Zinc Removal with Lignocellulosic Adsorbents; Interaction Mechanisms, from Biosorbent to Soil Conditioner

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Research Article

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Abstract

Batch experiments were performed to remove Zn2+ by adsorption process using organic residuals (pistachio, peanut, and almond) as an adsorbent. The adsorbents were characterized by FTIR spectra, SEM images and elemental analysis. The parameters of contact time, adsorbent dosage, pH and Zn2+ concentration were searched to define each effect on the process. Optimum adsorption of Zn2+ at pH 6, contact time 45 min at room temperature with 1.0 g adsorbent was found and the adsorption of Zn2+ was found to well describe Langmuir isotherm model and a pseudo-second-order rate equation. Intraparticle diffusion was applied to designate the rate-limiting step to the adsorption process. Functional groups on shell surfaces can cooperate with metal ions in many ways such as ion exchange, electrostatic interaction, complex formation, and physical adsorption. This study has shown that pistachio, peanut, and almond shell can be used for reducing Zn2+ from aqueous solutions as an eco-friendly, low-cost adsorbent. The end-product containing organic compounds and zinc can be used as a soil conditioner. Furthermore, the usage of the organic shell as a sorbent for the capturing of zinc from contaminated water ensures both the technical advantage and cost-effectiveness for the sustainable environmental management concept.

1. Introduction

The production of zinc over the world was 10.5 Mt in 2019 with help of roasting, electrolysis and pyrometallurgical process, purifying and electrodeposition. Zinc is one of the metals mostly utilized in industrial and agricultural processes, medicine, electroplating, mining, smelting, battery, paints and pigments, and pesticides due to its strong binding ability. However, the increasing production and excessive use of zinc have a growing concern about its eco-toxicological risks due to releasing into the environment. Zinc combination substances can be particularly toxic, and these elements are available from a wide variety of food sources. Zinc and its compound exposure exceed the permissible levels cause various health issues such as lung, bladder, breast, respiratory systems cancer, immune systems, gastrointestinal distress, and neurological signs. Therefore, the allowable level of 5.0 mg L⁻¹ in drinking water is released by the Environmental Protection Agency (EPA) and the World Health Organization (WHO).

Zinc, transition metal, are essential micronutrients as well as metal, and the body and human immune systems need zinc to function properly. Zinc is also an essential cofactor required for the performing of biological processes in all life and helps in the growth of cells. The lack of zinc deficiency brings about the loss of crops and retarded growth of plants. Moreover, the presence of organic materials effects nutrient ability and mobility, soil humidity and microorganism activity. Most of the nutrients cannot be taken by plant because of the presence of the complex structure form. However, many soil microorganisms convert complex forms into simple forms for taking up by the plant. So, the increase in soil organic contents results in an increase soil water holding capacity, microorganism activity, nutrients and mineral availability.
Wastes including soluble metals have to decrease allowable limits followed by secure disposal and recovery. Some conventional process has been widely used for the reduction of heavy metals from aquatic solution, for instance, ion exchange, chemical precipitation, electrolysis, adsorption, membrane technologies. However, most of these methods application has some limitation due to low efficiency and high operation costs. Among these, on the other hand, adsorption is called inexpensive, flexible, easy to operate in comparison to other processes and a highly effective method for the reduction of metal from polluted water and several researchers concentrated on the usage of cost-efficient and easily found sorbents. Organic residuals are usually acceptable as waste, have been applied at a reasonable cost and easily available adsorbents such as potato and banana peels, seed shells, tea leaves, coffee husks, eggshell, for the removal of heavy metals from aqueous solution. Researchers focus only on the adsorbent capacity and removal efficiency, rather than a comprehensive environmental protection approach to both metal removal and produced toxic end-products. These end-products, however, also contain valuable materials besides potentially hazardous materials. To identify the potential usage of the valuable by-products for sustainable environmental protection, it is useful to evaluate the composition of the products and usage areas.

The presence of lignin, cellulose and hemicellulose in pistachio, peanut, and almond shells make a valuable adsorbent for the purification of contaminated water by metals and further beneficial usage of final products. Peanut, pistachio, and almond are cultivated in the Middle East, the United States, and Mediterranean countries. Their annual production amount was about 47.0 million tons for peanuts, about 1.4 million tons for Pistachio, and about 3.2 million tons for almonds in 2019 (FAO, 2020.). The shell indicates about 35-40% of the total dry weight of peanut and 50% of pistachio, almond and annually shell produce is 16-19, 0.7, and 1.6 million tons respectively. Millions of tons of different agricultural wastes are burned or commonly discharged and disposed of at landfills resulted in odour and favouring microbial growth. Therefore, efficient researches are needed to find out a new adsorbent, recycle waste, is low-cost, obtaining end-products, and have a high adsorption capacity of heavy metals.

Removal of zinc from the receiving environment is very important to create a safe ecosystem. The main advantages of using organic waste as an adsorbent are the recovery of useful materials, and waste minimization. When zinc wastes are removes by organic residuals and recovery properly, it could be used beneficially for agriculture with zinc enriched organic soil conditioner. The usage of extremely chemical fertilizer causes deterioration of soil hypoxia, alkalinity, microbial and water imbalances due to farming activity. The restricted water and land resources put pressure on developing organic fertilizer/conditioner for sustainable agricultural development. It is very critical to improve physicochemical properties, chemical composition and nutrients contents in soil. Soil conditioners including organic materials are useful for releasing nutrients, holding water and also have a profitable effect on soil and plants. There has been renewed interest in compostable materials, and materials made from natural replenishable resources due to ecological concerns.
Some research was carried out related to heavy metal adsorption by using organic adsorbent, however, few focused on the removal mechanism and functional groups. Effective study is required to analyse the removal mechanism of the zinc on the adsorbent process and possible use of end-product for beneficial usage. Therefore, the research aim is to assess the possible removal mechanism, adsorption capacity and obtaining by-products in the removal of zinc ions from aqueous solutions, and also possible usage of end-product as a soil conditioner. Some kinetic, isotherm and thermodynamic equations were used to analyse the adsorption process. The possible removal mechanism of the metals is also explained with the help of FTIR spectra and SEM images. The effects of time, Zn$^{2+}$ concentrations, pH on metal removal efficiency were evaluated in batch experiments.

