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Removal of Cu (II) by Modified Magnetite Nanocomposite as a Nanosorbent

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Abstract: ***Present study reveals an effective* removal *method of Cu(II)) ions from water was investigated using silica-coated magnetite nanocomposite functionalized with EDTA as an nanosorbent. The nanosorbent was synthesized by co-precipitating iron salts followed by silica coating by sol-gel hydrolysis of TEOS. Further EDTA (Ethylene di-ammine tetra acetic acid) was functionalized on the surface of silica coating by sol-gel process. SEM image confirm the formation of magnetite nanopartilces with average diameter of 12-13 nm.. Silica-coating and the functionalisation of EDTA on its surface were confirmed by FT-IR. EDX study also confirmed the preparation of nanosorbent and the adsorption of Cu^{2+} ions on its surface as well . VSM study showed that nanosorbent was super paramagnetic at room temperature. Adsorption isotherm was well described by Langmuir adsorption model with maximumadsorption capacity of .099mole/gram. Adsorption mechanisms were ionexchange and electrostatic force of interactions. The metals loaded adsorbent was separated effectively by applying external magnetic field due to its superparamagnetic nature..The reaction parameters were optimized and it was found that at 10-15 minutes, at pH 5.5-6.5 and by taking 0.11gram adsorbent , 90-95% copper was adsorbed. The adsorbent stability in acidic and basic medium, its reusability and recyclability were also tested satisfactorily.***

Keywords: Nanocomposite, nanosorbents, Sol-gel hydrolysis, Adsorption isotherm

1. Introduction

Toxicity of heavy metals in ground water are of major concern for its hazardous effect on the environment **[**1**]** The sources of these toxic metals are anthropogenic activities like industrial wastes,vehicular pollution and natural causes like seepage from rocks,volcanic activity and forest fire may also contribute . In general heavy metal toxicity can cause chronic degenerative diseases and the symptoms are muscles and joint pain, mental disorders, gastro-intestinal disorders,chronic fatigue,vision problem, susceptibilty to fungal infection etc.Infact oxidation state of metals and the degree of the solubility of its different forms of salts defines its level of toxicity in water**[2]**. Although small quantities of heavy metals are essential for healthylife as they play key role in important biological activities but large amount of them may cause acute or chronic toxicity. For instance copper is an essential element in human metabolism,play a crucial roles in the development of bones,central nervous system and connective tissues. It is an integral part of certain imporatnt protein and enzymes. The acceptable limit of copper in drinking water is .05mg/l but normally its concentration vary from .01-.5mg/l which is tolerable and poses no serious health threat to human life as well other living organism. But when concentration of copper exceeds the 1.5 mg/l in water due to various natural sources and human activities it cuases serious health effects. Examples of natural sources are wind-blown dust, decaying vegetation, forest fires and sea spray. A few examples of human activities that contribute to copper release have already been named. Other examples are mining, metal production, wood production and phosphate fertilizer production. Because copper is released both naturally and through human activity it is very widespread in the environment. Copper is often found near mines, industrial settings, landfills and waste disposals. Most copper compounds will settle and be bound to either water sediment or soil particles. Soluble copper compounds form the largest threat to human health. Usually water-soluble copper compounds occur in the environment after release through application in agriculture .Hence it is necessary to remove copper from water by using cost-effective and environmentally friendly technique. Till now numerous processes are available to remove dissolved toxic metals from water including thermal, biological and chemical methods such as chemical precipitation, coagulation, solvent extraction, ultra filtration, electro dialysis, membrane separation, adsorption, ion exchange process etc **[3].**

Among various techniques adsorption is the most promising technique used in the removal of toxic metals from water Nowadays application of nanomaterials as a nanosorbents is attractive and efficient method for the removal of toxic metals from ground water **[4,5].**

The unique physico-chemical properties of nano materials such as size in nano range, larger surface area to volume ratio, high mechanical strength, easy surface functionalisation with different chemical groups etc ,makes them an efficient nanosorbents to be target selective for the pollutants in water purification **[6,7]** Several research groups are exploiting the unique properties of nanoparticles to develop high capacity and selective sorbents for metal ions and anions [8]

Iron oxide nano materials have special advantage in water purification technology due to its super paramagnetic property, least toxicity, biodegradable, environmentally friendly, easy and facile synthesis et.c [**9,10].**

Till now in various research studies iron oxide nanomaterials such as Fe_3o_4 and y-Fe_2O_3 and its composite with variety of inorganic and organic compounds have been successfully applied in water purification as a nanosorbents **[11, 12, 13],** photo catalysts and immobilization carrier. In present study silica-coated magnetite nanoparticles with its surface functionalized by ethylene di-ammine-tetra acetic acid (EDTA) is tested as a nanosorbents for the capturing of toxic metals from water. It has been found that EDTA-Si-Fe_3o_4, is an excellent adsorbent for toxic metals. Its removing capacity is far better than conventional sorbents .

