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Synthesis of coated magnetite nanoparticles by simple method to removal heavy ions from aquatic environments

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ABSTRACT

Preparation of magnetic nanoparticles coated with chitosan – silica (CS- coated Fe_3O_4 NPs) in one step by the co-precipitation method with some modifications, in the presence of different amounts of added chitosan is reported here. The magnetic property of the obtained magnetic composite nanoparticles was confirmed by X-ray diffraction (XRD) and magnetic measurements (VSM). Transmission electron microscopy (TEM) allowed the identification of spherical nanoparticles with about 30 nm in average diameter. Characterization of the products by Fourier transform infrared spectroscopy (FTIR) demonstrated that CS- coated Fe_3O_4 NPs were obtained. In this work we adopted a simple method for CS-coated Fe_3O_4 NPS obtaining, which could useful for heavier metal ions removal from water.

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INTRODUCTION

In the past several decades, magnetic nanomaterial of iron oxides (Fe_3O_4 NPs) have attracted much research interest due to their potential applications in many areas of chemistry, physics and material science based on their unique magnetic, physicochemical, and optical properties (Kim *et al*., 2007; Milano *et al*., 2010; Jadhav and Bonjiovanni, 2012; Dorniani *et al*., 2013; Dorniani *et al*.,2014;Gould, 2004; Ferrari, 2005). For applications are usually coated with polymers, bounded to the particle through organic linkers (Li *et al*., 2008). This type of coating is able to recognize specific molecules and ions for their binding and removal. Furthermore, in some cases it offers enhanced stability (Kekkonen *et al*., 2009). Magnetite nanoparticles coated polymer such as chitosan formed chains or oriented structure in external magnetic field (Lindlar and Boidt,2002; Woo *et al*., 2004). However magnetite particles were found to redistribute randomly when magnetic field was withdrew.

Different approaches had been used to generate magnetic chitosan materials such as blending (Mao *et al*., 2014; Lin *et al*. 2011), polymer micro gel template (Zhou *et al*., 2014) and co-precipitation methods(Hritcu *et al*., 2009).Most of traditional route to prepare magnetite/chitosan composite are co precipitation stoichiometric ferrous and ferric ions in presence of polymer with aqueous NaOH or $NH_3.H_2O$ directly , rapidly and without considering effects of magnetic field .On the otherhand , inorganic polymers , such as silica have been used as stabilizing agents for iron oxide and the silica coating has attractive properties including high biocompatibility (Mahmoudi *et al*., 2011), adsorption capacity , acid-base properties , insolubility in most solvents , chemical and thermal stability (Bai *et al*., 2006), in addition , silica can be grafted with a variety of functional groups, leading toconsiderable enhancement of their surface properties . Surface modification achieved by the attachment of in organic shells or/and organic molecules not only stabilizes the nanoparticles, eventually preventing their oxidation, but also provides specific functionalities that can be selective for ion uptake.This paperreports a simple method to prepare magnetite / silica / chitosan nano-compositeby the co-precipitation of magnetic nanoparticles in the presence of different chitosan concentration with some modification in this method, a detailed characterization of the products was carried out to demonstrate the feasibility of this method for obtaining chitosan-silica-magnetite nanoparticles in one stip. Also,in this work we carried-out a simple

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method for CS-coated Fe_3O_4 NPS obtaining, which could useful for heavier metal ions removal from water.

MATERIALS AND METHODS

2.1 Materials:

All reagents were high-purity grades from Aldrich and used without further purification: chitosan with low molecular weight (LMW), ferric chloride ($FeCl_3$. $6H_2O$, 99%), ferrous chloride [$Fecl_2$. $4H_2O$, 98%] tetraethylorthosilicate(TEOS≥98%), and ammonia solution (NH_3,28wt).

2.2 Synthesis Of Magnetite Nanoparticles:

The nanoparticles were prepared according to the method described by Massart, 1981,but without the use of hydrochloric acid. A total of 4.05g of $FeCl_3.6H_2O$ and 1.98g of $FeCl_2.4H_2O$ were dissolved in 100ml of distilled water; the solution was purged with nitrogen to agitate the mixture and prevent the oxidation of Fe^{2+} ions. After 30min of purging, 143ml of 0.7 mol/1NH_4OH was added dropwise into the solution and the now basified solution was purged for an additional 10 min. During the addition ofNH_4OH, it was noticed that the solution changed color from the original brown to dark brown and then to black.The precipitate was magnetically separated using a permanent magnet then washed with distilled water several times and allowed to dry in air. The resulting product was defined as M.