2. Materials And Methods

2.1. Materials and chemicals

Local dried nut manufactory provided pistachio, peanut and almonds hells. Previous to the ground and sieved, all shells were cleaned with deionized water and then dried out in the oven (Memmert Universal UN750, Germany) at 105°C for more than 24 h. The particle size of 0.5–1.2 mm was used the adsorbents for further studies.

The chemicals, Zn(Cl$_2$) (96% purity), HCl and NH$_4$OH, are of analytical grade and were provided from Merck Chemistry, Turkey. Deionized water (resistivity = 18.2 MΩ cm$^{-1}$) was produced from a Merck KGaA, Darmstadt, Millipore, Sigma system and used throughout the further study. Zn stock solution (1000 mg L$^{-1}$) was prepared with the help of exactly 2.09 g ZnCl$_2$ dissolved into 1 L pure water and the desired concentration of Zn$^{2+}$ was diluted for the study. The value of pH measured using a pH 510 Eutec pH-meter in solution (100 mg/L) was adjusted to 6 by using 0.1 mol/L HCl or 0.1 mol/L NH$_4$OH.

2.2 FTIR measurements

The surface chemistry was studied with the help of FTIR spectroscopy. FTIR spectra were recorded using a Perkin Elmer 400 FT-IR/FT-FIR) with a spectral resolution of 4 cm$^{-1}$. FTIR spectra for three adsorbents is demonstrated in Figure 1.

2.3 SEM Analyses

Scanning electron microscopy using a Zeiss Gemini 500-71-08 was used for surface properties of the shell samples. The Origin® software was used to smooth the data. SEM images (magnification of 20,000) of the almond, peanut and pistachio shells were taken with raw, and 10-minute intervals during removal of Zn$^{2+}$. SEM images is presented in (Fig. 2).

2.3. Analytical methods
Perkin Elmer Optima 2100 DV model inductively coupled plasma optical emission spectrometry (ICP-OES) was used to calculate the final Zn\(^{2+}\) concentrations after the designated contact time.

### 2.3. Batch studies

Adsorbent, 1.0 g for three shells in a 100 mL-glass conical flask under initial Zn\(^{2+}\) concentration of 5, 10, 25, 50, and 100 mg L\(^{-1}\), at a constant room temperature, was used for the batch studies (in Erlenmeyer flasks), for 45 min of contact time. The flask was shaken by a d ZHICHENG analytical model thermal shaker at 150 rpm with pre-fixed time, ranged from 5 to 45 min. 2 mL supernatants for each including the initial solution were used at pre-fixed time intervals before the Zn\(^{2+}\) concentration determination. The amount of Zn\(^{2+}\) ions in solutions (qe) were calculated by using equations (1):

\[
q_e = \frac{v(C_i-C_e)}{w}
\]  

(1)

where qe (mg g\(^{-1}\)) is the amount of metal ion removed from the solution, Co (initial) and Ce (final) concentrations (mg L\(^{-1}\)), V is the volume (L) and M the mass of shells (g).

The studies were carried out in duplicate to ensure reproducibility, reliability, and accuracy of the data and the Origin 9.0 program (Origin Lab, USA) was also used for all data.

### 2.4. Error Function Analyses

In this study, the average relative error, normalized standard deviation and marquardt’s percent standard deviation was also applied experimental data to confirm the best fitting. The equations are given below:

\[
AR\text{E} = \frac{100}{N} \sum_{i=1}^{N} \left| \frac{q_e^{\text{exp}} - q_e^{\text{cal}}}{q_e^{\text{exp}}} \right|_i
\]  

(2)

\[
MPSD = 100 \sqrt{\frac{1}{N-p} \sum_{i=1}^{N} \left( \frac{q_e^{\text{exp}} - q_e^{\text{cal}}}{q_e^{\text{exp}}} \right)^2}
\]  

(3)

\[
NSD = 100 \sqrt{\frac{1}{N-1} \sum_{i=1}^{N} \left[ \frac{q_t^{\text{exp}} - q_t^{\text{cal}}}{q_t^{\text{exp}}} \right]^2}_i
\]  

(4)

The MPSD, NSD and ARE shows more correct estimation of qe value\(^{12}\).

### 3. Results And Discussion

#### 3.1 Characterization of Adsorbents
Table 1 shows the chemical characteristic and composition of banana peel. As seen in the table the peel consists of lignin (28.82%), cellulose (28.82%), hemicellulose (28.82%), and ash (28.82%) due to organic residuals. Minerals composition of the peel is as follows:

Potassium, sodium, calcium, manganese, and other micro minerals.

