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Research Article
Equilibrium, Kinetic and Thermodynamic Studies of the Adsorption of Heavy Metals from Aqueous Solution by Thermally Treated Quail Eggshell

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Abstract
Background and Objective: Nowadays, the contamination of water resources by heavy metals has resulted in serious health issues. The metals in their elemental as well as chemically combined form are toxic, non-degradable and persistence in nature. Thus, there is need to develop a simple, efficient and economical method for removing dissolved heavy metals from water/wastewater. In the present study, it was aimed to prepare a new adsorbent from agricultural waste in order to remove Cu^{2+} and Zn^{2+} from aqueous solution. **Materials and Methods:** Calcium oxide (CaO) based material was prepared from quail eggshell, characterized and used as adsorbent for the removal of Cu^{2+} and Zn^{2+} from aqueous solution. Calcined quail eggshell at 900°C was studied and exhibited high adsorption capacity. The effects of variables affecting the adsorption process, contact time, adsorbent dosage, temperature and initial heavy metals concentration were investigated at fixed pH of 4.5. **Results:** At contact time of 30 min, adsorbent dosage of 1.5 g, temperature of 35°C and initial Cu^{2+} and Zn^{2+} concentration of 150 mg L^{-1}, the maximum heavy metals uptake could be achieved. Based on the value of correlation coefficient, the experimental results for Cu^{2+} best fitted the Langmuir isotherm model with monolayer adsorption capacity of 13.49 mg g^{-1}, while Freundlich isotherm model was best fitted to the experimental results for the Zn^{2+} adsorption. The kinetics and thermodynamic behaviours of the adsorption process were also investigated. **Conclusion:** The obtained results showed that the experimental data were in good agreement with pseudo-second-order kinetic model. The results from thermodynamic analysis revealed that the process is spontaneous and endothermic.

Key words: Copper ion, zinc ion, kinetics, thermodynamics, quail eggshell

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Data Availability: All relevant data are within the paper and its supporting information files.

INTRODUCTION

In recent years, the indiscriminate disposal of heavy metals and other contaminants into water bodies/resources has raised serious health concern. Generally, large concentrations of heavy metal compounds are discharged into the environment via industrial, agricultural and domestic processes[1]. Heavy metals are toxic, non-degradable and persistence in nature. Thus, lengthen exposure to heavy metals could cause serious health problems. For instance, exposure to copper ions can cause gastrointestinal disorder, vomiting and diarrhea[2], zinc ions at elevated concentration result in anaemia, pancreas damage, osteoporosis and even death[3]. The concentrations of copper and zinc ions that should be present in wastewater to be disposed to river environment according to the Nigerian Federal Environmental Protection Agency are less than 1.0 mg L^{-1} [4]. While, World Health Organization (WHO) maximum permissible limit for copper and zinc ions are 2.0 and 4.0 mg L^{-1}, respectively[5]. Thus, in order to maintain the acceptable limiting concentration for these toxic metals in wastewater, there is need to adopt a simple, efficient, inexpensive and economical method for removing them from wastewater[6]. Although several methods such as precipitation, ion exchange, electrochemical degradation, membrane technology and adsorption are being employed to remove heavy metals from wastewater, but it seems only adsorption method possesses those earlier mentioned attributes. The reasons have been that it is effective in removing from wastewater low concentrations of heavy metal ions[7] and also often used at industrial level[8].

Adsorption is a mass transfer process that requires a porous solid material called adsorbent to remove trace component (adsorbate) from fluid. The most generally used adsorbents are activated carbon, alumina, zeolite and molecular sieve which are very efficient in many different applications. However, they are expensive and for effluents containing metal ions activated carbon especially requires chelating agents to enhance its performance, thus increasing treatment cost. Therefore, the need of alternative low-cost sorbents has encouraged the search for new and cheap sorption processes for aqueous effluent treatment, as these materials could reduce significantly the wastewater-treatment cost[8]. It has been reported that some agricultural waste products[6,9-11], naturally occurring materials[12-13], microorganisms[14-17] and composite materials[18-19] have been used for toxic metal ions removal from wastewater. However, most of the adsorbents derived from these materials require activating agent and cumbersome process for synthesis. The process of culturing microorganisms and development of composite adsorbents are also complex and require expertise. In recent time, CaO based adsorbents have been derived from carbonated materials such as birds' eggshell[20-21], limestone[22] and snail shell[23].

Bird eggshells have been employed as adsorbents for removing heavy metals from wastewater[24-25]. However, quail eggshell has not been employed as an adsorbent to remove from wastewater two or more heavy metals ions simultaneously. Besides, thermodynamic properties of heavy metals (single or multicomponent) adsorption onto quail eggshell have not been established. Thus, in this study, quail eggshell was used as an adsorbent in the removal of copper and zinc ions from aqueous solution and was characterized to evaluate its morphological and chemical properties. The effects of various parameters, temperature, adsorbent dosage, contact time and initial heavy metal ions concentration, which influence the adsorption process, were investigated. Moreover, the equilibrium, kinetics and thermodynamic parameters of batch adsorption of Cu^{2+} and Zn^{2+} ions from aqueous solution were also evaluated.

MATERIALS AND METHODS

This study was carried out between the month of February, 2017 and July, 2017 at the Department of Chemical and Petroleum Engineering, College of Engineering, Afe Babalola University, Ado-Ekiti, Nigeria.

Materials: The waste quail eggshells were collected from Olusegun Obasanjo's farm, Ibadan, Nigeria. All chemical reagents and materials used in this study were of analytical grade. About 1000 mg L^{-1} stock solution each of Cu^{2+} and Zn^{2+} were prepared by dissolving required quantities of $Cu(NO_3)_2.3H_2O$ and $Zn(NO_3)_2.6H_2O$ in 1.0 L of distilled water. The pH of each of the stock solution was adjusted to 4.5 by adding several drops of HCl in order to prevent precipitation from taking place. From the stock solution prepared, desired initial concentrations of each heavy metal ion was prepared for each run and the concentration was analyzed using Atomic Absorption Spectrophotometer (AAS, Buck Scientific 210VGP, USA).