2.3Synthesis of Chitosan- Silica - Coated Magnetite Nanoparticles:

The procedure started with mixing a total of 0.99g $FeCl_2.4H_2O$ and 2.05g $FeCl_3$ in 50 mL of distilled water till complete dissolved.Then, the required amount of chitosan was added to the reaction mixture. Four concentrations by volumes of chitosan were used:25, 50, 75 and 100 ml from 0.2407gm.of chitosan in 100ml of 2% acetic acid. After this step the precursor TEOS (3ml) was carefully dropped into the reaction mixture usingasyrings, with mechanical stirring. The homogenization was performed for 15 min. After sonication for 15min. 143 ml of 0.7mol/L NH_4OH was added dropwise into the mixture with continuous mechanical stirring for 30 min. The coated particles were finally separated from the liquid using a permanent magnet, washed with distilled water several times, and allowed to dry at 60c°/3hrs. Finally,we also determined the effect of chitosan coating by varying the amount of chitosan added to the reaction mixture. In this regard, we studied the effect of four different amounts of chitosan, 25,50,75 and 100ml, which are equivalent to 0.5,1, 1.5 and 2%(w/v),respectively. The determine parameter of chitosan/ silica- coated magnetic nanoparticles is labeled asCSM_1,CSM_2,CSM_3 and CSM_4.

2.4Characterization of Nanocomposites:

Nanocomposites were analyzed by X-ray diffraction (XRD) of powdered samples using a Phillips multipurpose X-ray diffractometer with Cu k-α radiation.The size and shape of the nanoparticles were examined using a transmission electron microscope (TEM) (Model JEOL-1230, Japan).The IR spectra were recorded using a Fourier transform-infrared spectrophotometer (FT-IR).The sample and KBrwere pressed to form a table1.The magnetization values of the products were identified using vibrating sample magnetometer (Oxford) at the maximum external magnetic field of 1.2 Tesla at 25ºc.

2.5Pb^{+2} Removed by using Nanocomposite:

Typically , 50mg of dried nanocomposite were added to 50mL of 9 ppm pb^{+2} aqueous solution .Then, this mixture was ultrasonicated for 50 min at room temperature taking samples during the process each 10 min.After the nanocomposites were removed, the concentration of pb^{+2}in the samples was measured by atomic absorption spectrometer (specter AA 220model,Varian).

RESULTS AND DISCUSSION

3.1 Structure and shape at the support for nanoparticles:

The XRD pattern (Fig.1) of the Fe_3O_4 (M) nanoparticles prepared under standard conditions revealed diffraction peaks at 111 , 220 , 311 , 400 , 420 , 511 , 440 , etc. , which were the characteristic peaks of Fe_3O_4 crystals with a cubic spinel structure (Nedkov *et al*., 2004), it was clear that only the phases of Fe_3O_4 were detectable and there were no other undesired diffraction maximum as of the impurities that could be observed in the spectra , from the relatively wide half-peak breadth , it could be estimated that the particle size is quite small.From the XRD patterns , the average diameter that was calculated to be 13.7 nm using the scherrer equation ($D=K\lambda / B\cos\theta$, in which K is constant , λ is X-ray wavelength and B is the peak width of half maximum (Poulsen *et al*., 1995; Xu *et al*. 2007). Interestingly, it was observed that the diffraction patterns for the samples CSM_1, CSM_2, consisted of an amorphous structure, as clearly indicated in Fig1.The XRD patterns of the remaining samples CSM_3 and CSM_4 (not presented here) also showed an amorphous structure.The relatively low intensity reflections and absence of significant sharp diffraction peaks for the CSM_1 and CSM_2 patterns are probably due to the presence of SiO_2 on the surface of the magnetic nanoparticles. Xu *et al*. 2007, also suggested that the low intensity of the refection peaks could be attributed to the ultrafine crystalline structure of the magnetite particles used for the generation of silica-chitosan-coated nanoparticles. The particle size and morphology of magnetic nanoparticles coated with or without silica-chitosan were evaluated from the TEM

micrographs.It is noteworthy that the size distribution is 12-18 nm, which matched the value calculated using the scherrer equation, and that the nanoparticles are spherical in shape (Fig.2a) and their aggregation can be discerned clearly.In Fig.2b, c and d, the coated silica-chitosan layer can be observed as a typical core-shell structure of the Fe_3O_4/SiO_2/ chitosan nanoparticles.Thedisperseof the Fe_3O_4/SiO_2/chitosan nanoparticles was also improved, and the average size increased to about 30 nm.

