system and nervous system	0.006
Mercury	Rheumatoid arthritis, and diseases of kidneys, circulatory system and nervous system	0.00003

Table 1: The hazardous effects of heavy metals

MATERIALS AND METHODOLOGY

Iron (II) chloride tetrahydrate (99%), iron (III) chloride hexahydrate (98%), Benzoyl peroxide (BPO) and Acrylic acidwere purchased from Sigma-Aldrich. Ammonium hydroxide (25%), Lead(II) nitrate, Copper(II) nitrate and nickel(II) nitrate were purchased from Merck(MA, USA). All the chemicals were of analytical grade and used as received without further purification. Potato starch was obtained from potato peels after treatment. Potato peels were chosen as biomaterial because of their chemical stability, non-catalytic activity and local availability at very low cost.

Sample Preparation and Pre-Treatment

Potato peels were washed repeatedly with distilled water followed by filtration so as to remove dust and soluble impurities. The washed samples were oven dried at 100°C to constant weight. The cleaned

samples were then ground into powder and sieved to 150 – 250 µm particle size. The chemically activated samples were prepared by boiling starch powder in 0.1M NaOH for an hour at room temperature (70°C). The waste slurry was then heated to 120°C. Then it was washed several times with distilled water to remove any excess base until the water comes out becomes neutral and then dried at 100°C to constant weight.

Synthesis of starch-g-poly(AAc), (Graft copolymerization of acrylic acid onto treated potato starch)

The synthesis of graft copolymer is shown in Scheme 1. One gram of the treated potato starch (TPS)was dissolved in 100 ml distilled water with 0.1 N NaOH (0.4 g) solution, stirred at 70 ºC for 60 minutes before grafting was carried out with monomer. The definite amount of initiator (BPO) was added to the reaction mixture and allowed to react with starch for 10 minutes. Thereafter, definite amount of acrylic acid was added into the reaction mixture with continuously stirring at a particular temperature (70°C) for six hours. After cooling, the 25 ml ethanol was poured into above reaction mixture to precipitate it. The reaction mixture was kept for 24 hours at room temperature. The precipitates obtained were filtered and dried at 60 ºC in a hot air oven and weighed accurately. Different reaction parameters such as concentration and initiator concentration were optimized to get the maximum graft yield. Synthesized graft copolymers were washed thoroughly with acetone and then with distilled water to remove attached homopolymer from graft copolymer. Then they were dried in a hot air oven at 50 ºC. Synthesized graft copolymers were studied in metal ion removal.
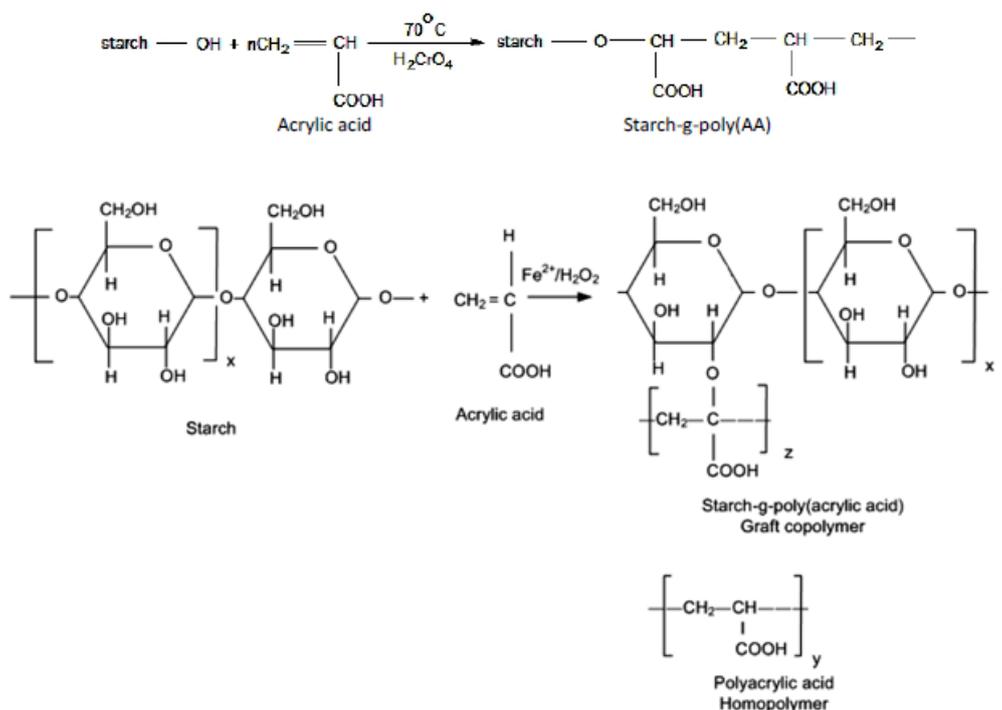
Scheme 1: Grafting of acrylic acid into starch

Different reaction parameters are summarized in Table 2.

Monomer type	Monomer concentration	Initiator concentration
Acrylic acid	0.5, 1 and 1.5 wt: wt % of the starch	0.01, 0.03 and 0.05 % of the monomer concentration

Table 2: Different reaction parameters

The percent grafting yield and grafting efficiency of starch-g-poly(Acrylic acid) were calculated as follow:

$$\text{Grafting yield (\%)} \ = \frac{W_3 - W_1}{W_1} \times 100 \qquad \qquad \text{Eqn} \qquad \qquad 1$$

$$\text{Grafting efficiency (\%)} \ = \frac{W_3 - W_1}{W_2} \times 100 \qquad \qquad \text{Eqn} \qquad \qquad 2$$

where W1 is the weight of starch before grafting, W2 is the weight of Acrylic acid before grafting and W3 is the total weight after grafting Acrylic acid onto the starch.

Synthesis of starch-g-poly(AAc), coated magnetic nanoparticles (MPS-MNPs)

MPS-MNPs were prepared by one step co-precipitation method. Briefly, 2.36 g $FeCl_3 \cdot 6H_2O$,0.86 g of $FeCl_2 \cdot 4H_2O$, and 1.5 g starch-g-poly(AAc)were dissolved in 40 mL of distilled water with vigorous stirring at 1000 rpm. After the solution was heated to 90 $^\circ$C,5 mL of25% NH_4OH was added. The reaction was continued for 1 h at 90 ∘C under constant stirring and nitrogen environment. The resulting nanoparticles were then washed with distilled water six times to remove the unreacted chemicals and dried in a vacuum oven. The codes and the compositions of the prepared nanocomposites are given in Table 3.

Code	Composition
MPS-MNP1	0.5 AA+ 0.01BPO +TPS+ Fe_2O_3
MPS-MNP2	0.5 AA+ 0.03BPO + TPS + Fe_2O_3
MPS-MNP3	0.5 AA+ 0.05BPO + TPS + Fe_2O_3
MPS-MNP4	1 AA+ 0.01BPO + TPS + Fe_2O_3
MPS-MNP5	1 AA+ 0.03BPO + TPS + Fe_2O_3
MPS-MNP6	1 AA+ 0.05BPO + TPS + Fe_2O_3
MPS-MNP7	1.5 AA+ 0.01BPO + TPS + Fe_2O_3
MPS-MNP8	1.5 AA+ 0.03BPO + TPS + Fe_2O_3
MPS-MNP9	1.5 AA+ 0.05BPO + TPS + Fe_2O_3

Table 3: Codes and compositions of the prepared magnetic nanogels

Characterization of the materials

- The functionalization of modified potato starch polymer onto the surface of Fe_3O_4 nanoparticle was detected by (Perkin-Elmer720) with a KBr pellet infrared spectrometer (Model 400) over the range of 4000–400 cm^{-1}.
- Transmission electron microscope (TEM, Jeol2100, 200Kv) was used to determine the size and morphology of magnetic particles.
- Thermo gravimetric analysis (TGA) was performed on a thermal analyzer (model Q600 SDT simultaneous DSC-TGA) to determine the magnetic content and thermal stability of the prepared MPS-MNPs. The X-ray diffraction (XRD) was carried out in a SHIMADZU diffractometer with high-intensity Cu Kα radiation (λ = 1.54065 Å) with the 2θ range from 10° to 90°.

