

WASTEWATER TREATMENT WITH CHITOSAN NANO-PARTICLES

MARAM T. H. ABOU KANA¹, MOHAMMED RADI² & MAHER Z ELSABEE³

^{1,2}National Institute of Laser Enhanced Sciences, Cairo University, Giza, Egypt

³Department of Chemistry, Faculty of Science, Cairo, Egypt

ABSTRACT

Chitosan interact with polyphosphate ions to form nanoparticles with different diameters depending on the mutual ratio among them. Three nanoparticles have been prepared and were characterized by spectral and X-ray diffraction tools. TEM analysis revealed there diameters. The nanoparticles were thoroughly studied for wastewater treatment such as the removal of Total Suspended Solid (TSS), Biochemical Oxygen Demand (BOD), Chemical Oxygen Demand (COD) and removal of six heavy metal cations (Cr, Cu, Fe, Mn, Pb, and Zn) from wastewater. These investigations were carried out to minimize the cost and obtain the optimum performance in wastewater treatment. The result showed that the dosage of nanoparticles increases the % efficiency of wastewater treatment, and the smaller the size of the nano chitosan the higher is its activity.

KEYWORDS: Chitosan Nanoparticles, Characterization, Wastewater Treatment

INTRODUCTION

Society's rapid evolution has increased the demand for water in every sector. At the same time, the continual production of great quantities of wastewater has led to the view that this should be considered as alternative water resource. Nevertheless, wastewater reuse poses a risk for public health and for this reason specific levels of quality are required. Conventional treatments do not reach the minimum quality standards, since effluents from such treatments continue to present a high number of pathogenic micro-organisms [Koivunen et al., 2003]. Consequently, there is a need for tertiary treatments such as water disinfection technologies.

Development of new technologies has extended the possibilities of wastewater reuse [Sonune and Ghate, 2004], and this may now be applied to agriculture at all levels, as well as to irrigation of sports grounds, urban uses, industrial uses, aquifer recharge, etc. At the same time, norms regarding the quality of water to be reused have become increasingly stringent, while tertiary treatments have in turn become increasingly sophisticated as they strive to obtain effluents of high quality.

Population explosion, haphazard rapid urbanization, industrial and technological expansion, energy utilization and waste generation from domestic and industrial sources have rendered many waters unwholesome and hazardous to man and other living resources. There are little or no stringent laws guiding environmental pollution. Hence, many industries discharge untreated or inadequately treated wastewater into water ways. A number of technologies have been developed over the years to remove organic matter (expressed as chemical oxygen demand, COD) from industrial wastewater. The most important technologies include coagulation/flocculation process [Amuda et al., 2006; Bromley et al., 2002], membrane filtration [Galambos et al., 2004], oxidation process [Martinez et al., 2003; Peres et al., 2004]. These methods are generally expensive, complicated, time consuming and requires skilled personnel. The high cost of coal-based activated carbons has stimulated the search for cheaper alternatives. Low cost and non-conventional adsorbent include agricultural by products such as nut shells, wood, bone, peat processed into activated carbons [Ahmedna et al. , 2000a; Ahmedna et al.,

2000b; Dastgheib et al. , 2001; Ng et al. , 2000a; Ng et al., 2000b; Bansode et al., 2004; Nomanbhay and Palanisamy, 2005] and biomass such as *Aspergillus terreus* [Azab et al. , 1989], *Pseudomonas* sp.[Hussein et al. , 2004], *Rhizopus arrhizus* [Preetha et al. , 2005] have been reported to be important adsorbents for the removal of metals and organics from municipal and industrial wastewater.

Activated carbon is a commonly used adsorbent in sugar refining, chemical and pharmaceutical industries, water and wastewater treatment, and as an adsorbent in point-of-use (POU) and point-of-entry (POE) home water filtration systems [Ng et al., 2003]. Increasing requirements for clearer and more polished effluent from many processes suggest that, barring the development of new technologies, industrial need for activated carbon will only increase in future [Ng et al., 2003]. However, its widespread use in wastewater treatment is sometimes restricted due to its higher cost. It is now recognized that adsorption using low-cost adsorbents is an effective and economic method for water decontamination.

Biosorbent gain wide attention as these are available in large quantities worldwide and are eco-friendly. The use of adsorbents containing natural polymers has received reorganization, in particular polysaccharides such as chitin and its derivate chitosan.

Chitosan of has drawn particular attention as effective biosorbent due to its low cost compared to activated carbon and its high contents of amino and hydroxyl functional groups showing high adsorption potential for various aquatic pollutants. This natural biomasses represents an attractive alternative to other biomaterials because of its physico-chemical characteristics, chemical stability, high reactivity, excellent chelation behavior with heavy metals and high selectivity toward pollutants [Ravi Kumar, 2000; Guibal, 2004; Varma et al., 2004; Gerente et al., 2007; Crini and Badot, 2008; Chatterjee et al., 2009; Guibal et al., 2005; Guibal et al., 2006; Guibal et al., 2007]. This work deals with the preparation of three chitosan nanoparticles with different diameters by the reaction of chitosan with tripolyphosphate (TPP). The concentration of TPP affects the diameter of the prepared nano particles. The behavior of these nano particles toward wastewater treatment has been investigated in details.

EXPERIMENTAL

Materials

Chitosan (purchased from Sigma with high M. Wt.), tripolyphosphate 85% (TPP) ((purchased from Sigma-Aldrich), Acetic acid and other solvents are used as received.