UV-Vis spectrophotometer technique is also applied to the determination of equilibrium Cu^{2+} metals ions concentration in the solutions with the help of calibration graph. This will helpful in the calculation of percentage recovery of toxic metal ions.

2. Materials and Methods

2.1 Materials

$FeCl_2.4H_2O$,$FeCl_3.6H_2O$,TEOS Tetraethoxysilane), EDTA (Ethylene-di- ammine tetra acetic acid) were purchased from Fisher scientific and Aldrich Chemical Reagent Co.Ltd. All reagents used in the synthesis were of analytical grade. The stock solution (.1M) of $CuSO_4.5H_2O$ for adsorption study was prepared by dissolving calculated amount of salts of metals in deionised water and different concentration of solution were obtained by diluting the stock solution.

2.2 Preparation method for EDTA-functionalized silica-coated magnetite nanocomposite.

The magnetite nanocomposite adsorbent was synthesized by co-precipitating ferrous and ferric salts in 1:2 molar ratios in basic medium at 90^0C with N_2 protection on ultrasonic stirrer**[14**] Silica coating was done by the hydrolysis and polycondensation of precursor TEOS (sol-gel process) followed by functionalisation of EDTA in slightly acidic medium (via sol-gel process).

2.3 Sample analysis method

Surface morphology and size of the synthesized nanocomposites was determined by SEM. FT-IR spectral analysis showed the confirmation of functionalisation of EDTA on the surface of silica-coated magnetite nanocomposite and also confirmed the adsorption of copper on the surface. Sample composition and elemental analysis was done by EDX spectral analysis .Super paramagnetic property was determined by using VSM.

2.4 Adsorption experiment

The adsorption of metal ions were studied by stirring(300rpm) fixed amount of nanosorbents with 10ml of .1M standard solution of metal ions for 15minutes at room temperature to achieve equilibration. After that metal loaded sorbent was magnetically separated. The concentration of unloaded metal ions in the solution was determined by the calibration graphs **Fig 6(a**) plotted by diluting concentration of standard solution in a fixed ratio and corresponding absorption is measured with the help of UV-Vis spectrophotometer at a fixed wavelength (λ_{max}). The concentration of adsorbed metal ions was calculated as a difference between the initial concentration in the solution and the final concentration after the equilibration. The amount of metal ions adsorbed at time t, qt in mg/gm is calculated as a mass balance equation- $q_t = \{C_o\text{-}C_{t\}}\ _{V/m.}$ Where C_O, $C_{t,}$ V, m are initial concentration of metal ions, concentration of metal ions after time t, volume of the solution, mass of the adsorbent.

The pH of the solution after equilibration was changed hence it was stabilized before magnetically separated. Percentage recovery factor (% R) was calculated by the following equation- % R = C_a/C_O x 100 where C_a, C_o are adsorbed concentration and initial concentration of metal ions.

2.5 Sorption Isotherms

Sorption isotherms were obtained by mixing .19gram of nanosorbents with 10ml metal solutions with different initial concentration ranging from .01 to .1 mol/L by adjusting the solutions PH = 6.5. Then the different concentration beakers were kept on ultra sonic stirrer for 15 minutes at constant temperature for adsorption. After adsorption and subsequent magnetic separation the final metal concentrations in the supernatant were measured.

2.6 Effect of adsorbent dosage

To observe the effect of adsorbent dosage on the adsorption capacity, 10ml of .1M metal solutions were taken and the PH of the solutions were adjusted at 6.5.Then various amount of adsorbents were added to the solutions on ultrasonic stirrer at constant temperature for 15 minutes. After the reaction and separation the residual metal ions were determined.

2.7 Effect of PH

The effect of PH on adsorption capacity was tested by mixing .19 gram of adsorbents with 10ml of .1M metal solutions with different PH value ranging from 2 to 6.5 under vibrating condition on ultrasonic stirrer for 15 minutes. After reaction and followed by magnetic separation the residual metal concentration were determined.

