Application of Snail Shell Chitosan as a Bioadsorbent in Removal of Copper (II) Ions from Wastewater

Oyekunle Ifeoluwa Peter, Oyegoke Jamal Adeyinka and Raji Ahmed Akolade

Department of Chemistry, Federal University of Technology, PMB 704, Akure, Nigeria

Abstract

Recently, various adsorbents have been employed in removing different heavy metals from wastewater particularly those that are toxic to man. This study was therefore conducted to examine the potency of chitosan obtained from snail shells to remove copper from wastewater by adsorption. The chitosan was subjected to Fourier transform infrared (FTIR) analysis which showed a strong band at 3425.69cm^{-1} that can be attributed to N-H and O-H stretching. The peak observed at 2939.61cm^{-1} indicated symmetric alkane −C-H stretching vibration or −OH stretch of carboxylic acids while that of 2546.12cm^{-1} can be assigned to -C≡C stretching vibration of alkynes. The presence of residual N-acetyl group was confirmed by the peak at 1643.41cm^{-1} (C=O stretching of amide I) and the peak at 1489.10cm^{-1} may be attributed to glycosidic linkage. The absorption band at 1149.61cm^{-1} can be attributed to be asymmetric stretching of the C-O-C bridge. The adsorption of copper by the chitosan was also studied under the effects of some process parameters and it was observed that removal efficiency of the chitosan increased with increase in contact time, adsorbent dosage and pH but decreased with increase in initial metal concentration. The adsorption of the copper ions was found to be aided by the presence of amine functional group on the chitosan and the mechanism of adsorption was chemisorption as the equilibrium data obtained from the study fitted better into the Langmuir isotherm model.

Introduction

Contamination of different water bodies by heavy metals has become a great concern because of the adverse effect on human, plants and animals (Li and Bai [1], Sharma et al. [2]). These heavy metals pose threat and are very harmful because they are non-biodegradable in nature, have long biological half-lives and have potential to be accumulated in the body (Manaham [3], Wilson and Pyatt [4]). Divalent metal ions such as lead, copper, cadmium, mercury and nickel can cause severe health problems in animals and human beings related to their ability to in bonding to proteins, nucleic acids and small metabolites in living organisms (Wiwit Alwi et al. [5]). Over the years, different ways of decontaminating waste water which include but not limited to chemical precipitation, nanofiltration, reverse osmosis, adsorption and ion exchange have been studied extensively. However, due to low cost, high efficiency, high availability of different adsorbents and easy handling, adsorption is specially gaining scientific focus. The treatment of wastewater using chitosan is considered an important application. Several research studies have highlighted the biosorbent ability of chitosan and their composite to remove pollutants from wastewater. Chitosan is a polyelectrolyte derivative of chitin which is the second most abundant naturally occurring biopolymer. Chitosan is an antibacterial, biocompatible, environment friendly, biodegradable material and has great potential for sorption of metals ions due to amino and hydroxyl groups in its chemical structure. The physico-chemical properties of chitosan are related to the presence of amine functional groups that makes it very efficient for binding cations from almost neutral solutions (Wiwit Alwi et al. [5]). The sorption capacity of chitosan is majorly controlled by its degree of deacetylaton which influences the physical, chemical and biological properties of chitosan, such as acid-base and electrostatic properties, self-aggregation, sorption property, ability to interact with other ions and biodegradability (Wiwit Alwi et al. [5]). Although, a number of researches are available on removal of heavy metals from wastewater by others methods, only few researches have been reported on the use of chitosan. Therefore, the current study examines the potency of chitosan obtained from snail shells to remove copper from wastewater by adsorption.

Materials and Methods

Sample collection and preparation

Snail shells were purchased from Oja-Oba market in Akure South Local Government

area, Ondo State, Nigeria. The shells were washed thoroughly to remove leaves, dirt and other impurities. They were dried at 100°C and pulverized into fine powder with the aid of a mechanical grinding machine. All chemicals used in this study were of analytical grade. The preparation of the chitosan was carried out in the analytical research laboratory, Chemistry Department of Federal University of Technology, Akure.