Preparation of Nano Chitosan

Chitosan solution (0.1 M) was prepared by dissolving 16 gm of chitosan in 1L of 2% acetic acid with stirring overnight at 60°C. 36.7 gm of TPP was dissolved in 1 liter of double distilled water to prepare 0.1 M solution. Chitosan nano particles of different degree of cross-linking (and diameters) was prepared by adding the chitosan solution drop wise to the TPP solution according to the following ratio (CS: TPP v/v), 1:1, 1:3, and 1:5. The formed nano chitosan were filtered and washed several times with double distilled water.

Characterization of Prepared Nano Chitosan

The prepared nano chitosan with different degree of cross-linking were characterized by TEM technique (JEOL-JEM-1400), XR diffraction pattern technique and The FTIR spectra were measured in KBr pellets in the transmission mode in the range 400-4000 cm^{-1} using Perkin-Elmer 2000 spectrophotometer.

Waste Water Samples Preparation and Jar-Testing Technique

Three fresh grab sewage samples were collected from a plant in the industrial city of Helwan. They were

transferred to the laboratory of the Abu Rawash treatment plant (ARTP). The treatment scheme of ARTP includes screening, grit removal, primary sedimentation and chlorination as represented in Figure 1. Jar testing experiments were carried out using the effluent of the grit removal from ARTP.

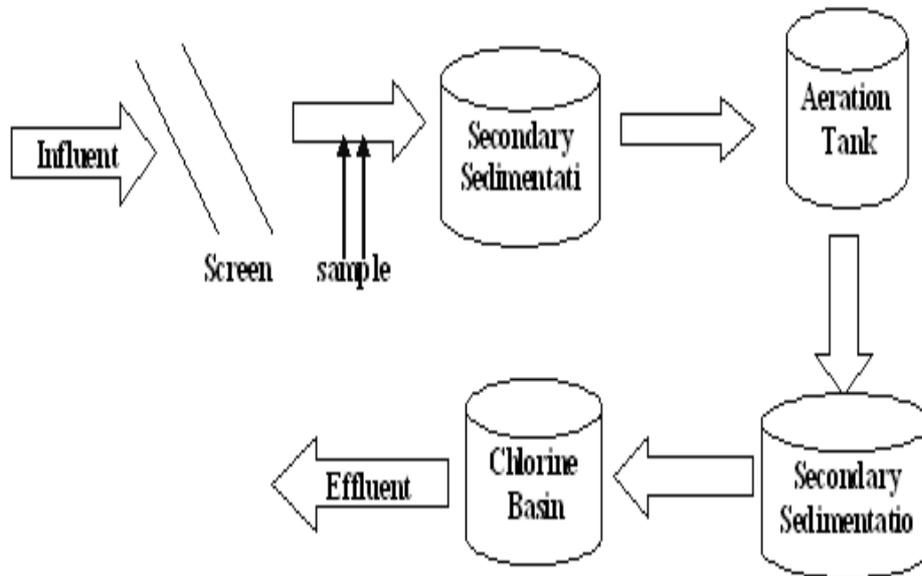


Figure 1: A Simple Flow Diagram of (Helwan Treatment Plant)



Figure 2: Jar-Test Apparatus

Chitosan nanoparticles with different sizes as coagulant dosages were added with the following concentrations: 0, 8, 16, 24, 32 and 40 mg/L to sewage samples. This was followed by an immediate initiation of 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 quiescent settling period of 30 minute was allowed. At the end of the settling period, a sample of the supernatant was analyzed for the different various parameters.

Analysis Measurements for the Strength of Waste

Chemical Oxygen Demand (COD) was carried out by using Closed Reflux –Tritimetric method while Total Suspended Solids (TSS) and Biochemical Oxygen Demand (BOD) are Approved by standard methods [Clesceri et al., 1998]. Sex heavy metals (Cr, Cu, Mn, Fe, Pb and Zn) are studied by atomic absorption spectroscopy.

RESULTS AND DISCUSSIONS

Characterization of Prepared Chitosan Nano Particles

FTIR Analysis

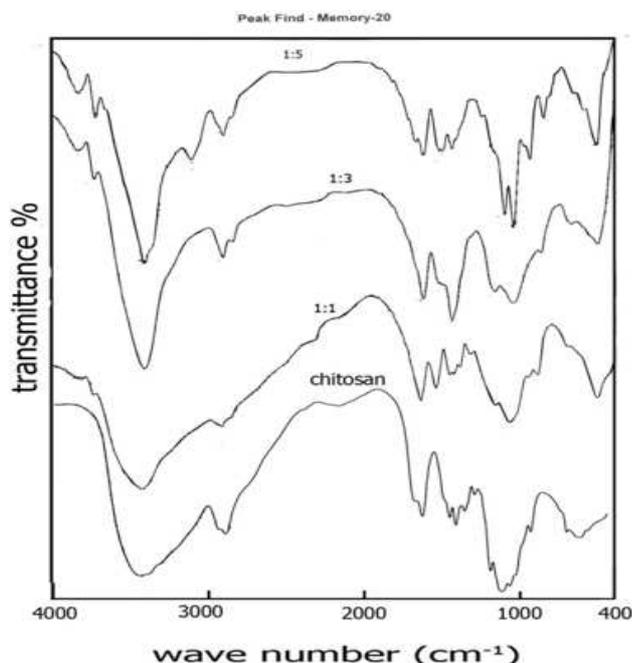
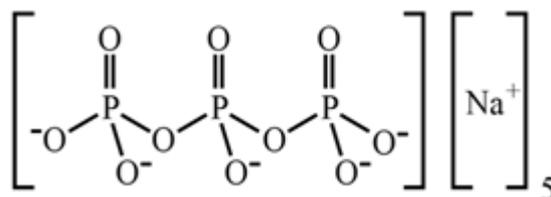