3.2 FT-IR Spectra Of The Magnetite Nanoparticles:

The FT-IR spectra of magnetite are shown in Fig3. A factor group analysis, reported in a classic IR study on spinels, suggested that there were four IR-active bands; however, in most cases, including magnetite, only two ofthem are observed between 400 and 800 cm^{-1}(White and De Angelis, 1967). In this study, magnetite showed a broadband that consisted of two slightly split peaks identified at 573 and 621 cm^{-1}; these peaks were attributed to the stretching vibration of the Fe-O bond and confirmed the occupancy of Fe^{+3} ions at tetrahedral sites in a manner consistent with that reported in the literature (Ma *et al*., 2005; Guang-she *et al*., 2001; Li *et al*., 2010). On the low- frequency side of the broad band, we observed that the weak peaks appearing at 432 and 453 cm^{-1} correspond to the presence of the Fe^{+3}–O^{-2} bond at octahedral sites (Maity and Agrawal, 2007). In contrast, we found a broad peak near 3380 cm^{-1} and a sharp peak near 1635 cm^{-1}, which were attributed to the stretching and binding vibrations of the hydroxyl groups. These peaks confirm the presence of adsorbed water on the surface ofmagnetite (Ti *et al*., 2006). However, the peaks at 1383 and 1453 cm^{-1}resluted from the stretching vibration of the C-O bonds in CO_2,which might come from air. Figure 3 shows the IR spectrum of the chitosan–silica-coated magnetite nanoparticles.It was clear that the characteristic adsorption bands of the Fe-O bond (Fe^{+3}–O^{-2}) of the silica – chitosan coated magnetite nanoparticles shift tohigher wave numbers of591,637,435,and 469 cm^{-1}, respectively, compared with that of uncoated nanoparticles (in 573, 621 , 432 and 453cm^{-1}). The absorption bands at around 1037,800, and 469 cm^{-1} reflect the Si-O-Si asymmetry, Si-O-Si symmetric starching vibrations, and deformation mode of Si-O-Si, respectively (arruebo *et al*., 2006). The bands at 591 and 970cm^{-1} are possibly because of the Fe-O-Si and Si-O-Si stretching vibrations caused by the perturbation of the metallic ion in the SiO_4tetrahedrarespectively (Chang *et al*.,2006).In accordance with that reported in the literature (Guo *et al*.,2010; Chen *et al*., 2009) the characteristicabsorption bands for chitosan in Fig 3appear at 3360 (O-H and N-H stretching vibrations),2862 (C-H stretching vibrations), 1650(N-H bending vibrations), 1420 (C-N stretching vibrations) and a group of bands for 1100 to 1020cm^{-1}(C-O-C and C-O stretchingvibrations).Thus, it was concluded that all the silica and chitosan in the final product is chemically bound to the surface of magneticnanoparticles .However, the possibility that some magnetic nanoparticles remained uncoated cannot be dismissed. Once the FTIR results demonstrated that the precipitation reactions carried out with TEOS and chitosanrendered magnetic nanoparticles coated by these silica and polymer.

3.3 Magnetic Property of Coated Magnetite:

The effect of magnetic coating on magnetic property may be evaluated from the data of analysis. This analysis utilizes a power of the external magnetic field to produce a hysteresis curve describing the magnetic properties of samples. This curve resulted from analysis of coated magnetite is expressed in Fig 4 , and magnetic parameters including saturation filed value (M_s), corecivity filed (H_c)and permanent magnetization (M_r) can be calculated and presented in Table1. From Fig 4 seems that all magnetite (coated and uncoated) give small curve area indicating low energy for magnetization and are classified as soft magnet. This assumption is supported by the low $H_c$valuesof the samples. The value of $H_c \neq 0$ for Uncoated and coated magnetitesindicates ferromagnetic properties of the samples. The difference in magnetization value between bare Fe_3O_4 nanoparticles and Fe_3O_4–silica–chitosan particles can be attributed to the nonmagnetic organic components which can reduce the total magnetization to different extent (Guo *et al*., 2010). Lin *et al*., 2010) reported that coating magnetite with amino-silica material leads to decrease of magnetization. It was explained that this decrease was ascribed to the contribution of the nonmagnetic NH_2/SiO_2 layer to the total of the particles.

