

# Removal of heavy metal from industrial wastewater using modified activated coconut shell carbon

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## Abstract

The present study was undertaken to develop a cost effective biosorbent and to study the biosorption process involved in the adsorption of heavy metal-contaminated industrial wastewater using the developed biosorbent. Coconut shell carbon was modified with chitosan and/or oxidizing agent (phosphoric acid) to produce composite adsorbent. The adsorption efficiency of the adsorbent was evaluated by measuring the extent of adsorption of zinc (II) in synthetic beverage industrial wastewater. Operational parameters such as pH, agitation time and adsorbent concentration, initial ion concentration and particle size were also studied. Adsorption data fitted well with the Langmuir and Freundlich models. However, Langmuir isotherm displayed a better fitting model than Freundlich isotherm because of the higher correlation coefficient that the former exhibited, thus, indicating to the applicability of monolayer coverage of the zinc (II) on the surface of adsorbent.

Desorption studies were carried out with NaOH and quantitative recovery of the metal was evident. The dominant sorption mechanism is ion exchange. The use of agricultural waste (coconut shell) and aquatic waste (chitin) to produce activated carbon potentially leads to the production of a highly effective adsorbent generated from less expensive raw materials that are from renewable resources.

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**Keywords:** Coconut shell; Chitosan-coated carbons; Heavy metals; Industrial wastewater; Adsorption isotherms

## 1. Introduction

Rapid industrialization has led to increased disposal of heavy metals into the environment. The tremendous increase in the use of the heavy metals over the past few decades has inevitably resulted in an increased flux of metallic substances in the aquatic environment. The metals are special because of their persistency in the environment. At least 20 metals are classified as toxic, and half of these are emitted into the environment in quantities that pose risks to human health [1]. The ability of a water body to support aquatic life as well as its suitability for other uses, however, depends on many trace elements.

Trace concentrations of zinc (Zn) are important for the physiological functions of living tissue and regulate many biochemical processes. However, just like other heavy metals, when Zn is discharged into natural waters at increased concentrations

in sewage, industrial wastewater or from mining operations it can have severe toxicological effects on humans and aquatic ecosystems [2]. A similar experience is the minamata mercury-poisoning episode in Japan [3].

Hence, it is essential to remove Zn from industrial wastewaters before transport and cycling into the natural environment.

A number of technologies have been developed over the years to remove heavy metals from industrial wastewater. The most important technology includes coagulation/flocculation [4,5]. Other conventional chemical methods include precipitation, ion-exchange, electrochemical processes and membrane technology. All the chemical methods have proved to be much costlier and less efficient than the biosorption process [6]. In addition, chemical methods increase the pollution load on the environment.

Biosorption, a biological method of environmental control can be an alternative to conventional waste-treatment facilities.

Natural biopolymers are industrially attractive because of their capability of lowering transition metal-ion concentrations to parts per billion concentrations [7].

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Biomaterials that are available in large quantities or certain waste from agricultural operations may have potential to be used as low cost adsorbents, because they represent unused resources that are widely available and environmentally friendly [8]. Some investigators have reported processing of pecan and coconut shells wastes into chars with sufficient densities and high porosity for the treatment of industrial and municipal wastewaters [9,10]. The sorption properties of coconut shell are due to the presence of some functional groups, such as carboxylic, hydroxyl, and lactone, which have a high affinity for metal ions [11]. In recent years, development of surface modified activated carbon has generated a diversity of activated carbon with far superior adsorption capacity [7]. The use of coconut shell with surface modification to improve its metal removal performance would add to its economic value, help reduce the cost of waste disposal, and most importantly, provide a potentially inexpensive alternative to existing commercial activated carbon [7,10,12,13].

Low cost and non-conventional adsorbents include agricultural by-products such as nut shells, wood, bone, peat, coconut shells, processed into activated carbons [9,12,14–21] and biomass such as *Aspergillus tereus* [22] *Rhizopus arrhizus* [6], these have been reported to be important adsorbents for the removal of heavy metals and organics from municipal and industrial wastewater.

Among these low cost adsorbents, chitosan has the highest sorption capacity for several metal ions [7,10,23]. Chitin (2-acetamido-2-deoxy- $\beta$ -D-glucose-(N-acetylglucan) is the main structural component of molluscs, insects, crustaceans, fungi, algae and marine invertebrates like crabs and shrimps [23,24,7,25].

Chitosan (2-acetamido-2-deoxy-B-D-glucose-(N-acetyl glucosamine) is a partially deacetylated polymer of chitin and is usually prepared by deacetylation of chitin with a strong alkaline solution as shown in Fig. 1.