The characteristic functional group identifies with the help of the FTIR spectroscopic analysis. The FTIR spectrums, scanned in the range of 450–4000 cm\(^{-1}\), are demonstrated in Figure 1. The spectra revealed a number of absorption peaks, indicating the complexity of the adsorbents. As seen at Figure 1, the band at 3276 cm\(^{-1}\) is indicating a number of hydroxyl groups (-OH) resulted from lignin, cellulose, hemicellulose in/on pistachio shell. The band near 2843 and 2150 cm\(^{-1}\) is the stretching vibration of C–H in alkanes, aldehydes and a carboxylic acid, and C≡C bond. The peak near 1722 cm\(^{-1}\) is the stretching vibration of C=O in aldehydes and ketones. There is a complex set of absorptions unique to each compound in the fingerprint region (1500 cm\(^{-1}\) to 500 cm\(^{-1}\)) of the spectrum. It is described with the help of references instead of interpreting the peaks visually. The band around 1423, 1251, and 1148 cm\(^{-1}\) represents C=C alkanes, -NO\(_2\) asymmetric nitro compound, and \(-\text{CH}_3\), \(-\text{CH}_2\) from alkanes, respectively. The peak 1026 cm\(^{-1}\) represents the C–O bond in cellulose. Peanut and almond shell also includes cellulose, hemicellulose and lining compounds, so similar spectra peaks came out as can be seen in Figure 1. The adsorbent peak gives valuable information concerning the bond –OH groups, C=O stretching, secondary amino group, carbonyl/carboxyl group -C=C- functional group were mostly taken part in adsorption process.

The SEM images of pistachio, peanut and almond shell are also demonstrated in Fig. 2 (a, b, c). It can be seen from the SEM images; shells consist of the considerable number of heterogeneous pore layers.

### 3.2 Contact time effect

Figure 3 demonstrates the effect of time on Zn reduction by shells. In the first 30 min, the removal rate increases quickly reaching a minimum of 83% for all adsorbents and then increases in contact time has no critical effect on the rate and equilibrium was reached in about 45 min. Initial Zn\(^{2+}\) removal was rapid due to large availability of functional groups on the adsorbent surface brought about the binding of metal ions on the adsorbent. The slow filling of functional groups on shells resulted in a decrease of Zn ions in the solution and then a decrease in the removal rate of Zn\(^{2+}\) in the final stage (30-45 min) (see Figure 3).

### 3.3 Effect of the pH

The characteristic of sorbent surface and ionization of the heavy metal is effected by pH. The adsorption capacity is, similarly, effected by pH due to the ability of hydrogen ions to change the adsorbent surface properties\(^13\). The formation of metal hydroxide, slightly soluble in the solution, depends on the optimum pH value. Batch experiment was performed at pH values between 3.0 and 10.0. Figure 3 shows the effects of pH on the removal of Zn\(^{2+}\). The removal efficiency of Zn\(^{2+}\) sharply changed for all adsorbents.
when the pH was increased from 3 to 6 and however, the removal rate fluctuated or decrease with increased of pH values (pH=9.0).

Kaur et al.\textsuperscript{14} pointed out that the positive charges find lower than that of pH 5.6, and negative charges higher than pH 5.6, and low adsorption percentage obtained at below pH values of 5.6. It can be explained by the fact that the positively charged functional groups on adsorbent repulse to Zn\textsuperscript{2+} ions. Furthermore, the chelation and the formation of metal hydroxide occurs with increasing pH result in enhancing the removal of zinc. The maximum removal rate was obtained at pH 6.0. These results are in compliance with the previous studies\textsuperscript{15} informed that maximum removal of zinc by using apple pulp, and barley straw was achieved pH values 6.0 and 5.0, respectively. pH values are bigger than 5 bring about the formation of soluble hydroxyl complexes or precipitates.

Zn\textsuperscript{2+} exist at pH 1.0 and 6.0 in the solution according to The Atlas of Eh- pH Diagrams. A negative surface charge on the adsorbent occurred with high pH values. The electrostatic repulsive force was effected and reduced by lower pH\textsuperscript{16} The neutral pH was favourable for the absorption of Zn\textsuperscript{2+} due to H\textsuperscript{+} was high at lower pH, which concluded filling the existing binding site of adsorbents and prevented from Zn\textsuperscript{2+} adsorption on the shell. Moreover, pH value greater than 6.0, the HO\textsuperscript{-} is dominant, resulted in a low removal rate due to dual competition occurred for the binding site between anions and metals.

### 3.4 Effect of adsorbent dose

Adsorption dose is the critic for the designation of the adsorbent capacity for a predetermined amount of the adsorbate. Adsorbent dose effect on the removal of metal ions is given in Figure 3. The shell dosage was increased from 0.25 g to 8.0 g at fixed pH and room temperature.

The removal rate of Zn\textsuperscript{2+} increased significantly from 68\% to 82\% for Peanut due to the adsorbent dosage increase number of functional and active sites that resulted in removal efficiency. A similar trend is also valid for the peanut and almond (see Figure 3). The adsorbent dose increase from 0.25 to 8.0 g increase the removal efficiency first and then continues steadily. However, equilibrium removal capacity is decreased. It can be explained with the relatively more existing reaction and binding sites in the surface area at lower adsorbent dose. Optimum adsorbent dosage was selected as 1.0 g for the further batch experiments.

### 3.5 Adsorption Isotherm

The sorbate and adsorbent interaction is well described for the equilibrium isotherm. Freundlich\textsuperscript{17}, Langmuir\textsuperscript{18}, Temkin\textsuperscript{19}, Dubinin-Radushkevich\textsuperscript{20} isotherm models applied data obtained from the batch experiment, performed with altering initial Zn\textsuperscript{2+} concentrations ranging from 5 to 100 mg/L, to express the interactions. Isotherm linearized form of equations, parameters and correlation coefficients is given in Table 3.

\textit{Freundlich Isotherm;
The Freundlich isotherm is known as an empirical model and is mostly used for the description of the heterogeneous adsorption having different energies of sorption. Freundlich isotherm is accepted that the formation of the monolayer is limitless with the reversible adsorption. The value of the Freundlich constant \((1/n)\) informs the adsorption intensity and the heterogeneous surface of the adsorbent. Furthermore, the sorption process is thought to be acceptable on the condition the value of \(n\) ranges between 1 and 10. As \(1/n\) indicate that \(1/n = 0\) is irreversible process, \(0 < 1/n < 1\) is favourable adsorption and \(1/n > 1\) unfavourable or cooperative adsorption. The value of \(1/n\) for \(\text{Zn}^{2+}\) was calculated lower than unity and these were bigger than 0.99 for three adsorbent follows (see Table 3). It was concluded that the adsorption conditions were favourable, and an ion exchange process occurs in the uneven adsorption surface layer. The adsorption capacity of pistachio, peanut and almond is as follows 17.28, 20.95, and 23.77 mg/g, respectively.