Table 1: magnetic parameters of magnetite and coated magnetite

Samples	M_s(emu/g)	H_c(x10^{-2} Tesla)	M_r(emu/g)
M	69.28	1.76	16.33
CSM_1	36.54	1.82	7.22
CSM_2	33.15	1.82	8.12

CSM_4	14.05	1.12	3.45

3.4 Pb^{+2} Removed by using Nanocomposite:

The final test in this study was to evaluate the efficiency of the obtained composite in pb^{+2}removal from a $pb(NO_3)_2$ aqueous solution . This test is based on the ability of different concentrations of chitosn to chelate heavy metal ions through its amino groups. For this, the composites prepared with 0.5% (w/v) and 2% (w/v) chitosan were evaluated. Figure 5 shows that the pb^{+2} concentration drops from its initial value (9ppm) to around 5.4in the first 10 minutes in the assay when the compositewasprepared with 0.5% (w/v) chitosan.Then,it slowly decreasedtoattain a final value of 4 ppm at the end of the test. In the assay carried out with the composite prepared with 2% (w/v) chitosan, value 7.5 and 5.4ppm were attained in the first 10 minutes and at the end of the assay,respectively. From here, a removal efficiency of 53.2% for the CSM_1nanoparticles prepared with 0.5%(w/v) chitosan and of 39.6% for those CSM_4 with 2%(w/v) chitosan were prepared,which is surprising because of a direct relation between removal efficiency and chitosan content in the evaluated composites was expected. This indicate that the nanoparticles prepared with the higher chitosan content have a smaller total amount of amino groups on their surface , which really means that they have less total surface area than the nanoparticles with 0.5(w/v) chitosan. A possible explanation for this behavior is that contents of chitosan as higher as 2%(w/v), under the conditions used in this study, favor the aggregation of chitosan –silica –coated nanoparticles.In turn, this would lead to an increase in the final nanocompoiste size and as a consequence, to a decrease in thetotal surface area.

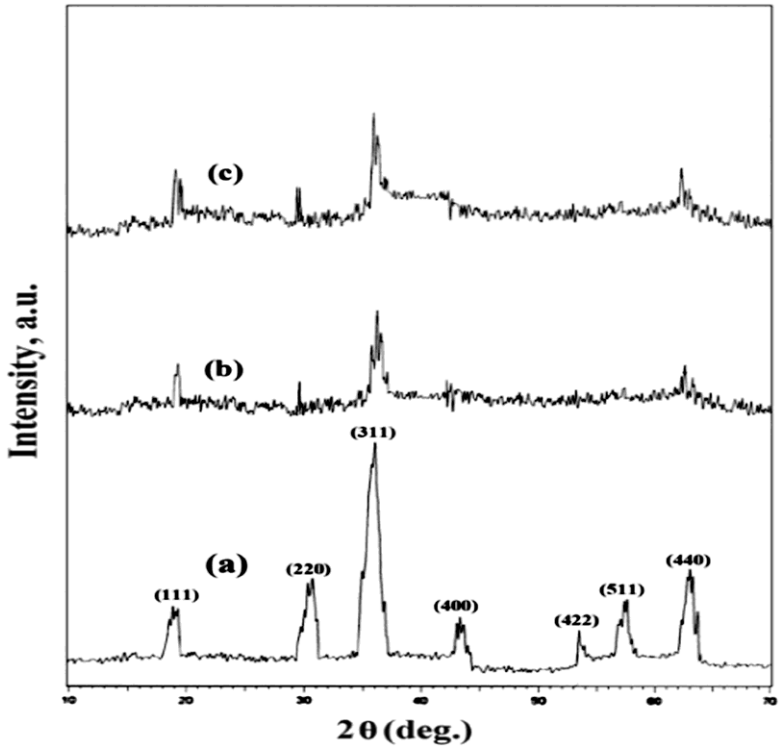

Fig. 1: XRD patterns of (a)uncoated magnetite nanoparticles (b) CSM1 and (c) CSM2