Yang and Zall [26] reported that chitosan can chelate five to six times greater concentrations of metals than chitin. They further reported this property to be related to the free amino groups exposed in chitosan because of deacetylation of chitin. Chitosan is slightly soluble at low pHs and possesses problems for developing commercial applications. Also, the active binding sites of chitosan are not readily available for sorption. The sites are reported to be soft and have a tendency to agglomerate or form gel in aqueous solutions. Transport of metal contaminants to the binding sites plays a very important role in process

design. Therefore, it is necessary to provide physical support and increase the accessibility of the metal binding sites for process applications [7].

The objectives of this work were to coat chitosan and/or oxidizing agent such as phosphoric acid on the surface of coconut shell with a view to investigating the adsorptive capacity of the activated carbons (adsorbents) by varying pH of solution, agitation time, adsorbent concentration, initial ion concentration and particle size during the treatment of zinc ion in aqueous solution.

## 2. Materials

Synthetic beverage industrial wastewater was employed for the adsorption studies. Reagents were prepared by dissolving AR grade chemicals (Sigma–Aldrich, Germany), in deionized water.

An experimental solution containing Zn (II) was prepared by diluting 1 mL of stock solution of the metal to the desired concentrations. The ranges of concentrations of Zn (II) prepared from stock solution were varied between 5 and 30 mg/L. The pH of experimental solution was adjusted by using 0.1N NaOH and/or 0.1N H<sub>2</sub>SO<sub>4</sub>. A stock solution of Zn (II) was obtained by dissolving the exact quantity of zinc nitrate in deionized water.

## 3. Method

### 3.1. Preparation of char from coconut shell

Preparation of char from coconut shell was carried out as previously described [13]. Coconut shells were pulverized and sieved to 2.0–3.0 particle size. Pulverized sample (15 g) was pyrolyzed, in a furnace (Carbolite, CTE 12/75). During pyrolysis, nitrogen gas at a flow rate 0.1 m<sup>3</sup>/h was used as purge gas. The furnace temperature of 600 °C was maintained for 2 h. The weight loss of the sample was determined by the difference in the weight of the sample before and after pyrolysis. The pyrolyzed sample was crushed into powder form.

### 3.2. Preparation of chitosan gel

A method described by Nomanbhay and Palanisamy [7] was employed. A 50 g of chitosan was slowly added to 1 L of 10 wt% oxalic acid with constant stirring. The mixture was heated to 40–50 °C to facilitate mixing. The chitosan was allowed to cool at room temperature and a whitish viscous gel of chitosan–oxalic acid mixture was obtained.

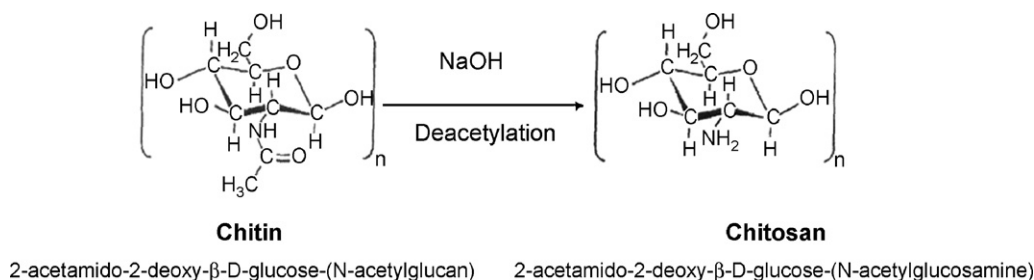


Fig. 1. Conversion of chitin to chitosan by deacetylation.

### 3.3. Preparation of granular activated carbons

#### 3.3.1. Acid-treated coconut shell carbon

For phosphoric acid activation, the previously described method of Amuda and Ibrahim [13] with slight modification was employed. The pulverized coconut shell was washed with deionized water until leachable impurities due to acid and adherent powered were removed. The sample was then treated with 50 wt.% phosphoric acid in an incubator at 110 °C for 24 h. It was later soaked with deionized water until the solution pH was stable. Then, the adsorbent was soaked in 27% NaHCO<sub>3</sub> (w/v) till any residual acid left was removed as evident by the lack of lead phosphate precipitate upon introduction of a few drops of lead nitrate to sample of the wash water. The acid-treated coconut shell carbon (ACSC) was then dried overnight in an oven (Mettler, England) at 110 °C, cooled at room temperature and stored in desiccators until use. A yield of 38% was determined for the coconut shell carbons.

#### 3.3.2. Surface modification of ACSC and coconut shell carbon (CSC) with chitosan

The previously described method of Babel and Kurniawan [10] for surface modification of coconut shell carbon with chitosan was employed.

ACSC (500 g) was slowly added to dilute chitosan gel (chitosan gel–water, v/v heated to 50 °C) and mixing was carried out at 150 rpm for 24 h. The chitosan coated ACSC (CACSC) was then washed with deionized water and dried at 102 °C for 2 h before use. The same process was applied to CSC to obtain chitosan coated coconut shell carbon (CCSC). A yield of 29% was determined for the chitosan coated carbons.

