



Article Info

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Adsorption efficiency of chitosan obtained from *Schistocerca gregaria* for Fe²⁺ and Zn²⁺ metals

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A number of technologies for wastewater treatment have been developed and used over the years, but adsorption comes into prominence and gained wide recognition due to its simple handling, flexibility in design, high efficiency, reversible nature for multiple uses, high-quality treatment, and adsorbent availability. Chitosan obtained from desert locust (*S. gregaria*) exoskeleton emerged as best candidate as a sorbent for heavy metals removal via adsorption process in aqueous solution. Isolation of chitosan involved three main stages, includes demineralization, deprotenization and deacetylation. Chitosan was characterized using Fourier Transform Infrared Spectroscopy (FTIR) and X-ray diffraction (XRD). The affinity of chitosan for Fe (II) and Zn (II) ions solutions adsorbed under different conditions was evaluated using atomic adsorption spectroscopy. And the result showed that the equilibrium percentage adsorption of Fe²⁺ was 95 %, 95 %, 96 %, 96.2 %, and 95.8 % and the quantity of Fe²⁺ adsorbed was 5.98, 5.96, 6, 6.1 and 5.98 (mg/g) while the equilibrium percentage adsorption of Zn²⁺ was 78 %, 83 %, 86 %, 87 %, and 89 % and the quantity of Zn²⁺ adsorbed was 5, 5.2, 5.3, 5.4 and 5.6 (mg/g) at contact time 10, 20, 30, 40 and 50 mins. The effect of adsorbent dose and contact time were studied, as the result revealed that increment of adsorbent dosage which provides more binding sites used for metal adsorption, leads to the increase in quantity of Fe²⁺ and Zn²⁺ adsorbed and their percentage removal.

Keywords: *Schistocerca gregaria*, chitosan, bio-adsorption, heavy metal.

1. Introduction

Heavy metals are used in many industries for different purposes and discharge to the environment through effluents with industrial wastage. Heavy metals are one of the categories of water pollutants which are potentially toxic to humans and other living species (Gamage, *et al.*, 2023). The heavy metals of most concern from various industries include lead (Pb), zinc (Zn), iron (Fe), copper (Cu), arsenic (As), cadmium (Cd), chromium (Cr), nickel (Ni) and mercury (Hg) which have been also recognized as poisonous to environment and human health even if present in trace amount (Begum *et al.*, 2021). Hence heavy metal contamination has been a critical problem (Pooja *et al.*, 2022). Heavy metal removal from wastewater is an issue of concern, a number of technologies have been developed and used over the years, such as chemical precipitation, ion exchange, chemical oxidation, reduction, reverse osmosis, and ultra filtration, among others these methods, adsorption comes into prominence and gained wide recognition due to its simple handling, flexibility in design, high efficiency, reversible

nature for multiple uses, high-quality treatment, and adsorbent availability (Praipipat *et al.*, 2023). But recently attention has been shifted towards the use of low cost and available adsorbent made from renewable resources (Ngamsurach *et al.*, 2022). Chitosan being the low cost adsorbent and derived from renewable source has emerged as best candidate as a sorbent for heavy metals removal via adsorption process in aqueous solution (Gamage *et al.*, 2023).

Chitosan is direct polysaccharide that occurs naturally and it is primarily made up of β -(1,4)-connected glucosamine segments (2-amino-2-deoxy- β -d-glucopyranose) in addition to recurring quantities of *N*-acetyl glucosamine segments (2-acetamino-2-deoxy- β -d-glucopyranose) (Ya and Yung, 2020). Chitosan is by far the most common cationic (-NH₂) biopolymer on the planet (Ya and Yung, 2020). Chitosan is soluble in inorganic and organic acids solutions ($pH < 6$), because of the protonation (H⁺) of its amino groups. Also due to its polycationic nature, it can combine alongside

polyanions to form polyelectrolyte compound (Aranaz *et al.*, 2021). OH and NH₂ functions in chitosan enable it for the creation of a variety of derivatives with enhanced characteristics for specific applications (Korma *et al.*, 2018). Chitosan has the potential to reduce and solve some environmental pollution problems for creating 'Greener' environment and it is a renewable polymer in this application. Some of the properties that are commercially attractive are polymeric, including natural decomposition, non-toxic to both the environment and humans, with no side effects or allergic effects if implanted in the body.

Chitosan occurs naturally in the environment in large quantities and run second in abundance to cellulose. It has an amine functional group which is strongly reactive with metal ions which results in novel binding properties for metal ion such as zinc, iron, copper, nickel and chromium (Zhang, *et al.*, 2020). The present study aimed to investigate the applicability of chitosan for some selected heavy metals (Iron and Zinc) adsorption from wastewater. The chitosan used in this work was prepared from *Schistocerca gregaria* (Desert Locust). The structure of chitosan is presented schematically in Figure 1.