2.8 Effect of contact time

To investigate the effect of contact time on the adsorption capacity,.19 gram of adsorbents were mixed with 10 ml of .1M metal solutions by adjusting PH 6.5 followed by stirring at constant temperature on ultratasonic stirrer for different time interval ranging from 2 to 15 minutes .After adsorption and subsequent separation the residual metal concentration were determined.

2.9 Desorption and reusability

Desorption study was investigated using .1M HCl solution as an eluant to elute metal ions from the adsorbent. For this .19 gram adsorbent was loaded with 10ml metal solution followed by separation of metal loaded sorbent magnetically. After thorough washing with distilled water the metal loaded adsorbent was mixed with 10ml of .1M HCl and kept on ultrasonic stirrer for15 minutes at room temperature. After the elution the unloaded adsorbent was separated magnetically and the metal concentration was measured in the supernatant. Recovered adsorbent was reused for adsorption of metal ions.

3. Result and Discussions

3.1 Characterization of EDTA-Functionalized-Si-coated magnetite nanocomposites as nanosorbent

Fig (1) showed the SEM images of the nanosorbents to reveal the surface morphology and size. It was found that the size of the nanosorbents were spherical in shape with average diameter of 18nm.

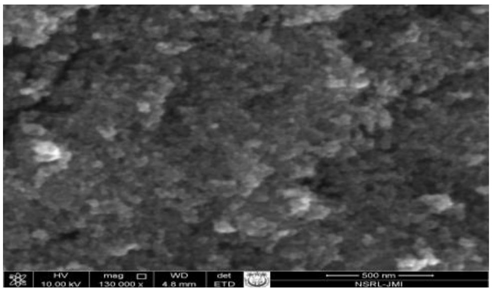


Figure1: (a) magnetite nanosorbents

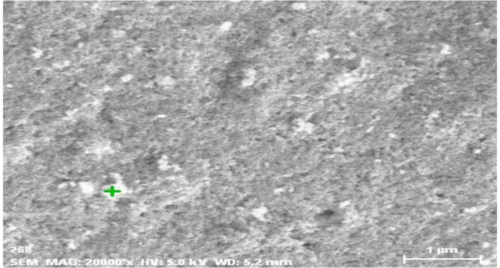


Figure 1: (b) Adsorbed Cu^{2*}ions on the surface of magnetite nanosorbents

FT-IR spectra were analyzed and showed in **Fig(2)** to find out whether EDTA was functionalized on the surface of silica-coated magnetite nanocomposites and the metal adsorption behavior. **Fig 2(a)** showed the spectra of bare magnetite nanoparticles with characteristic peak of Fe-o bond stretching vibration at 595cm^{-1}**. Fig2 (b**) showed a new peak at 1095.9cm^{-1}for Si-OH bond indicating that the silica had been coated on the surface of magnetite nanoparticles. Fe-O-Si peak could not be seen due to the overlapping with Fe-O peak. In **Fig 2(c)** a new peak was observed at 1680cm^{-1} for –C-O stretching vibration in –COOH functional group. Hence confirming the binding of EDTA on the surface of silica-coated magnetite composites. **Fig (3)** revealed the red shift of peak of –C-O bond thus attesting the binding of metal ions with –COOH by substituting the hydrogen ions (H^+) to form a –COO-Metal complex. It also revealed that the binding of metal ions with –COOH were guided by ion exchange and electrostatic interaction mechanism.

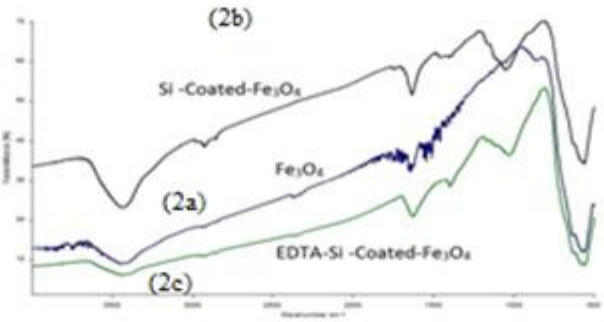


Figure 2: FT-IR spectra

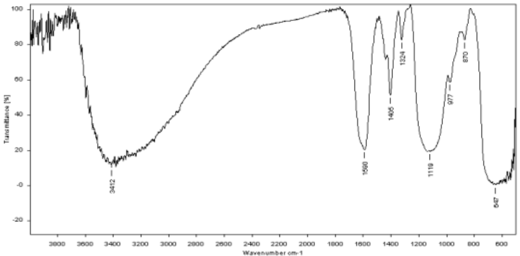


Figure 3: FT-IR spectra of Cu^{2+}ions on the surface of magnetite nanosorbent

Fig 4 (a) and (b) showed the EDX spectra of naosorbents before and after Cu (II) metal loaded on the nanosorbents. Results showed that the observable peak of Cu (II) was seen clearly **Fig 3(b)** while nanosorbents laden with Cu (II) ions.