The CACSC and CCSC were then soaked in 0.5% NaOH solution till any residual acid was removed. These were then rinsed extensively with deionized water and dried in an oven (Mettler, England) at 102 °C for 2 h, cooled at room temperature and stored in desiccators.

### 3.4. Measurement of characteristics of adsorbents

The previously described methods of Ahmedna et al. [18] were employed for the measurement of characteristics (such as surface area, bulk density, ash content, pH and iodine value) of the adsorbents. The measurements are presented in Table 1.

Table 1  
The characteristics of the adsorbents

Parameters	Adsorbents			
	CACSC	CCSC	ACSC	F-300
Surface area (m <sup>2</sup> /g)	902	670	668	628
Bulk density (g/mL)	0.60	0.49	0.52	0.47
Ash content (%)	2.70	5.62	1.45	6.53
pH	5.90	9.60	5.50	7.40
Iodine value (mg/g)	190	210	172	132

### 3.5. Batch adsorption studies

Batch adsorption studies were carried out using CACSC, CCSC, ACSC and CAC (Calgon carbon-F-300; Calgon carbon Inc.).

Batch experiments were conducted at ambient temperature using the optimum conditions of all factors that influence adsorption such as adsorbent dose, pH, initial ion concentration, particle size and agitation time. Wastewater (100 mL) containing Zn (II) was placed in a 250 mL Erlenmeyer flask and 1.5 g/L adsorbent was added. The mixture was mechanically agitated at 200 rpm on a reciprocate shaker. The Zn (II) concentration of the treated wastewater was analyzed at time interval between 0 and 180 min using standard methods recommended for examination of water and wastewater [27].

The removal efficiency (*E*) of adsorbent on Zn (II) and distribution ratio (*K<sub>d</sub>*) were measured as follows:

$$E (\%) = \frac{C_i - C_f}{C_i} \times 100, \quad (1)$$

where *C<sub>i</sub>* and *C<sub>f</sub>* are the initial and final equilibrium concentration of Zn (II) (mg/L) in wastewater, respectively, and

$$K_d = \frac{\text{amount of Zn in adsorbent}}{\text{amount of Zn in solution}} \times \frac{V}{M} \text{ (mL/g)}, \quad (2)$$

where *V* is the volume of the solution (mL) and *m* is the weight of the adsorbent (g).

The removal efficiency (%) and *K<sub>d</sub>* (mL/g) can be correlated by the following equation [28]:

$$\text{removal efficiency (\%)} = \frac{100K_d}{K_d + V/m}. \quad (3)$$

All the experiments were duplicated to ensure accuracy, reliability and reproducibility of the collected data. Relative error did not exceed ±0.01.

## 4. Results and discussion

### 4.1. Adsorption dynamics

#### 4.1.1. Effect of pH

The effect of pH on the adsorption of Zn (II) is presented in Fig. 2. The pH of the aqueous solution is an important operational parameter in the adsorption process because it 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 reaction [7]. Thus, the role of hydrogen ion concentration was examined on the Zn (II) removal efficiency. The pH was varied from 1 to 11, other operational parameters (adsorbent dosage, agitation time, initial ion concentration and in case of CACSC, particle size) were kept at the optimum and temperature and agitation speed were kept at 25 °C and 200 rpm, respectively.

From Fig. 2, it is shown that increasing pH of the solution from 2 to 6 caused linear increase in Zn removal efficiency. The removal efficiency remained almost constant above pH 6. This may be due to the formation of soluble hydroxyl complexes.

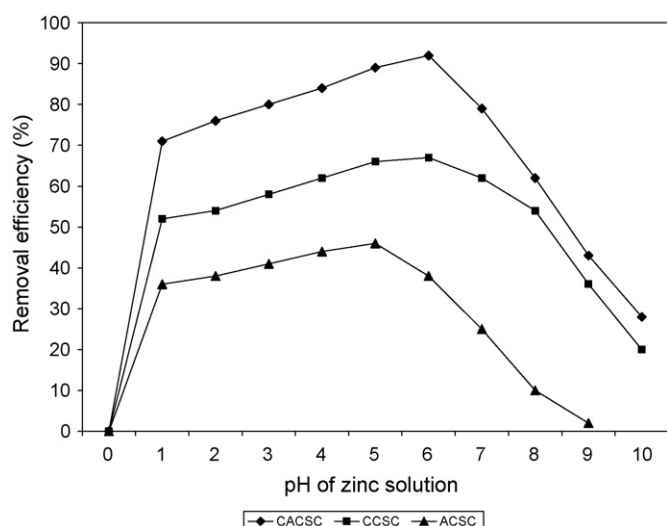


Fig. 2. Effect of pH on the adsorption of Zn (II) on the adsorbents. Zn (II) dosage: 25 mg/L; agitation time: 3 h; agitation speed: 200 rpm; dose of each adsorbent: 30 g/L; temperature of solution: 25 °C.