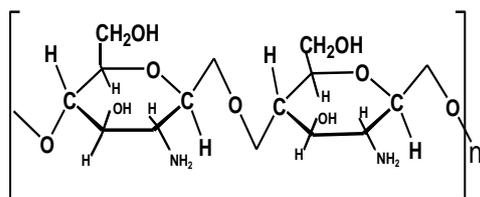


Figure 1: Structure of chitosan

2. Materials and Methods

2.1 Preparation of chitosan

Dried, matured *Schistocerca gregaria* (Desert Locust) which were used for chitosan preparation was purchased from the Sokoto State Old Market. Pretreatment stage was introduced as the first stage prior to the common procedure of chitosan isolation. At the pretreatment stage, the exoskeleton of *Schistocerca gregaria* (Desert Locust) was washed, dried inside oven for 2 hours at 50°C and crushed using motor as well as pestle. A powdered sample was obtained and sieved as described by (Ngamsurach *et al.*, 2022). The prepared exoskeletons were demineralized using 5% HCl (1:15 w/v) at 30°C for 60 mins. The mixture was cooled, filtered, the residue was washed with tap water, rinsed 3 times with distilled water to neutrality and then dried (Kaya *et al.*, 2013). After that the demineralized exoskeleton was deproteinized using 3% NaOH solution (1:50w/v) at 30°C for

60mins, the mixture was filtered via whatman filter paper then the residue was washed with distilled water. The resulting material was chitin which was dried (Kaya *et al.*, 2013; Andressa, *et al.*, 2021). The chitin obtained from the above process was deacetylated using 50% NaOH (1:50 w/v) solution at 120°C for 120mins to produce chitosan. The resultant chitosan was washed completely to neutrality using distilled water and oven dried for 24 hours at 50 °C (Amelia *et al.*, 2021). The prepared chitosan was characterized by Fourier transformed infrared (FT-IR) spectroscopy to determine the functional group present. The crystallinity of chitosan in powder form was studied by X-ray diffraction method (Varma and Vasudevan, 2020).

2.2 Study of heavy metal adsorption by prepared chitosan

2.2.1 Preparation of heavy metals solutions

Iron and Zinc solution (1000 mg/L) were prepared by dissolving 2.71g and 2.08g of FeSO₄ and ZnCl₂ salt into 1000 cm³ volumetric flask containing distilled water until homogeneous solution was obtained. This solution was kept as stock solution; 100 mL of 50 mg/L was prepared by serial dilution from stock solution 1000 mg/L by measuring 5cm³ into standard volumetric flask and making it up to the mark with distilled water.

2.2.2 Removal of heavy metals from wastewater

Twenty-five (25) cm³ of 50 mg/L of Fe²⁺ and Zn²⁺ solution was taken into different conical flasks containing 0.2g of chitosan. The mixture was placed and shake using an orbital shaker at 180 rpm at a contact time of 10minutes. The solution was allowed to settle for 5 minutes and then filtered, filtrate of each Fe²⁺ and Zn²⁺ solution was analyzed using atomic adsorption spectroscopy (AAS 306) to determine the amount of iron and zinc absorbed by chitosan. Effect of contact time was studied by changing only reaction time to 20, 30, 40 and 50 minutes and keeping other parameters constant and the above mentioned procedure was repeated one time. Effect of adsorbent dose of chitosan powder on amount of metal uptake was studied by increasing the adsorbent dose to 0.4, 0.6, 0.8, and 1.0g and keeping other parameters constant and the above mention procedure was repeated one time. Amount of iron and zinc adsorbed under different conditions was evaluated using atomic adsorption spectroscopy (Sewvandi and Adikary, 2011).

3. Results and Discussion

3.1 FTIR Spectrum

FT-IR analysis was performed to confirm the structure of the chitosan prepared from *Schistocerca gregaria* exoskeleton through the identification of bands characteristic of this polymer. Results of FTIR analysis of chitosan prepared from *Schistocerca gregaria* (Desert Locust) exoskeleton are presented in Figure 2. The characteristic peaks that confirms the identity of chitosan were detected, these includes, the N–H and O–H stretching bands around 3630 cm⁻¹, oxygen stretching (C–O–C) glycosidic linkage bands around 1125 cm⁻¹, (C–O) in primary OH group bands around 976 cm⁻¹, and 1634 cm⁻¹ corresponding to the free amino group (–NH₂) at C₂ of glucosamine. The yielded results were closed to the 3358, 1653, 1151 and 940 cm⁻¹ band peaks obtained in the studies conducted earlier for commercial shrimp chitosan by Ibitoye *et al.*, (2018). Mohammed, *et al.*, (2013) reported the amide I band as 1658 cm⁻¹ and the amine band as 1632 cm⁻¹ for prawn shells chitosan. It was observed that the 1540 cm⁻¹ absorption band which is attributed to protein was absent, hence confirming the effectiveness of deproteinization. Also the presence of a peak around 1634 cm⁻¹ which is the characteristic of amino group proves the success of deacetylation and this indicates the successful formation of chitosan biopolymer.