Adsorbent preparation and characterization: The waste quail eggshells were first soaked for a day and washed thoroughly with tap water to get rid of all dirt and organic matters adhered to it, followed by another washing with distilled water. Then, the neatly washed eggshells were oven dried at 110°C for 12 h to get rid of water. The dried eggshells were ground by mechanical grinder to get the fine powder. Thereafter, the fine eggshell powder was passed through sieve mesh of 0.3 mm to obtain finest eggshell powder. The obtained eggshell powder was then calcined in a muffle furnace at a temperature of 900°C for 4 h. The adopted heating rate was 10°C min^{-1} and after the calcination time was attained, the calcined quail eggshell sample was immediately removed from furnace before the furnace temperature drop to room temperature[26]. The activated eggshell sample was then kept in a sealed glass bottle to prevent formation of carbonate and hydroxide.

The morphology and topography of the raw and calcined eggshell adsorbents were examined by scanning electron microscope (SEM-JEOL-JSM 7600F). Fourier Transform Infra Red (FTIR) analysis was carried out on both raw and thermally treated quail eggshell adsorbents in order to identify various functional groups present on their surfaces and compared, by using FTIR spectroscope (FTIR- IR Affinity-1S Shimadzu, Japan). Moreover, the chemical compositions of both raw and calcined adsorbents were determined by XRF machine.

Batch equilibrium studies: Batch adsorption process was carried out by bringing in contact the calcined eggshell adsorbent with aqueous solution containing Cu^{2+} and Zn^{2+} in a set of each 250 mL conical flasks. The flasks were agitated in a temperature controlled water bath shaker (SearchTech Instrument) operating at a constant stirring speed of 150 rpm. The adsorption process was conducted under the following operating conditions: Adsorption temperatures were 25, 30, 35, 40, 45, 50°C, contact time were 30, 60, 90, 120, 150 and 180 min, adsorbent dosages were 0.05, 0.1, 0.5, 1.0, 1.5 and 2.0 g and initial Cu^{2+} and Zn^{2+} concentrations were 150, 200, 250, 300, 350 and 400 mg L^{-1}.

After the equilibrium was attained, each sample was filtered to obtain solution containing un-adsorbed Cu^{2+} and Zn^{2+} that is free from adsorbent and the concentration of each metal ion was analyzed by Atomic Absorption Spectrophotometer (AAS, Buck Scientific 210VGP, USA). The removal percentage, E_A (%) and amount of metal ions adsorbed at equilibrium, (mg g^{-1}), of each cation were calculated as follows[19, 25]:

$$E_A = \frac{(C_o - C_e)}{C_o} \times 100(\%) \tag{1}$$

E_A : Amount of equilibrium adsorbed
C_o : Initial concentration (mg L^{-1})
C_e : Concentration at equilibrium (mg L^{-1})

$$q_e = \frac{(C_o - C_e)\ V}{W} \tag{2}$$

q_e : Amount of metal ions adsorbed at equilibrium (mg g^{-1})
C_o : Initial concentration (mg L^{-1})
C_e : Concentration at equilibrium (mg L^{-1})
V : Volume of the solution (L)
W : Mass of calcined eggshell adsorbent (g)

The batch kinetic study was also carried out by using method similar to equilibrium analysis. The heavy metal ions solution was taken at particular time intervals and the concentration of Cu^{2+} and Zn^{2+} were similarly measured[6]. The amount of Cu^{2+} and Zn^{2+} adsorbed at preset time t, (mg g^{-1}), was calculated as follows[6]:

$$q_t = \frac{(C_o - C_t)\ V}{W} \tag{3}$$

q_t : Amount of metal ions adsorbed at preset time t, (mg g^{-1})
C_o : Initial concentration (mg L^{-1})
C_t : Concentration at present time (mg L^{-1})
V : Volume of the solution (L)
W : Mass of calcined eggshell adsorbent (g)

Adsorption isotherms: In this study, the experimental data for Cu^{2+} and Zn^{2+} adsorption onto calcined quail eggshell were fitted to the two-parameter isotherm models (Langmuir and Freundlich models). The Langmuir and Freundlich isotherm models are given in equations (4) and (5), respectively as follows[25]:

$$q_e = \frac{q_{max} b C_e}{(1 + b C_e)} \tag{4}$$

q_e : Amount of metal ions adsorbed at equilibrium (mg g^{-1})
q_{max} : Maximum adsorption capacity (mg g^{-1})
C_e : Equilibrium concentration of metal in solution (mg L^{-1})
b : Langmuir equilibrium constant

$$q_e = k_F C_e^{1/n} \tag{5}$$

q_e : Amount of metal ions adsorbed at equilibrium (mg g^{-1})
k_F : Freundlich constant
C_e : Equilibrium concentration of metal in solution (mg L^{-1})
n : Adsorption intensity

The parameters contained in isotherm model equations (4) and (5) were evaluated by non-linear curve fitting, using excel solver and the model that best fitted to the isotherm data was chosen based on value of correlation coefficient (R^2). The experimental data is assumed to be well predicted by the model, when the R^2 value is closer to unity.

A dimensionless constant referred to as separation factor (R_L) can be employed for identifying the type of adsorption using the Langmuir equilibrium constant (b) and the highest initial concentration of adsorbate (C_o, mg L^{-1}) as given in Equation (6)[9].

$$R_L = \frac{1}{(1+bC_O)} \quad (6)$$

R_L = 0 indicates irreversible adsorption, $0<R_L<1$ means favourable adsorption
R_L = 1 implies linear adsorption and $R_L>1$ suggests unfavourable adsorption

Adsorption kinetic studies: Kinetic modeling is very important in adsorption process as it helps in determining the required residence time of adsorbent in the adsorption system[6]. Various adsorption kinetic models have been used to describe the rate of adsorption of trace component onto porous solid surface. The most commonly used kinetic models for the adsorption process are pseudo-first-order and pseudo-second-order.

In this study, the Lagergren pseudo-first-order and pseudo second-order kinetic models given in equations (7)[27] and (8)[28] were employed to analyze the adsorption kinetics of Cu^{2+} and Zn^{2+} based on experimental data obtained. More so, the sorption rate, h (mg g^{-1} min^{-1}) was calculated using Equation (9).