The onset of metal hydrolysis and precipitation begin at  $\text{pH} > 6$  [29]. The hydrolysis of metal ions occurs by the replacement of metal ligands in the inner co-ordination sphere with the hydroxyl group. This replacement occurs after the removal of the outer hydration sphere of metal ions. Adsorption may not be related directly to the hydrolysis of the metal ion, but instead, outer hydration sphere that precede hydrolysis [30]. The hydrogen ion concentration increases if pH is low (below 3), thus, competitive adsorptions between  $\text{H}^+$  and  $\text{Zn}^{2+}$  result in low adsorption efficiency of Zn ion.

Zinc removal efficiency ranged between 45% and 93% for CACSC; 32% and 55% for CCSC, and 12% and 50% for ACSC over pH range of 2–6. Zinc, like other metals, such as chromium, depending on the pH, is known to exist as anion. At low pH, the amine group on chitosan is protonated to varying degree [7]. The surface acidity was due to the introduction of several oxygen-containing functional groups [31].

It was calculated [32], from the  $\text{pK}_a$  of chitosan that the extent of protonation is 9, 50, 91 and 99% at pH 7.3, 6.3, 5.3 and 4.3, respectively. This led to the interaction between amine functional groups and the zinc anion. Increasing the pH above 6 led to the gradual decrease of the degree of protonation of the chitosan adsorbent functional group which in turn led to decreased Zn removal efficiency. Above the  $\text{pK}_a$  value the chitosan adsorbent will be negatively charged.

Acid activation of coconut shell carbon (CSC) using phosphoric acid (forming ACSC) improved the electrostatic interaction between chitosan and the ACSC. Thus, more active sites were available for the adsorption of Zn at low pH conditions. In their own study, Olin et al. [33] reported enhancement of hydrophilic property and hence improvement in the hydrodynamic flow of metal ion to the acidic surface oxides on the carbon surface.

For the ACSC, the removal efficiency of zinc increased slightly between pH 2 and 5, above pH 6, there was gradual decrease in removal efficiency up to pH 11. At  $\text{pH} > 6$ , the pres-

ence of oxygen-containing functional groups conferred negative charge on the adsorbent surface and hence repulsive electrostatic interaction resulted between the adsorbent and the metal ions [7].

For the CCSC, the low active binding sites, as a result of less acidic oxide surface caused low adsorption capacity for Zn on CCSC.

#### 4.1.2. Effect of adsorbent concentration

Fig. 3 presents Zn removal efficiency as function of adsorbents dosage. The dose of the adsorbents was varied between 1 and 30 g/L, other operational parameters (pH, agitation time, initial ion concentration and particle size) were kept at the optimum and temperature and agitation speed were kept at 25 °C and 200 rpm, respectively.

From the results in Fig. 3, increasing dose of the adsorbents increased Zn removal efficiency. This is expected because more binding sites for ions are available at higher dose of adsorbents. However, increasing the dose of the adsorbents above 18 g/L for CCASC, 21 g/L for CCSC or 27 g/L for ACSC yielded no increase in the Zn removal efficiency. The highest Zn removal efficiency for CACSC was 90% at 18 g/L dose of the adsorbent; whereas 21 g/L dose of CCSC exhibited 58%, while 25 g/L dose of each of ACSC and F-300 had 52% and 50% Zn removal, respectively.

These observations suggest that adsorption of Zn ion in the wastewater is related to carbon surface area. CACSC having highest surface area (902  $\text{m}^2/\text{g}$ ) had highest Zn removal efficiency, followed by CCSC with 670  $\text{m}^2/\text{g}$ ; ACSC with 668  $\text{m}^2/\text{g}$  and the least was F-300 with 628  $\text{m}^2/\text{g}$ . Furthermore, at certain dose of adsorbent, adsorption peak is reached and hence, no adsorption of metal ion to the adsorbent. Also, the amount of free ions in solution remains constant [7]. The difference in the surface modification of the adsorbents conferred on them different degree of removal efficiency. According to Toles et al. [19], the formations of metals, including zinc, into anions depend on the pH. They further reported that amine group