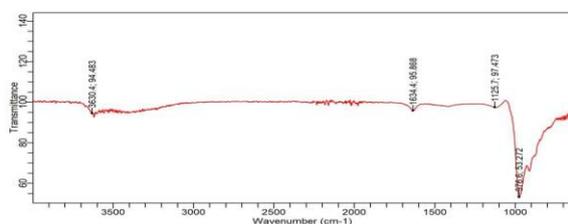


Figure 2. FTIR Spectrum of prepared chitosan prepared.

3.2 XRD Spectrum

Results of XRD analysis of chitosan prepared from *Schistocerca gregaria* (Desert Locust) exoskeleton are presented in Figure 3. The XRD analysis was performed to reveal the crystalline structure of the chitosan from the exoskeleton of *Schistocerca gregaria*. From the XRD spectrum pattern in Figure 3. A total of two peaks,

including one sharp and one weak peak, around 19.01, and 20.48° and many noisy peaks were observed. The appearance of only two peaks and many noisy peaks were ascribed to the amorphous structure and this indicated the destruction of the crystalline structure of the chitosan. This is in line with result from similar studies by Kaya, *et al.*, (2014) Two sharp peaks were observed in the chitosan produced from *C. barbarus* at approximately 10.92° and 20.08° (Kaya *et al.*, 2014). The peaks around 26, 27 and 28 can be attributed to the remaining minerals which as reported by Kaya, *et al.*, (2014) were absent, and this shows the effectiveness of demineralization process.

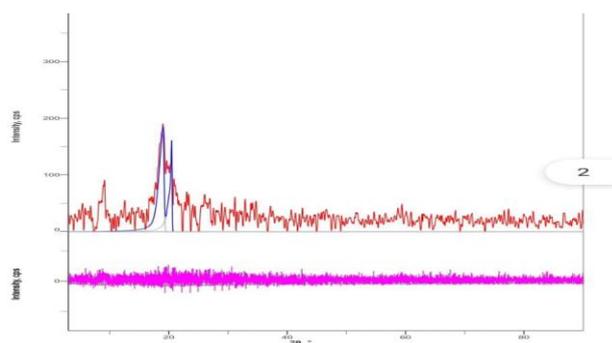


Figure 3. XRD Spectrum of prepared chitosan

3.3 Heavy Metals Adsorption Studies

The results of Fe²⁺ and Zn²⁺ adsorption process using chitosan prepared from *Schistocerca gregaria* (Desert Locust) exoskeleton as adsorbent under different conditions are presented in Figures 4, 5, 6 and 7.

3.3.1 Effect of Contact Time on the Removal of Fe²⁺ and Zn²⁺

The effect of contact time on the removal efficiency of Fe²⁺ and Zn²⁺ from wastewater were studied and presented in Figures 4 and 5. It was observed that different optimum times were observed for the Fe²⁺ and Zn²⁺ removal on the adsorbents. The equilibrium percentage adsorption of Fe²⁺ was 95 %, 95 %, 96 %, 96.2 %, and 95.8 % and the quantity of Fe²⁺ adsorbed was 5.98, 5.96, 6, 6.1 and 5.98 (mg/g) while the equilibrium percentage adsorption of Zn²⁺ was 78 %, 83 %, 86 %, 87 %, and 89 % and the quantity of Zn²⁺ adsorbed was 5, 5.2, 5.3, 5.4 and 5.6 (mg/g) at contact time 10, 20, 30, 40 and 50 mins.