Preparation of chitosan

The chitosan was prepared based on the method proposed by (Wan Ngah and Fatinathan [6]). 100g of the powder was weighed into the conical flask and de-proteinised using 1.2M NaOH, boiled at 70°C for one hour and washed severally with de-ionized water. The sample obtained was thereafter demineralized using 0.7M HCl, boiled at 70°C for 15mins and washed severally with de-ionized water. The resulting sample was deacetylated using 50% NaOH, boiled at 100°C for 3hrs, washed and filtered repeatedly until the filtrates became neutral. Thereafter, it was oven-dried, cooled and sieved to obtain 280-300 micrometer mesh size. It was later transferred into a labeled sample bottle and stored under air-tight condition. The prepared sample was divided into four parts for effective sample utilization and 1g of the chitosan prepared the from snail shells was taken for FTIR analysis.

Preparation of stock solution

1000ppm of Cu^{2+} was prepared by dissolving 3.929g of copper (II) sulphate pentahydrate ($CuSO_4.5H_2O$) in 1 litre of distilled water.

Preparation of working solution

The working solution used during the experiments is obtained from the stock solution using the equation:

$$M_1V_1 = M_2V_2.$$

For the purpose of batch adsorption study, 20ppm was prepare in 100ml by pipetting 1ml of 1000ppm into a 100ml standard flask and the made up to mark using distilled water. The percentage removal of metal from the aqueous solution by the each chitosan can be determined using:

$$\% \ removal = \frac{C_0 - C_1}{C_0} \times 100,$$

where C_0 is the concentration of the metal before adsorption and C_1 is the concentration of the metal after adsorption.

The adsorption capacity of the biosorbent q_e can be calculated as:

$$q_e = \frac{C_0 - C_1}{m} \times V,$$

where *m* is the mass of the adsorbent used and *V* is the volume of the aqueous solution.

Characterization of chitosan

The surface chemistry of the synthesized chitosan was characterized using FTIR-8400S Fourier Transform Infrared Spectrophotometer at National Research Institute for Chemical Technology, Zaria, Nigeria.

Results and Discussion

Characterization of chitosan

FTIR analysis was used to identify the type of functional groups present in the chitosan. In Figure 1, a strong band at 3425.69cm^{-1} can be attributed to N-H and O-H
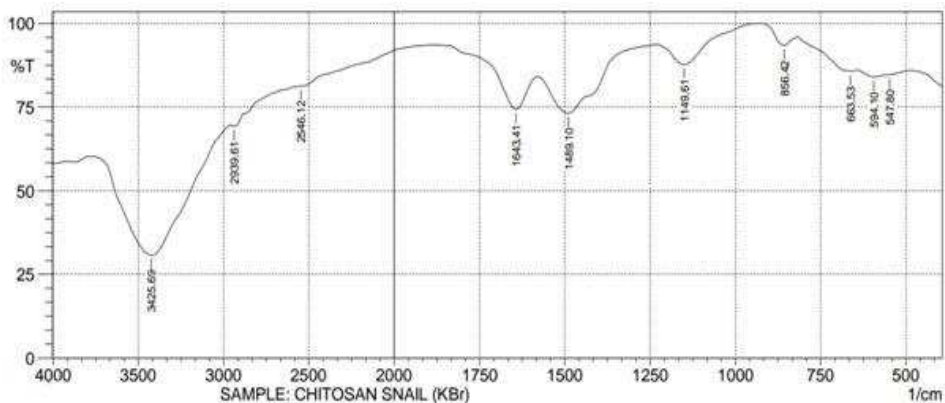

Figure 1. FTIR spectra of synthesized chitosan.

stretching. The peak observed at 2939.61cm^{-1} indicated symmetric alkane –C-H stretching vibration or –OH stretch of carboxylic acids while that of 2546.12cm^{-1} can be assigned to -C≡C stretching vibration of alkynes. The presence of residual N-*acetyl*

group was confirmed by the peak at $1643.41cm^{-1}$ (C=O stretching of amide I) and the peak at $1489.10cm^{-1}$ may be attributed to glycosidic linkage. The absorption band at $1149.61cm^{-1}$ can be attributed to be asymmetric stretching of the C-O-C bridge. All bands are found in the spectra of samples of chitosan reported by (Vino et al. [7], Song et al. [8]).

