Effect of pH, adsorbent dosage, time and temperature for the removal of copper and zinc from wastewater by chitosan nanoparticles

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Abstract : Chitosan nanoparticles synthesized in the laboratory were used for the removal of copper and zinc from synthetically prepared wastewater. These nanoparticles are produced by interaction of chitosan with sodium tripolyphosphate. The synthesized particles were characterized using scanning electron microscopy and Fourier-transform infrared spectroscopy . Batch adsorption studies were conducted to study the effects of pH, adsorption dosage, contact time and temperature. The optimum conditions obtained were 200 mg adsorbent dose, 360 min contact time, and pH 5 for copper and 150 min contact time, 200 mg adsorbent dose and pH 7 for zinc.

***IndexTerms* - Adsorption; Chitosan nanoparticles; copper; Zinc; wastewater.**

1 INTRODUCTION

Heavy metal pollution due to rapid industrialization and growth in world pollution is a serious threat to environment and all forms of life [1]. The toxic metals are emitted to the environment from various industries in such a quantity that pose risk to human health [2]. Because of their toxicity and non-biodegradability they cause a lot of diseases and disorders. Zinc, copper, mercury, nickel, cadmium , etc. are considered as toxic metals of particular concern in waste water treatment. Copper plays an important role in all living organisms. It is widely used in industries because of its high electrical and thermal conductivity, high recyclability and attractive appearance [3] and good corrosion resistance. Copper is one of the most toxic heavy metal to the living organisms. Excessive intake of copper causes hemolysis, nephro toxic effects or even death [4,5]. Zinc is used in many industries for preparing large number of zinc alloys and compounds. The extensive intake of zinc may cause toxic effects such as mutagenesis, carcinogenesis, and teratogenesis as a result of bioaccumulation [6].

Many treatment processes which has been used to remove heavy metals from wastewater includes precipitation and coagulation, electro dialysis, ion exchange, membrane filtration, flotation, adsorption, and reverse osmosis [7]. Most of these processes are of high cost. Adsorption is used many industries for purification of water due to its low cost and applicability on large scale. Adsorption is being done using activated carbon which adsorbs dissolved organic substances in the water. In order to avoid the high cost of activated carbon many low-cost adsorbents has been used and tested to remove heavy metal ions [7-8] . Different adsorbents have been used include wood sawdust modified sugarcane bagasse [9], rice husk ash [2], modified flax shive, waste activated sludge, waste biomass, Lignite, and chitosan [10,11]. There are so many adsorbents still used and also new adsorbents are developed due to the increase in demand for the treatment of industrial wastewater. Recently, a number of studies were carried out on low cost adsorbents for the removal of heavy metals from water. One of such kind is the waste produced from fishery waste was used in this study. Chitosan is a low cost adsorbent which is biocompatible and biodegradable polymer and it is produced by alkaline deacetylation of chitin.

Chitosan is a basic polysaccharide and partially deacetylated polymer of glucosamine which is obtained after alkaline deacetylation of chitin. It consists of β-(1-4-2- acetamido-2-deoxy-D-glucose) units and is the second most abundant natural biopolymer on earth after cellulose [12,13]. It is found in crustacean shells and cell walls of fungus. Chitosan is soluble in dilute acids. The solubilisation of chitosan occurs by the protonation of the –NH2 function on the C-2 position of the D-glucosamine repeat unit, where the polysaccharide is converted to a polyelectrolyte in acidic media [15]. Chitosan is the only natural cationic polymer and it is used in many applications for wastewater treatment. In the present study chitosan nanoparticles were prepared by the dropwise addition of chitosan solution to the TPP solution and characterized using scanning electron microscopy(SEM) and Fourier-transform infrared spectroscopy(FTIR). Batch adsorption studies were conducted to study the effects of pH, adsorption dosage, contact time and temperature.

2 Experimental

2.1 Materials

All the chemicals used were of analytical reagent grade. Zinc sulphate heptahydrate and copper sulphate pentahydrate were used for preparation of stock solutions. Hydrochloric acid and Sodium hydroxide were used to adjust the solution pH. TPP was used for making chitosan nanoparticles. Water from Millipore water purification system was used for conducting the experiments. Batch adsorption tests were conducted in incubated shaker.

