Seafood wastes as an attractive biosorbent: Chitin-based shrimp shells

BAHADIR T.[1], GÖK G.[2], ÇELEBİ H.[3,*], ŞİMŞEK İ.[4], GÖK O.[5]

[1]Environmental Engineering Department, Engineering Faculty, Aksaray University, Centre Campus, 68100, Aksaray, Turkey
[2]Environmental Engineering Department, Engineering Faculty, Aksaray University, Centre Campus, 68100, Aksaray, Turkey
[3]Environmental Engineering Department, Engineering Faculty, Aksaray University, Centre Campus, 68100, Aksaray, Turkey
[4]Environmental Engineering Department, Engineering Faculty, Aksaray University, Centre Campus, 68100, Aksaray, Turkey
[5]Environmental Engineering Department, Engineering Faculty, Aksaray University, Centre Campus, 68100, Aksaray, Turkey
*corresponding author:
e-mail: hakanaz.celebi@gmail.com

Abstract In recent years, water quality deteriorated with Zn (II) ions has started to take place among the important environmental problems. Zn (II) is a primary type of toxic and bioaccumulative pollutant commonly found in industrial wastewater. Biosorption is the most practical method in the treatment of water contaminated with Zn (II). Researchers have evaluated the biosorption efficiency with various innovative adsorbents in the aquatic environment recently. In this study, the biosorption capacity of chitin based shrimp shell waste (Cht-SSW) was investigated in Zn (II) containing wastewater. Initial findings showed that Cht-SSW is an effective biosorbent due to high porosity and functional groups. Within the scope of the study, the effects of Cht-SSW dose, contact time, pH and temperature on the treatment efficiency of Zn (II) were evaluated by batch mode experiments. The surface morphology and functional groups of Cht-SSW used in the study were determined using FT-IR and SEM. The isotherms and kinetics confirmed that Cht-SSW has high value of adsorption capacity. Experimental results point out Cht-SSW is a biosorbent that eco-friendly, economical, easily available and efficiently (4e) on the removal of Zn (II) from aqueous solution.

Keywords: Biosorption, Chitin, Seafood waste, Shrimp shell, Zinc ion

1. Introduction

Although the environment has been defined as a water, air and soil environment in which humans, plants, animals and microorganisms live together in a certain harmony, it is under the threat of various pollutants. Metallic chemical elements and metalloids that are toxic to the environment and humans today are called "heavy metals". The most important reasons why these are among environmental problems are bioaccumulation and toxicity (Crans and Kostenkova, 2020). It has been determined in the literature that these inorganic-originated heavy metal pollutants react with some organic substances and turn them into even more toxic metal-organic complex pollutants (Hong et al., 2020; Tahoon et al., 2020). These pollutants can originate from a wide variety of natural formations and anthropogenic activities (Briffa et al., 2020; Sall et al., 2020). Especially Cd, Cu and Zn are three types of heavy metals that are frequently found in surface waters at high concentrations according to the quality standards determined by the European Union (Delahout et al., 2020). Table 1 shows the properties and concentration values of Zn (II) on the international scale (USEPA, 2019; WHO, 2017). Some conventional methods such as ion exchange, chemical precipitation, ultrafiltration, reverse osmosis, and adsorption are preferred to reduce and remove Zn (II) concentrations in contaminated water sources to the desired levels (Adewuyi, 2020; Pal et al., 2021). Biosorption is an effective process that has very high treatment potential in aquatic environments contaminated with various pollutants such as Zn (II) (Escudero et al., 2019; Senthilkumar et al., 2018).

In this study, biosorption which is preferred as an alternative to conventional treatment methods of toxic heavy metals was performed with an efficient and cost-effective biosorbent prepared from seafood-based waste. Chitin, the main component of shellfish such as crab and shrimp, is the most widely used type of biopolymer after cellulose (Santos et al., 2020; Eddya et al., 2020; Suryawanshi et al., 2019). Today, although some approaches such as waste recycling, zero waste, and life cycle analysis with industrial symbiosis have become increasingly important, large quantities of shells of seafood such as shrimp is discarded as waste without too much evaluation in all world countries. Therefore, it was thought that the treatment of waste with waste could be achieved by using such waste materials in the treatment process. For this purpose, the biosorption capacity of Cht-SSW was investigated. In the scope of the study, the effects of CHT-SSW dose, contact time, pH and temperature on the removal efficiency of Zn (II) were evaluated by batch mode experiments.