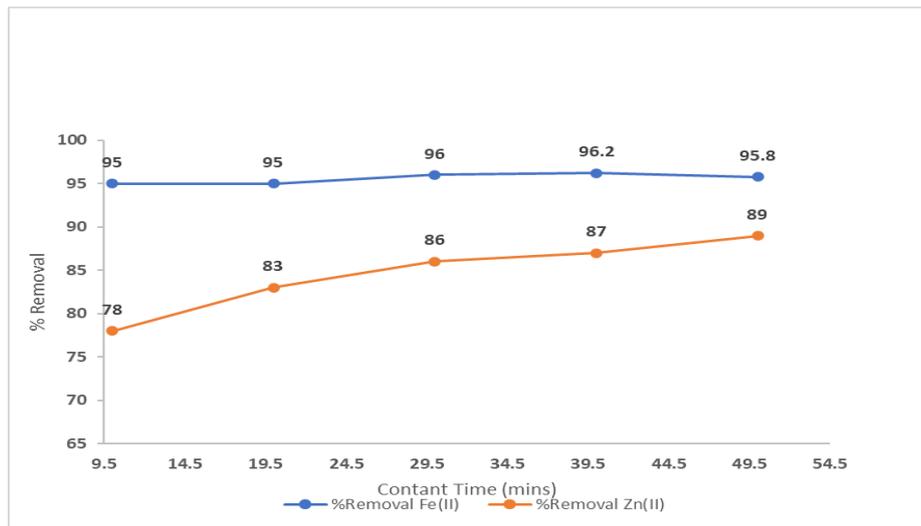


Figure 4. Effect of contact time on the adsorption of Fe²⁺ and Zn²⁺

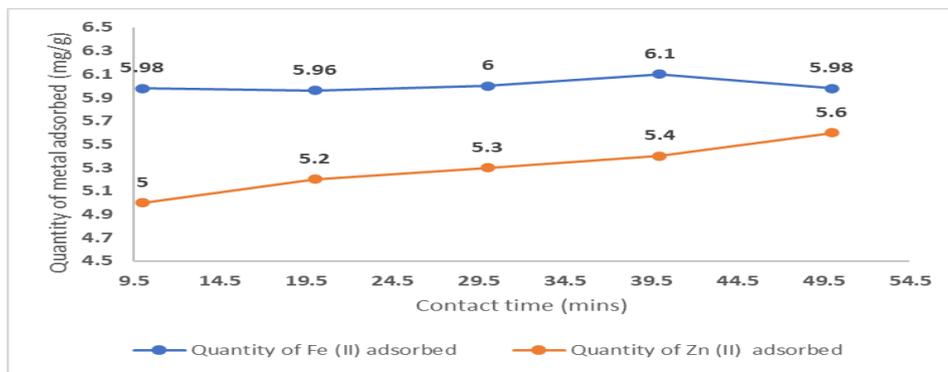


Figure 5. Effect of adsorbent dosage in the adsorption of Fe²⁺ and Zn²⁺.

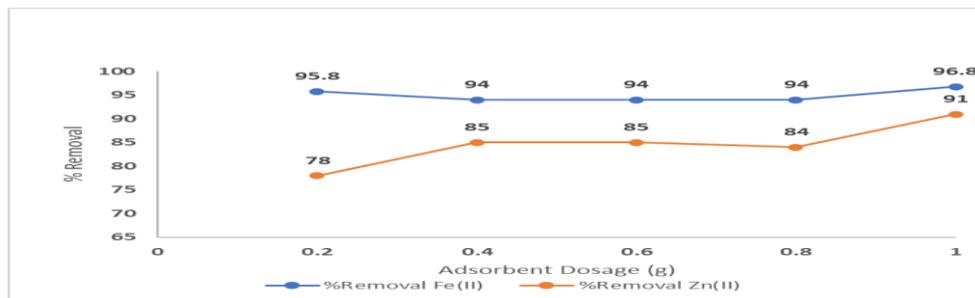


Figure 6. Effect of contact time on the adsorption of zinc Fe²⁺ and Zn²⁺

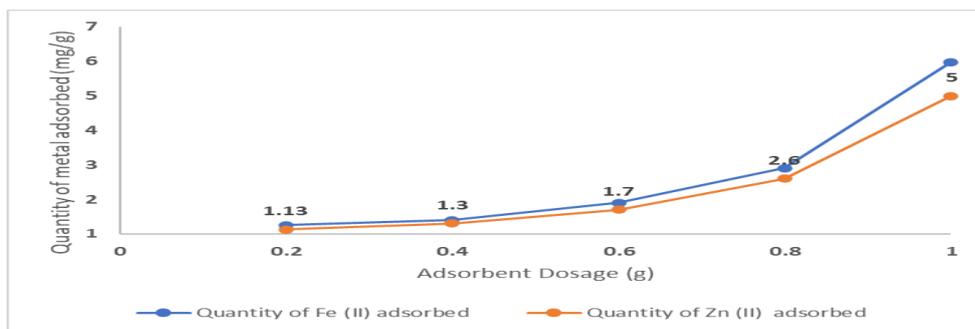


Figure 7. Effect of Adsorbent dosage on the adsorption of Fe²⁺ and Zn²⁺

The obtained value was higher than 35.1, 44.733, 45.33, 46.6 and 46.83% reported by Garima, (2016), for Zn (II) removal efficiency using chitosan, at contact time of (10, 20, 30, 40 and 50minutes). It was observed that adsorption was considerably successful because significant percentage removal of Fe²⁺ and Zn²⁺ were achieved and also quantity of Fe²⁺ and Zn²⁺ were removed after the process. Optimum Fe²⁺ and Zn²⁺ percentage removal was observed at 50 minutes' contact time.