2.2 Methods

Stock solution of 10 mg/L of copper solution is prepared dissolving 39.28mg CuSO4.5H2O in 1L of distilled water. 10mg/L of zinc solution is prepared by adding 43.96mg ZnSO4.7H2O in 1L of distilled water. Concentration of copper and zinc solutions was measured using Atomic Absorption Spectrophotometer. Chitosan solution of 0.1M was prepared by dissolving 16gm of chitosan in 1L of 2% acetic acid with stirring at 600C. 36.7g of TPP was dissolved in 1L of distilled water to prepare 0.1M solution [14]. Chitosan nanoparticles are prepared by the dropwise addition of chitosan solution to the TPP solution. The formed nanochitosan was filtered and washed several times with distilled water. Nanoparticles obtained were characterized using SEM and FTIR.

Adsorption experiments were performed in the laboratory in a shaker by varying the parameters that affects adsorption of copper and zinc to chitosan nanoparticles. The effect of adsorbent dosage, pH, time of shaking and temperature was studied. Chitosan nanoparticles were added with the following concentrations: 0, 8, 16, 32 and 40 mg/L to stock samples. This was followed by an immediate flash mixing by 300 rpm for 10 minutes. The mixing rate was then reduced to 30 rpm and held at this level for 20 minute. Finally, a settling period of 30 minute was allowed.

3 Results and Discussion

3.1 Characterization of chitosan nanoparticles

The FTIR (Fig.1) spectra of chitosan nanoparticles show a broad band at 3440cm-1 showing the stretching vibration of NH and OH groups in chitosan. The band around 2915cm-1can be attributed to stretching vibration of C-H. The band at 1065cm-1 is due to the combined effects of C-N stretching vibration of primary amines and the C-O stretching vibration of the primary alcohol in chitosan. The SEM image of chitosan nanoparticles is depicted in Figure 2. The well shaped particles with average diameter of about 28nm are seen.

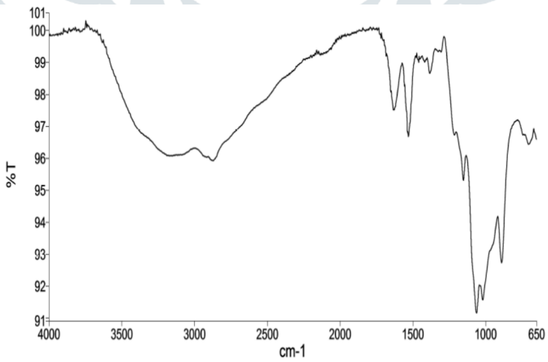

Fig 1. FTIR spectra of chitosan nanoparticles

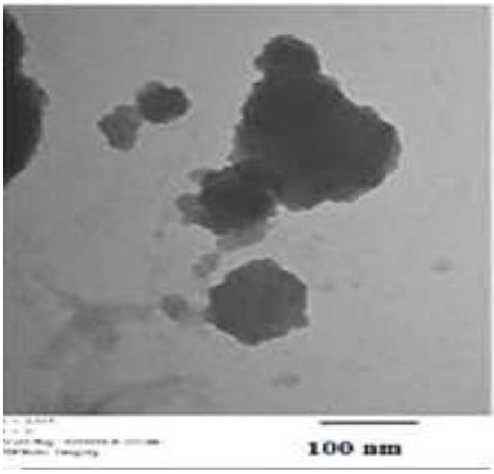

Fig 2. SEM analysis of nanoparticles

3.2 Copper

3.2.1 Effect of pH

Figure 3 show that pH has influenced the removal efficiency of the copper ions in aqueous solution. The results showed that Cu removal was increased to maximum and then decreased with variation in pH from 4 to 9. The maximum % removal of Cu was about 88% at pH 5. When pH was lower than 5 the dominant species of copper was free Cu and was mainly involved in the adsorption process. When the pH greater than 5, copper ions started to form precipitate as Cu (OH)2. Increases in metal removal with increased pH is due to the decrease in competition between proton and cations for same functional groups and by decrease in positive surface charge, which results in a lower electrostatic repulsion between surface and metal ions. Decrease in adsorption at higher pH is due to formation of soluble complexes. The adsorption of Cu ion was mainly influenced by solution pH.