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (7)$$

q_e : Amount of metal ions adsorbed at equilibrium (mg g^{-1})
q_t : Amount of metal ions adsorbed at preset time t, (mg g^{-1})
k_1 : Pseudo-first-order
t : Time

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (8)$$

q_t : Amount of metal ions adsorbed at preset time t, (mg g^{-1})
q_e : Amount of metal ions adsorbed at equilibrium (mg g^{-1})
k_2 : Pseudo-second-order
t : Time

$$h = k_2 q_e^2 \quad (9)$$

h : Sorption rate (mg g^{-1} min^{-1})
q_e : Amount of metal ions adsorbed at equilibrium (mg g^{-1})
k_2 : Pseudo-second-order

In order to identify the mechanism of Cu^{2+} and Zn^{2+} adsorption onto eggshell, intraparticle diffusion model given in equation (10) was applied.

$$q_t = k_D t^{1/2} + C \quad (10)$$

q_t : Amount of metal ions adsorbed at preset time t, (mg g^{-1})
k_D : Intraparticle diffusion rate constant (mg g^{-1})
C : Intercept
t : Time

Adsorption thermodynamic study: The parameters that describe the thermodynamic behaviour of adsorption of Cu^{2+} and Zn^{2+} onto thermally treated quail eggshell were evaluated using equations (11-13). The equilibrium constant (K_c) was calculated using equation (13) reported by Mohammed-Ridha *et al.*[2].

$$\Delta G° = -RT \ln K_C \quad (11)$$

ΔG : Change in standard Gibbs free energy (kJ mol^{-1})
R : Universal Gas Constant
T : Temperature
K_c : Equilibrium constant

$$\Delta G° = \Delta H° - T\Delta S° \quad (12)$$

ΔG : Change in standard Gibbs free energy (kJ mol^{-1})
ΔH : Change in enthalpy (kJ mol^{-1})
ΔS : Change in entropy (J mol^{-1} K^{-1})
T : Temperature

$$K_C = \frac{C_{ad}}{C_e} \quad (13)$$

K_c : Equilibrium constant
C_{ad} : Adsorbed heavy metals concentration
C_e : Equilibrium concentration of metal in solution (mg L^{-1})

RESULTS AND DISCUSSION

The SEM analysis results, in Fig. 1a and b, revealed the surface morphology of raw and thermally activated eggshell, respectively. The morphology of the raw eggshell adsorbent was observed to be rough, possessed particles that were irregular in shape and had no pores for heavy metals adsorption.