Similarly, high quantity of Fe²⁺ and Zn²⁺ were adsorbed at 50 minutes. It was observed that the final concentration after the adsorption process was 2.1, 2.3, 2.0, 2.9 and 2.1mg/ml for iron (II) while 10.0, 8.1, 7.0, 6.2 and 5.2mg/ml was obtained for zinc (II) which are within the world health organization (WHO) allowable limit of 0.3 mg/l. However, it was observed that contact time highly affect the adsorption process as the result revealed that increases in contact time lead to the increase in quantity of iron (II) and zinc (II) adsorbed and increase in percentage removal (Figures 4 and 6). Because adsorption sites are well exposed and more diffusion process take place, due to increase in contact time.

3.3.2 Effect of Adsorbent Dosage on the Removal of Fe²⁺ and Zn²⁺

The effect of adsorbent dosage on the removal efficiency of Fe²⁺ and Zn²⁺ from wastewater were also studied and presented in Figures 5 and 7. The equilibrium percentage adsorption of Fe²⁺ was 95.8 %, 94 %, 94 %, 94 %, and 96.8 % and the quantity of Fe²⁺ adsorbed was 1.25, 1.4, 1.9, 2.9 and 5.98 (mg/g). while the equilibrium percentage adsorption of Zn²⁺ was 78 %, 85 %, 85 %, 84 %, and 91 % and the quantity of Zn²⁺ adsorbed was 1.13, 1.3, 1.7, 2.6 and 5 (mg/g) with adsorbent dosage of 0.2, 0.4, 0.6, 0.8 and 1.0g.

The obtained values were close to 91.4, 93.8, 94.3, 95.4 and 95.5% reported by Garima, (2016), for Zn (II) removal efficiency using chitosan, with adsorbent dosage of (50, 100, 150, 200 and 250mg). It was observed that significant percentage removal of Fe²⁺ and Zn²⁺ were achieved and also quantity of Fe²⁺ and Zn²⁺ were removed after the process. Also, from the result it was observed that optimum Fe²⁺ and Zn²⁺ percentage removal was observed with 1.0 g chitosan powder adsorbent. Similarly high quantity of Fe²⁺ and Zn²⁺ were adsorbed with 1.0g chitosan and this may be due to increment of adsorbent dosage which provides more binding sites used for metal adsorption. This showed that adsorbent dosage affects the adsorption process. However, a further increase in adsorbent dosage from 0.2 to 0.4, 0.6 and 0.8

led to a decrease in the percentage removal of both Fe²⁺ and Zn²⁺ which may be as a result of accumulation of adsorbent at one place thereby preventing the metal iron from the accessing the adsorption site efficiently, hence reducing the available active sites for adsorption process.

It was observed that the final concentration after the adsorption process was 2.1, 2.8, 2.8, 2.6 and 1.6 mg/ml for iron (II) while 10.6, 7.2, 7.0, 8.0 and 4.5mg/ml was obtained for zinc (II) and both the obtained concentration are within the world health organization (WHO) allowable limit of 0.3mg/l. the presence abundant vacant sites on the surface of the adsorbent and the rapid occurrence are always controlled by the diffusion process from the bulk solution to the adsorbent surface, thereby attaining equilibrium. At these points, the rate of sorption is equal to the rate of desorption and the equilibrium was achieved.

4. Conclusion

Chitosan was successfully synthesized from *S. gregaria* (Desert Locust). FTIR spectra of chitosan showed the characteristics band energies of standard chitosan sample. According to the results, optimum Fe²⁺ and Zn²⁺ adsorption was observed in the solution with 1.0 g chitosan powder at 50 minutes contact time, chitosan adsorbent dose, and reaction time highly effect on iron and zinc adsorption as shown by the result. According to the study chitosan may be a good candidate for heavy metals removal from wastewater. Chitosan may offer an alternative to traditional coagulants in wastewater treatment. The availability of chitosan and its unique properties make it an exciting and promising agent for the heavy metal removal from waste water.

Conflict of interest

The authors declare no conflict of interest.

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