**Langmuir isotherm;**

The Langmuir adsorption model defines the monolayer adsorption and exists only one active side for binding ions and refers the adsorption sites on the adsorbent’s surface are homogenous. There is no interaction between adsorbent and adsorbate. The Langmuir constant \((RL)\) gives information about the affinity of the sorbent for the binding ions. If \(RL > 1\), the adsorption is undesirable; \(RL = 1\), it is linear; \(0 < RL < 1\) it is desirable; \(RL = 0\), it is irreversible.

The experimental data of pistachio, peanut and almond shells applied the Freundlich equations demonstrated that the correlation coefficient \((R^2)\) and validity equations of \(\text{Zn}^{2+}\) was followed as 0.996 (Pistachio), 0.998 (Peanut), and 0.998 (Almond). Values of \(1/n\) for adsorption on the shells were calculated as 0.912 for pistachio, 0.988 for peanut, and 0.943 for almond. These values confirmed that desirable adsorption occurs for the removal of metal ions by the organic adsorbents. The maximum adsorption capacity \((q_{\text{max}})\) was 17.28, 20.95, and 23.77 mg/g for pistachio, peanut, and almond, respectively.

Figure 4 presents the comparison of the experimental values and the predicted amount of equilibrium for pistachio, peanut and almond shell. As demonstrated in Fig. 4, the data calculated values by Langmuir isotherm is close to the experimental data and the best isotherm for predicting the amount of \(\text{Zn}^{2+}\) adsorbed on the shells at equilibrium. Furthermore, the values of ARE, NSD and MPSD error analysis are well fit to Langmuir isotherms provides a better model for the reduction of \(\text{Zn}^{2+}\) (see Table 3).

The adsorbate–adsorbent interactions, in a homogenous distribution of binding energy, are generally defined by applying to Temkin isotherm. On the contrary, The Dubinin-Radushkevich isotherm is mostly applied to define the adsorption mechanism and nature using a Gaussian energy distribution onto a heterogeneous surface for the porous adsorbents. The average free energy \((E)\) in the D–R isotherm value for \(\text{Zn}^{2+}\) was calculated as follows for Zn: 7.90 kJmol\(^{-1}\) (Pistachio), 7.33 kJmol\(^{-1}\) (Peanut), and 8.70 kJmol\(^{-1}\) (Almond), (see Table 2). These results indicated that physical sorption took place for the reducing
3.6 Kinetic studies

To analyse the adsorption process, diffusion rate and mechanism of Zn\(^{2+}\) the Elovich \(^{12}\), Lagergren pseudo-first-order \(^{21}\), and the pseudo-second order model \(^{22}\), and the intra-particle diffusion model \(^{23}\) were applied, and the linearized equations, and the correlation coefficient is given in Table 4. The pseudo-first order equation is defined with one reactant concentration dependency or the reversible reactions, while the pseudo-second order is defined with the concentration of one second or two primary reactants dependency. The comparison of the isotherm model results was demonstrated in the Table 4. The coefficients \((R^2)\) of Zn\(^{2+}\) on the shells were calculate more than 0.99 for pseudo-second order. So, the pseudo-second order is well described in comparison to the pseudo first order in the adsorption process of Zn\(^{2+}\)(See Table 4). Previous researchers \(^{24}\) pointed out that pseudo-second order is more applicable than pseudo-first order to analyse the sorption rate of most sorbents in the aqueous medium. Similar results were found to reduce Zn\(^{2+}\) by using shells and our results are in line with previous studies.

Intra-particle diffusion plot was not linear. As seen in figure 5, it can be separate a few linear regions, and the results demonstrated that not only intra-particle diffusion is rate-limiting mechanism in the process, but also the diffusion played an important role the. Correlation coefficient \((R^2 < 0.891)\) shown that the adsorption process was governed by more than one mechanism such as external mass transfer and internal particle diffusion. It was also in concordance with the fact that the adsorption followed the pseudo second-order model. The internal particle diffusion rate constants were 3.411 mg/g/ min\(^{1/2}\) for pistachio, 1.429 mg/g/min\(^{1/2}\) for peanut, and 1.667 mg/g/min\(^{1/2}\) for almond, respectively (see table 4). The rate constants demonstrated the adsorption by shells was the fastest in the reaction rate of pistachio, in comparison to peanut and almond.

4. Removal Mechanism Of Zinc

Heavy metals and functional groups interaction is complex and effected by adsorbent properties, porous structure, surface area and functional groups, pH of the solution, metals chemistry in solution, binding characteristics effects adsorption behaviours. The heavy metals adsorption process is mostly carried out by mechanism of ion exchange, electrostatic interaction, complex formation, surface complexation, physical adsorption, and/or precipitation \(^{14}\). Each mechanism specific role depends on functional groups of organic adsorbent, ionization of metals, and aqueous environment \(^{25}\). The main constituents of the three used organic residuals are lignin, cellulose and hemicellulose, and also other components is, lipids, proteins, simple sugars, and ash, having a different ratio. Cellulose consists of 49.39% oxygen, 44.44% carbon, and 6.17% hydrogen with having a linear chain. The organic polymer chemical formula of cellulose is an \((C_6H_{10}O_5)n\), and n refers the number of glucose groups \(^{26}\). The chemical formula of
hemicellulose, an important component of plant materials, is \((C_6H_8O_4)\) m and is composed of glucose, xylose, Omethyl-gluconic acid and galacturonic acid. The aliphatic hydroxyl (\(-OH\)) and ether (C–O–C) groups are active groups in cellulose and hemicellulose chains. Lignin with the chemical formula \([C_9H_{10}O_3(och3) 0.9–1.7]n\) is a highly branched polymer having phenolic units including trans-p-coumaryl, trans-coniferyl and trans-sinapyl. There are a number of active site in aliphatic and aromatic hydroxyl groups, lignin, double bonds and phenyl groups. There are a number of active sites on/in the shell, such as \(-\text{COOH}, \ -\text{OH}, \ -\text{CH}_3, \ -\text{NO}_2, \ -\text{CH}_2, \ -\text{CH}\), amino acids and so on, involving in the heavy metal removal process.