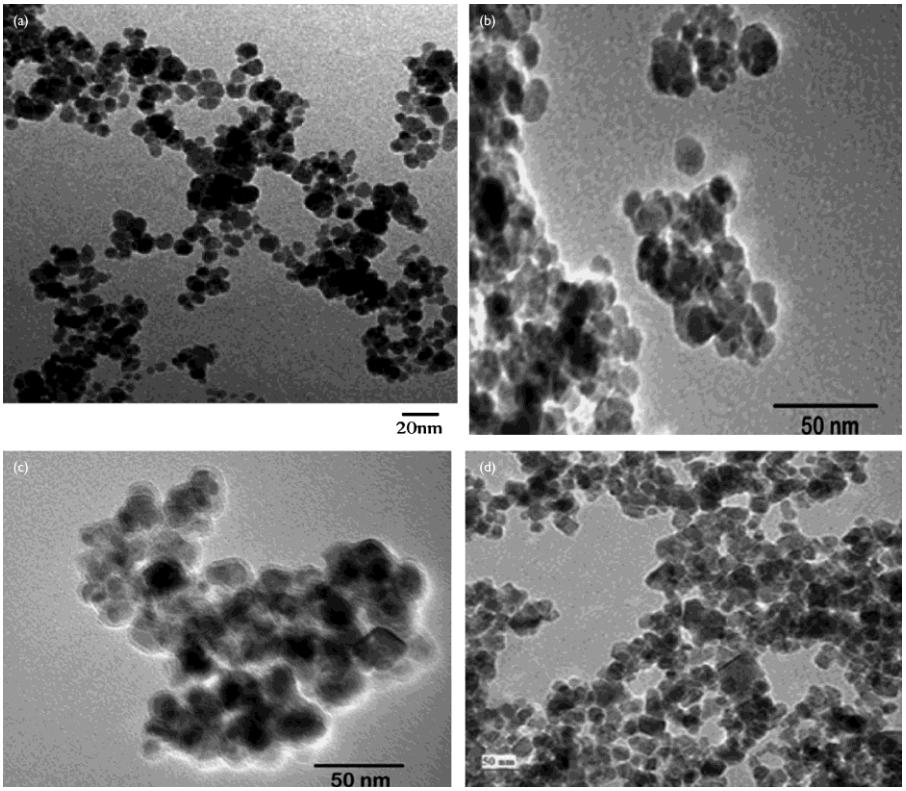

Fig. 2: TEM images of (a) uncoated Magnetite nanoparticles, (b) CSM2, (c) CSM3 and (d) CSM4