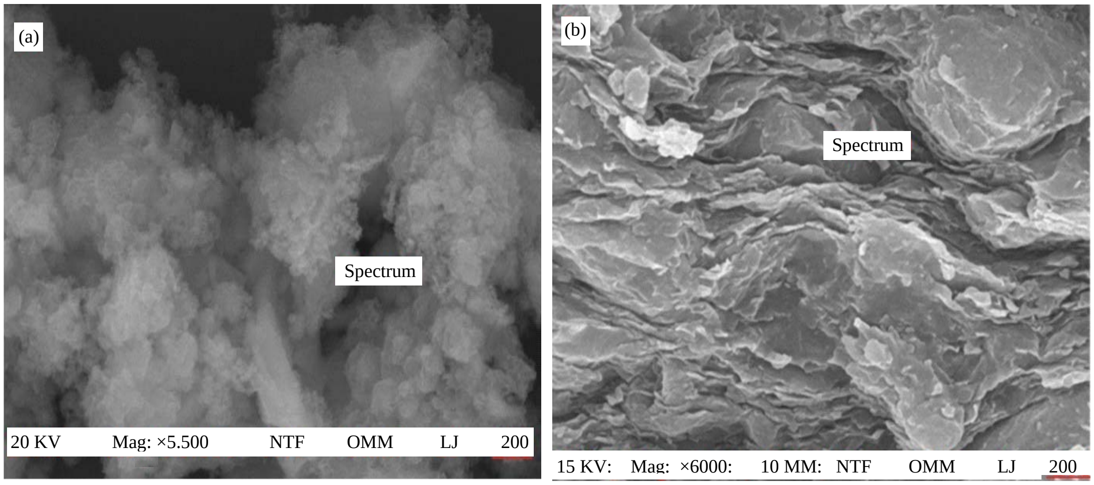

Fig. 1(a-b): SEM images for (a) Raw eggshell and (b) Calcined eggshell adsorbent

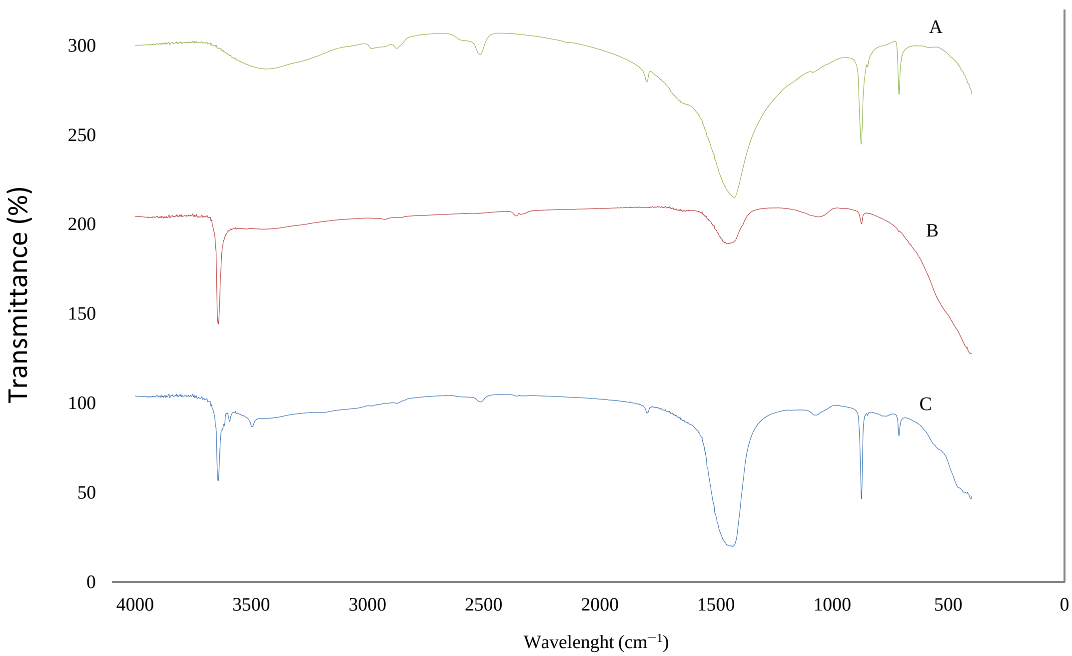

Fig. 2: FT-IR spectra of A- raw, B-calcined and C-used quail eggshell adsorbents

Table 1: XRF analysis result for the raw and calcined eggshell adsorbent

		Chemical composition (wt%)								
Material	Conditions	Al_2O_3	SiO_2	P_2O_5	SO_3	SnO	CaO	F_2O_3	MgO	Others
Raw	Oven dried at 110°C, 3 h	0.37	0.29	0.57	1.26	0.68	95.80	0.20	0.12	1.37
Calcined	Activated at 900°C, 4 h	0.40	0.33	0.50	0.63	0.56	97.63	0.20	0.43	1.05

The chemical composition analysis of both raw and calcined eggshell as depicted in Table 1 revealed that the CaO content constitutes larger percentage in eggshell. However, the percentage of CaO increased after calcination process as can be seen in Table 1. This implies that the $CaCO_3$ originally contained in raw eggshell has been decomposed into CO_2 and CaO.

The FT-IR spectra of raw, calcined and used eggshell adsorbents are shown in Fig. 2. Upon calcination, some of the peaks in raw adsorbent varnished or shifted and also, new

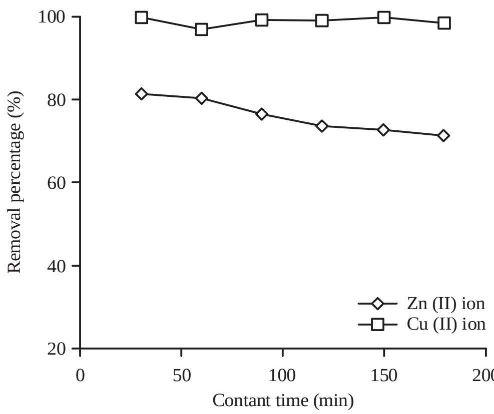

Fig. 3: Effect of contact time on removal percentage of Cu^{2+} and Zn^{2+} at constant initial heavy metal concentration = 350 mg L^{-1}, adsorbent dosage = 1.5 g and temperature = 30°C

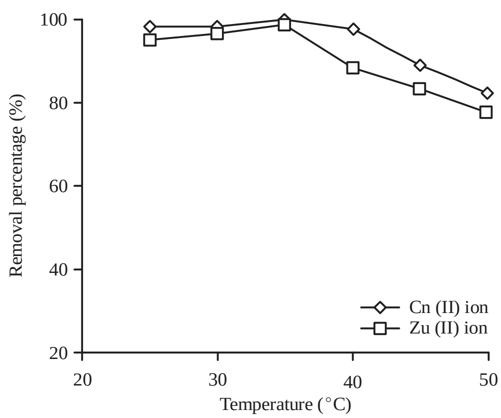

Fig. 4: Effect of temperature on removal percentage of Cu^{2+} and Zn^{2+} at constant initial heavy metal concentration = 350 mg L^{-1}, adsorbent dosage = 1.5 g and contact time = 30 min

Table 2: Isotherm parameters and correlation coefficients for adsorption of Cu^{2+} and Zn^{2+} onto eggshell

Isotherm	Cu^{2+}	Zn^{2+}
Langmuir		
q_{max} (mg g^{-1})	13.49	11.52
b (L mg^{-1})	0.149	0.0138
R^2	0.9927	0.9775
R_L	0.0165	0.1538
Freundlich		
k_F (mg g^{-1} (L $mg^{-1})^{1/n}$)	3.62	0.74
n	3.08	2.12
R^2	0.9727	0.9827

peaks were formed. These observations imply that transformation had occurred after thermal treatment of the raw adsorbent.

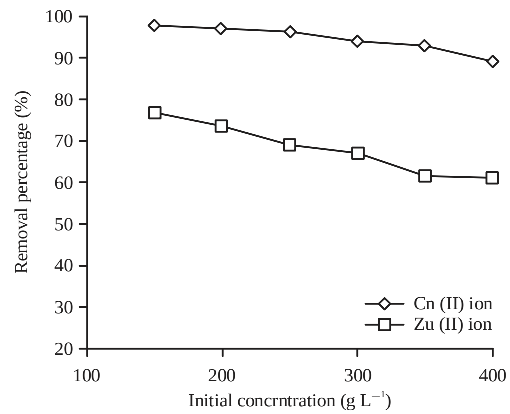

Fig. 5: Effect of initial concentration on removal percentage of Cu^{2+} and Zn^{2+} at constant temperature = 35°C, adsorbent dosage = 1.5 g and contact time = 30 min

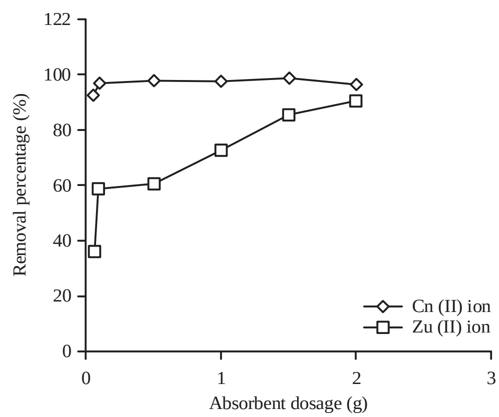

Fig. 6: Effect of adsorbent dosage on removal percentage of Cu^{2+} and Zn^{2+} at constant initial heavy metal concentration = 350 mg L^{-1}, temperature = 35°C and contact time = 30 min

The effects of various adsorption parameters on the heavy metals removal from aqueous solution were investigated and the results, as shown in Fig. 3-6, indicated that those variables considered have significant influence on adsorption process.