**Physical Adsorption**

The physical adsorption is effected by adsorbent surface area, porosity and the nature of heavy metals. The adsorption enhances the functional groups, heterogeneity, and polarity of adsorbent via electrostatic attraction and ion-dipole forces. Cellulose, hemicellulose found in the shells contain hydroxyl groups (\(-OH\)) involved in corporate binding with heavy metals. The carboxyl group dissociates to \(-\text{COO}^–\) and \(H^+\) in aquatic solution, and most of the carboxyl group transforms to \(-\text{COO}^–\) under the certain pK, provide reducing the cationic heavy metal efficiently.

**Electrostatic Interaction**

The electrostatic interaction is created as a result of divalent metals and negatively charged functional groups on the adsorbent. However, this happens secondary and are very weak. The aqueous pH, and point of zero charges of the adsorbent are key for the frequency of electrostatic interaction. Fujisawa et al. informed that the C6-carboxyl group of oxidized cellulose presents at the pKa value of 2.8–3.7. Therefore, the carboxyl groups were dissociated and associated with the Zn\(^{2+}\) ions due to the working pH value is 6.0. The metal complexes formation can be defined with the help of the Lewis acid-base theory, where acid is the acceptor of electron pairs from a base. Three adsorbent shell is represented by S, and the protonation equilibria for the amino group, \(-\text{NO}_2\) and the hydroxyl of C-6, \(-\text{OH}\) is as follows;

\[
\begin{align*}
S-O-\text{NO}_2 + H^+ & \rightarrow HO-S-\text{NO}_2 \\
H_1S + H & \rightarrow S \\
S-HO-\text{NO}_2 + H^+ & \rightarrow O-S-\text{NO}_3^+ + H_2O \\
S + H & \rightarrow HS
\end{align*}
\]

where \(H_1S\) is the completely deprotonated unit, the shell dimeric unit with C-6 hydroxyl group protonated, and HS, the fully protonated sites.

**Ion-exchange**
The other main heavy metal removal process is that ion exchange takes place with the availability of carboxyl and hydroxyl functional groups include oxygen. The functional group chemistry and metal ion size are critical for the process efficiency. Chemical and physical adsorption is the main mechanism between adsorbent and adsorbate. Chemical adsorption is mostly leaded by mainly ketones and esters contain carboxyl group and polar groups on the adsorption surface. Specifically, an acidic functional group plays a critical role the removal of heavy metals by organic adsorbents. Zinc removal rate increased at pH 6.0 due to negatively adsorption surface increased. pH was adjusted by using NH₄OH in this study, resulting in hydroxide to form the Zn(HO)₂ salt. This indicated that the removal of Zn²⁺ was a deposition reaction due to working pH is 6.0. Based on the results, one of the adsorption mechanism is cation exchange due to removal efficiency effected by pH. Hu et al. pointed out that the formation of metal hydroxide was carried out in solution at neutral pH or alkaline conditions, and metal hydroxyl salt precipitates out in aqueous. In this work, the formation of the metal carboxylate occurs on the basis of the exchange of divalent metal with the proton in the carboxyl groups due to NH₄OH was the pH buffering agent. The ion exchange process is most likely defined by the following equations:

\[
\text{RCOOH} + \text{NH}_4\text{OH} \rightarrow \text{RCOONH}_4 + \text{H}_2\text{O},
\]

\[
2\text{RCOONH}_4 + \text{ZnCl}_2 \rightarrow 2\text{RCOOZn} + \text{NH}_4\text{Cl}
\]

\[
\text{S-OH} + \text{Zn}^{2+} \rightarrow \text{S-O-Zn}^+ + 2\text{H}^+
\]

\[
\text{S-NO}_2 + \text{Zn}^{2+} \rightarrow \text{S-NO-Zn}^+ + \text{H}_2\text{O}^+
\]

\[
\text{S-COOH} + \text{Zn}^{2+} \rightarrow \text{S-COO-Zn}^+ + 2\text{H}^+
\]

The salt reaction with shell hydroxyl groups are mostly as follows;

\[
\text{S-OH} + \text{Zn(OH)}_2 \rightarrow \text{S-O- ZnOH} + \text{H}_2\text{O}
\]

\[
\text{S-NO}_2 + \text{Zn(OH)}_2 \rightarrow \text{S-NO- ZnOH}
\]

**Surface Complexations and Chelation**

Surface complexations occur with multi atom structures and metal-functional group interaction and important process in adsorption. The carboxyl/carbonyl functional groups bind heavy metals, creating a complexation. Ali et al. pointed out that chemical adsorption may be the rate controlling step due to forming chemical bonds with exchange or sharing of electrons between sorbent and sorbate in process. Zn²⁺ present in aqueous as cations at neutral pH can be reduced with the help of surface complexion or electrostatic attraction. The complex species associated with equilibrium can be defined by the following equations;

\[
\text{S} + \text{Zn}^{2+} \rightarrow \text{SZn}^{2+}
\]
Zn\textsuperscript{2+} + S + H \rightarrow SHZn\textsuperscript{2+}