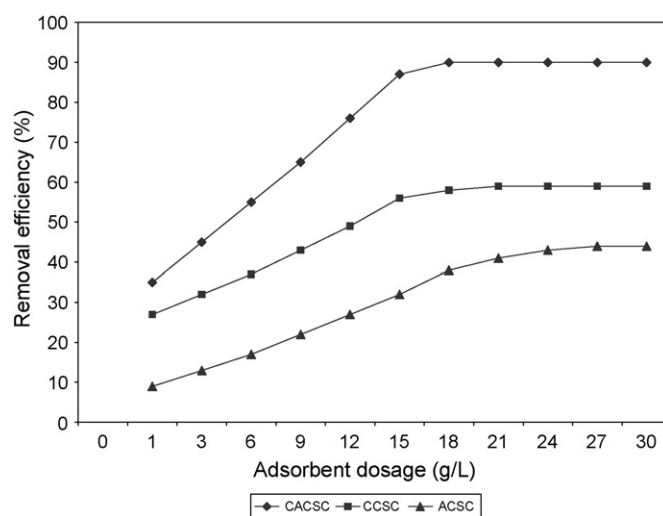


Fig. 3. Effect of dose of the adsorbents on the removal efficiency of Zn (II). Zn (II) dosage: 25 mg/L; agitation time: 3 h; agitation speed 200 rpm; pH of solution: 6; temperature of solution: 25 °C.



on chitosan is protonated to different degrees at low pH. The  $\text{NH}_3^+$  group on the chitosan is chiefly responsible for interaction with anions and negatively charged surfaces [7]. Oxidation of nutshell carbon with mineral acids has been implicated to introduce more acidic C=O groups on the surface of nutshell carbons. This would enhance the electrostatic interaction between chitosan and the more negatively charged CACSC, thus, preventing agglomeration of chitosan [7]. Formation of more acidic surface oxides on CACSC than CCSC enhanced efficient coating of chitosan, enhanced its hydrophilic character and hence improved the hydrodynamic flow. This could be responsible for high adsorption capacity of CACSC over CCSC. The least adsorption capacity was exhibited by ACSC. At higher pH (>5) the presence of oxygen-containing functional groups, makes the adsorbent surface negatively charged and hence repulsive electrostatic interaction between the adsorbent and anions occurred [7].

#### 4.1.3. Effect of agitation times

Equilibrium time is another important operational parameter for an economical wastewater treatment process. Fig. 4 depicts Zn removal efficiency as function of agitation time. From the Fig. 4, it is shown that increase in agitation time increased removal efficiency until equilibrium adsorption was established; other parameters such as pH, adsorbent dosage, initial ion concentration and, in case of CACSC, particle size were kept at the optimum and temperature and agitation speed kept at 25 °C and 200 rpm, respectively.

Equilibrium adsorptions were established within 120 min for CACSC and CCSC in which case Zn removal efficiencies were 90% and 75%, respectively. For the ACSC, equilibrium adsorption was established at about 300 min in which case 52% Zn removal efficiency was achieved. With these results, CACSC with highest binding sites for metal require shorter time to achieve a high Zn removal efficiency.

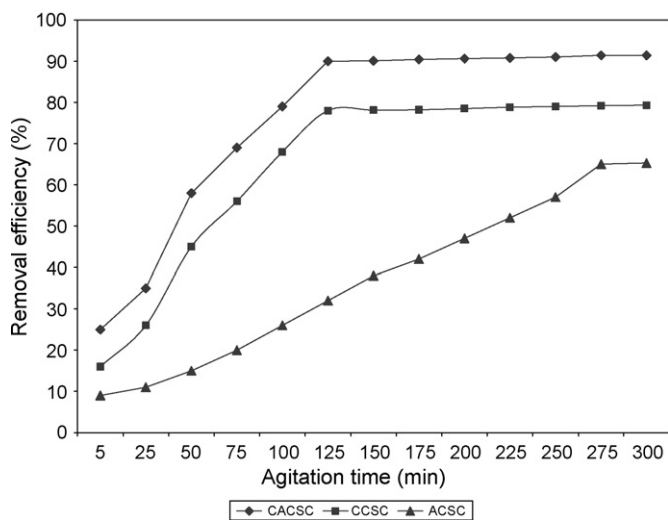


Fig. 4. Effect of agitation time on removal efficiency of Zn (II) by the adsorbents. Zn (II) dosage: 25 mg/L; agitation speed: 200 rpm; dose of each adsorbent: 30 g/L; pH of solution: 6; temperature of solution: 25 °C.

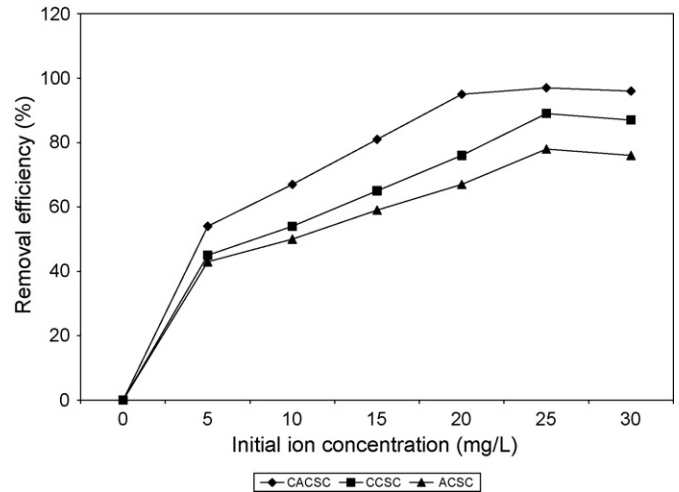


Fig. 5. Effect of initial ion concentration on removal efficiency of Zn (II) by the adsorbents. Agitation time: 3 h; agitation speed: 200 rpm; dose of each adsorbent: 30 g/L; pH of solution: 6; temperature of solution: 25 °C.