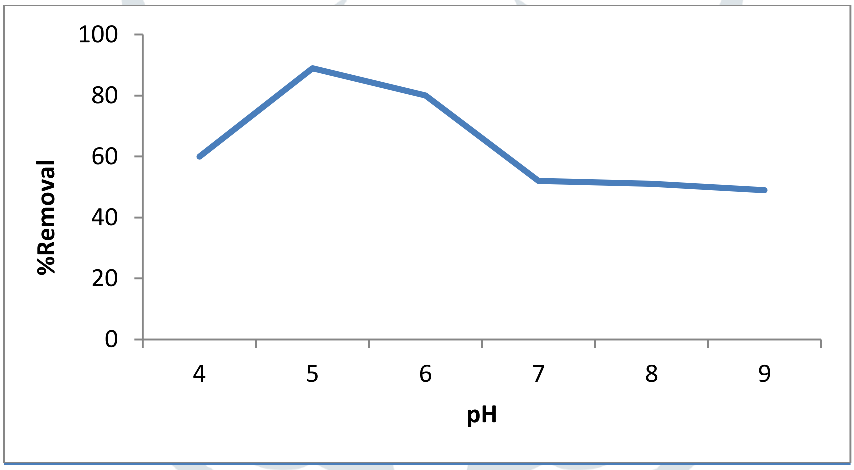

Fig 3. Effect of pH on adsorption of copper

3.2.2 Effect of contact time

Figure 4 indicated that percentage removal was increased with an increase in contact time. All parameters such as pH of solution and dose of adsorbent were kept constant. The results showed that Cu removal was increased from 15 to 88% with the contact time variation from 10 to 360 minutes. From 360 to 400 minutes, the percentage removal remains constant (88%), which showed that equilibrium was reached at 360 minutes. Thus the result shows that the optimum contact time for maximum removal (88%) of Cu was 360 minutes.

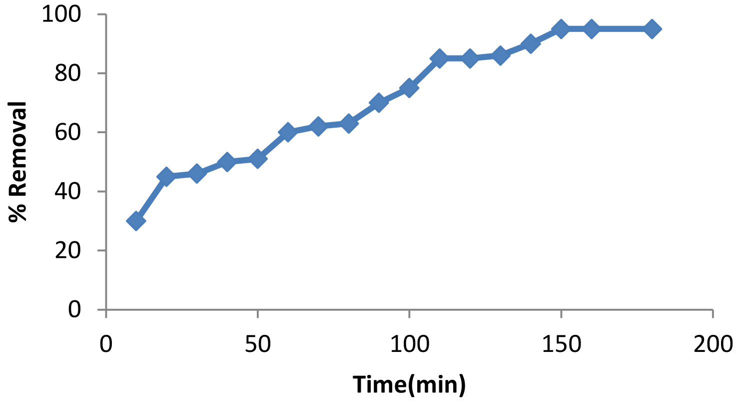

Fig 4. Effect of contact time on adsorption of copper

3.2.3 Effect of adsorbent dose

Adsorption efficiency was studied by varying the amount of adsorbents from 50 to 200 mg keeping other parameters such as pH and contact time constant. The figure 4.6 shows that removal efficiency of the copper is improved with increasing adsorbent doses. This may be due to the fact that the higher dose of adsorbents provides the greater availability of exchangeable sites for the ions. From the figure 5 it is clear that the no further increase in adsorption after a certain amount of adsorbent was added . The maximum % removal of Cu was about 87.17% at the dosage of 200 mg.