Zn\textsuperscript{2+} + S + OH \rightarrow Zn\textsuperscript{2+}SOH

Furthermore, chelation is the other mechanism. A chelate is composed of a metal ion and a chelating agent, and molecules can be linked to bonds with a metal ion, resulting from the low competitive adsorption of hydrogen ions at high pH. There is a close link between pH and adsorbent surface functional groups, effect on the adsorption capacity due to the low pH increase solubility. Saito et al.\textsuperscript{32} pointed out that divalent metals removal with an ion exchange process by using TEMPO-oxidized cellulose is less efficient at pH values of 2.5–2.7 due to free carboxylic acids present at lower pH values. It can be explained the fact that most functional groups are protonated in acidic conditions and occur weak contents between the metal ions and protons. A combination of metal chelation and ion exchange governed metal adsorption on the shell, mainly with carboxyl functional groups. Metals removal by organic compound took place through a surface complexation-ligand exchange mechanism between organic adsorbent active sites and metal ions.

**Diffusion**

Fernández-López et al.\textsuperscript{33} pointed out that some information relating to the adsorbent surface, chemical/physical reaction, and diffusion, the proper reaction rate is described by the sorption kinetic models. The pseudo-second-order equation defined well the adsorption of Zn\textsuperscript{2+} on the three adsorbents considering correlation coefficients (R\textsuperscript{2}) (see Table 4). So the adsorption-complexation interactions through electron exchange or sharing are the main sorption process. Ho and McKay\textsuperscript{22} is pointed out that chemisorption could be the rate-limiting step in all adsorption processes due to valence forces through exchange or sharing of electrons between sorbent and sorbate.

The particle size and shape of the adsorbent effects the pore diffusion of the metal ions. Therefore, an intra-particle diffusion model was applied to define the adsorption kinetics due to the porous structure of the shells. The first plot refers to the external surface adsorption in the intra-particle diffusion model. The First stage is the fastest adsorption process due to the presents of unbinding sites. The second part, the gradual adsorption stage, is defined with intra-particle diffusion of the metal ions through the pores of shell particles. The final equilibrium stage represents the intra-particle or both film and intra-particle diffusion due to the low metal ions remain in the solution. Furthermore, Khanjani et al.\textsuperscript{34} highlighted that the divalent cations bridge the carboxylate groups between fibrils and fibers, cause to the solidification of the film within a time required for diffusion through the film thickness to be completed. During the adsorption of Zn\textsuperscript{2+} onto the shells, sequencing steps take place and are represented in Figure 6. Metal ions removal by adsorption process occurs through metals ions go towards from solution to adsorbent surface via external diffusion; diffusion of the metal ions towards boundary layer to adsorbent surface via film diffusion; metals ions go towards from surface to interior of the adsorbent via inter-particle diffusion, and metal ions adsorption on the surface active site by chemical reaction via ion-exchange, complexation and/or chelation.
SEM images were taken at 10 minutes interval through the adsorption process to obtain further information about the adsorption interaction between Zn$^{2+}$ ions and the shell (in Fig 6). It can be seen from the SEM analyses that shells consist of a considerable number of heterogeneous pore layers. Figure 6 demonstrates the formation of complexes in some regions on the shell surface after the sorption. Similarly, FTIR spectra of the shell at 10-minute intervals during Zn$^{2+}$ adsorption showed that functional groups of hydroxyl, carbonyl/carboxyl play important roles in the adsorption of heavy metals, and zinc adsorption by the shells increased over time. Furthermore, this adsorption resulted in changing the peaks and transmittances (see Table 7).

The spectroscopic analysis of the pistachio shell during the removal process demonstrated the peak transmittance shifted from 87.0 to 80.0 % (3276 cm$^{-1}$) for hydroxyl groups, and 94.0 to 87.0% for the peak of 2056 cm$^{-1}$ of alkanes, aldehydes and carboxylic groups (C$\equiv$H); 1722 cm$^{-1}$ assigned for aromatic C-C transmittance decrease 6.0%; 1148 cm$^{-1}$ assigned for C=O ester and carboxyl groups transmittance altered from 93.0 to 87.5%. The band at 3331 cm$^{-1}$ is indicating a number amount of hydroxyl (-OH) groups is produced from lignin, cellulose, hemicellulose, the transmittance decreased 11.0% for the almond shell. The peak near 2918 cm$^{-1}$ is the stretching vibration of C–H in alkanes, aldehydes and an carboxylic acid, and changed to 16.5% % end of the process. Furthermore, the peak at 3272 cm$^{-1}$ refers to the hydroxy groups (–OH) transmittance changed from 84.0 to 79% (30 min) for the peanut shell. It is most likely that surface adsorption through their complexation with phenolic -OH group occurs. The bands at 1728-1606 cm$^{-1}$ for peanut were linked with the aromatic carbonyl/carboxyl C=O and the aromatic C=C stretching modes, and changes of these peaks after adsorption started surface complexation of Zn$^{2+}$ by delocalized electrons. The peak near 1728 of transmittance changed 9.0% (30 min), is the vibration of C=O in aldehydes and ketones for almond. Similarly, the peaks at around 1597 and 1504 cm$^{-1}$ were assigned to C-O vibrations of hydroxyl groups or C-H stretching vibrations resulted from cellulose, hemicellulose and lignin and that of transmittance shifted 11.5% and 16.5 %, respectively. The bands between 1226, 1148 and 1011 cm$^{-1}$ were associated with C=O, -OH, -COOH stretching vibration of carboxyl groups resulted in transmittance change of 10.0 and 11.0% (see table 7). Other shell spectra peak and transmittance changes in the designated interval in the adsorption process were given in Table 7. As seen in Table 7, the transmittance shifts informed that the bond –OH groups, C=O stretching, secondary amino group, carboxyl group -C-C- functional group were mostly taken part in the adsorption process. The -OH and -COOH group were involved in the adsorption process due to C=O and –OH functional groups changed after zinc adsorption. These changes could be explained by ion-exchange mechanism between adsorbent and adsorbate. Furthermore, the electrostatic interaction and co-precipitation/inner-sphere complexation results from ion exchange reactions between metal ions and cations. As seen in Table 3, the metal adsorption capacity of pistachio shell is lower than peanut and almond shell. It can be explained the fact that the much lignin content in the peanut and almond than the pistachio attributes to metal uptake efficiency. The high electron ability and density towards participation in conjugation concludes toward to metal complexes. Furthermore, the complex formation and coordination affinity of lignin is much higher compared to cellulose and hemicellulose.
The actives groups can cooperate with ions in many ways, as shown in Figure 6. It can be concluded that the electrostatic interaction, ion exchange, diffusion, formation of complex, and precipitation of Zn ions, and Zn ions sorption by surface functional groups are the mechanism of the metal ions removal process.