Table 1. Concentration and specific properties of Zn (II) in water

Metal	Permissible Limits (mg/L)			Chemical Properties			
	WHO	**USEPA**	**EU**	**Density (g/cm^3)**	**Mol. Weight (g/mol)**	**$LogK_{OW}$**	**K_{OC}**
Zn^{2+}	5.0	5.0	C-I <0.045, C-V >0.12	7.134	65.4	-0.471	1.20
Hazards	Nausea; skin irritation; spasms; vomiting; anemia; impaired immune function; Neutropenia						

2. Materials and Methods

2.1. Chemicals Used and Stock Solution

All the chemicals used in the experiments were at analytical purity level. To prepare a 1000 mg/L zinc stock solution, 100 mg/L solutions, which were prepared by diluting the weighed 4.176 g of $ZnCl_2$ from stock solution after dissolving with deionized water in 1 L volumetric flask, were used. In this study, 0.1 M HCl and NaOH chemicals were obtained from Merck Company (Merck, Darmstadt, Germany) to adjust the pH of the solutions. In addition, the initial pH of the solutions was measured with a HANNA pH 211 brand pH meter.

2.2. Preparation and Characterization of the Adsorbent

For Cht-SSW, which was the seafood waste used in the research, shrimp was purchased from fishermen. Cht-SSW was manually removed in laboratory environment and washed several times with pure water at room temperature for 24 hours to avoid any dirt, salt, and color problems before being used as an adsorbent. After the washing process, a number of methods including demineralization and deproteinization were applied to extract chitin contained in the structure of Cht-SSW (Celikci et al., 2020; Narudin et al., 2020; Kandile et al., 2018). Prior to the experiment, any other chemical or physical processes were not used. Functional groups of Cht-SSW, whose effectiveness as an adsorbent would be examined, were measured by the Fourier Transform Infrared Spectrometer (FTIR) (Thermo Scientific-Nicolet iS5) at spectra in the range of 400-4000 cm^{-1}. On the other hand, the surface morphology and element type of Cht-SSW were examined by the scanning electron microscopy (SEM) (Hitachi-SU 1510) and X-ray Fluorescence Spectrometry (XRF) (Rigaku-NEX-CG) devices, respectively.

2.3. Zn (II) Adsorption in Aqueous Solution

Adsorption studies were performed in glass equipment working in a discrete layout. 250 mL closed-mouth Erlenmeyer flasks with a working volume of 100 mL were used. The prepared Erlenmeyer flasks were treated with three repetitions in a ZHICHENG analytical model thermal shaker at a constant mixing speed of 150 rpm and a constant temperature of 20 °C. Adsorption experiments were conducted under appropriate conditions respectively according to the parameters of pH, time, Cht-SSW dose and temperature, which determine the basic mechanism. For the calculation of the adsorbed amount, samples filtered from filters with a pore diameter of 0.45 µm were given to the Perkin Elmer 2100DV brand (USA) Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) device, and the results were recorded according to standard deviation (≤5%) values. Experimental data were adapted to kinetic, isotherm models, and thermodynamic conditions (data were not shown). The optimal model shows the most likely adsorption mechanism. After the adsorption reaches equilibrium, the values of Zn (II) adsorption efficiency "AY (%)" and the Zn (II) adsorption capacity by the unit amount of Cht-SSW "q_e (mg/g)" were calculated based on the following formulas:

$$q_e = \frac{(C_0 - C_e) \text{ x V}}{1000 \text{ x m}} \quad (1)$$

$$AY\,(\%) = \frac{(C_0 - C_e)}{C_0} \text{x}100 \quad (2)$$

Where; C_0 and C_e: initial and final concentrations of Zn (II) (mg/L), m: Cht-SSW (mg) amount, V: volume of solution (mL).