Effects of pH

Figure 2 shows the adsorption capacity of Cu (II) for different pH. pH is an important parameter for adsorption of metal ions from aqueous solution because it
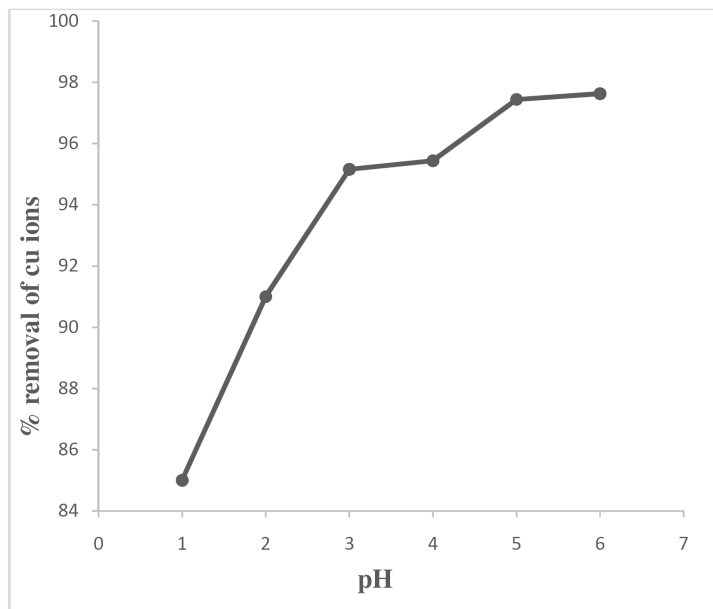
Figure 2. Variation of percent Cu^{2+} removal with change in pH value (adsorbent dosage = 0.5g, shaking speed = 250rpm, contact time = 50mins).

affects the solubility of the metal ions, concentration of the counter ions on the functional groups of the adsorbent and the degree of ionization of the adsorbate during the reaction. As shown in Figure 2, the adsorption of the copper ions is a function of the pH. The highest adsorption was observed at pH 6 with 97.63% which was slightly higher than that obtained at pH 5. After the pH 6, there was no visible increase in the percentage adsorption indicating the equilibrium has been reached. This phenomenon may be

explained as due to repulsive forces between Cu^{2+} on the surface of the adsorbent and Cu^{2+} in the aqueous phase and electrostatic balance between the protonated amine sites and Copper (II) ions (Guibal et al. [9]).

Effect of contact time

The adsorption of Cu^{2+} from aqueous solution was studied by varying the time of intimate contact between the chitosan and the synthesized wastewater containing the copper. Figure 3 below depicts the graphical illustration of the percentage copper
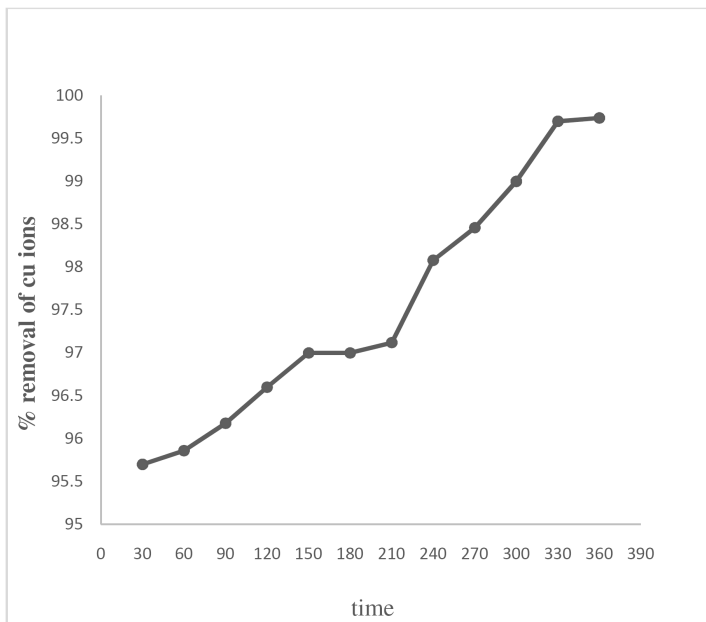

Figure 3. Variation of percent Cu^{2+} removal with contact time (adsorbent dosage = 0.5g, pH = 3, shaking speed = 250rpm, contact time = 50mins).

removal against the time of intimate contact. It was found out that, there was a significant increase in amount of Cu^{2+} adsorbed between contact time 30mins to 150mins. However, between contact time 150 to 210mins there was a very little increase in the percentage adsorbed after which there was a significant increase up to contact time 330mins after which no significant increase was observed which implied that the adsorbent was saturated.