5. Thermodynamic Studies

The thermodynamic parameter is critical for the evaluation heat change of the adsorption processes and the spontaneity. It is the fact that energy cannot be lost or gained, and the entropy change is the only driving force in an isolated system. Therefore, standard Gibbs free energy ($\Delta G^o$), standard enthalpy ($\Delta H^o$) and standard entropy ($\Delta S^o$) values called thermodynamic parameters, were also determined to explain the thermodynamic nature of the adsorption process. The following equation could be used for the calculation of the amounts of $\Delta H^o$ and $\Delta S^o$

$$\ln(K^o) = -\frac{\Delta H^o}{R} \cdot \frac{1}{T} + \frac{\Delta S^o}{R}$$

$$K^o = \frac{(1000 \text{ Kg molecular weight of adsorbate}) \cdot \text{[Adsorbate]}^o}{\gamma}$$

where $\gamma$ is the coefficient of activity (dimensionless), [Adsorbate]$^o$ is the standard concentration of the adsorbate (1 mol L$^{-1}$), R (8.314 J mol$^{-1}$ K$^{-1}$) is the gas constant and T (Kelvin) is the absolute temperature of the aqueous solution. $K^o$ is the equilibrium constant that is dimensionless. The standard equilibrium constant (L mol$^{-1}$) should be recalculated by multiplying the number of moles of water per litter of solution to obtain the dimensionless constant$^{36}$.

Values of Gibbs’ free energy are −1.696, −1.743 and −1.775 kJ/mol for the sorption of Zn$^{2+}$ on the pistachio, peanut and almond, respectively. The spontaneity of sorption of Zn$^{2+}$ onto the shells were resulted from the negative value of the Gibbs’ free energy. Lima et al. $^{36}$ pointed out that the values of $\Delta G^o$ should be negative to occur the adsorption. It is more likely that Zn$^{2+}$ ions and shell surface interaction results in the endothermic nature of the process, and is also called the diffusion process and the deprotonation reaction.

6. Comparison Study Of Shells

A comparison of shell adsorption capacity with other organic adsorbents was performed to find out the applicability of pistachio shell for Zn$^{2+}$ removal process (see Table 5). The presence of active functional groups effects the capacity of adsorbents. FTIR study of shell reveals that it has many metal-binding groups. It is difficult to direct the comparison of different adsorbents due to different experimental
conditions, chemical and physical characteristics of the adsorbent. However, the results indicated that Zn$^{2+}$ adsorption capacity of pistachio, peanut and almond shell is higher than the recently used adsorbent reported in Table 5.

Liu et al.\textsuperscript{37} reported that Zn$^{2+}$ removal rate by using watermelon rind solution having maximum adsorption capacity is 6.845 mg g$^{-1}$. The adsorption capacity was as follows; 17.72 mg g$^{-1}$ (Pistachio), 20.95 mg g$^{-1}$ (Peanut), 23.68 mg g$^{-1}$ (Almond) in this study.

According to Feizi and Jalali\textsuperscript{38}, the walnut shell was used for the removal of zinc from aqueous solutions and informed the maximum adsorption capacity of 33.3 mg/g. Similarly, Çoruh et al.\textsuperscript{39} used activated almond shell for reduction of zinc from aqueous solution and reported maximum adsorption capacity of 5.54 mg/g. Furthermore, the maximum adsorption capacity of pistachio, peanut and almond were lower than with walnut shell, modified pecan shell, but the adsorption capacity was higher than that of spent coffee ground, apple pulp, almond shell. As seen in Table 5, the shells can be used as a low-cost and efficient adsorbent for the adsorption of metal ions. The electronegativity, tendency, molecular size and of heavy metal ions makes adsorption capacity different. The comparison of the adsorption capacity values with the reported research indicates that the residual of pistachio, peanut and almond is of a better adsorbent in reducing Zn$^{2+}$ from aqueous solution.

7. Use Of End-product As A Conditioner

Chemical fertilizers are applied to increase crop yield in many years. However, Cultivation trends, currently, focus on using bio-organic fertilizer/conditioner instead of chemical fertilizers due to high costs, contamination, and inappropriate application causing soil quality degradation\textsuperscript{40}. The world trend is to protect soil biodiversity while producing quality crops with respect to sustainability. Organic fertilizers, produced organic wastes, are cheap nutrient sources and enhance crop production in low-input agriculture. Furthermore, organic waste increases soil organic carbon and microbial activity that helps provides nutrients and recycling them for plant growth. The presents of microbial population and activities is an indication of soil quality\textsuperscript{41}.