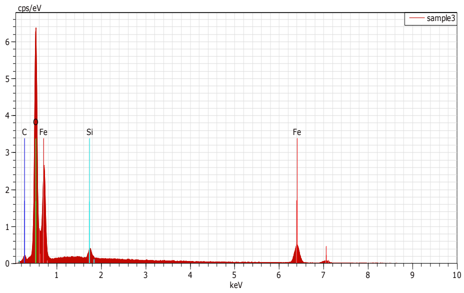


Figure 4: (a) EDX spectra of magnetite nanosorbents

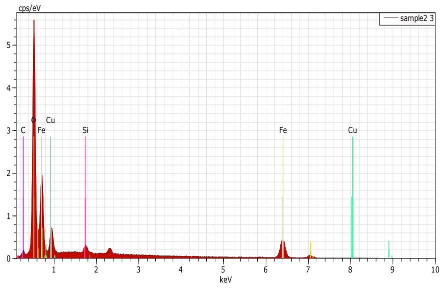
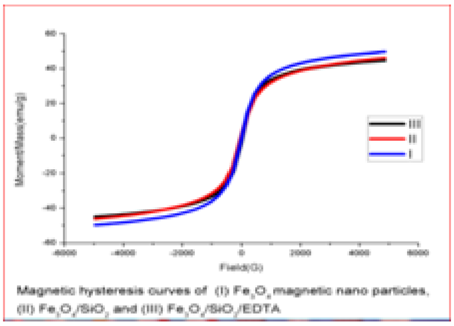


Figure 4: (b) EDX spectra of Adsorbed Cu^{2+}ions on the surface of magnetite nanosorbent

(Fig 5) revealed the saturation magnetization curves for magnetite, silica-coated magnetite and EDTA-Functionalized-Silica-coated magnetite nanocomposites. Saturation magnetization values were observed as 51emu/g, 46emu/g and 44emu/g respectively at room temperature. Although saturation magnetization value for the nanocomposite is less than the bare magnetite but enough to carry out magnetic separation from aqueous solution.



Magnetic hysteresis curves of (I) Fe_3O_4 magnetic nano particles, (II) Fe_3O_4/SiO_2 and (III) $Fe_3O_4/SiO_2/EDTA$

Figure 5: VSM study

3.2 Adsorption isotherms

To determine the sorption capacity of the nanosorbents, sorption studies were carried out with varying initial concentration of metal solutions ranging from .02-.1mol/l at constant temperature. **Fig 6 (b)** showed the equilibrium adsorption isotherms for Cu (II) ions on the nanosorebnts. Generally the two most common adsorption models, Langmuir and Freundlich models **[15,16]** were used to describe the adsorption behaviour. Langmuir adsorption equation is described as below

$$\mathbf{1/q_e=1/q_m\, b\, C_e+ 1/q}$$

where qe is the equilibrium adsorption capacity of adsorbent toward Cu(II) (mg/g), Ce is the equilibrium Cu(II) concentration in solution (mg/L), qm is the maximum capacity of adsorbent (mg/g), and b is the Langmuir adsorption constant pertaining to the energy of adsorption (L/mg).The maximum adsorption co-efficient (q_m) was calculated as .099mol/gram for the Langmuir adsorption isotherm model. It was noticed that during the functionalisation of EDTA, its optimized amount played a crucial role in suitable size distribution and optimal adsorption capacity. Finally it was noticed that the synthesized nanosorbent (EDTA@Si-Fe_3O_4) was comparable to the best sorbents(salicylic acid @Si- Fe_3O_4, NH_2@ Fe_3O_4) synthesized earlier for metal adsorption capacity(16-20). % removal recovery factor for the synthesized sorbent was found to be 98% at optimized reaction parameters. The values of q_m and b were calculated by the slope and intercept of the linear plot of $1/q_e$ versus $1/C_e$.The correlation coefficients of Langmuir.950 thus revealing that the data were well fitted for the isotherm.