Adsorption and desorption of heavy metal ions

Pb^{2+}, Cu^{2+} and Ni^{2+} ions adsorption experiments were conducted using batch equilibrium technique in aqueous solutions at pH range 2-5.5and at 25–55 $^\circ$C. In general, an average of 20 mg of dry magnetic nanoadsorbents placed with 10 mL of Pb^{2+}, Cu^{2+} and Ni^{2+}solution of 50 mg L^{-1}in a 50 ml bottles. The bottles were stoppered and shaken in a thermostatic shaker operated at 250 rpm for different time intervals 15, 30, 60, 90 and 120 minutes. Then the bottles were placed on permanent Nd–Fe–B magnet to remove magnetic nanoadsorbents and the supernatant was collected after magnetic decantation. The concentrations of Pb^{2+}, Cu^{2+} and Ni^{2+} ions were measured using flame atomic absorption spectrometer /ZEEnit 700P/Analytikjena Co./Germany.

The solution pH was adjusted by 0.1N NaOH or 0.1N HCl. For the non-competitive experiments, the initial Pb^{2+}, Cu^{2+} and Ni^{2+} ion concentrations used were 50 -250 mg L^{-1} and the pH used was 5.5. At various time intervals, samples were collected after magnetic decantation and the concentrations of studied pollutants were determined. In the competitive adsorption experiments, the metal ions were added in equal mass concentration (each 50 mg L^{-1})to a 10 mL solution contained in the vial. The vials were shaken for 2 h to ensure equilibrium before the magnetic nanoparticles were removed and the concentrations of remaining metal ions were measured as mentioned previously. The removal efficiency of MPS-MNPs was calculated from the following relationship:

$$\% \text{ Removal efficiency} = \frac{\text{The amount of cation Absorbed}}{\text{Initial cation Concentration}} \times 100 \qquad \text{Eqn.3}$$

Desorption study was conducted using 0.01 M phosphoric acid as desorbing agent. It was examined by adding 10 mL of the desorption eluent to the metal-sorbed MPS-MNPs. After shaking at 250 rpm for 3 h, the solid phase MPS-MNPs were collected by magnetic decantation and the concentration of each pollutant in the supernatant was measured. The reusability was checked by following the above adsorption–desorption process for four cycles.

RESULTS AND DISCUSSION

Synthesis and characterization of MPS-MNPS:

The compound	The most important peaks	Peak interpretation
Starch	A strong band at 2983cm^{-1} A strong band at 1166cm^{-1} A strong absorption peak at 3323cm^{-1} A strong absorption band at 816 cm^{-1}	C-H stretching vibration assigned to the ether bonds O–H stretching of the hydroxyl groups of glucose unit C–O stretching of alcohol
Starch-g-poly(AAc)	A strong band at 3200-3500cm^{-1} A strong absorption band at 1780 cm^{-1}	O–H stretching of carboxylic group C=O stretching vibration
MPS-MNP1	A wide strong band at 3200-3500cm^{-1} A strong absorption band at 1780 cm^{-1} A strong peak at 590 cm^{-1} Two peaks appeared at 1628 and 1400 cm^{-1}	O–H stretching of carboxylic group C=O stretching vibration Stretching vibration of Fe-O Bands of COOFe[33]

**Table 4: The most important peaks and their interpretation**
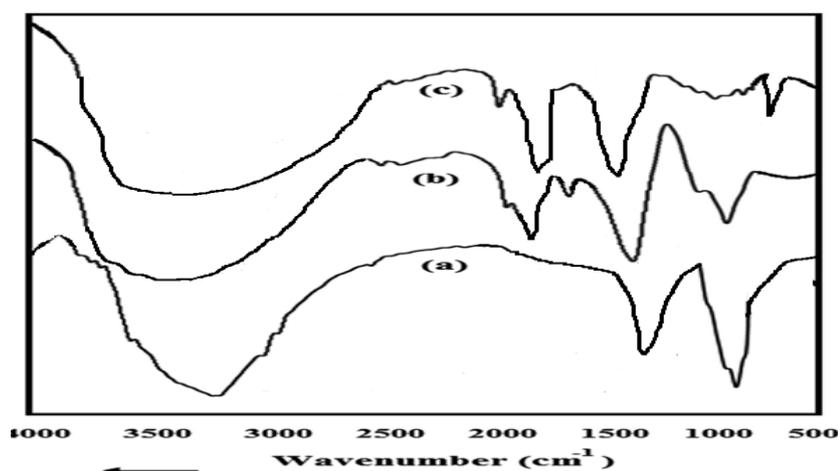
Figure 2: FT-IR spectra of a- Starch, b- Starch-g-poly(AAc) and c-MPS-MNP1

Starch-g-poly(AAc), coated magnetic nanoparticles (MPS-MNPs) were synthesized by simple co-precipitation where iron ions (Fe^{2+} and Fe^{3+}) and Starch-g-poly(AAc)polymer as shown in scheme 1. The functionalization of Starch-g-poly(AAc) on magnetic nanoparticles was confirmed by FTIR spectroscopy. Fig.

2(A) shows the FTIR spectrum of starch extracted from potato peels, Figure 2(B) shows the FTIR spectrum of Starch-g-poly(AAc) and Figure 2(C) shows FTIR spectrum polymer coated Fe_3O_4 nanoparticles (MPS-MNP1) in the 4000–400 cm^{-1} wave number range. The most important characteristic peaks for each one and their interpretation are given in Table 4.

Grafting and fabrication of potato starch

The magnetite particle sizes and the effect of monomer and crosslinker concentration are illustrated in Figure 3(a-e). Figures 3(a) shows the TEM image for non-coated magnetite nanoparticles which display the largest particle size distribution with evidence of aggregation of magnetite magnetic particles. Figures 3(b) and 3(c) show the growth of polymer coating around magnetite in MPS-MNP1 and MPS-MNP2 as the percent of crosslinker increased from 0.01 to 0.03wt/wt of potato starch. Figure 3(d) and 3(e) show complete polymer coating of MPS-MNP5 and MPS-MNP8 magnetite nanoparticles. TEM analysis demonstrates that the fabrication of magnetite with starch-g-poly(AAc) increases the size distribution of the magnetite nanoparticles and prevents particle aggregation due to the dispersion of magnetite within the polymer matrix. They also show that the coating of the oxide particles is not uniform due to non-uniform growth of polymer chains. The magnetite nanoparticle sizes were found to be consistent with the results from XRD analysis