Zinc is an essential micronutrient and effects most of physiological processes\textsuperscript{42,43}. It is most likely to develop the potential phytotoxicity at leaf tissue concentrations above 0.2 mg g$^{-1}$ dry matter\textsuperscript{44}. Phytotoxicity leads to a decrease in yield and photosynthetic performance, as photochemical reactions, carbonic anhydrase activity, biosynthesis of Chls and cell membrane integrity affect. The presence of major nutrients concentrations and the microelements forms for plant usage is effected by soil pH, effecting also total Zn concentration and activity in soil solution, and high pH reduces the total Zn concentration and activity\textsuperscript{45}. Calcareous soil lacks nutrients, especially N, P, micro-nutrients, and soil organic matter, resulted in weak soil–plant productivity. Bio-organic conditioners decreases nutrient losses and enhance plant growth in calcareous soil\textsuperscript{41}.
As seen in Table 1 and 2, fresh shells contain organic materials, nutrients and mineral and then holding zinc with functional groups make it valuable soil conditioner/amendments. The composition and concentration of the growth media effects to zinc uptake by the plants depend of plant species, and the form of present a divalent cation or as complexes with organic ligands increase the uptake. The working pH for the adsorption process for three adsorbents is 6.0, so resulted in producing end-products pH value of 6.0 due to studying in a controlled environment. The ideal soil pH for plant growth is between 6.0 and 8.0 called neutral soil. The end-product can also be used for reducing pH of the alkaline and high alkaline soil (pH>8).

8. Cost-benet Estimations

Activated carbon is used commonly in the adsorption process due to its porous, carbon contents and removal capacity of the pollutants. For that reason, the price of pistachio, peanut and almond shell was compared with commercial activated carbon price for using adsorbent in the adsorption process. Table 6 indicates that the typical prices of organic adsorbent and commercial activated carbon prices. The activated carbon price is extremely expensive in comparison to the shells, though the market prices for chemicals and activated carbon tend to change all over the world. It is very important to produce a cost-effective adsorbent for the removal of metal ions from solutions considering the high environmental benefits. Furthermore, to use of agricultural shell waste as an adsorbent could provide an economical advantage at least 48 times in comparison to that of the activated carbon cost. Furthermore, the usage of the organic shell as an adsorbent for the capturing of zinc from contaminated water ensures both the technical advantage and cost-effectiveness for the sustainable environmental management concept.

9. Conclusions

This study has shown that pistachio, peanut and almond shell can be used for reducing Zn$^{2+}$ from aqueous solutions as an eco-friendly, low-cost adsorbent. Langmuir models and the pseudo second order is well-fitted sorption isotherm and kinetics for the shells, respectively. The maximum adsorption capacity of pistachio, peanut and almond is as follows; 59.52 mgg$^{-1}$, 54.64 mgg$^{-1}$, and 51.81 mgg$^{-1}$, respectively. Adsorption ability of the adsorbent for Zn$^{2+}$ uptake was as followed: Pistachio > Peanut > Almond. The results of the kinetic experiments implied that the rate-controlling sorption for Zn$^{2+}$ only was not the intra-particle diffusion.

Functional groups on shell surface can cooperate with metal ions in many ways, electrostatic interaction, physical adsorption, ion exchange, surface complexation, chelation and precipitation. The by-product of present study can also be used for the alkaline and high alkaline soil (pH>8) to balance the Ph. Furthermore, the by-product containing organic compounds and zinc can be used as a soil conditioner for sustainable agriculture, resulting in reducing the disposal cost of the by products for sustainable environmental management.
### Abbreviations

| Abbreviation | Definition |
|--------------|------------|
| KF | Freundlich constant (mg/g) (L/g)\(^{1/n}\) |
| 1/n | Freundlich exponent |
| KL | Langmuir isotherm constant (L/mg) |
| KT | Tempkin isotherm constant (L/mg) |
| \(k_{1p}\) | Pseudo-first order kinetic model constant (1/h) |
| \(k_2\) | Pseudo-second order kinetic model constant (gmg\(^{-1}\)h\(^{-1}\)) |
| kp | Intra-particle diffusion kinetic model constant (gmg\(^{-1}\)h\(^{-0.5}\)) |
| R\(^2\) | Correlation coefficient |
| MPSD | Marquardt’s percent standard deviation |
| ARE | Average relative error |
| NSD | Normalized standard deviation |
| P | Number of parameters in isotherm |
| N | Number of experimental measurements |
| Ce | Equilibrium concentration (mg/L) |
| C0 | Initial concentration (mg/L) |
| C\(_t\) | Concentration at time t (mg/L) |
| \(q_e\) | Amount of metal ion adsorbed at equilibrium (mg/g) |
| E | The mean adsorption energy (kJ/mol) |
| qm | Monolayer sorption capacity (mg/g) |
| T | Time (h) |
| T | Temperature (K) |
| R | Ideal gas constant (JK\(^{-1}\)mol\(^{-1}\)) |
| kd | The distribution constant for Gibbs' free energy |
| V | Volume of the solution (L) |
| W | Amount of adsorbent used (g) |

### Declarations

The author declares no competing financial interest or personal relationships that could have appeared to influence the work presented in this paper.
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**Tables**

Due to technical limitations the Tables are available as downloads in the Supplementary Files.

**Figures**
Figure 1

Three adsorbent FTIR spectra and functional groups
Figure 2

SEM images of three adsorbent (Fresh, 10, 20 and 30 min)
Figure 3

Effect of contact time, pH and Adsorbent dosage on removal of zinc
Figure 4

The predicted amount of adsorption at equilibrium by different isotherm models and the experimental values

Figure 5

Intra-particle diffusion plots of the pistachio (a), peanut (b) and almond (c) for zinc
**Figure 6**

Possible adsorption mechanisms of Zn+2

**Supplementary Files**

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