#### 4.1.4. Effect of initial ion concentration

The percentage removal of Zn (II) ion by the adsorbent initially increased rapidly with increasing Zn concentration and slowed down when Zn concentration reached 25 mg/L (Fig. 5). At lower concentrations, Zn ion in the solution would interact with the binding sites and thus facilitated 100% adsorption. At higher concentrations, more Zn ions are left un-adsorbed in solution due to the saturation of binding sites. This indicates that energetically less favourable sites become involved with increasing ion concentrations in the aqueous solution. The Zn ion adsorption is attributed to different mechanisms of ion-exchange processes as well as to the adsorption process. During the ion-exchange process, Zn ions had to move through the pores of the adsorbent mass, but also through channels of the lattice, and they had to replace exchangeable cations. Diffusion was faster through the pores and was retarded when the ions moved through the smaller diameter channels. In this case, the Zn ion sorption could mainly be attributed to ion-exchange reactions in the micropores of the adsorbents. Fig. 6 presents  $K_d$  as a function of Zn ion concentration. The  $K_d$  values increased with the decreasing concentration of Zn ion. In other words, the  $K_d$  values increased as dilution of Zn ion in solution proceeds. Maximum percentage Zn (II) ion removal of 97, 89 and 78 was achieved when 25 mg/L Zn (II) ion concentrations was adsorbed with 30 g/L of CACSC, CCSC and ACSC, respectively.

#### 4.1.5. Effect of particle size of the adsorbent on sorption of metal

The adsorption experiments were carried out using various particle sizes of the CACSC only because it is the adsorbent that proved most efficient compared to CCSC and ACSC. The particle sizes used were 0.63, 0.80, 1.00, 1.25, 1.50 and 1.60 mm, respectively.

Other parameters such as pH of aqueous solution, adsorbent concentration, initial ion concentration and agitation time were kept at the optimum; temperature and agitation speed were kept at 25 °C and 200 rpm, respectively.

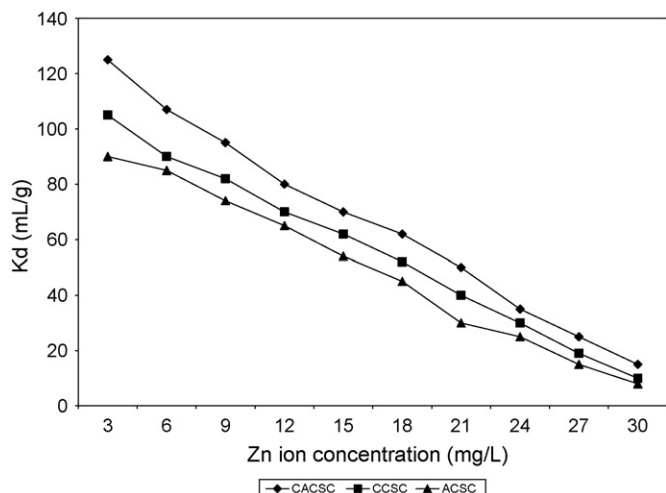


Fig. 6. Distribution ratio of the adsorbents as function of Zn ion concentrations. Agitation time: 3 h; agitation speed: 200 rpm; dose of each adsorbent: 30 g/L; pH of solution: 6; temperature of solution: 25 °C.

The percentage removal of Zn ion at different particle sizes showed that the percentage removal rate increased with decrease in particle size (Fig. 7).

The higher adsorption level achieved by smaller particle size of the adsorbent may not be unconnected to the fact that smaller particles give large surface areas. There is tendency that smaller particles produce shorter time to equilibrate [34]. Particle sizes of 1.00 and 1.25 were found to yield highest percentage removal of Zn (II) ion.

#### 4.2. Adsorption isotherms

Adsorption isotherms can be generated based on numerous theoretical models where Langmuir and Freundlich models are the most commonly used. The Langmuir model assumes that uptake of metal ions occurs on a homogenous surface by monolayer adsorption without any interaction between adsorbed ions.