Effect of adsorbent dosage

The percentage adsorption of Cu^{2+} by the synthesized chitosan was found to increase with increasing quantity of the adsorbent from 0.1 to 1.0 g/l. Thus may however be attributed to increase in binding sites of the adsorbent as more adsorbent were added (Lingamdinne et al. [10]). Based on the data in Figure 4, maximum adsorption of the synthesized chitosan was achieved with 1.0g/l.
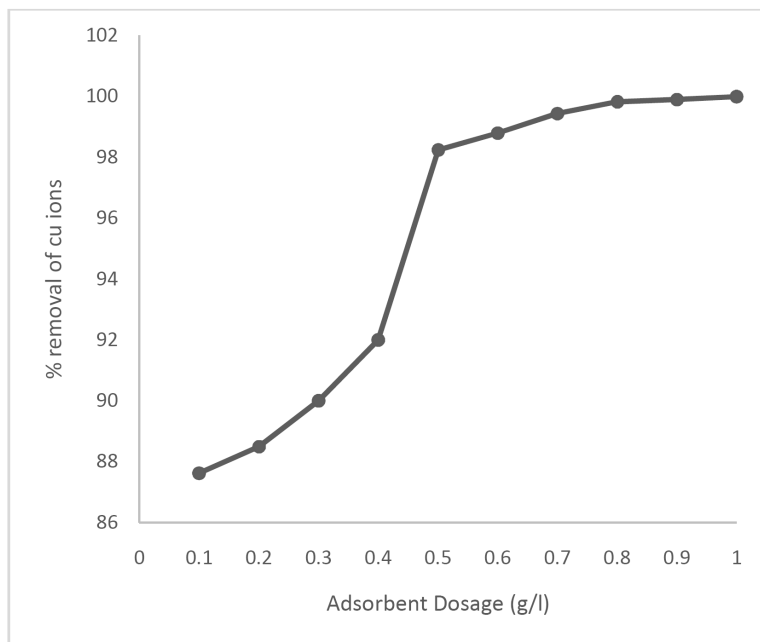

Figure 4. Variation of percent Cu^{2+} removal with adsorbent dosage (pH = 3, shaking speed = 250rpm, contact time = 50mins).