3. Results and Discussion

3.1. Effect of pH on Zn (II) adsorption

pH is an important medium parameter since it affects both the adsorbent and the type of pollutant being adsorbed. As the pH changes, the adsorption efficiency also changes due to the strong change in the hydrogen (H^+) and hydroxyl (OH^-) ions present in the medium. Pourbaix graphs were used to accurately evaluate Zn forms in the Zn (II) containing water samples that were chemically analyzed. According to the Pourbaix graph, while the major types found at pH≥7 are Zn^{+2}, they are $Zn(OH)_2$, $HZnO_2^-$ and ZnO_2^{-2} at pH ≥ 9 (Takeno 2005). It is difficult to determine the level of pollution in water; as heavy metals cannot dissolve at pH≥7. Therefore, adsorption experiments were conducted in the pH range of 2-12 (Figure 1). As a result of discrete experiments conducted between different pH values, the maximum Zn (II) removal efficiency (82.41%) was found at pH 6.32. The maximum Zn (II) yield recorded for a medium close to the weak acidic level may be a result of interaction between cations in solution and functional groups at the adsorption regions of Cht-SSW. In our study, the decrease in the removal of Zn (II) under strongly alkaline conditions (pH>7.0) may have been caused by the electrostatic binding of ions to the surface of Cht-SSW or by the concentration of excessive OH- radicals. It is also a known fact that adsorption efficiency is shaped based on the loading of the adsorbent surface.

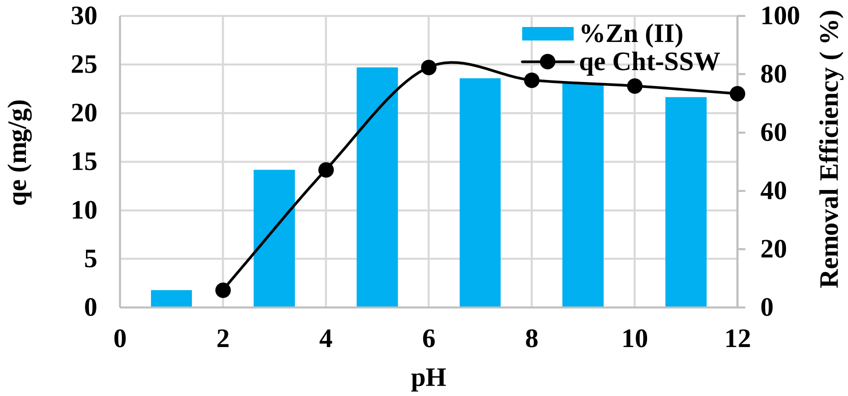

Figure 1. Effect of solution pH on the removal efficiency of Zn (II) using Cht-SSW.

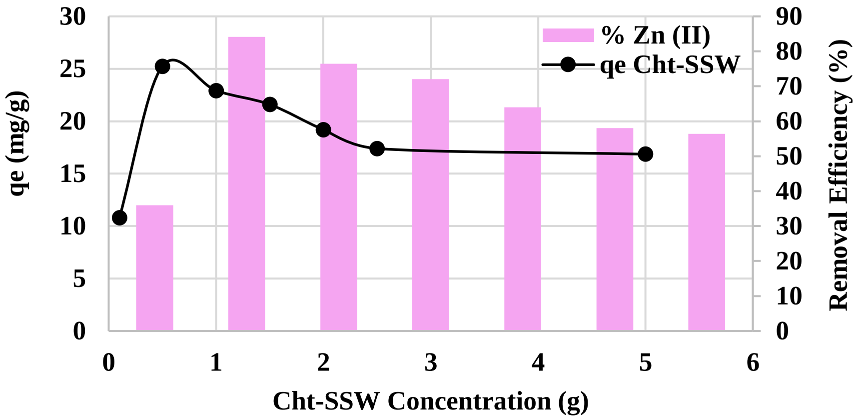

Figure 2. Effect of Cht-SSW dose on the removal efficiency of Zn (II) using Cht-SSW.