Figure 3: FTIR Spectra of Chitosan and its Nano Particles of Different Degree of Cross Linking

The FTIR spectra of chitosan and its nanoparticles show a characteristic broad band at 3440 cm^{-1} revealing the stretching vibration of NH, and OH groups in chitosan. This broad band narrows with increasing the extent of cross linking in chitosan nano particles. The band at 2915 cm^{-1} can be attributed to C-H stretching vibration while the stretching mode of the acetylated amine appears near 1650 cm^{-1} (amide I). The band at 1323 cm^{-1} is due to O=C-O groups stretching frequency while the bands at 1150 cm^{-1} and 1100 cm^{-1} may be interpreted as asymmetric C-O-C etheric bridge stretching vibration mode and C-O group deformations, respectively. The band around 1065 cm^{-1} is attributed to the combined effects of C-N stretching vibration of primary amines and the C-O stretching vibration from the primary alcohol in chitosan. The mechanism of cross linking of chitosan with TPP to form nano particles is mainly by ionic interaction. Chitosan is polycationic when dissolved in acid with protonated $-\text{NH}_3^+$ sites. STPP ($\text{Na}_5\text{P}_3\text{O}_{10}$) when dissolved in water dissociates to give negative O^- ions (Scheme 1) which may compete with the Na^+ ions to interact with the $-\text{NH}_3^+$ of chitosan.



Scheme 1: A Representation of the TPP Molecule

XRD Analysis

X-ray diffraction patterns of chitosan nano particles with different sizes are shown in Fig 2. However, the peak of the semicrystalline structure of chitosan has been reformatted (and drastically reduced, especially the band at $10\ 2\theta$) in the diffractogram of chitosan nanoparticles depending upon the degree of crosslinked with sodium tripolyphosphate as shown in figure 4.

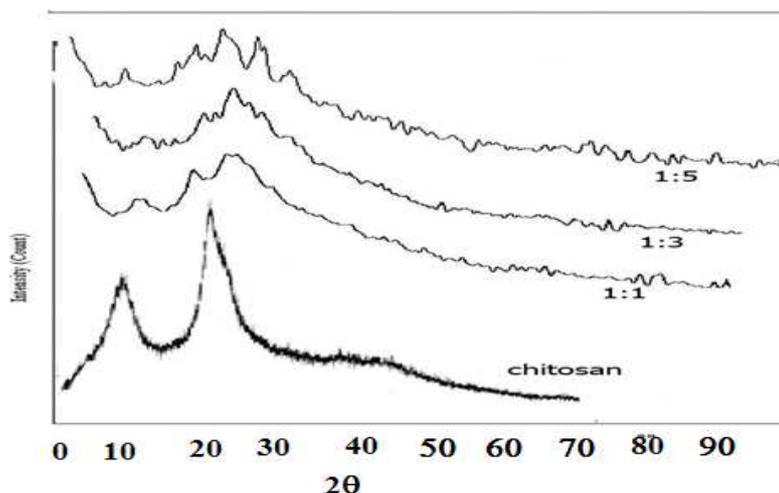


Figure 4: XRD Pattern of Chitosan and its Nanoparticles with Different Degree of Crosslinking Diameter of Chitosan Nanoparticles

The TEM images of chitosan nanoparticles of different chitosan:TPP ratios were depicted in Figure (5). The well shaped particles with average diameter of about 10, 24, and 28 nm representing 1:5, 1:3 and 1:1 ratios, respectively, were achieved. The majority of the particles are spherical. Spherical molecular polymers have large surface area, indicating that large number of effective sites could exist in the surface to adsorb the molecules in aqueous media.

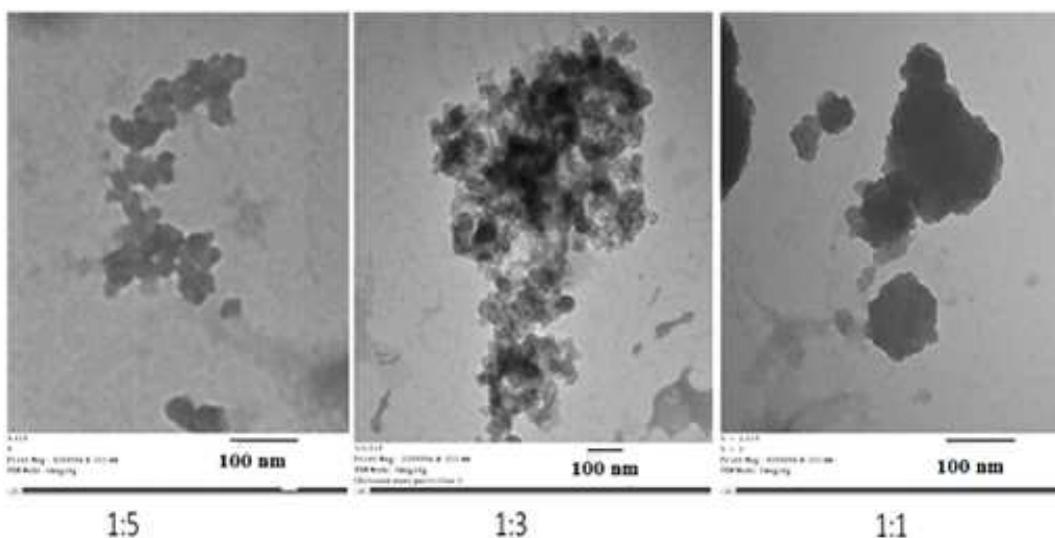


Figure 5: TEM Images of Different Sizes of Chitosan Nanoparticles

Effect of Sizes and Dosages of Nano Chitosan on Wastewater Treatment

The size and dosage of nano chitosan as adsorbent are important parameters for the adsorption process because these factors determine the capacity of an adsorbent for a given initial concentration of the adsorbate. These parameters were thoroughly studied for the TSS, BOD, COD and six heavy metals removal from waste water. These investigations were carried out to minimize the cost and obtain the optimum performance in waste water treatment. The result showed that not only the dosage of adsorbent increases the % efficiency of wastewater treatment, but also the size of nano chitosan.