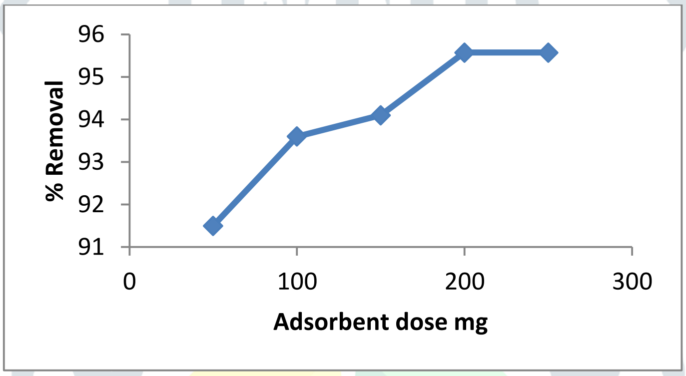

Fig 5. Effect of adsorption dosage on % removal of copper

3.2.4 Effect of temperature

The temperature shows a negative effect on adsorption of copper on to chitosan. The effect of temperature on removal of copper ion was studied within the range of 25-55^{0}C. Other parameters such as pH of solution and dose of adsorbent were kept constant. With increase in temperature from 25-55^{0}C the percent removal of copper ions decreased from 83.3% to 75.37%. From the figure 6 it is clear that the low temperatures are in favour of copper ion removal. This may be due to the tendency for the copper ions to escape from the solid phase to the bulk phase with an increase in temperature of the solution.

3.3 ZINC

3.3.1 Effect of pH

Figure 7 indicates that pH influenced the removal efficiency of the zinc ions in aqueous solution. The results show that Zn removal was increased to maximum and then decreased with pH variation from 5 to 9. The maximum percentage removal of Zn was about 97.3% at pH 7. When pH was below 7 the dominant species of zinc was free Zn and was mainly involved in the adsorption process. When the pH greater than 7, zinc ions forms precipitate as $Zn(OH)_2$.

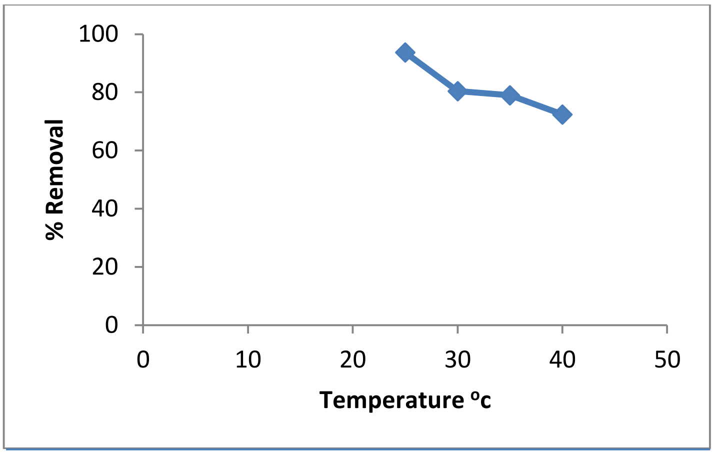

Fig 6. Effect of temperature on adsorption of copper

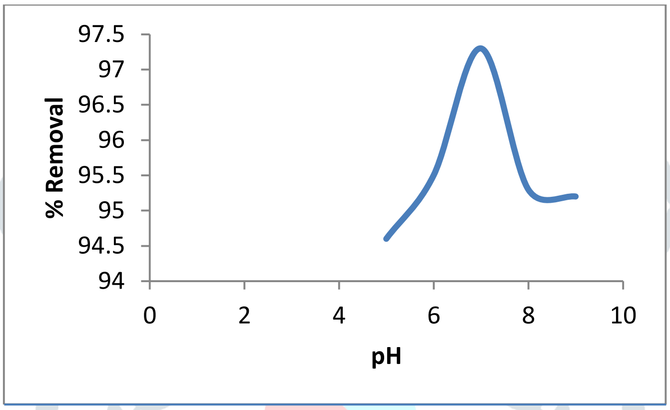

Fig .7 Effect of pH on adsorption of zinc

3.3.2 Effect of contact time

From Fig 8, it is seen that the rate of percent removal of zinc was higher at the beginning. This is be due to the larger surface area of the adsorbent being available for the adsorption of zinc ions. Equilibrium was reached after 150 minutes indicating that the adsorption sites are well exposed.