The nonlinear plot of amount of metal ion adsorbed at equilibrium (q_e) against equilibrium concentration (C_e) for Cu^{2+} and Zn^{2+} are displayed in Fig. 7 and 8, respectively. The isotherm models parameters which were determined using excel solver are presented in Table 2.

Figures 9a and b indicated that the kinetic data of Cu^{2+} and Zn^{2+} cannot be well predicted by pseudo-first-order model. Thus, the kinetic data of the heavy metal ions were

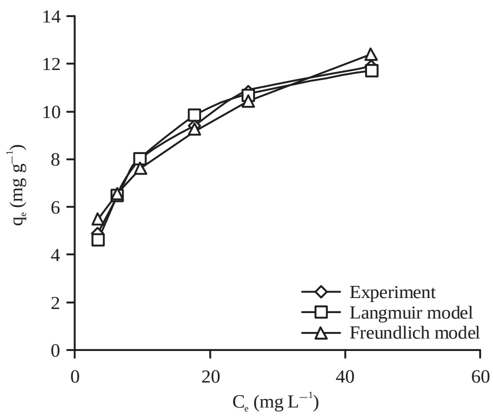

Fig. 7: Adsorption isotherm of Cu^{2+} based on the Langmuir and Freundlich models at 35°C

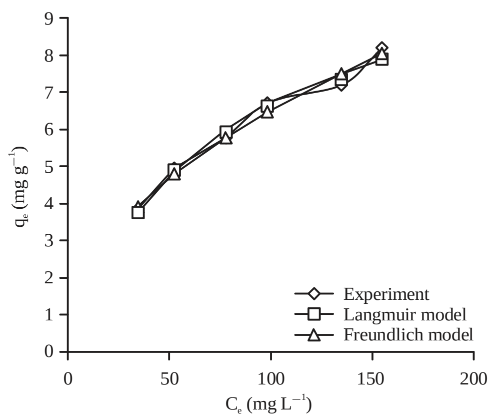

Fig. 8: Adsorption isotherm of Zn^{2+} based on the Langmuir and Freundlich models at 35°C

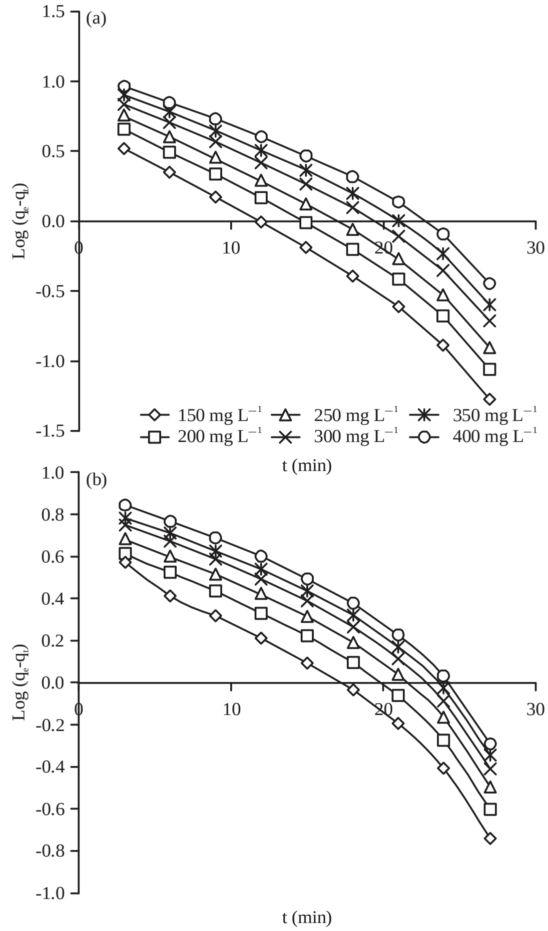

Fig. 9(a-b): Pseudo-first-order kinetics for adsorption of (a) Cu^{2+} (b) Zn^{2+} onto eggshell

further analyzed using pseudo-second-order kinetic model given in Equation (10) and the results for adsorption kinetics of Cu^{2+} and Zn^{2+}, as shown in Fig. 10a and b, indicated that the experimental data agreed excellently well with pseudo-second-order kinetic model. However, the plot of q_t against $t^{1/2}$, as shown in Fig. 11a and b, revealed the mechanism of Cu^{2+} and Zn^{+} adsorption onto eggshell.

The adsorption kinetic parameters contained in pseudo-first-order and pseudo-second-order models are calculated from Fig. 9 and 10 and their values are listed in Table 3 and 4. However, having obtained the pseudo-second-order rate constants, K_2 (g mg^{-1} min^{-1}) for each of the initial concentration, the sorption rate, h (mg g^{-1} min^{-1}) was evaluated and the results are presented in Table 3 and 4 as well. More so, the values of intraparticle diffusion rate constants (mg g^{-1} min$^{0.5}$) for all the initial Cu^{2+} and Zn^{2+} concentrations, which can be evaluated from the slope of linear plot of q_t against $t^{1/2}$ (Fig. 11a and b) are listed in Table 3 and 4.

The values of thermodynamic parameters for Cu^{2+} and Zn^{2+} adsorption onto eggshell, as shown in Table 5, indicated that the adsorption is a temperature dependent process.

Characterization of adsorbents: Thermal treatment of quail eggshell at 900°C for 4 h led to particle rearrangement and formation of pores on its surface as can be seen in Fig. 1b. However, the pores observed on the activated eggshell were as a result of elimination of adsorbed gases, organic matter and moisture content[29]. Moreover, the changes in structure of the eggshell upon calcination might be due to its compositional changes. As widely reported in the literature, the major component in raw eggshell is calcium carbonate, $CaCO_3$, which was decomposed into calcium oxide (CaO) and carbon dioxide (CO_2) after calcination. This observation is corroborated by XRF analysis (Table 1) and is attributed to why thermally treated quail eggshell adsorbent had improved performance in heavy metals adsorption.