TSS Removal

The initial concentration of TSS was determined colorimetrically according to standard methods [Clesceri et al., 1998]. This initial concentration of TSS of the untreated beverage wastewater (raw materials) was 140, 210 and 230 mg/l in case of 1:1,1:3 and 1:5 [chitosan:TPP] respectively.

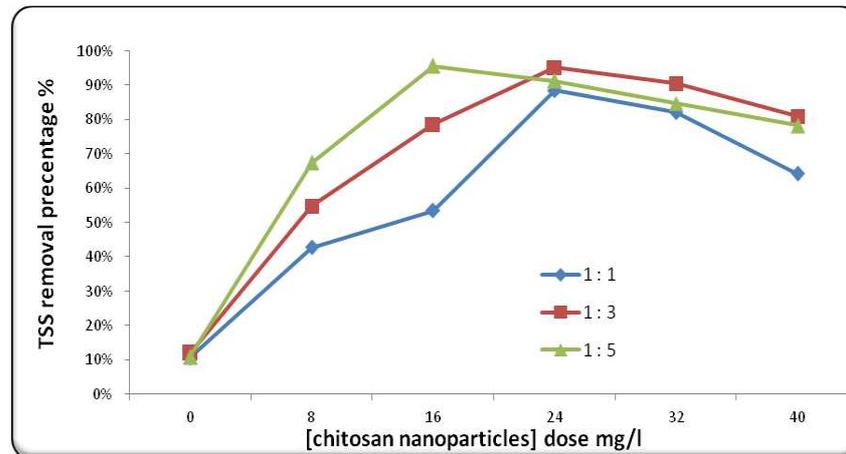


Figure 6: Effect of Different Doses and Sizes of Nano Chitosan on % of TSS Removal

The removal percentage of TSS because of the effect of the different dosages and three sizes of chitosan nanoparticles was represented by figure 6. It shows that for the chitosan:TPP ratio (1:1) the best dose was 24 mg/l which result in removal of 88.5%, and for the ratio (1:3) the best dose was 24mg/l which gives removal 95.21% and for the ratio (1:5) the best dose is 16 mg/l which gives maximum removal of 95.75%

BOD Removal

The initial concentration of BOD was determined colorimetrically. This initial concentration of BOD of the untreated beverage wastewater (raw materials) was 154, 260 & 275 mg/l in case of 1:1,1:3 and 1:5 [chitosan : TPP] respectively

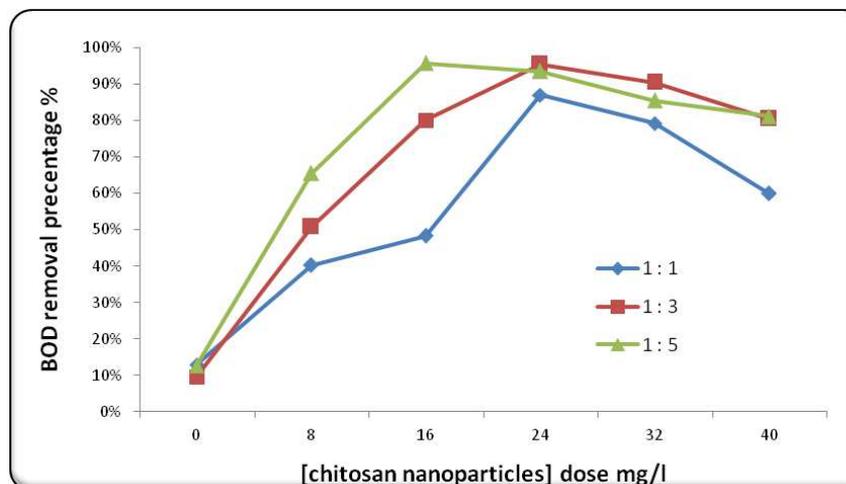


Figure 7: Effect of Different Doses and Sizes of Nano Chitosan on % of BOD Removal

BOD removal percentage from the waste water due to different dosages and three sizes of chitosan nanoparticles was represented by figure 7. It shows that, for the ratio (1:1) the best dose was 24 mg/l which gives removal 87%, and for the ratio (1:3) the best dose was 24mg/l which gives removal 95.38% and for the ratio (1:5) the best dose 16 mg/l which gives removal 95.64%.

COD Removal

The initial concentration of COD was carried out by using Closed Reflux –Titrimetric method. This initial concentration of COD of the untreated beverage wastewater (raw materials) was 225, 310 & 340 mg/l in case of 1:1,1:3 and 1:5 [chitosan : TPP] respectively.