3.3.3 Effect of adsorbent doses

The removal efficiency of the zinc was improved on increasing adsorbent doses as depicted in Fig.9. This may be due to the fact that the higher dose of adsorbents provides the greater availability of exchangeable sites for the ions. From the figure it is clear that the no further increase in adsorption occurs after a certain amount of adsorbent was added. The maximum % removal of Zn was about 95.57% at the dosage of 200 mg.

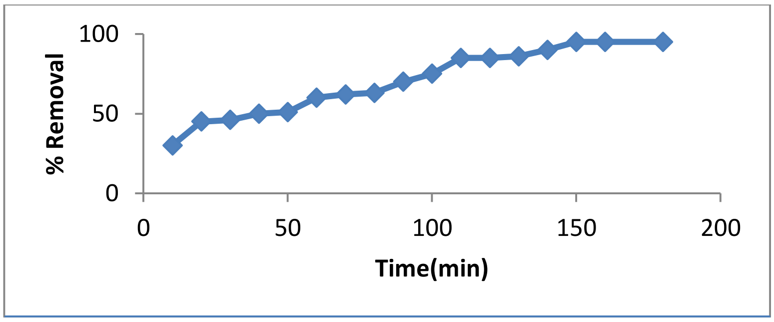

Fig. 8. Effect of contact time on adsorption of zinc

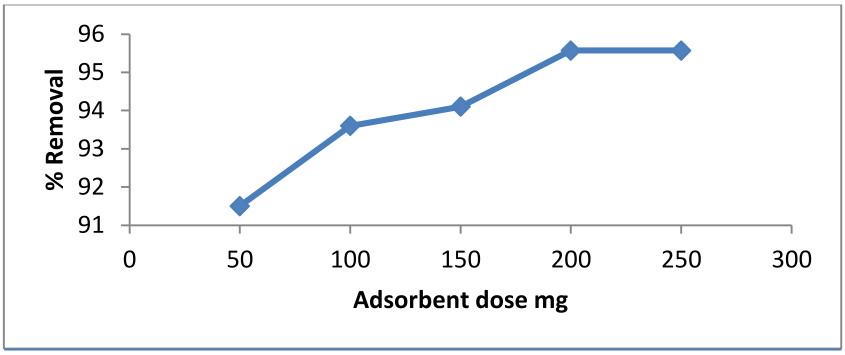

Fig 9. Effect of adsorbent dose on adsorption of zinc

3.3.2 Effect of temperature

From figure 10, it is clear that the low temperatures are in favour of zinc ion removal. This may be due to the tendency for the zinc ions to escape from the solid phase to the bulk phase with an increase in temperature. The result shows that adsorption mechanism related with removal of zinc is physical in nature. The adsorption process takes place from the electrostatic interaction, which is in general related with low adsorption heat. This implies that the adsorption process was exothermic in nature.