a

b

c

d

e
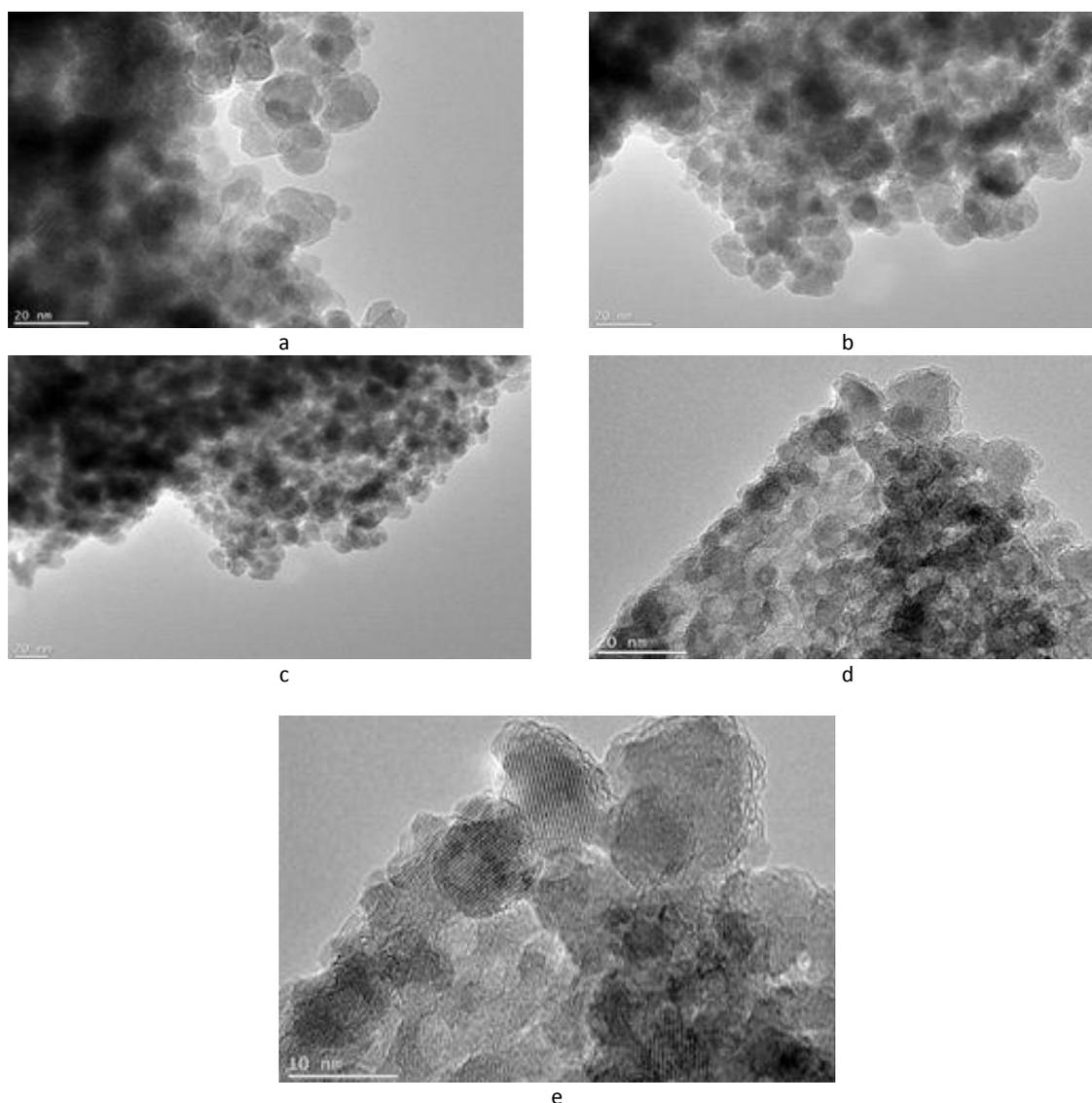
**Figure 3: TEM of a- non coated magnetite particles, b-MPS-MNP1, c-MPS-MNP2
d- MPS-MNP5 and e- MPS-MNP8**

XRD analysis

Figure 4 shows XRD pattern for MPS-MNP1 as a selected sample due to its highest content of magnetite. It can be seen that there is one sharp peak and several weak diffraction peaks. This reveals that the resultant nanopraticle contains Ferric oxide in its core and confirming its high magnetite content.
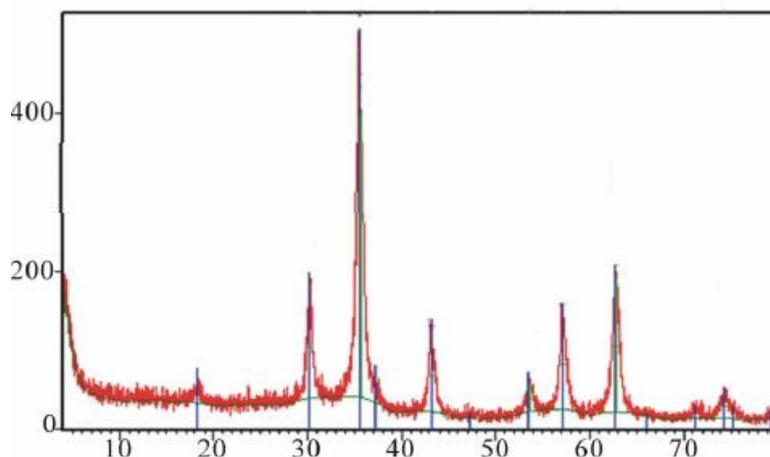

Figure 4: XRD pattern for MPS-MNP1

Factors affecting graft polymerization

The effect of monomer and initiator concentrations on grafting polymerization is shown in Table 5. The data reveals that grafting yield and grafting efficiency increase by increasing AAc contents. This may be attributed to that, as monomer concentration increases the active site of grafted starch increases. On the other hand, grafting yield and grafting efficiency increase by increasing initiator content from 0.01 to 0.03 and decreases by increasing imitator content to 0.05.This was due to increase in the active sites on starch at optimum value of initiator. Further increase in initiator concentration leads to homopolymerization due to increase in number of active radical species, which results in decreased grafting [34].

AAC concentration	Grafting yield	Grafting efficiency	Initiator concentration	Grafting yield	Grafting efficiency
0.5	10	65	0.01	5	60
1	20	75	0.03	30	80
1.5	40	85	0.05	10	70

Table 5: Effect of monomer and initiator concentrations on grafting polymerization

Factors affecting removal efficiency

Effect of contact time

Figure 5(a-c) show absorption isotherms for of Pb^{2+}, Cu^{2+} and Ni^{2+}ions adsorbed by a fixed concentration of the substrate (50 mg/L) for MPS-MNPs. It is obvious that there is rapid binding of the metal to the sorbent followed by slow increase until a state of equilibrium in 60 minutes was reached. Equilibrium time is one of the important parameters for an economical wastewater treatment system. After equilibrium state, a slight decrease in the adsorption efficiency was observed and it may be due to the mobilization of some adsorbed metal ions as a result of continuous shaking of the solution. It was found that MPS-MNP5 achieved complete metal removal for both $Ni^{2+}$and $Cu^{2+}$and 70% removal for Pb^{2+}. This may be explained on the bases of ionic radii. Ni ions with the least ionic size were observed to have adsorbed at a faster rate followed by Copper ions then Lead ions. Therefore, the smaller the ionic size, the greater its affinity to reactive sites. It is possible that the metal with smaller ionic size would diffuse faster through the adsorbent pores faster than the bulkier ions like Pb^{2+}. Thus the adsorption of cations with larger ionic radii would be less likely compared with smaller