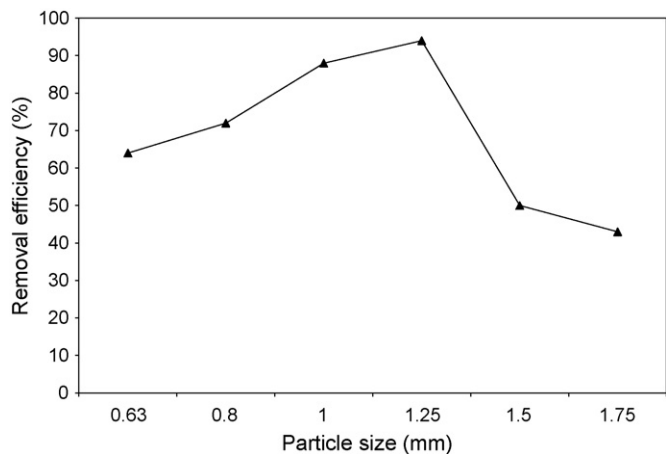


Fig. 7. Effect of particle size on removal efficiency of Zn (II) by CACSC. Zinc dosage: 25 mg/L; agitation time: 3 h; agitation speed: 200 rpm; dose of each adsorbent: 30 g/L; pH of solution: 6; temperature of solution: 25 °C.

The model takes the following form:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \tag{4}$$

where  $C_e$  is the equilibrium concentration (mg/L),  $q_e$  the amount of metal ion adsorbed at specified equilibrium (mg/g),  $Q_0$  and  $b$  are the Langmuir constants related to adsorption capacity and energy of adsorption. The essential characteristics of Langmuir isotherm model can be explained in terms of a dimensionless constant separation factor or equilibrium parameter  $R$  [35], which is defined by

$$R = \frac{1}{1 + bC_0} \tag{5}$$

where  $b$  is Langmuir constant (L/mg) and  $C_0$  is initial concentration (mg/L). It has been shown using mathematical calculations that parameter  $R$  indicates the shape of the isotherms [35] as follows:

Values ( $R$ )	Types of isotherm
$R > 1$	Unfavorable
$R = 1$	Linear
$0 < R < 1$	Favorable
$R < 0$	Irreversible

On the other hand, the Freundlich equation [36] is an empirical equation based on adsorption on a heterogeneous surface. The equation is commonly represented by

$$q_e = K_f C_e^{1/n} \tag{6}$$

where  $K_f$  and  $1/n$  are the Freundlich constants characteristics of the system, indicating the adsorption capacity and the adsorption intensity, respectively.

Therefore, a plot of  $\log q_e$  versus  $\log C_e$  enables the constant  $K_f$  and  $1/n$  to be determined. The Langmuir and Freundlich isotherms for the adsorbents prepared from coconut shell are presented in Figs. 8 and 9, respectively. The plots of  $1/q_e$  against  $1/C_e$  are linear (Fig. 8), showing the applicability of Langmuir isotherm to all types of adsorbent tested.

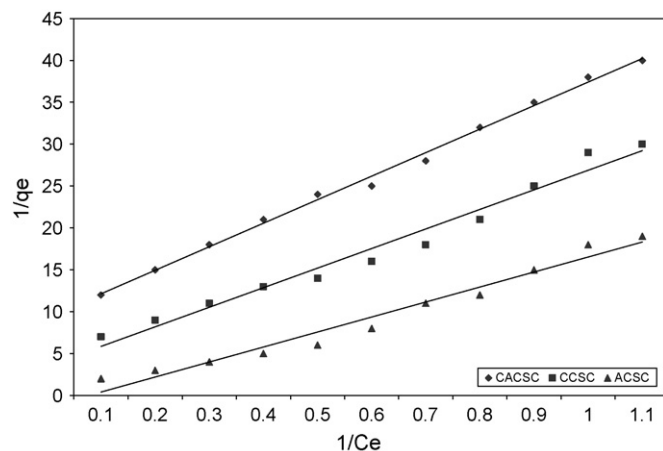


Fig. 8. Langmuir adsorption isotherms for the adsorption of Zn (II) by the adsorbents.

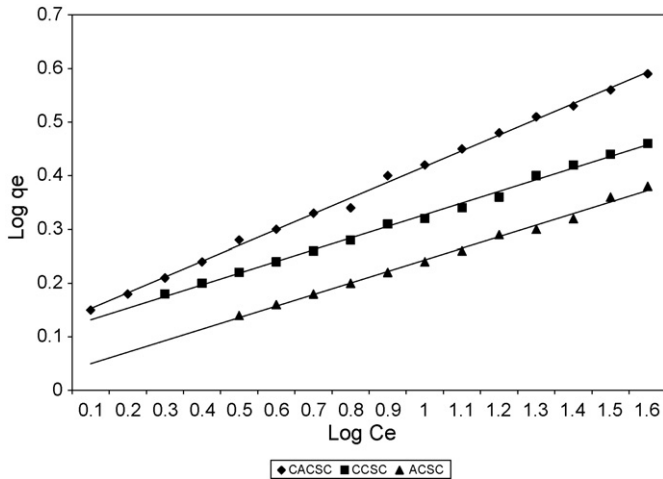


Fig. 9. Freundlich adsorption isotherms for the adsorption of Zn (II) by the adsorbents.