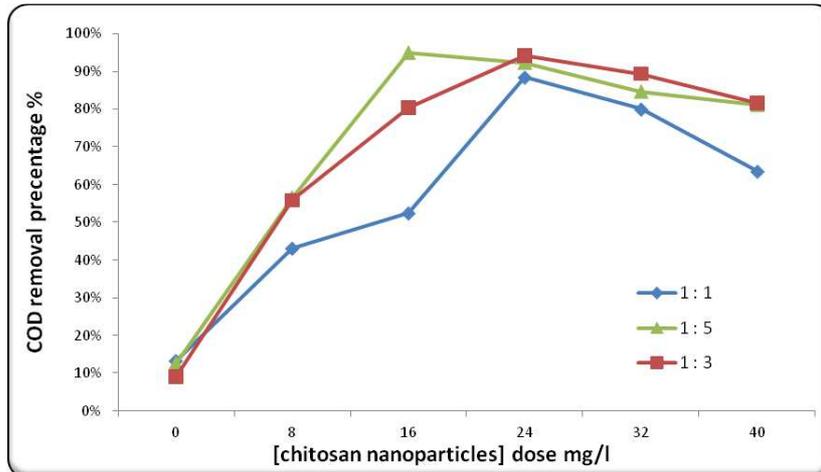


Figure 8: Effect of Different Doses and Sizes of Nano Chitosan on % of COD Removal

The removal percentage of COD from waste water due to effect of the different dosages and the three sizes of chitosan nanoparticles was shown in figure 8. It shows that, for the size (1:1) the best dose was 24 mg/l which gives removal 88.44%, and for size (1:3) the best dose was 24mg/l which gives removal 94.19% and for size (1:5) the best dose 16 mg/l which gives removal 95%

Cr Removal

The initial concentration of Cr as heavy metal was detected for untreated waste water (raw materials) by atomic absorption spectroscopy. It was 0.267, 0.293& 0.352 mg/l in case of 1:1, 1:3 and 1:5 [chitosan: TPP] respectively.

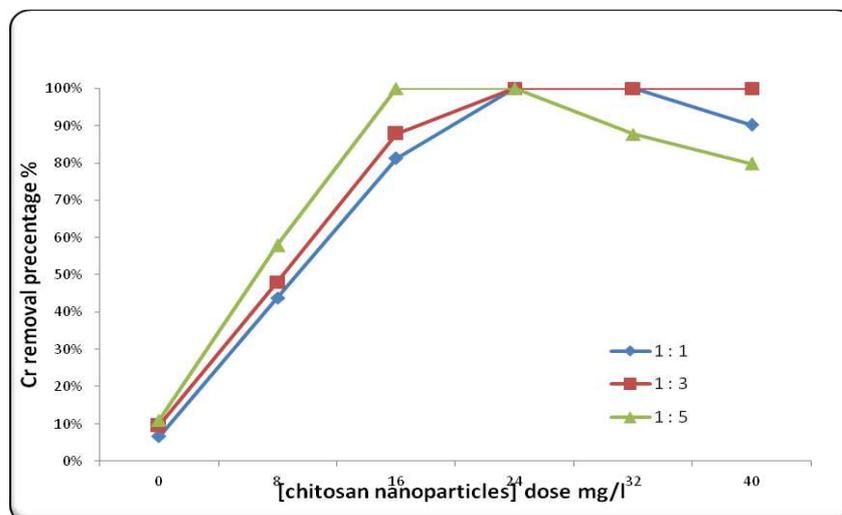


Figure 9: Effect of Different Doses and Sizes of Nano Chitosan on % of Cr Removal

The removal percentage of Cr from waste water due to effect of different dosages and the three sizes of chitosan nanoparticles was presented in figure 9. It shows that, for the ratio (1:1) the best doses were 24 mg/l and 32mg/l which give 100% removal of Cr. So, the best dose is 24mg/l, and for the ratio (1:3) the best doses was 24, 32 and 40 mg/l which give 100% removal of Cr. So the best dose is 24 mg/l. On the other hand, in case of ratio (1:5) the best dose 16 and 24mg/l which give 100% removal, so for this size the best dose is 16 mg/l.

Cu Removal

The initial concentration of Cu as heavy metal in untreated waste water (raw materials) was 0.085, 0.132& 0.186 mg/l in case of 1:1,1:3 and 1:5 [chitosan : TPP] respectively.

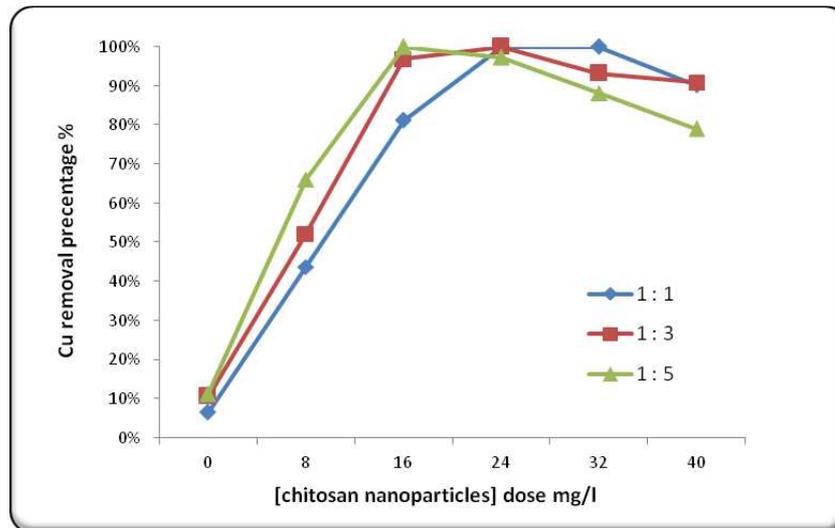


Figure 10: Effect of Different Doses and Sizes of Nano Chitosan on % of Cu Removal

The removal percentage of Cu from the different doses and three sizes of chitosan nanoparticles are shown in figure 10. It shows that for the ratio (1:1) the best doses was 24 mg/l and 32mg/l which gives 100% removal so that the best dose is 24mg/l, and for the ratio (1:3) the best dose was 24mg/l and for the ratio (1:5) the best dose is 16 mg/l which gives removal of 100%.