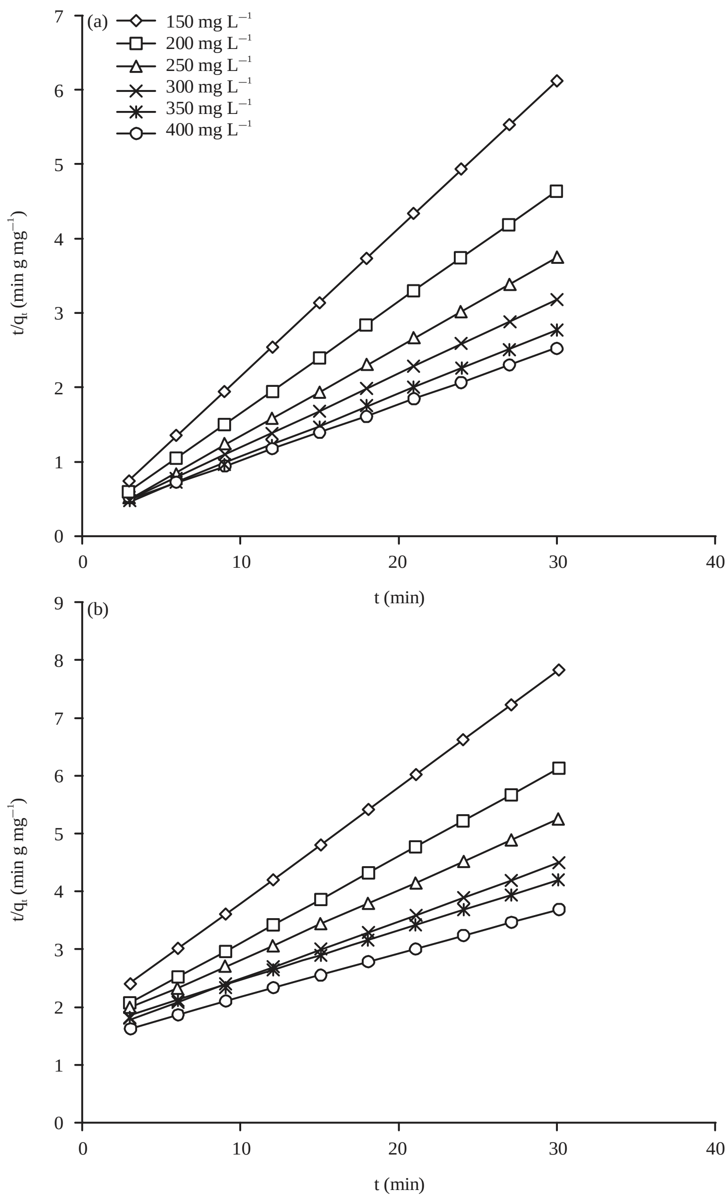

Fig. 10(a-b): Pseudo-second-order kinetics for adsorption of (a) Cu^{2+} and (b) Zn^{2+} onto eggshell

Table 3: Kinetic models and parameters of adsorption of Cu^{2+} onto eggshell

	Pseudo-first-order		Pseudo-second-order			Intraparticle diffusion	
C° (mg L⁻)	k_1 (min⁻¹)	R^2	k_2 (g mg⁻¹ min)	R^2	h (mg g⁻¹ min⁻¹)	k_D (mg g⁻¹ min$^{0.5}$)	R^2
150	0.1644	0.9815	0.2789	0.9998	6.6509	0.1937	0.8180
200	0.1566	0.9804	0.1537	0.9999	6.8303	0.3289	0.8299
250	0.1529	0.9802	0.0991	0.9992	6.8823	0.4782	0.8406
300	0.1412	0.9722	0.0528	1.0000	5.2850	0.7766	0.8645
350	0.1363	0.9695	0.0360	0.9996	4.9043	1.0330	0.8791
400	0.1271	0.9637	0.0203	1.0000	3.6049	1.4534	0.9096

The chemical composition of CaO increased after calcination of eggshell as can be seen in Table 1. This implies that the $CaCO_3$ originally contained in raw eggshell has been decomposed into CO_2 and CaO[26]. Generally, thermal activation of carbonated materials at higher temperature leads to evolution of adsorbed gases and transforms the components into several metal oxides with synergetic effect as can be seen in the XRF analysis result in Table 1. This is corroborated by

Table 4: Kinetic models and parameters of adsorption of Zn^{2+} onto eggshell

	Pseudo-first-order		Pseudo-second-order			Intraparticle diffusion	
C° (mg L^{-1})	k_1 (min^{-1})	R^2	k_2 (g mg^{-1} min)	R^2	h (mg g^{-1} min^{-1})	k_D (mg g^{-1} $min^{0.5}$)	R^2
150	0.1149	0.9647	0.0222	1.000	0.5538	0.6755	0.9712
200	0.1082	0.9529	0.0140	1.000	1.000	0.9066	0.9786
250	0.1050	0.9438	0.0088	1.000	0.6138	1.1216	0.9846
300	0.1036	0.9425	0.0068	1.000	0.6789	1.3344	0.9873
350	0.1006	0.9388	0.0046	1.000	0.6193	1.4932	0.9936
400	0.1006	0.9387	0.0040	1.000	0.9867	1.7037	0.9938

Table 5: Thermodynamic parameters for Cu^{2+} and Zn^{2+} adsorption onto eggshell

	Cu^{2+}				Zn^{2+}			
T(K)	K^c	ΔG°	ΔH°	ΔS°	K_c	ΔG°	ΔH°	ΔS°
298	53.945	-9.880	87.047	0.252	2.744	-2.500	55.505	0.178
303	55.497	-10.117			1.831	-1.524		
308	152.84	-12.878			1.268	-0.607		
313	41.918	-9.721			0.895	-0.288		
318	8.066	-5.519			0.616	-1.279		
323	4.653	-4.128			0.501	-1.857		