Effect of initial metal concentration

Figure 5 shows the adsorption capacity of Cu (II) for different initial metal concentration. It was observed that the percentage of removal decreased increase in initial metal concentration. The low percentage removal at higher metal concentration can be traced to increased ratio of initial number of moles of copper to the vacant sites available. Therefore, the data obtained from the table revealed that copper adsorption was dependent on the initial metal concentration.
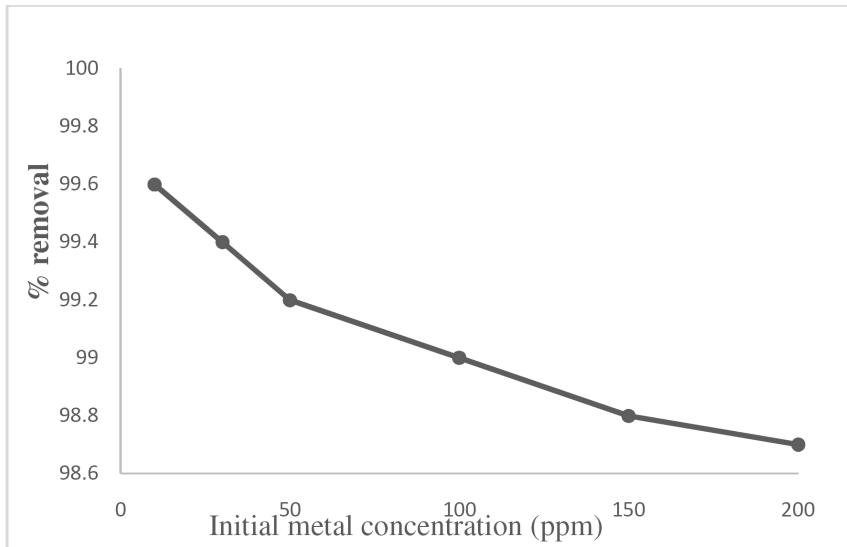
Figure 5. Variation of percent Cu^{2+} removal with initial metal concentration (pH = 3, shaking speed = 250rpm, contact time = 50mins).
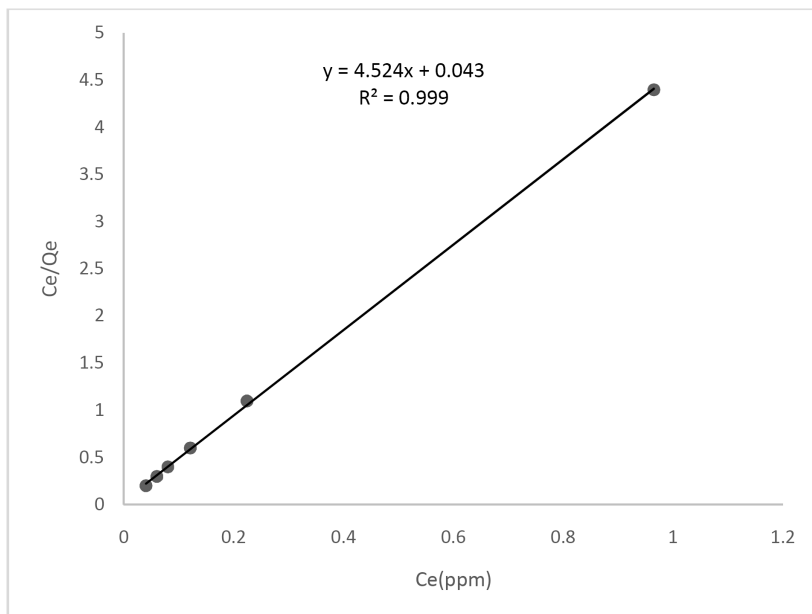
Adsorption Isotherm

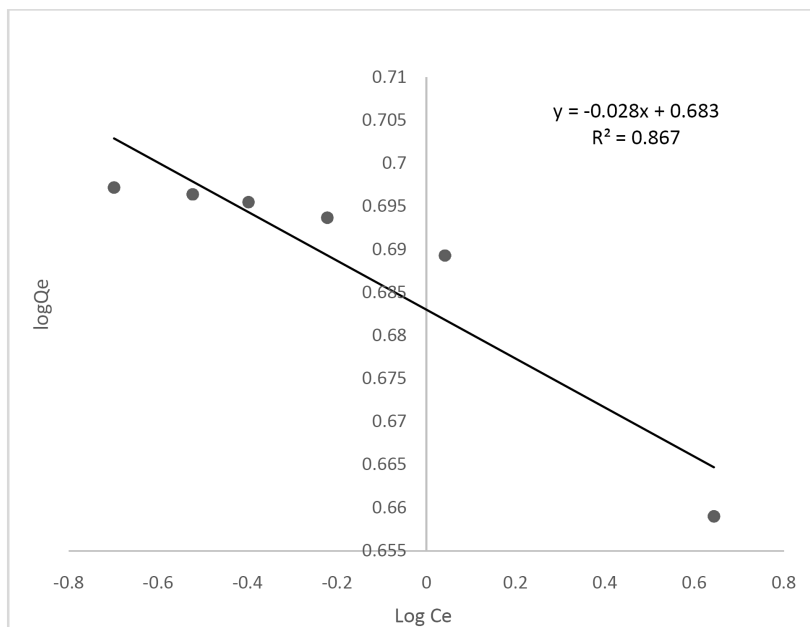**Figure 6.** Langmuir isotherm model for adsorption of copper.

Figure 7. Freundlich isotherm model for adsorption of copper.

The adsorption isotherm is usually employed in the mechanism of adsorption of the adsorbate by the adsorbent used. From Figures 6 and 7, which depict the Langmuir and Freundlich adsorption isotherm onto chitosan for copper, the coefficient of correlation indicated that the experimental data fitted better into the Langmuir isotherm which made it safe to conclude that copper tends to be chemically adsorbed, i.e., chemisorption is favoured which is peculiar to Langmuir isotherm. This observation was also reported by (Asandei et al. [11], Ng et al. [12]).