ionic radii. Our findings run parallel to those obtained by Igwe et al. [35]. They stated that during sorption of metal ions, the ions of smaller ionic radii tend to move faster to potential adsorption. This has been observed on other biological adsorbents as reported earlier [35, 36]. On the base of the structure of sorbents, it was found that there is an optimum concentration of monomer and crosslinker to attain maximum efficiency of metal removal above and below which the metal ion uptakes decreases.
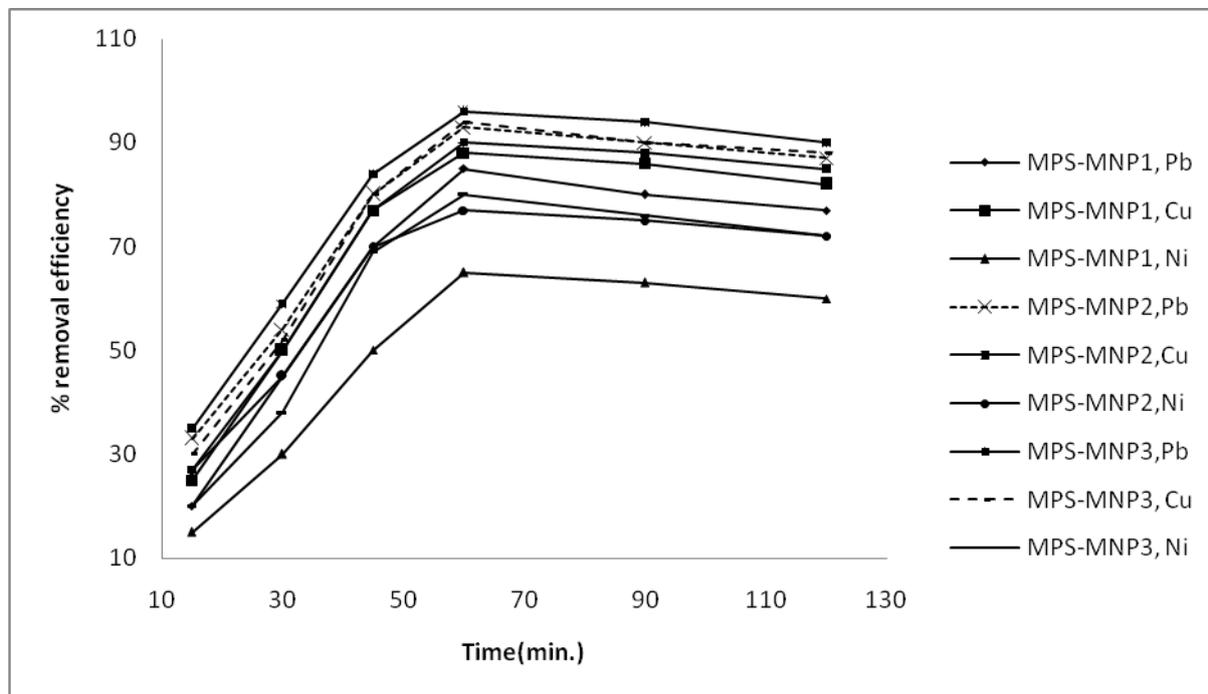
Figure 5a: Effect of contact time on removal efficiency of MPS-MNP (1-3) for the investigated metal ions at pH5.5 and at 35°C.
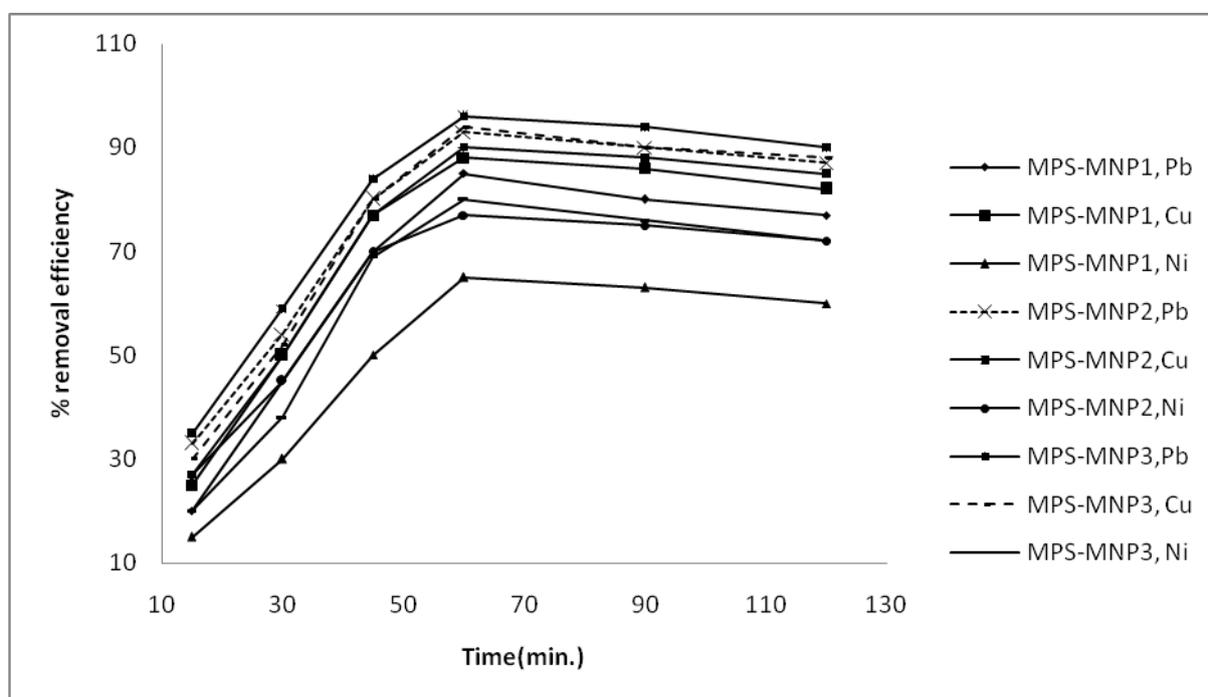
Figure 5b: Effect of contact time on removal efficiency of MPS-MNP (4-6) for the investigated metal ions at pH 5.5 and at 35°C.
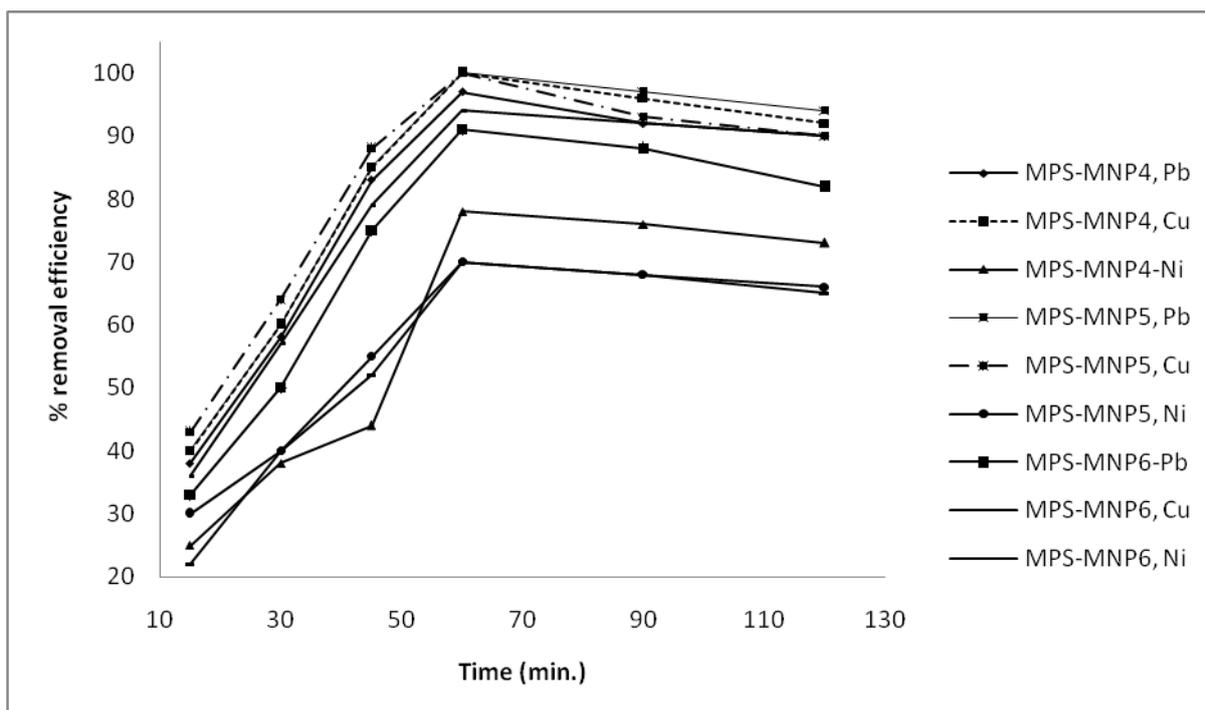
Figure 5c: Effect of contact time on removal efficiency of MPS-MNP (7-9) for the investigated metal ions at pH 5.5 and at 35°C.