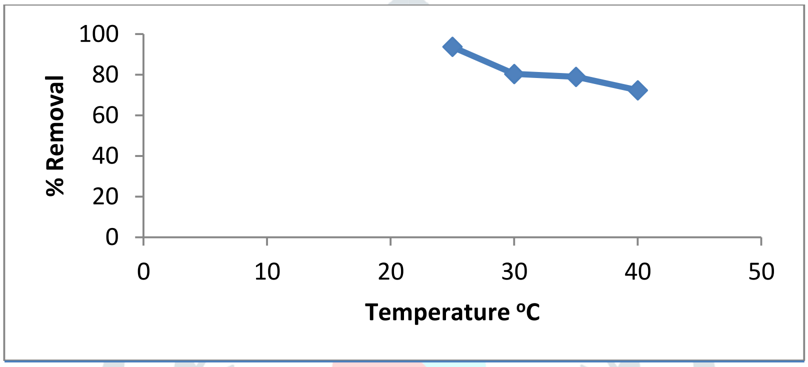

Fig. 10 Effect of temperature on adsorption of zinc

4 Conclusion

Chitosan nanoparticles were synthesized and characterized in laboratory and were used for the removal of heavy metals such as zinc and copper from the wastewater. The results show that the optimum dosage of adsorbent for removal of copper and zinc was 24mg/L. Influence of process parameters such as pH, adsorbent dosage, contact time, temperature were at moderate levels such that they can affect the removal efficiencies of the heavy metals. The optimum pH of solution for zinc and copper removal were found to be 5 and 7 respectively. Within the scope of the experimental investigation, the optimum temperature was found to be 25^0C.The optimum time for adsorption of zinc and copper was found to be 150 min and 360 min respectively. Therefore removal of copper and zinc is effectively performed using adsorption on chitosan nanoparticles.

References

[1]. A. Chen, C. Yang, C. Chen and C. W. Chen (2009), The chemically crosslinked metal-complexed chitosan for comparative adsorptions of Cu(II), Zn(II), Ni(II) and Pb(II) ions in aqueous medium, *Journal of Hazardous Materials*, 163., 1068-1075.

[2]. A. K. Shrivastava (2009), A Review on Copper Pollution and its Removal from Water Bodies by pollution Control Technologies, *IJEP*, 29. , 552-560.

[3]. P. Saha, S. Datta, S. K. Sanyal (2008), Study on the Effect of Different Metals on Soil Liner Medium, *Indian Sci. Cruiser*, 22., 50-56.

[4]. A. Ozer, D. Ozer, A. Ozer (2004), The adsorption of copper (II) ions on to dehydrated wheat bran (DWB): determination of the equilibrium and thermodynamic parameters, *Process Biochemistry*, 39., 2183-2191.

[5]. R. Gustavo et al (2007), Enhanced copper release from pipes by alternating stagnation and flow events. *Env. Sci Tech*, 41. , 7430-7436.

[6].R. Gustavo et al (2007), Enhanced copper release from pipes by alternating stagnation and flow events. *Env. Sci Tech*, 41. , 7430-7436.

[7]. Nora Savage, Mamadou S Diallo. Nanomaterials and water purification: opportunities and challenges. Journal of Nanoparticles Research 2005: 7:331-342.

[8]. M. Madhava Raoa, A. Rameshb, G. Purna Chandra Raoa, K. Seshaiah (2006), Removal of copper and cadmium from the aqueous solutions by activated carbon derived from Ceiba pentandra hulls, *Journal of Hazardous Materials*, 129. , 123–129.

[9]. F. Fenglian, Q. Wang (2011), Removal of heavy metal ions from wastewater, *Journal of Environmental Management*, 92 . , 407-418.

[10]. F.V. Pereira, L.V.A. Gurgel, S.F. de Aquino, and L.F. Gil (2009). Removal of Zn^{2+} from Electroplating Wastewater Using Modified Wood Sawdust and Sugarcane Bagasse, *ASCE*, 135. , 341-350.

[11]. P. K. Dutta, J. Dutta, V. S. Tripathi (2004), Chitin and chitosan: Chemistry, properties and applications, *Journal of scientific & industrial research*, 63. , 20-31.

[12] M. Rinaudo (2006), Chitin and chitosan: properties and applications, *Prog Polym Sci*., 31, 603–632.

[13] Yusmanir (2014), Treatment of wastewater printing ink by process coagulation using chitosan nanoparticles, *International journal of management, information technology and engineering*, 2, 35-44

[14]. R. Ramya, P. Sankar, S. Anbalagan and P.N. Sudha (2011), Adsorption of Cu (II) and Ni (II) ions from metal solution using crosslinked chitosan-g-acrlonitrile copolymer. *International journal of environmental science*, 1, 1323-1338.

[15]. A. Shafaei, F. Z. Asthiani, T. Kaghazchi (2007), Equilibrium studies of the sorption of Hg(II) ions onto chitosan. *Chem. Engg. Journal*, 133. , 311-316.