Fe Removal

The initial concentration of Fe as heavy metal in untreated waste water (raw materials) was 4.788, 6.315 and 6.923 mg/l in case of 1:1, 1:3 and 1:5 [chitosan: TPP] respectively.

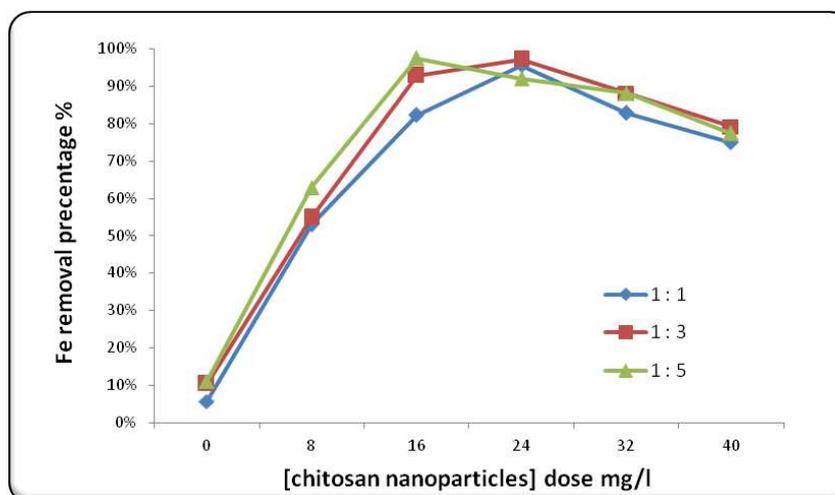


Figure 11: Effect of Different Doses and Sizes of Nano Chitosan on % of Fe Removal

The removal percentage of Fe from the different doses and the three sizes of chitosan nanoparticles are represented by figure 11. It shows that for the ratio (1:1) the best doses was 24 mg/l which gives removal 95.49% and for the ratio (1:3) the best dose was 24mg/l which gives removal 97.15% and for the ratio (1:5) the best dose 16 mg/l which gives removal of 97.38%.

Mn Removal

The initial concentration of Mn as heavy metal in untreated waste water (raw materials) was 0.192, 0.273 and 0.312 mg/l in case of 1:1, 1:3 and 1:5 [chitosan : TPP] respectively.

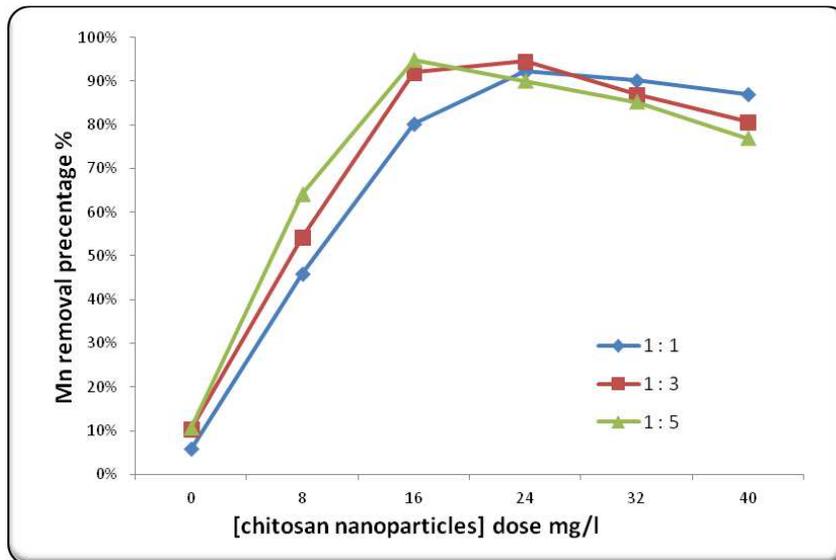


Figure 12: Effect of Different Doses and Sizes of Nano Chitosan on % of Mn Removal

The removal percentage of Mn from the different doses and the three sizes of chitosan nanoparticles also are presented in figure 12. It shows that for the ratio (1:1) the best doses was 24 mg/l which gives removal 92.19% and for the ratio (1:3) the best dose was 24mg/l which gives removal 94.50% and for the ratio (1:5) the best dose 16 mg/l which gives removal 94.87%.

Pb Removal

The initial concentration of Pb as heavy metal in untreated waste water (raw materials) was 0.070, 0.120 and 0.136 mg/l in case of 1:1,1:3 and 1:5 [chitosan : TPP] respectively.