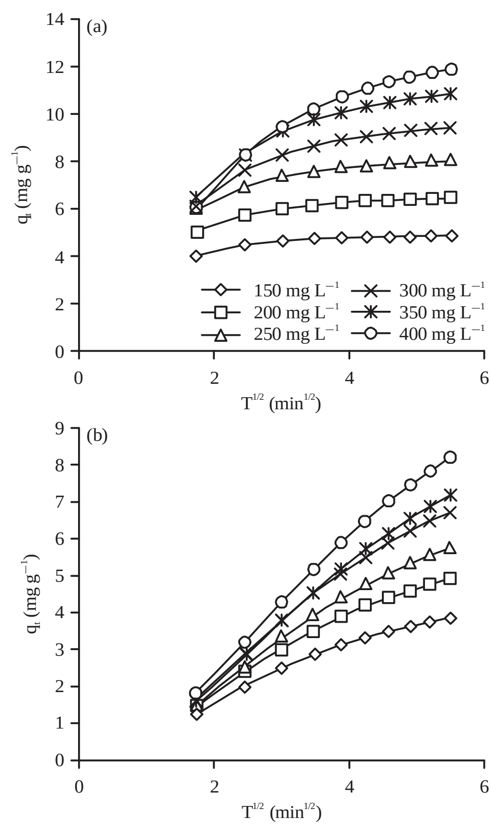

Fig. 11(a-b): Intraparticle diffusion plot for adsorption of (a) Cu^{2+} (b) Zn^{2+} onto eggshell

SEM analysis and is attributed to why calcined quail eggshell possessed high adsorption capacity. This finding is in line with the study reported by Eletta *et al.*[21].

The broad adsorption band at 3433.41 cm^{-1} for raw eggshell and sharp peaks at 3641.73 cm^{-1} for both calcined and used quail eggshells in Fig 2 are attributed to O-H stretching vibration mode which confirms the presence of moisture on the surface of the adsorbent. The adsorption peaks observed for raw eggshell at 1429.73, 875.71 and 711.76 cm^{-1} are attributed to C-O asymmetric stretching, out of plane bend and in-plane bend vibration modes respectively of from $CaCO_3$[30]. In the case of calcined eggshell, as depicted in Fig. 2, the appearance of peak at 1031.95 cm^{-1} implies that carbonate in raw eggshell had been converted to CaO. However, reappearance of peaks 1429.30, 873.78 and 711.76 cm^{-1}, as well as sharp peak at 3641.73 cm^{-1} for used eggshell as can be seen in Fig. 2, is as a result of its exposure to carbon dioxide and moisture, which led to the formation of carbonate and hydroxide. These are given by reactions.

$$CaO + CO_2 \rightarrow CaCO_3 \quad (14)$$

$$CaO + H_2O \rightarrow Ca(OH)_2 \quad (15)$$

The changes observed in the spectrum of used eggshell indicated the possible participation of functional groups present on the surface of the calcined eggshell in adsorption process[6].

Effect of contact time: The effect of contact time on the removal percentage of Cu^{2+} and Zn^{2+} from aqueous solution is shown in Fig. 3. It was noticed that the heavy metals uptakes increased with increase in contact time. The adsorption of Cu^{2+} and Zn^{2+} onto eggshell was more pronounced at 30 min contact time. The Cu^{2+} uptake was more than that of Zn^{2+}. However, as the adsorption progressed with longer time, the removal percentage of Zn^{2+} continued to decrease, as can be seen in Fig. 1, the equilibrium time varied between 60-90 for Cu^{2+} and 60-80 min for Zn^{2+}.

Effect of temperature: The effect of the operating temperature during the removal of Cu^{2+} and Zn^{2+} by eggshell was also investigated over the range of 25-50°C. The effect of different values of temperatures on heavy metals uptake using adsorbates initial concentration of 350 mg L^{-1}, adsorbent dosage 1.5 g in 30 min contact time is shown in Fig. 4. The removal percentage of both Cu^{2+} and Zn^{2+} increased from 25-35°C when the metals uptake dropped as presented by Fig. 4. The maximum heavy metals uptake recorded at the temperature of 35°C is attributed to increased kinetic energy and mass transfer of the cations[31].

Effect of initial Cu^{2+} and Zn^{2+} concentration: The influence of initial concentration of Cu^{2+} and Zn^{2+} on their removal percentages by eggshell adsorbent was studied by considering various values of initial concentrations between 150-400 mg L^{-1}. It was noticed that the removal percentage of cations decreased from 97.67-89.03% and from 76.87-61.25% for Cu^{2+} and Zn^{2+}, respectively by increasing initial concentration from 150-400 mg L^{-1} as shown in Fig. 5. This observation revealed that the adsorbent dosage of 1.5 g provided enough active bonding sites for the adhesion of metal ions when the initial concentration was 150 mg L^{-1}. Meanwhile, increasing the initial heavy metals concentration above 150 mg L^{-1}, the active bonding sites become saturated and the adsorbent capacity becomes exhausted due to non-availability of adsorption sites[2,32].

Effect of adsorbent dosage: The removal percentage of heavy metals from wastewater solely relies on the amount of adsorbent. The influence of eggshell dosage on adsorption of Cu^{2+} and Zn^{2+} from wastewater was investigated by varying the mass of calcined eggshell from 0.05-2.0 g. The results are depicted in Fig. 6, the removal efficiency of both Cu^{2+} and Zn^{2+} was found to increase with the increase in eggshell dosage. This observation revealed that increasing the mass of eggshell could provide enough adsorption sites for the metal ions and also, increase the contact between the cations and eggshell.

Adsorption isotherms: It was found that the Langmuir model gave the best fit with experimental results for Cu^{2+} based on R^2 value, thus indicating that eggshell would provide monolayer and homogeneous adsorption for Cu^{2+}. A similar observation was reported for adsorption of Cu^{2+} on clay[12]. Meanwhile, based on R^2 value as well, Freundlich model provides a good fit to the experimental data for Zn^{2+}. The maximum adsorption capacities (q_{max}) were obtained to be 13.49 and 11.52 mg g^{-1} for Cu^{2+} and Zn^{2+}, respectively as shown in Table 2. Langmuir model constant (b) for Cu^{2+} and Zn^{2+} were found to be 0.149 and 0.0138 L mg^{-1}, respectively. This result implies that there was strong affinity between Cu^{2+} and eggshell[31]. However, the values of Freundlich adsorption intensity (n) for both Cu^{2+} and Zn^{2+} were greater than one as can be seen in Table 2. This indicates that the condition of adsorption of Cu^{2+} and Zn^{2+} onto eggshell is a favourable type[9]. The values of separation factor (R_L) for Cu^{2+} and Zn^{2+} in this study have been found to be 0.0165 and 0.1538, respectively, thus indicating that the adsorption of Cu^{2+} and Zn^{2+} onto calcined eggshell is favourable at 35°C.