Effect of pH

The pH of the aqueous solution is an important operational parameter in the adsorption process because it affects the solubility of the metal ions, concentration of the counter ions on the functional groups of the sorbent and the degree of ionization of the sorbent during the reaction. The active sites on the sorbent can either be protonated or deprotonated depending on the pH while at the same time the sorbent speciation in a solution also depends on the pH.
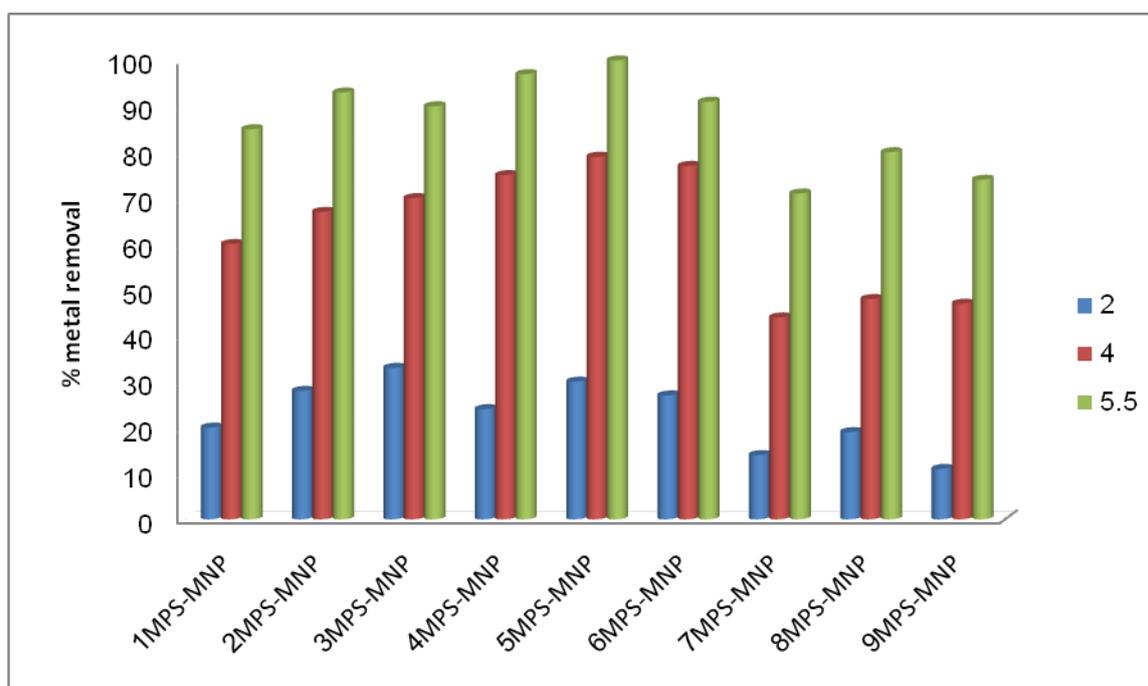
**Figure 6a: Effect of pH (2, 4, 5.5) on % removal efficiency of MPS-MNPs for removal of Cu ions at 35°C.**
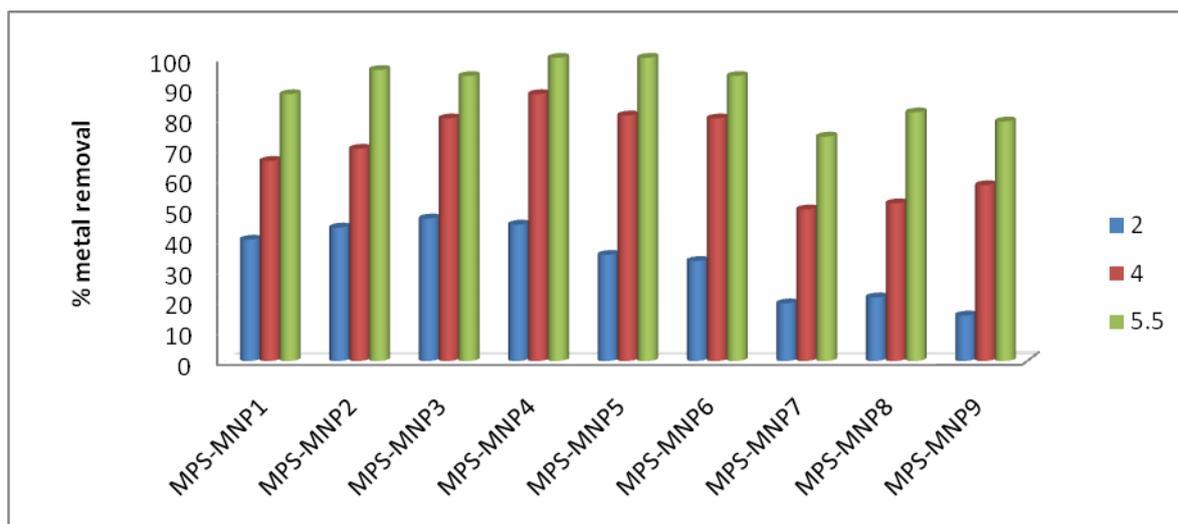
Figure 6b: Effect of pH (2, 4, 5.5) on % removal efficiency of MPS-MNPs for removal of Ni ions at 35°C.
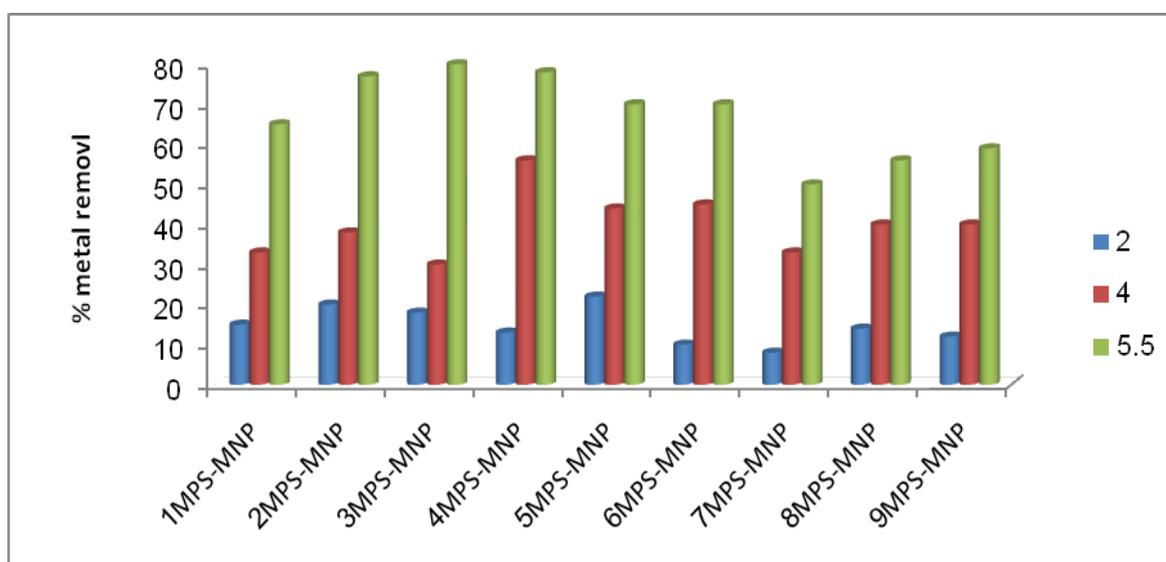

Figure 6c: Effect of pH (2, 4, 5.5) on % removal efficiency of MPS-MNPs for removal of Pb ions at 35°C

The effect of solution pH on the adsorption of metal ions by MPS-MNPs was studied at pH values 2, 4 and 5.5, 35°C, and an initial ion concentration of 50 mg/L, Figure 6(a-c). The adsorption studies at pH > 6 were not conducted because of the precipitation of Cu (OH)$_2$ from the solution. As shown in Figure 5(a-c), there is an obvious sharp decrease in the adsorption effectiveness for all the prepared nanosorbents when the acidity of the solution increases, i.e. from pH 5.5 to pH 4 to pH 2. This low adsorption efficiency at lower pH value could be referred to the sufficiently high hydrogen ion concentration, which led to the strong competitive adsorption [36]. Our findings match those obtained by Bhattit et. al. [37]. It can also observed that the order of metal ion uptake is Ni^{2+}> Cu^{2+}> Pb^{2+}. The set of nanosorbents that have complete polymer coating around the magnetic nanoparticles showed the best performance. This finding agrees with the data obtained from TEM images.