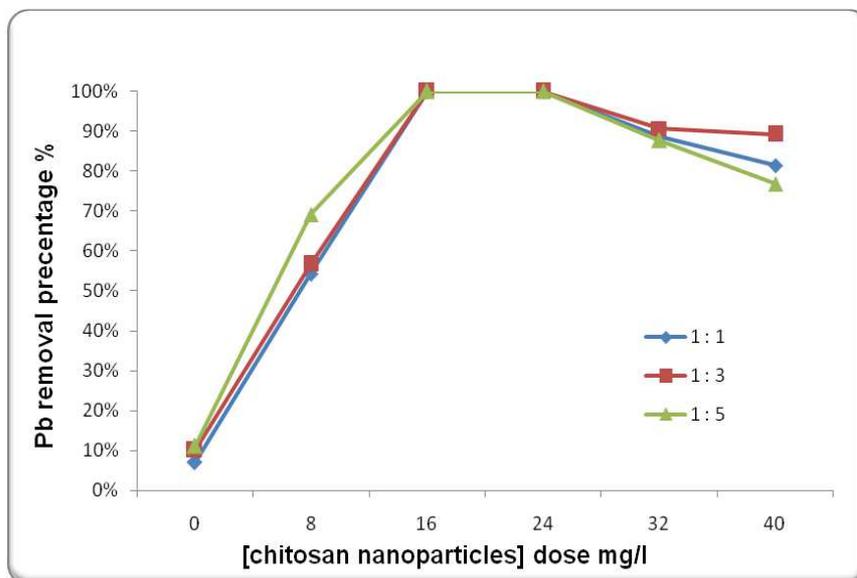


Figure 13: Effect of Different Doses and Sizes of Nano Chitosan on % of Pb Removal

As shown in figure 13, all three sizes of doses 16 mg/l and 24 mg\l give 100 % removal of Pb in waste water. So, nano chitosan of dose 16 mg\l has the best effect of treatment.

Zn Removal

The initial concentration of Zn as heavy metal in untreated waste water (raw materials) was 0.738, 1.426 and 1.513 mg/l in case of 1:1, 1:3 and 1:5 [chitosan : TPP] respectively.

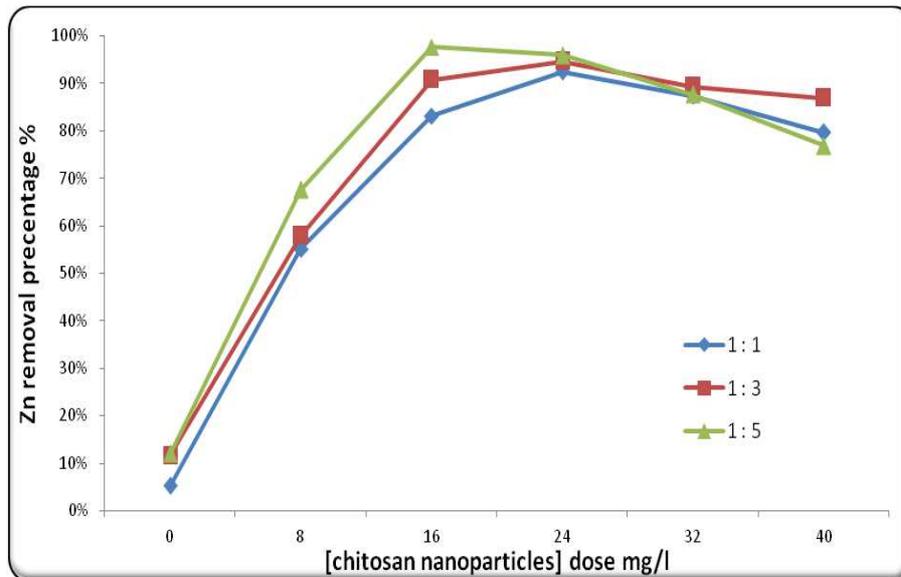


Figure 14: Effect of Different Doses and Sizes of Nano Chitosan on % of Zn Removal

The removal percentage of Zn from the different doses and the three sizes of chitosan nanoparticles were presented in figure 14. It was shown that, for the ratio (1:1) the best doses was 24 mg/l which gives removal 92.4% and for the ratio (1:3) the best dose was 24mg/l which gives removal 97.69% and for the ratio (1:5) the best dose 16 mg/l which gives removal 97.67%.

CONCLUSIONS

The results of the present investigation showed that, the dosages of 16 & 24 mg/l of chitosan nanoparticles were the optimum dosages for maximum removal in all treatment. This behavior could be explained based on charge density character of the nano chitosan. Compared to the other coagulants, chitosan nano particles have a high charge density. The charge density of the polymer increased when polymer adsorption increased. Therefore, this signifies the rapid destabilization of the particles. On the other hand, there was a drastic drop for the percentage of wastewater treatment up 32 & 40 mg/l dosages of the chitosan nanoparticles. This poor performance was due to the phenomenon of excess polymer is adsorbed on the colloidal surfaces and producing restabilized colloids. Thus, there were no sites available on the particle surfaces for the formation of interparticle bridges. The restabilized colloidal particles can become positively charged and cause the electrostatic repulsion among the suspended solids.

It is noted also that, the smallest size of nano chitosan (~ 10 nm) has the greatest surface area of effective sites which exhibited maximum uptake capacity and so highest treatment percentage of wastewater. Chitosan nano particles can serve as an environmentally friendly material for waste water treatment.

REFERENCES

1. Ahmedna, M., Marshall, W. E., Rao, R. M., 2000a. Production of granular activated carbons from select agricultural by products and evaluation of their physical, chemical, and adsorptive properties. *Bioresource Technol.* 71, 113-123.
2. Ahmedna, M., Marshall, W. E., Rao, R. M., 2000b. Surface properties of granular activated carbons from agricultural by – products and their effects on raw sugar decolorization. *Bioresource Technol.* 71, 103- 112
3. Amuda, O. S., Amoo, I. A., Ajayi, O. O., 2006. Performance optimization of coagulation/flocculation process in the treatment of beverage industrial wastewater, *J. Hazard. Mater.* 129, 69-72.