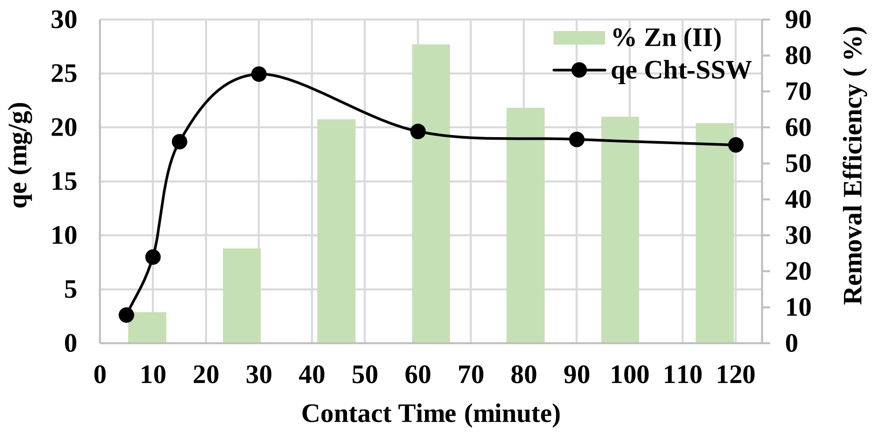

Figure 3. Effect of Contact time on the removal efficiency of Zn (II) using Cht-SSW.

3.2. Quantity of Cht-SSW adsorbent

The effect of Cht-SSW quantity on the Zn (II) adsorption process was examined by changing it in the range of 0.1-5.0 g at 150 rpm and at 20 °C in 100 mL of Zn (II) solution. The percentage of Zn (II) increased first up to the level of 0.5 g as the dose of Cht-SSW increased; however, it was partially decreased in later quantities (Figure 2). Zn (II) fell to levels of 36.00, 84.12, 76.43, 72.00, 64.00, 58.00, and 56.42% for Cht-SSW doses that have yield percentages of 0.1, 0.5, 1.0, 1.5, 2.0, 2.5 and 5.0 g, respectively. This can be based upon the active adsorbent surface area and higher adsorption capability. Maximum Zn (II) removal efficiency (84.12%) was achieved using a 0.5 g optimal quantity. Many researchers have tried different adsorbents to efficiently remove Zn (II) ions from wastewater. Other studies in the literature presents similar findings for Zn (II) adsorption by using various adsorbents. However, most of the used adsorbents are of the modified type, and the use of raw adsorbents or waste materials is quite limited. The external and internal surface physical morphology of Cht-SSW, characterized by methods such as SEM, XRF and FITIR, were determined according to international standards in the Aksaray University Scientific and Technological Application and Research Center Laboratories (data is not shown).

3.3. Interaction between Cht-SSW and Contact Time

Contact time is the time required for the adsorption process to reach equilibrium, and when adsorption studies conducted with boron is examined, it is understood that adsorption balance can usually occur over long periods of time. As can be seen in Figure 3, the contact time relationship between Cht-SSW and Zn (II) has a significant effect. The adsorption of Zn (II) was examined on Cht-SSW in the range of 5-120 minutes, as a function of time. Efficiency initially increased rapidly and reached a maximum level of 83.14% within 30 minutes of contact time for Cht-SSW. The higher removal rate in the first phase of the adsorption process may have been caused by the larger empty surface area of Cht-SSW for Zn (II) adsorption.

4. Conclusions

The current experimental study results showed that the adsorption of the heavy metal Zn (II) onto Cht-SSW depended on pH, contact time, temperature, and Cht-SSW quantity. The maximum removal efficiency of Cht-SSW was calculated as approximately 83% for Zn (II) under ideal conditions. Optimal conditions for the Zn (II) adsorption process on Cht-SSW were obtained as 0.5 g/L, 6.32, 20 °C, and 30 minutes for Cht-SSW dose, pH, temperature, and contact time, respectively. In order to better understand the adsorption of Zn (II), the effects of thermodynamics, different isotherms and kinetic models on adsorption efficiency were also examined (the data is not shown). This study clearly showed that in order to remove Zn (II) from aqueous solutions, Cht-SSW could be effectively used as a practical, effective, high-capacity, cost-effective, and environmentally friendly adsorbent.

References

Adewuyi A. (2020), Chemically modified biosorbents and their role in the removal of emerging pharmaceutical waste in the water system, *Water*, **12,** 1551.