Effect of Temperature

The effects of temperature on the removal of metal ions by MPS-MNPs were investigated at aqueous solution of pH 5.5 and at temperature range 25-55°C and an initial metal ion concentration of 50 mg/L. As shown in Figure 7 (a-c), the % removal efficiency for the biosorbents increased with the increase in temperature from 25-35°C, revealing that the adsorption process was endothermic. But there is a sharp decrease in the efficiency above 35°C. One possible explanation was that the metal ions were well hydrated. They have to lose part of hydration sheath in order to be adsorbed. This dehydration process of metal ions

needed energy [38]. At higher temperatures, some desorption occurs due to the shrinkage of the sorbent and release some of the absorbed ions resulting in increasing the ion concentration in the solution again.
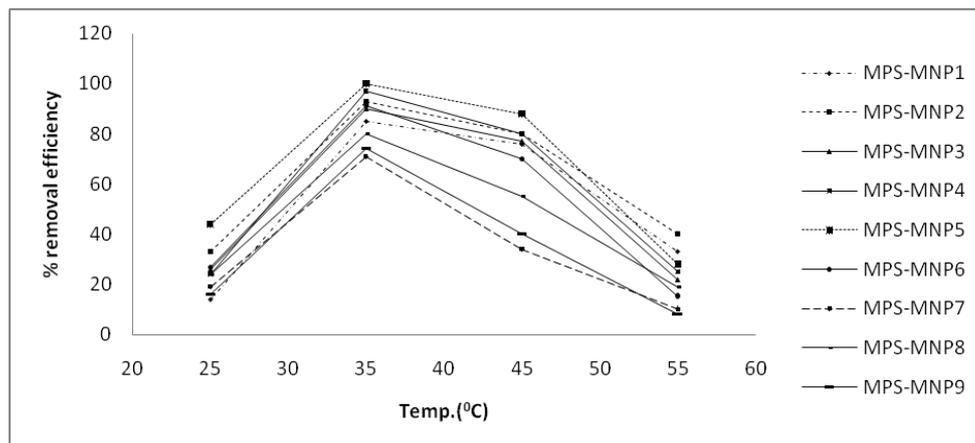

**Figure 7a: Effect of temperature on % removal efficiency of MPS-MNPs for removal of Cu ions at pH 5.5**
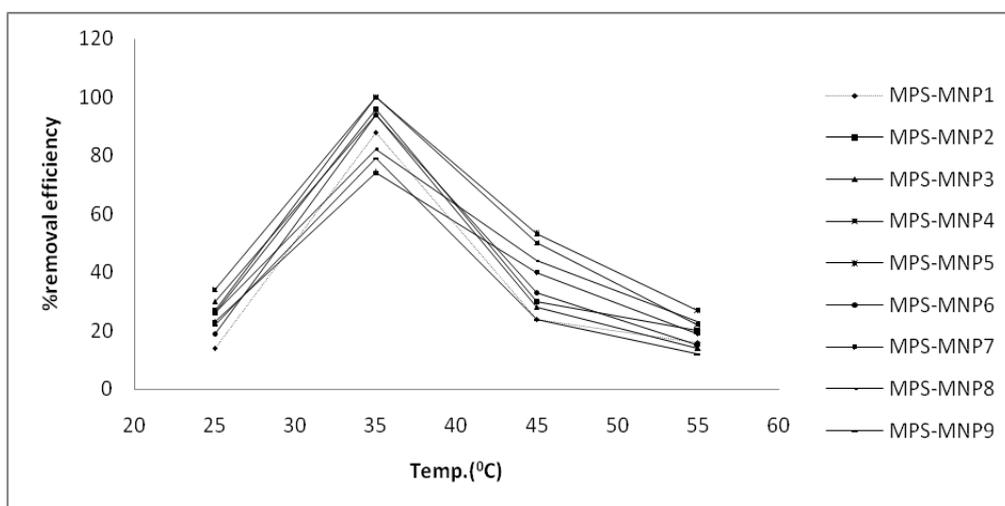
Figure 7b: Effect of temperature on % removal efficiency of MPS-MNPs for removal of Ni ions at pH 5.5
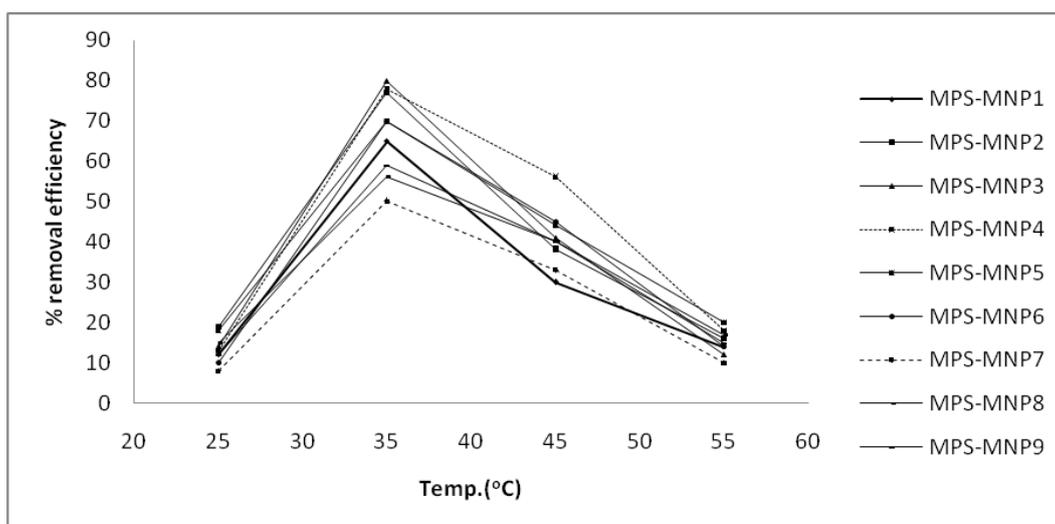

Figure 7c: Effect of temperature on % removal efficiency of MPS-MNPs for removal of Pb ions at pH 5.5

Competitive adsorption

The selectivity of MPS-MNPs sorbents towards specific metal ion was investigated by preparing of stock solution containing equal concentrations of the three investigated metal ions at optimum adsorption conditions. As shown in Figure 8, the adsorption efficiency of the biosorbents towards Ni and Cu ions is more pronounced. The uptake of Pb ions is much lower than the other two metal ions. This finding may be attributed to the smaller ionic size of both Ni and Cu ions relative to Pb ions. Eliga et al [39] stated that the order of removal of heavy metals by some cellulosic biosorbents was Mn (II)>Pb (II) due to difference in ionic sizes.
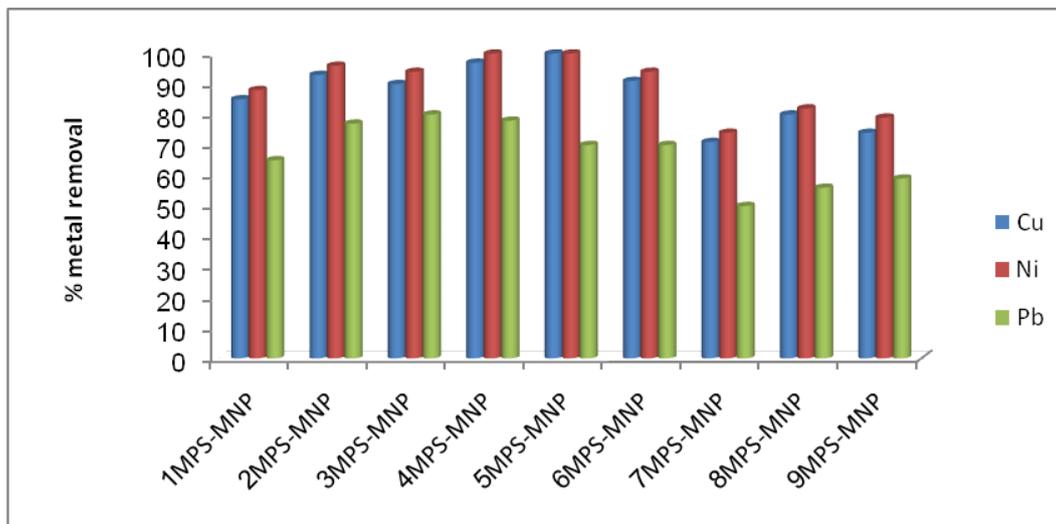