Adsorption kinetic studies: By plotting $\log(q_e\text{-}q_t)$ against t (Fig. 9a and b), the pseudo-first-order parameters were determined and summarized in Table 3 and 4 for Cu^{2+} and Zn^{2+}, respectively. The R^2 values for all initial concentrations of the heavy metal ions considered within the operating limit of experimental conditions are generally lower than 0.982 as can be seen in Table 3 and 4. In that case, the kinetic data of Cu^{2+} and Zn^{2+} cannot be well predicted by pseudo-first-order model. This outcome is actually expected, because many researchers have reported similar results[1,6,33].

The parameters contained in the model were obtained from the plot of t/q_t against t (Fig. 10a and b). The values of R^2 for the second-order kinetic model were determined and presented in Table 3 and 4. Results presented in Table 3 and 4 imply that the experimental data agreed excellently well with pseudo-second-order kinetic models. The values of R^2 for all the initial concentrations are approximately equal to 1. According to Khambhaty *et al.*[34], the good compliance of the adsorption of Cu^{2+} and Zn^{2+} onto eggshell with second-order kinetic model is attributed to the fact that two reactions occur, first one occurs very fast and quickly attains equilibrium, while the second reaction is slow and proceed for long time. However, having obtained the pseudo-second-order rate constant K_2 (g mg^{-1} min^{-1}) for each of the initial concentration, the sorption rate, h (mg g^{-1} min^{-1}) was calculated using equation (11) and the results are presented in Table 3 and 4 as well. The values of sorption rate (h) were found to be in the range 3.6049-6.8823 mg g^{-1} min^{-1} for Cu^{2+} adsorption onto eggshell, while those of Zn^{2+} were obtained to be in the range 0.5538-1.00. As can be seen in Table 3, the highest initial adsorption rate was recorded when Cu^{2+} initial concentration was 250 mg L^{-1}, this implies that Cu^{2+} reached the surface of the eggshell adsorbent in a shorter period of time at the initial concentration of 250 mg L^{-1} compared to others[9,28]. Meanwhile, there was increase in driving force for mass transfer of Zn^{2+} onto eggshell when its initial concentration was 200 mg L^{-1}. This observation was corroborated by the obtained value of sorption rate at initial concentration of 200 mg L^{-1} as can be seen in Table 4.

The model parameters (K_D and C) and R^2 were calculated from the plot of q_t against $t^{1/2}$ (Fig. 11a and b). The slope of the plot was regarded as the intraparticle diffusion rate constant, (mg g^{-1} $min^{0.5}$). As can be seen in Fig. 11a and b, it is obvious that the adsorption of Cu^{2+} and Zn^{2+} onto eggshell comprises of two phases, which include diffusion of adsorbates to the external surface of the adsorbent and intraparticle diffusion. The first linear portion of the plot implies boundary layer effect[33], while the second linear portion represents slow adsorption phase. In this case, the intraparticle diffusion model cannot be regarded as rate-limiting step, because R^2 values for intraparticle model are smaller than those for pseudo-second-order kinetic as can be seen in Table 3 and 4.

Adsorption thermodynamic study: The negative values of ΔG° at different temperatures imply that the adsorption of Cu^{2+} and Zn^{2+} onto eggshell is spontaneous in nature as seen in Table 5. The positive value of ΔS° signifies the degree of disorderliness at the interface of solid-liquid system during the adsorption of Cu^{2+} and Zn^{2+} onto prepared adsorbent[35]. More so, the positive value of ΔH° indicates the adsorption is endothermic. Similar observations were reported for Cu^{2+} adsorption onto clay by Mohammed-Ridha *et al.*[2] and for Zn^{2+} adsorption onto rice husk by Elham *et al.*[36]. However, the large values of ΔH° for Cu^{2+} and Zn^{2+} as contained in Table 5 indicated that the interaction between these cations and thermally treated quail eggshell was strong[37]. Moreover, since the values of ΔH° for the heavy metal ions are higher than 40 kJ mol^{-1} as can be seen in Table 5, the adsorption of Cu^{2+} and Zn^{2+} onto calcined eggshell can be regarded as chemisorption[38]. Quail eggshell is found to possess a relatively high adsorption capacities of 13.49 and 11.52 mg g^{-1} for Cu^{2+} and Zn^{2+}, respectively and these imply that it could be considered a suitable agricultural waste based adsorbent for the removal of Cu^{2+} and Zn^{2+} from aqueous solution, mostly when compared with Cu^{2+} adsorption on chicken eggshell (8.4 mg g^{-1})[29] and removal of Zn^{2+} by rice husk (0.3 mg g^{-1})[36]. However, the process adopted in this study was considered simple and economically feasible as no activating agent and precursor were used, yet it provided an adsorbent that showed better performance for heavy metals removal from aqueous solution.

CONCLUSION

Adsorption of Cu^{2+} and Zn^{2+} onto thermally treated quail eggshell had been investigated. The result revealed that maximum Cu^{2+} and Zn^{2+} uptake from the process was achieved at contact time of 30 min, adsorbent dosage of 1.5 g, temperature of 35°C and initial Cu^{2+} and Zn^{2+} concentration of 150 mg L^{-1}. Equilibrium data for Cu^{2+} were well predicted by Langmuir isotherm model with monolayer adsorption capacity of 13.49 mg g^{-1} at 35°C, while the data obtained for Zn^{2+} were well represented by Freundlich isotherm model. The kinetics and thermodynamic studies were also carried out. Experimental data for the adsorption of the heavy metals were best fitted with pseudo-second-order kinetic model. Thermodynamic evaluation showed that the heavy metals adsorption onto eggshell was spontaneous and endothermic.

SIGNIFICANCE STATEMENTS

This study discovers the possible way of converting agricultural wastes to useful products which can be used in various applications including wastewater treatment. This study will help the researcher to uncover the usefulness of quail eggshell which has not been fully explored in wastewater treatment process. Thus, a new theory on the development and characterization of quail eggshell as an agricultural waste based adsorbent for water/wastewater treatment may be achieved and documented. Moreover, thermodynamic properties of copper and zinc ions adsorbed on thermally treated quail eggshell may be established.

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