4. Azab, M. S., Peterson, P. J., 1989. The removal of Cd from wastewater by the use of biological sorbent *Water Sci. Technol.* 21, 1705-1706.
5. Bansode, R. R., Losso, J. N., Marshall, W. E., Rao, R. M., Portier, R. J., 2004. Pecan shell – based granular activated carbon for treatment of chemical oxygen demand (COD) in municipal wastewater. *Bioresource Technol.* 94, 129-135.
6. Bromley, D., Gamal El-Din, M., Smith, D. W., 2002. A low cost treatment process to reduce phosphorus and suspended solids in liquid wastes from animal farm operations. *Proc. 4th international livestock waste manage. Symp. Technol. Expo.* Malaysia society of animal production, penang, Malaysia. p. 215.
7. Chatterjee, S., Lee, D. S., Lee, M. W., Woo, S. H., 2009. Congo red adsorption from aqueous by using chitosan hydrogel beads impregnated with nonionic or anionic solutions surfactant. *Bioresour. Technol.* 100, 3862–3868.
8. Clesceri, L. S., Greenberg, A. E., Eaton, A. D., 1998. Standard methods for the examination of water and wastewater. 20th ed. American public health association, Washington.
9. Crini, G., Badot, P-M., 2008. Application of chitosan, a natural aminopolysaccharide, for dye removal from aqueous solutions by adsorption processes using batch studies: A review of recent literature, *Prog. Polym. Sci.* 33, 399-447.
10. Dastgheib, S. A., Rockstraw, D. A., 2001. Pecan shell activated carbon: synthesis, characterization, and application for the removal of copper from aqueous solution. *Carbon* 39, 1849-1855.
11. Galambos II, Molina, J. M., Jaray, P., Vatai, G., Bekassy-Molnar, E., 2004. High organic content industrial wastewater treatment by membrane filtration. *Desalination* 162, 117-120.
12. Gerente, C., Lee, V. K. C., Cloirec, P. L. E., McKay, G., 2007. Application of Chitosan for the Removal of Metals From Wastewaters by Adsorption—Mechanisms and Models Review, *Crit Rev Environ Sci Technol* 37, 41-127.
13. Guibal, E., 2004. Interactions of metal ions with chitosan-based sorbents *Sep. Purif. Technol.* 38, 43-74.
14. Guibal, E., Touraud, E., Roussy, J., 2005. Chitosan interactions with metal ions and dyes: dissolved-state versus solid-state application. *World, J Microb Biotechnol.* 21, 913–920.
15. Guibal, E., Vooren, M. V., Dempsey, B. A., Roussy, J., 2006. A review of the use of chitosan for the removal of particulate and dissolved contaminants. *Sep Sci Technol.* 41, 2487–2514.
16. Guibal, E., Roussy, J., 2007. Coagulation and flocculation of dye-containing solutions using a biopolymer (chitosan). *React Funct Polym* 67, 33–42.
17. Hussein, H., Ibrahim, S. F., Kandeel, K., Moawad, H., 2004. Biosorption of heavy metals from wastewater using pseudomonas sp. *Electronic J. Biotechnol.* 7, 24 – 29.
18. Koivunen, J., Siitonen, A., Heinonen-Tanski, H., 2003. Elimination of enteric bacteria in biological-chemical wastewater treatment and tertiary filtration units, *Water Res.*, 37, 690–698.
19. Martinez, N. S. S., Fernandez, J. F., Segura, X. F., Ferrer, A. S., 2003. Preoxidation of an extremely polluted industrial wastewater by the Fenton's reagent. *J. Haz. Mat.* B101, 315-322.

20. Ng, C., Losso, J. N., Marshall, W. E., Rao, R. M., 2000a. Physical and chemical properties of selected agricultural by products – based activated carbons and their ability to adsorb geosmin. *Bioresour. Technol.* 84, 177-185.
21. Ng, C., Losso, J. N., Marshall, W. E., Rao, R. M., 2000b. Freundlich adsorption isotherms of agricultural by products based powdered activated carbons in a geosmin - water system. *Bioresour. Technol.* 85, 131- 135.
22. Ng, C., Marshall, W. E., Rao, R. M., Bansode, R. R., Loss, J. N., Portier, R. J., 2003. Activated carbon from pecan shell: process description and economic analysis. *Ind Crops Prod* 17, 209–217.
23. Nomanbhay, S. M., Palanisamy, K., 2005. Removal of heavy metal from industrial wastewater using chitosan coated oil palm shell charcoal. *Electronic J. Biotechnol.* 8, 43 – 53.
24. Peres, J. A., Beltran de Heredia, J., Dominguez, J. R., 2004. Integrated Fenton's reagent - coagulation/ flocculation process for the treatment of cork processing wastewaters. *J. Haz. Mat.* 107, 115-121.
25. Preetha, B., Viruthagiri, T., 2005. Biosorption of zinc (II) by *Rhizopus arrhizus* equilibrium and kinetic modeling *African J. Biotechnol.* 4, 506 – 508.
26. Ravi Kumar, M. N. V., 2000. A review of chitin and chitosan applications *React. Funct. Polym.* 46, 1-27.
27. Sonune, A., Ghate, R., 2004. Developments in wastewater treatment methods, *Desalination*, 167, 55–63.
28. Varma, A. J., Deshpande, S. V., Kennedy, J. F., 2004. Metal complexation by chitosan and its derivatives *Carbohydrate Polymers*, 55, 77–93.