Figure 8: competitive adsorption experiment for the prepared MPS-MNPs sorbents

Reusability of the prepared biosorbents

Sorption-desorption experiments were carried out four rounds in order to investigate the reusability of the prepared sorbents. The data obtained from these experiments are illustrated in Fig.9 (a-c) for Ni, Cu and Pb ions respectively. It is clear that the removal efficiency of the modified potato starch sorbents was the same in the first and second rounds followed by slight decrease in the third round then remarkable decrease in the last round. This may be explained by the decomposition of parts of gel structure by the desorbing effluent [40, 41]. This finding proves the economic importance of the modified potato starch for two reasons. First, they were prepared from abundant natural waste material and second they are reusable several times with reasonable efficiency.
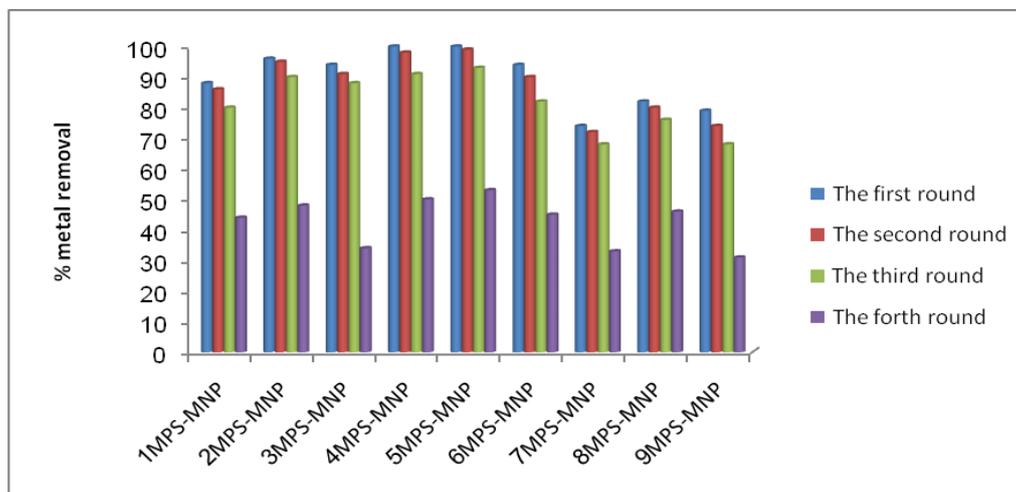

**Figure 9a: Reusability MPS-MNPs in removal of Ni ions at four rounds**
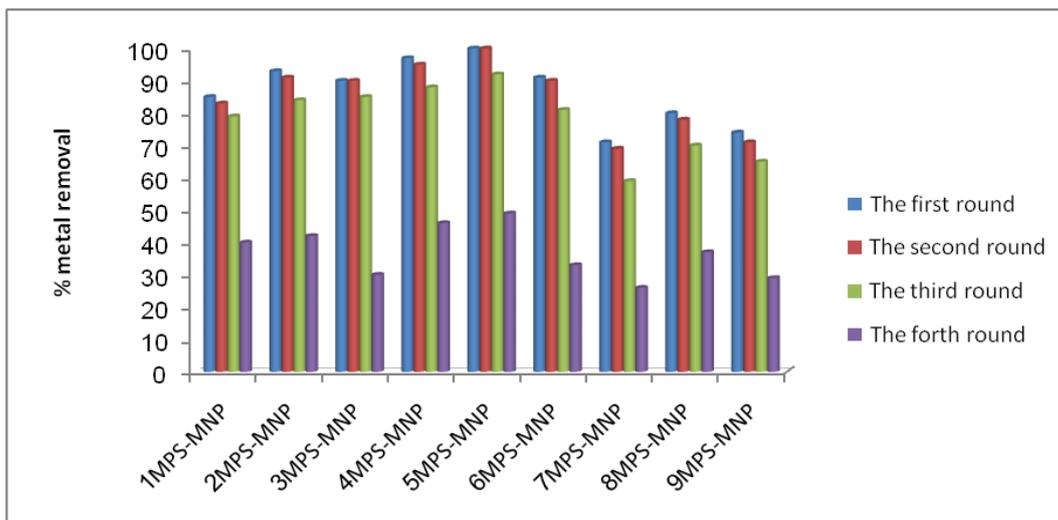
**Figure 9b: Reusability MPS-MNPs in removal of Cu ions at four rounds**
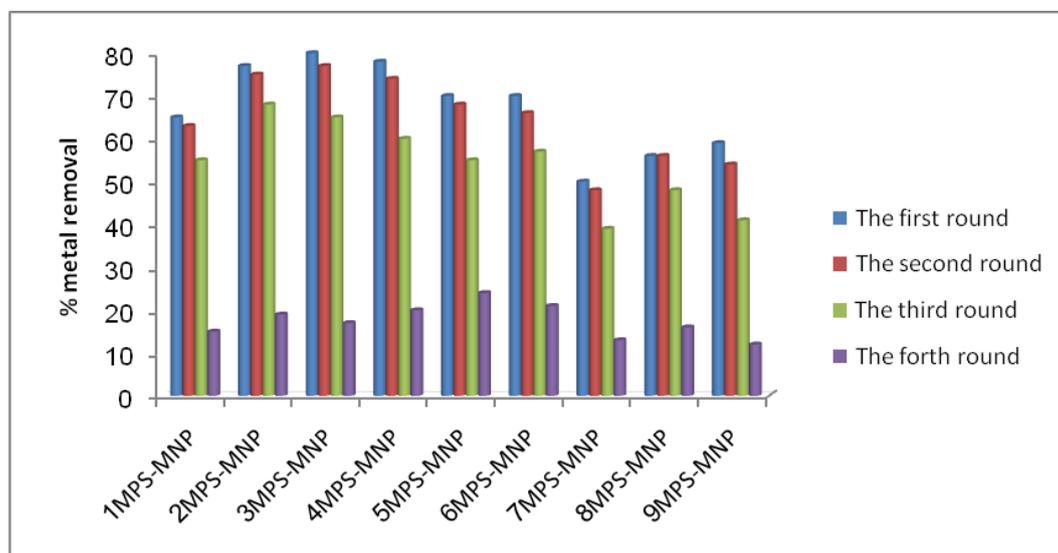
Figure 9c: Reusability MPS-MNPs in removal of Pb ions at four rounds

CONCLUSIONS

Treated potato starch was grafted with different weight ratios of acrylic acid in presence of different ratios of benzoyl peroxide as crosslinker. The grafted potato starch was then fabricated with iron oxide to prepare modified potato starch magnetic nano particles, MPS-MNPs. The nanosorbents were used as biosorbents in order to eliminate some heavy metals from waste water. The obtained data revealed that the biosorbents were effective in removing Nickel, Copper and Lead from waste water. It was found that the removal efficiency was dependent on several factors such as pH of the medium, the temperature at which the sorbents applied and the contact time between the metal ions and the sorbents. The data showed that the maximum removal efficiency was achieved at pH 5.5 and temperature 35°C.

REFERENCES

[1]   V. Lenntech, Rotterdamseweg, the Netherlands, Sources of Heavy Metals (1998-2011).
[2]   Gupta, N., Kushwaha, A. K., &Chattopadhyaya, M. C. (2012). Adsorptive removal of Pb^{2+}, Co^{2+} and Ni^{2+} by hydroxyapatite/chitosan composite from aqueous solution. Journal of the Taiwan Institute of Chemical Engineers, 43, 125–131.

[3]   Heidari, A., Younesi, H., &Mehraban, Z. (2009). Removal of Ni(II), Cd(II), and Pb(II) from a ternary aqueous solution by amino functionalized mesoporous and nanomesoporous silica. Chemical Engineering Journal, 153, 70–79.

[4]   Fernández, M., Villalonga, M. L., Fragoso, A., Caob, Ba˜nos, M., Villalonga, R., (2004). Chymotrypsin stabilization by chemical conjugation with Ocarboxymethyl- polycyclodextrin. Process Biochemistry, 39, 535–539.

[5]   Futalan, C. M., Kan, C. C., Dalida, M. L., Hsien, K. J., Pascua, C., Wan, M. W., et al. (2011). Comparative and competitive adsorption of copper, lead, and nickel using chitosan immobilized on bentonite. Carbohydrate Polymers, 83(2), 528–536.

[6]   Gupta, V. K., &Nayak, A. (2012). Cadmium removal and recovery from aqueous solutions by novel adsorbents prepared from orange peel and Fe_2O_3 nanoparticles. Chemical Engineering Journal, 180, 81–90.