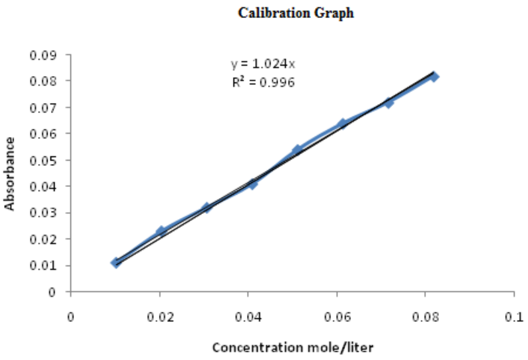


Figure 6: (a) Calibration graph of Cu (II)

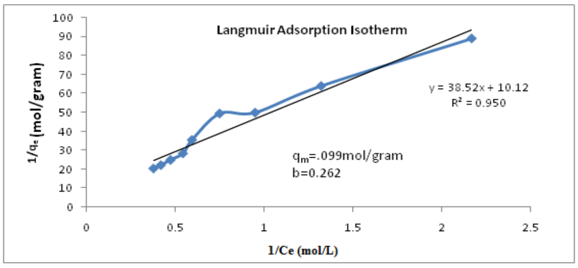


Figure 6: (b) Langmuir Adsorption Isotherm Copper (II) ions.

3.3 Effect of pH and its optimization

The pH dependence may suggest that the surface adsorption phenomenon is caused by mainly ion exchange mechanism. It has been found that if the PH of the reaction medium is lower (Acidic medium), the concentration of H^+ ions is higher and the competition between metal ions and protons for the binding of the chelating sites increases. For higher pH (Basic medium), the concentration of hydroxide ions increases and metal ions tend to be precipitated by hydroxide ions. Therefore optimization of pH is necessary for quantitative recovery of metals. For this, adsorption study was conducted over the pH range from 2 to 10 by keeping other parameters constant. The effect of pH on ion exchange of $Cu^{2+}$was studied at room temperature by varying the pH of reaction medium from 5-7.5 (**Fig 7).**

Because at this PH range availability of free lone pair of electrons on oxygen and nitrogen atoms are higher and good chance to coordinate with metal ions. When pH was below 5, the recovery of metals was decreased appreciably due to enhanced competition of protons with metal ions for the binding sites of donor atoms. It had been also observed that only minor change in pH can lead to the abrupt change in adsorption of metal ions. Hence considering all these factors pH 6.5 was selected as an optimal pH value for all subsequent experiments.

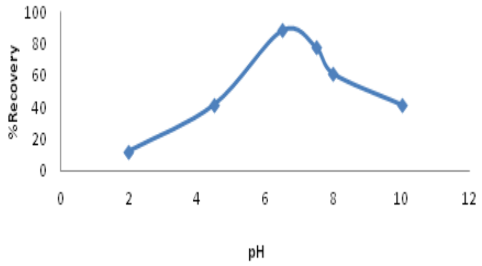


Figure 7: %Recovery of Copper (II) ions at pH-range (2-12) .

3.4 Effect of adsorbent and its optimization

Amount of nanosorbents is another important parameter that has to be optimized for quantitative recovery .In this regard the influence of adsorbent amount was tested in the range of .04gm to .19 gm for the adsorption of metal ions. According to the result obtained from (**Fig 8)** it was observed that quantitative recoveries were obtained when nanosorbent amount was above.13 gram. It also showed that there is no further increase in recovery of metal ions when the amount of nanosorbent was above.19 gm. This may be attributed to the non availability of free lone pair of electrons on oxygen or nitrogen atoms on the surface of nanosorbent as surface binding sites were fully occupied by metal ions. Hence .19 gm nanosorbent was taken as an optimal value for further experiment.