Conclusion

The results obtained from the study revealed that the use of chitosan for removal of copper ions in wastewater is technically feasible, environmentally friendly and with high efficiency. The adsorption of the copper ions was found to be aided by the presence of amine functional group on the chitosan and the mechanism of adsorption was chemisorption as the equilibrium data obtained from the study fit better into the Langmuir isotherm model. Process parameters such as adsorbent dosage, temperature, contact time, initial metal ion concentration and pH also play different roles in establishing the removal efficiency of copper in wastewater with chitosan. It is

recommended that alongside the FTIR used to characterize the chitosan synthesized from the snail shells, Scanning Electron Microscopy (SEM), X-ray Diffraction (XRD) should also be used to determine the crystallinity and morphology respectively.

References

[1] N. Li and R. Bai, Development of chitosan-based granular adsorbents for enhanced and selective adsorption performance in heavy metal removal, *Water Sci. Technol.* 54 (2006), 103-113. https://doi.org/10.2166/wst.2006.736

[2] R. K. Sharma, M. Agrawal and F. M. Marshall, Heavy metal (Cu, Zn, Cd and Pb) contamination of vegetables in urban India: A case study in Varanasi, *Environ. Pollut.* 154 (2008), 254-263. https://doi.org/10.1016/j.envpol.2007.10.010

[3] S. E. Manaham, *Environmental Chemistry*, 8th ed., Lewis Publisher, Boca Raton, Florida, 2005.

[4] B. Wilson and F. B. Pyatt, Heavy metal dispersion, persistence, and bioaccumulation around an ancient copper mine situated in Anglesey, UK, *Ecotoxicol. Environ. Saf.* 66 (2007), 224-231. https://doi.org/10.1016/j.ecoenv.2006.02.015

[5] Wiwit Alwi, M. Lutfi Firdaus, Habibus Syakura, Syukri Arief, Syukri Darajat and Ghufira, Utilization of shrimp shells as biosorbent to remove heavy metal Cu and Zn in aquatic samples, 3rd International Conference on Biological, Chemical & Environmental Sciences (BCES-2015), Kuala Lumpur (Malaysia), Sept. 21-22, 2015.

[6] W. S. Wan Ngah and S. Fatinathan, Adsorption of Cu(II) ions in aqueous solution using chitosan beads, chitosan-GLA beads and chitosan-alignate beads, *Chemical Engineering Journal* 143 (2008), 62-72. http://dx.doi.org/10.1016/j.cej.2007.12.006

[7] A. B. Vino, P. Ramasamy, V. Shanmugam and A. Shanmugam, Extraction, characterization and *in vitro* antioxidative potential of chitosan and sulfated chitosan from Cuttlebone of Sepia aculeata Orbigny, *Asian Pacific Journal of Tropical Biomedicine* 2 (2012), S334-S341. https://doi.org/10.1016/S2221-1691(12)60184-1

[8] C. Song, H. Yu, M. Zhang, Y. Yang and G. Zhang, Physicochemical properties and antioxidant activity of chitosan from the blowfly *Chrysomya megacephala* larvae, *Int. J. Biol. Macromol.* 60 (2013), 347-354. https://doi.org/10.1016/j.ijbiomac.2013.05.039

[9] E. Guibal, M. Van Vooren, B. A. Dempsey and J. Roussy, A review of the use of chitosan for the removal of particulate and dissolved contaminants, *Sep. Sci. Technol.* 41 (2006), 2487-2514. https://doi.org/10.1080/01496390600742807

[10] L. P. Lingamdinne, J. R. Koduru, Y. L. Choi, Y. Y. Chang and J. K. Yang, Studies on removal of Pb(II) and Cr(III) using graphene oxide based inverse spinel nickel ferrite nano-composite as sorbent, *Hydrometallurgy* 165 (2016), 64-72. https://doi.org/10.1016/j.hydromet.2015.11.005

[11] D. Asandei, L. Bulgariu and E. Bobu, Lead (II) removal from aqueous solutions by adsorption onto chitosan, *Cellul. Chem. Technol.* 43 (2009), 211-216.

[12] J. C. Y. Ng, W. H. Cheung and G. McKay, Equilibrium studies of the sorption of Cu(II) ions onto chitosan, *J. Colloid Interface Sci.* 255 (2002), 64-74. https://doi.org/10.1006/jcis.2002.8664