[7]   Gupta, V. K., &Rastogi, A. (2009). Biosorption of hexavalent chromium by raw and acid-treated green alga Oedogoniumhatei from aqueous solutions. Journal of Hazardous Materials, 163(1), 396–402.

[8]   Gupta, V. K., Ali, I., &Saini, V. K. (2007a). Adsorption studies on the removal of Vertigo Blue 49 and Orange DNA13 from aqueous solutions using carbon slurry developed from a waste material. Journal of Colloid and Interface Science, 315(1), 87–93.

[9]   Ayoub, A. S. and Rizvi, S. S. H., An overview on the technology of cross-linking of starch for nonfood applications. Journal of Plastic Film and Sheeting, 2009. 25(1): 25-45.

[10]   Crini, G. (2005). Recent developments in polysaccharide-based materials used as adsorbents in wastewater treatment. Progress in Polymer Science, 30, 38–70.

[11]   Ahalya N, Ramachandra TV, Kanamadi RD (2003). Biosorption of heavy metals. Res. J. Chem. Environ., 7: 71-78.

[12]   Feng, Y., Gong, J. L., Zeng, G. M., Niu, Q. Y., Zhang, H. Y. and Niu, C. G., (2010). Adsorption of Cd (II) and Zn (II) from aqueous solutions using magnetic hydroxyapatite nanoparticles as adsorbents. Chemical Engineering Journal, 162, 487–494.

[13]   Tran, H. V., Tran, L. D., & Nguyen, T. N. (2010). Preparation of chitosan/magnetite composite beads and their application for removal of Pb(II) and Ni(II) from aqueous solution. Materials Science and Engineering C, 30, 304–310.

[14]   Banerjee, S. S., & Chen, D. H. (2007). Fast removal of copper ions by gum arabic modified magnetic nano-adsorbent. Journal of Hazardous Materials, 147, 792–799.

[15]   Zhu, H., Jia, S., Wan, T., Jia, Y., Yang, H. and Li, J., (2011). Biosynthesis of spherical Fe3O4/bacterial cellulose nanocomposites as adsorbents for heavy metal ions. Carbohydrate Polymers, 86, 1558–1564.

[16]   Gupta, N., Kushwaha, A. K., & Chattopadhyaya, M. C. (2012). Adsorptive removal of Pb^{2+}, Co^{2+} and Ni^{2+} by hydroxyapatite/chitosan composite from aqueous solution. Journal of the Taiwan Institute of Chemical Engineers, 43, 125–131.

[17]   Juang RS, Shiau RC (2000). Metal removal from aqueous solutions using chitosan-enhanced membrane filtrations. J. Membane. Sci., 765: 159-167.

[18]   Kim, M. and Lee, S.-J., Characteristics of crosslinked potato starch and starch-filled linear low-density polyethylene films. Carbohydrate Polymers, 2002. 50(4): 331-337.

[19]   Pourjavadi, A., Ayyari, M., Amini-Fazl, M.S., Taguchi Optimized Synthesis of Collagen-g-poly(acrylic acid)/kaolin Composite Superabsorbent Hydrogel. European Polymer Journal, 2008. 44: p. 1209-1216.

[20]   Aydin H, Bulut Y, Yerlikaya C (2008). Removal of Cu(II) ion from aqueous solution by adsorption onto low-cost adsorbents. J. Environ. Manage., 87: 37-45.

[21]   Crini, G. (2005). Recent developments in polysaccharide-based materials used as adsorbents in wastewater treatment. Progress in Polymer Science, 30, 38–70.

[22]   Kim B. S., Lim S.-T., Removal of heavy metal ions from water by cross-linked carboxymethyl corn starch. Carbohydrate Polymers, 39 (3), pp. 217-223, (1999).

[23]   Abia AA, Horsfall M, Didi O (2003). The use of chemically modified and unmodified cassava waste for the removal of Cd, Cu, and Zn ions from aqueous solution, Biores Technol., 90: 345- 348.

[24]   Abia AA, Asuquo ED (2006). Lead (II) and nickel (II) adsorption kinetics from aqueous metal solutions using chemically modified and unmodified agricultural adsorbents. Afr. J. Biotechnol., 5(16): 1475-1482.

[25]   Liu, Y., Wang, W., & Wang, A. (2010). Adsorption of lead ions from aqueous solution by using carboxymethyl cellulose-g-poly (acrylic acid)/attapulgite hydrogel composites. Desalination, 259, 258–264.

[26]   Mahlambi, M. M., Malefetse, T. J., Mamba, B. B., & Krause, R. W. (2010). Cyclodextrin-ionic liquid polyurethanes for the removal of organic pollutants and heavy metals from water: Synthesis and characterization. Journal of Polymer Research, 17, 589–600.

[27]   Sen G., Kumar R., Ghosh S., Pal S., A novel polymeric flocculant based on polyacrylamide grafted carboxymethyl starch. Carbohydrate Polymers, 77 (4), pp. 822-831, (2009).

[28]   Xie G., Shang X., Liu R., Synthesis and characterization of a novel amino modified starch and its adsorption properties for Cd(II) ions from aqueous solution. Carbohydrate Polymers, 84 (1), pp. 430-438, (2011).

[29]   Nair, K. P., Breedveld, V. and Weck, M., Complementary hydrogen-bonded thermo-reversible polymer networks with tunable properties. Macromolecules, 2008. 41(10): 3429-3438.

[30]   Amuda OS, Amoo IA (2006). Coagulation/flocculation process and sludge conditioning in beverage industrial wastewater treatment. J. Haz. Mater., 747: 778-783.

[31]   Amuda OS, Alade A (2006). Coagulation/flocculation process in the treatment of abattoir wastewater. Desalination, 796: 22- 31.

[32]   Amuda, OS, Amoo, IA, Ajayi OO (2006). Performance optimization of coagulation/ flocculation process in the treatment of beverage industrial wastewater. J. Haz. Mater, 129(1-3): 69-72.

[33]   Badruddoza, A. Z. M., Tay, A. S. H., Tan, P. Y., Hidajat, K., &Uddin, M. S. (2011). Carboxymethyl-β-cyclodextrin conjugated magnetic nanoparticles as nanoadsorbents for removal of copper ions: Synthesis and adsorption studies. Journal of Hazardous Materials, 185, 1177–1186.

[34]   Pathania, D.; Sharma, Synthesis and characterization of graft copolymers of methacrylic acid onto gelatinized potato starch using chromic acid initiator in presence of air, R. Adv. Mat. Lett.2012, 3, 136. DOI: 10.5185/amlett.2011.8297

[35]   Igwe JC, Ogunewe DN, Abia AA (2005). Competitive adsorption of Zn (II), Cd (II) and Pb (II) ions from aqueous and non- aqueous solution by maize cob and husk. Afr. J. Biotechnol., 4(10): 1113-1116.

[36]   Qiu Y, Cheng H, Xu C, Sheng SD (2008). Surface characteristics of crop-residue-derived black carbon and lead(II) adsorption. Water Res., 42: 567-574.

[37]   Bhatti HN, Mumtaz B, Hanif MA, Nadeem R (2007). Removal of zinc ions from aqueous solution using Moringaoleifera Lam. (horseradish tree) biomass. Process Biochem., 42: 547-553.

[38]   Abdel-Raouf M., Abdul-Raheim A., El-Kafrawy A., Maysour N., Ibraheim A. & Abdel-Azim A., (2013) PHEMA magnetic nanogels for removing of Cu ions from aqueous solution, International Journal of Chemistry and Material Science, Vol. 1(2): 036-044.

[39]   Egila JN, Dauda BEN, Jimoh T (2010). Biosorptive removal of Mn (II) ions from aqueous solution by AmaranthushydridusL. stalk wastes. Afr. J. Biotechnol., 9(48): 8192-8198

[40]   Okuo MJ, Oviawe AP (2007). Selective sorption of mixed Heavy Metal ions using Cassava fiber modified with Citric acid. J. Chem. Soc. Niger., 32(2): 247-253.

[41]   Amuda OS, Amoo IA (2006). Coagulation/flocculation process and sludge conditioning in beverage industrial wastewater treatment. J. Haz. Mater., 747: 778-783.