Briffa J., Sinagra E., Blundell R. (2020), Heavy metal pollution in the environment and their toxicological effects on humans, *Heliyon*, **6,** e04691.

Celikci N., Ziba C.A., Dolaz M. (2020), Synthesis and characterization of carboxymethyl shrimp chitosan (CMSCh) from waste shrimp shell, *MANAS Journal of Engineering*, **8**, 77-83.

Crans D.C., Kostenkova K. (2020), Open questions on the biological roles of first-row transition metals, *Communications Chemistry*, **3,** 104.

Delahut V., Raskovic B., Salvado M.S., Bervoets L., Blust R., De Boeck G. (2019), Toxicity and bioaccumulation of Cadmium, Copper and Zinc in a direct comparison at equitoxic concentrations in common carp (Cyprinus carpio) juveniles, *PLoS One*, **15,** e0220485.

Eddya M., Tbib B., El-Hami K. (2020), A comparison of chitosan properties after extraction from shrimp shells by diluted and concentrated acids, *Heliyon*, **6**, e03486.

Escudero L.B., Quintas P.Y., Wuilloud R.G., Dotto G.L. (2019), Recent advances on elemental biosorption, *Environmental Chemistry Letters*, **17**, 409-427.

Hong Y.J., Liao W., Yan Z.F., Bai Y.C., Feng C.L., Xu Z.X., Xu D.Y. (2020), Progress in the research of the toxicity effect mechanisms of heavy metals on freshwater organisms and their water quality criteria in China, *Journal of Chemistry*, **2020**, 1-12.

Kandile N.G., Zaky H.T., Mohamed M.I., Nasr A.S., Ali Y.G. (2018), Extraction and characterization of chitosan from shrimp shells. *Open Journal of Organic Polymer Materials*, **8,** 33-42.

Narudin N.A.H., Mahadi A.H., Kusrini E., Usman A. (2020), Chitin, chitosan, and submicronsized chitosan particles prepared from Scylla serrata shells, *Materials International*, **2**, 0139-0149.

Pal P., Pal A., Nakashima K., Yadav B.K. (2021), Applications of chitosan in environmental remediation: A review, *Chemosphere*, **266**, 128934.

Sall M.L., Diaw A.K.D., Gningue-Sall D., Aaron S.E., Aaron J.J. (2020), Toxic heavy metals: impact on the environment and human health, and treatment with conducting organic polymers, a review, *Environmental Science and Pollution Research*, **27,** 29927-29942.

Santos V.P., Marques N.S.S., Maia P.C.S.V., de Lima M.A.B., de Oliveira Franco L., de Campos-Takaki G.M. (2020), Seafood waste as attractive source of chitin and chitosan production and their applications, *International Journal of Molecular Sciences*, **21**, 4290.

Senthilkumar R., Reddy Prasad D.M., Lakshmanarao G., Krishnan S., Naveen Prasad B.S. (2018), Ocean-based sorbents for decontamination of metal-bearing wastewaters: a review, *Environmental Technology Reviews*, **7,** 139-155.

Suryawanshi N., Jujjavarapu S.E., Ayothiraman S. (2019), Marine shell industrial wastes–an abundant source of chitin and its derivatives: constituents, pretreatment, fermentation, and pleiotropic applications-a revisit, *International Journal of Environmental Science and Technology*, **16,** 3877-3898.

Tahoon M.A., Siddeeg S.M., Alsaiari N.S., Mnif W., Rebah F.B. (2020), Effective heavy metals removal from water using nanomaterials: a review, *Processes*, **8,** 645.

Takeno, N. Atlas of Eh-pH diagrams (Intercomparison of thermodynamic databases). Geological survey of Japan open file report, 419, 1-287 (2005).

WHO, Guidelines for Drinking-Water Quality, Brazil, 2017. https://apps.who.int/iris/bitstream/handle/10665/254637/9789241549950-eng.pdf;jsessionid=347132493F49421E89E02B7B25E34359?sequence=1.

USEPA, National Primary Drinking Water Regulations. United States Environmental Protection Agency, Washington, DC. (2019). https://www.epa.gov/ground-water-and-drinking-water/national-primary-drinking-water-regulations.