Table 2  
Langmuir and Freundlich constants for the adsorption of Zn (II) at 25 °C

Adsorbent	Langmuir constants			Freundlich constants		
	$b$ (L/mg)	$q_e$ (mg/g)	$R^2$	$K_f$	$1/n$	$R^2$
CACSC	2683	60.41	0.997	10.59	0.59	0.975
CCSC	2010	50.93	0.995	9.67	0.49	0.955
ACSC	1695	45.14	0.996	7.47	0.38	0.952

$R^2$  = correlation coefficient.

Freundlich isotherm was also a representative for the Zn adsorption by all type of adsorbent tested. The two models fitted well for the adsorption studies; however, Langmuir isotherm had a better fitting model than Freundlich isotherm. This is as a result of higher correlation coefficient exhibited by Langmuir isotherm (Table 2), thus indicating to the applicability of monolayer coverage of the Zn on the surface of the adsorbents. This can be explained by the fact that activated charcoal has a small surface area for metal adsorption therefore, monolayer adsorption occurred on its surface, in spite of any surface modification [7]. Table 3 shows comparison of Langmuir sorption capacities of Zn (II) ion to some agricultural by-products carbons and adsorbents employed in this study. For the Freundlich model, the constant  $K$  and  $n$  were calculated for the Zn ion (Table 2). The numerical value of  $1/n < 1$  indicates that adsorption capacity is only slightly suppressed at lower equilibrium concentrations.

Table 3  
Comparison of the Langmuir constants for Zn adsorption onto adsorbents

Adsorbent	$q_e$ (mg/g)	References
<i>Mangifera indica</i>	32.44	[37]
Coal ash	15	[38]
Wood ash	12	[39]
Natural zeolite	13.40	[28]
Fly ash	46.6	[40]
Clay mineral	13.72	[41]
CACSC	60.41	This study
CCSC	50.93	This study
ACSC	45.14	This study

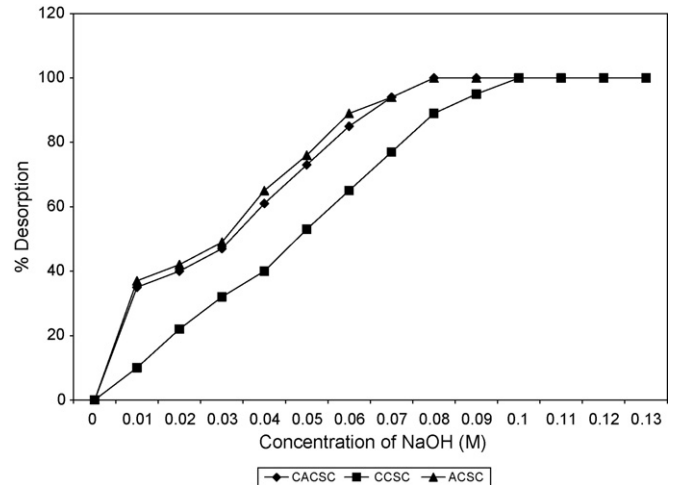


Fig. 10. Sodium hydroxide concentration—NaOH (M) as function of % desorption of Zn (II) from the adsorbents.

This isotherm does not predict any saturation of the sorbate; thus infinite surface coverage is predicted mathematically, indicating to multilayer adsorption on the surface [28].

#### 4.3. Desorption studies

After the adsorbent was saturated with the metal ions, it was regenerated with different concentrations of sodium hydroxide. The quantitative recovery of metal ions is possible (Fig. 10). Complete desorption of Zn ion from the adsorbents was achieved between 0.08 and 0.1 M sodium hydroxide solution. This confirms that ions exchange is the phenomenon of the adsorption process.

### 5. Conclusion

The composite adsorbent (chitosan-coated acid treated coconut shell carbon) exhibited effectiveness in the removal of Zn from aqueous solution. The removal efficiency was controlled by solution pH, adsorbent concentration and agitation times, initial ion concentration and particle size. Adsorption data fitted well with the Langmuir and Freundlich models. However, Langmuir isotherm displayed a better fitting model than Freundlich isotherm because of the higher correlation coefficient that the former exhibited, thus, indicating to the applicability of monolayer coverage of the Zn (II) on the surface of adsorbent. Using coconut shells and aquatic waste such as chitin to produce activated carbons potentially provide a less expensive raw material, a highly effective adsorbent as well as producing activated carbon processed from renewable resources instead of non-renewable ones.

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