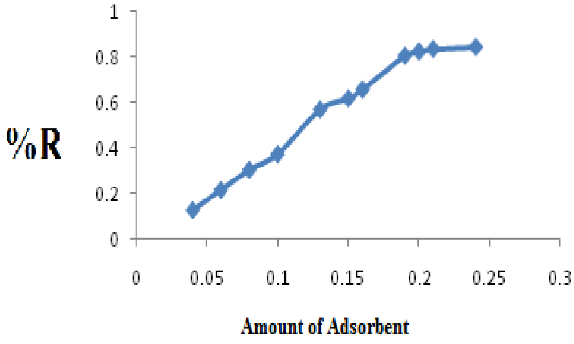


Figure 8: %Recovery of Copper (II) ions

3.5 Effect of time and its optimization

It was found that metal ions deposition on the surface of nanosorbent was time dependent. In this regard effect of time on adsorption was tested through a range of 5 minutes to 20 minutes. (**Fig 9)** showed the adsorption of the metal ions by the nanosorbent as a function of time at neutral PH (7). It was observed that time below 5 minutes adsorption was negligible and above 10 minutes adsorption of metal ions was increased appreciably.` Hence percentage removal of metal ions increased rapidly and there after it rose slowly before attaining a saturation value in 15 minutes. A further increase in contact time had a negligible effect on the percent removal. Hence in all subsequent experiments; the equilibrium time was maintained at 15minutes.The metal uptake versus time curves, are single, smooth and continuously leading to saturation suggesting the possible monolayer coverage of metal ions on the surface of the adsorbent. The percent metal removal is higher in the beginning due to greater number of surface sites available for the sorption of the metal. The maximum recoveries of Cu^{2+} were found. (99 %) at pH=6.5. The percentage uptake of metal ions is highly dependent upon the initial concentration of metal ions and the nanosorbent.

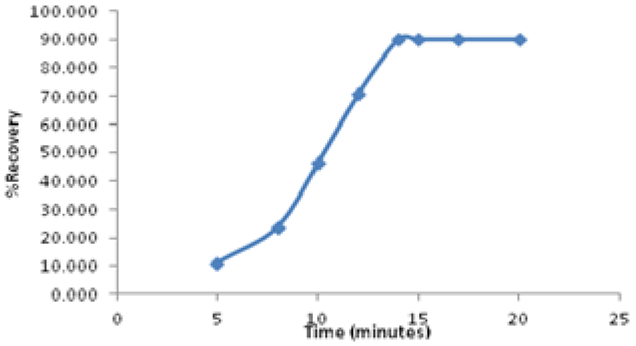
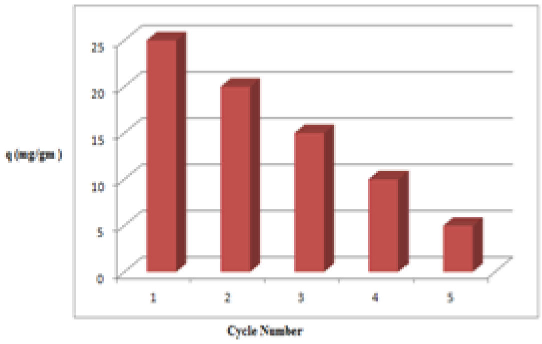


Figure 9: %Recovery of Copper (II) ions at various time intervals.

3.6 Desorption and Recycling

Desorption behaviour was studied by mixing 10 ml of.1M HCl as an eluant with .19 gram of nanosorbent on ultrasonic stirrer for 15 minutes at room temperature. It was found that desorption efficiency of HCl was much better(93%) when compared with other eluant like HNO_3 due to the high affinity of Cu^{2+}ions with HCl. Although the desorption capacity was decreased with increasing number of regeneration cycle but remained satisfactory till five cycles were completed (**Fig 10)**.



4. Conclusion

In present study synthesis and adsorption behaviour of EDTA@Si-Coated Fe_3O_4 was investigated for the removal of $Cu^{2+}$from aqueous systems. Reaction parameters were optimized to achieve monodispersed and stable colloidal solution of nanosorbent in aqueous systems. FT-IR spectra elucidated the successful functionalisation of EDTA on the surface of Si-coated Fe_3O_4 nanoparticles. EDX analysis provided the evidence of Cu^{2+}uptake from aqueous solution by the nanosorbent. The effects of PH, initial concentration of copper ions, amount of adsorbent and contact time on the adsorption capacity were studied in detail. It was found that by optimizing these parameters % recovery of copper metal ions from aqueous solution was turn out to be 90-98%. Adsorption isotherm was described by Langmuir equation with maximum adsorption capacity of .099mol/gram. Adsorption mechanisms of copper ions uptake on the surface of nanosorbent were ion-exchange between hydrogen ions of free carboxylic acid group of nanosorbent and copper ions from the aqueous solution and electrostatic interactions between copper ions and nanosorbent. Desorption experiments showed that .1 M HCl solutions was an efficient eluant with 92.5% of copper ions released from the nanosorbent from the first regeneration cycle. Its efficiency decreased in further regeneration cycles but remained satisfactory till the fifth cycles were completed. Hence it is concluded that the magnetite nanosorbent is potential alternative for copper ions removal from waste water due to its high adsorption capacity and easy separation ability.

5. Acknowledgement

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