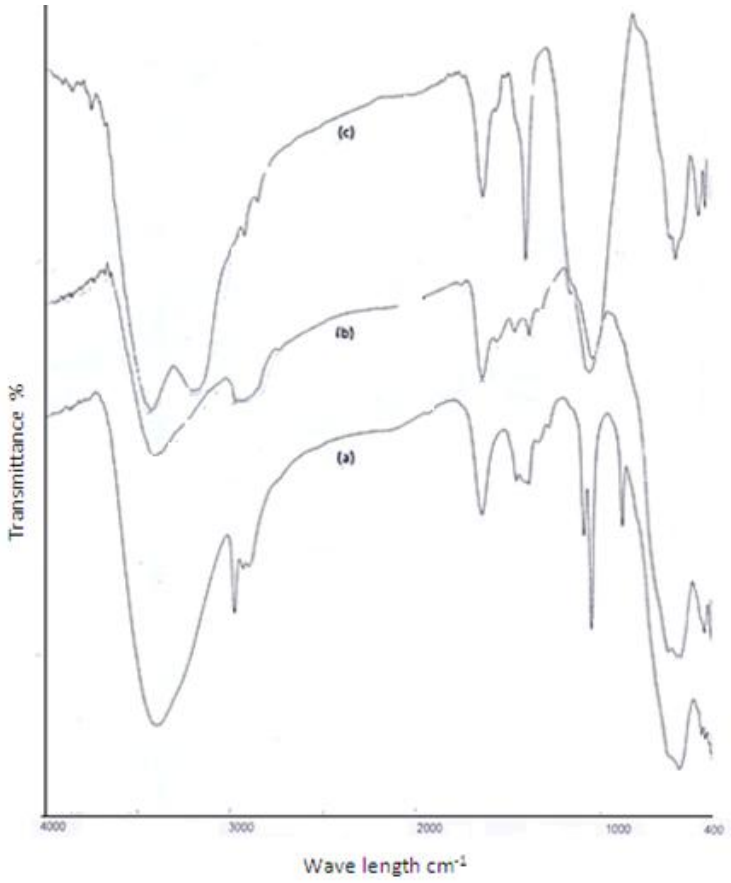

Fig. 3: FTIR of (a) uncoated Fe_3O_4 (b) CSM1 and (c) CSM4

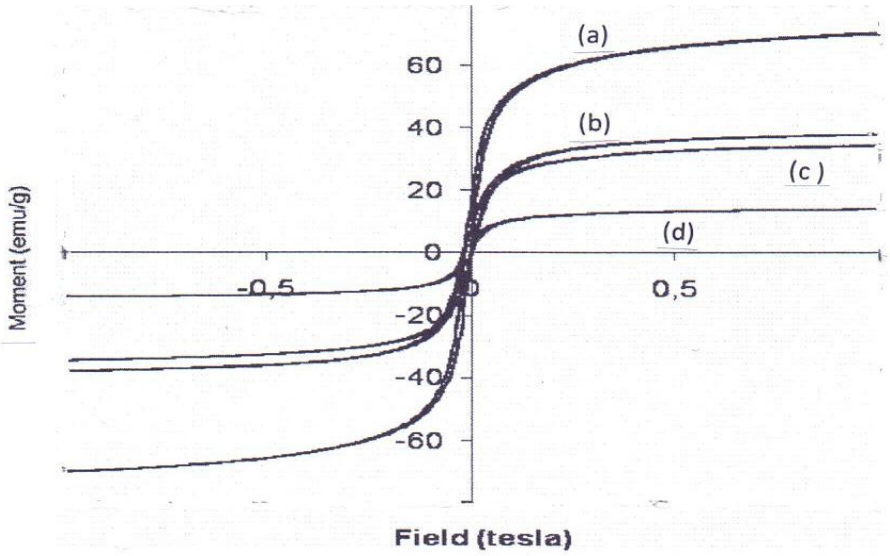

Fig. 4: Magnetization curves of magnetite materials; (a) uncoated Fe_3O_4 (b) CSM1 (c) CSM2 and (d) CSM4

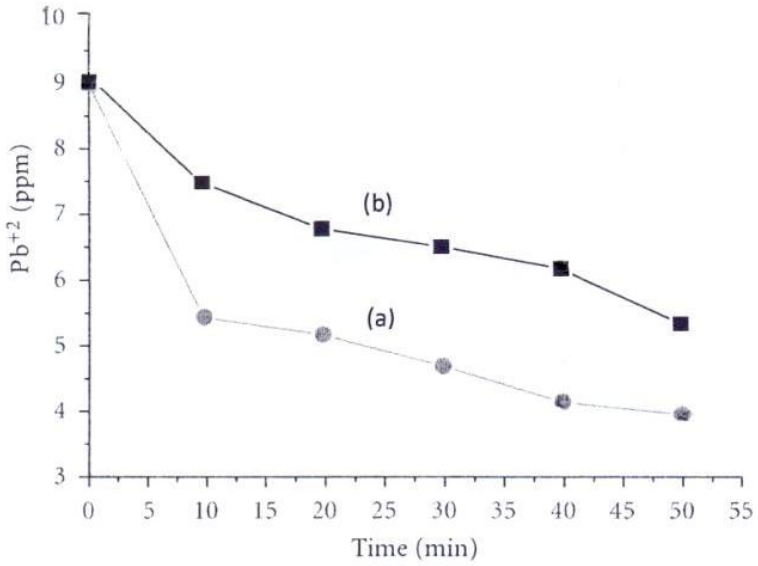

Fig. 5: Pb^{+2}removal as a role of time using chitosan – silica coated magnetic nanoparticles prepared with (a) 0.5 and (b) 2% (w/v) chitosan.

Conclusion:

From these results it can be concluded that Fe_3O_4 magnetic nanoparticles and Cs-coated Fe_3O_4 NPs with excellent properties have been successfully prepared using the chemical co-precipitation technique with some modifications. The XRD results indicate that the composites were in the nanoscopicphase. Based on the TEM images, the diameters of the coated magnetite particles were determined to be about 30nm. The silica coating appeared to be effective in protecting the magnetite from being converted to other oxide species .The presence of amino group in coated samples are effective for separation and removal of heavy ions from aquatic environments.

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