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Research Article

Preparation and Characterization of Composite Anthill-Chicken Eggshell Adsorbent: Optimization Study on Heavy Metals Adsorption Using Response Surface Methodology

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Abstract

Background and Objective: The generation of wastewater containing heavy metals has become an issue as their release into the environment has increased as a result of industrialization. This wastewater contains amounts of heavy metals that are harmful to human beings and aquatic species. This present study was aimed to develop mixed anthill-chicken eggshell as composite adsorbent and use to remove heavy metals contained in an aqueous solution via adsorption process. **Materials and Methods:** The stock solution was prepared by dissolving desired amount of Cu(II) and Zn(II) nitrate in a known volume of deionized water. After preparation of anthill and eggshell powders, the mixed anthill-eggshell preparation conditions were optimized by maximizing the heavy metals uptakes using Central Composite Design (CCD) of response surface methodology (RSM) in design expert 7.0.0 as an optimization tool. The fitness of the developed models was evaluated by analysis of variance (ANOVA- Type III). **Results:** Findings revealed that the predicted Cu(II) and Zn(II) ions uptakes from the two suggested models agreed reasonably well with the experimental values. The obtained data showed that at 863.78°C calcination temperature, 4 h calcination time and eggshell/anthill mixing ratio of 1.86, the percentages of Cu(II) and Zn(II) ions removed from aqueous solution by optimal composite anthill-eggshell adsorbent were 97.89 and 99.34% respectively. **Conclusion:** The analyses results revealed that composite anthill-eggshell adsorbent was porous, possessed active functional groups on its surface and made up of active mixed metal oxides with close interaction.

Key words: Adsorption, anthill, eggshell, central composite design, heavy metals

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Competing Interest: The author have declared that no competing interest exists.

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

INTRODUCTION

Heavy metals are among some of the contaminants which often find their ways into open stream. However, their presence in water causes serious health issue to humans and aquatic species. This is because heavy metals have great tendency to pile up in soil, water and wastewater through which they enter into the food chain[1]. To this end, it is necessary to adopt a novel approach in getting rid of these toxic substances from water and wastewater before disposal. According to literature, several methods of removing heavy metals from water and wastewater had been reported. These methods include precipitation, membrane separation, ion-exchange, ultrafiltration and adsorption[2], among these techniques, adsorption is frequently used for the removal of heavy metals from aqueous solution due to its simplicity[2]. Adsorption is the process that describes the attachment of solute present in fluid onto porous solid surface called adsorbent. It is a mass transfer process.

However, the most common industrial adsorbents are activated carbon, silica gel and alumina. All these adsorbents are generally expensive, especially in developing countries of the world. As a result of these, there is need to create an avenue through which locally source materials from our environments are being converted into effective adsorbents, for removing inorganic/organic solutes contained in wastewater. Several agricultural waste and naturally occurring materials have been used for the production of adsorbents for the removal of contaminants from wastewater. These include coconut shell[3], rice straw[4], clay[5], kenaf fiber[6], cassava peel[7], grain sorghum[8], oil palm fiber[9], sawdust[10], soil[11] and many more. Recently, the use of composite adsorbents such as montmorillonite-supported magnetite nanocomposite[12], Chitosan-montmorillonite composites[13], Ti-pillared montmorillonite[14] and many more for heavy metals removal from aqueous solutions have also been reported. Recently, low cost adsorbents have been synthesized from waste chicken eggshells[1] and clay materials[2].

Eggshells are part of the wastes generated from household, food processing industries and poultries[15]. According to Sharma *et al.*[16], calcium carbonate constitutes larger amount in dry eggshell. Other components include magnesium carbonate, phosphate, organic matter and traces of some metals. It is therefore possible to synthesis from it an adsorbent with high adsorptive capacity due to the intrinsic pore structure, the large $CaCO_3$ content and its large availability. Many researches had been conducted on the use of waste chicken eggshells as a source CaO based adsorbent for removing contaminants from wastewater[1,17,18].

Anthill is a siliceous fireclay that is formed at the entrances of subterranean dwelling of ant colonies[19]. Anthill is a naturally occurring material and has numerous applications. For instance, it has been used in making ceramic[19], refractories[20], cement, bricks and sand casting[21] and catalyst for biodiesel production[22]. However, as reported by Srinivasan[23], raw, chemically and thermally treated clays have been employed in some cases as adsorbents for the removal of heavy metals from aqueous solutions. To mention but a few, Mohamed *et al.*[2] reported adsorption of Cu(II) ion onto natural clay while Etci *et al.*[24] removed lead and cadmium ions from aqueous solution via batch adsorption process using beidellite (low and natural clay mineral) as adsorbent.

Meanwhile, the adsorption capacity of adsorbents derived from those aforementioned materials depends on method of preparation adopted and also preparation conditions[3]. This is because adsorbent preparation variables such as activation temperature, activation time and mixing proportion if it involves impregnation influence the morphology and textural features of the synthesized adsorbent. As a result of these, it is pertinent to optimize the preparation conditions of the adsorbent in order to establish favorable conditions that will provide adsorbent with high adsorptive capacity. In assessing the influence of these parameters on the performance of the adsorbent, it is highly important to employ an experimental design that will be objective. In this regard, Response Surface Methodology (RSM) has been found worthy to analyze the interactions of two or more variables[3]. This design tool has been widely used in many chemical engineering operations[25-27]. The RSM has been previously used in optimization of preparation conditions of various biomass derived adsorbents such as palm oil fronds[28], marine algae[29], coconut husk[3], kenaf fiber[6].

The aim of this current study was to develop composite adsorbent from waste chicken eggshell and anthill and use for the removal of Cu(II) and Zn(II) ions from aqueous solution. It also aimed to optimize the preparation conditions of the new composite adsorbent in order to establish favorable conditions that will result in high heavy metals uptake.

MATERIALS AND METHODS

This study was carried out between the months of December 2016-April 2017 at the Department of Chemical and Petroleum Engineering, Afe Babalola University, Ado-Ekiti, Nigeria.

Preparation of composite anthill-eggshell adsorbent: The waste chicken eggshells used for this study were collected from students' cafeteria 1, Afe Babalola University (ABUAD), Ado-Ekiti, Nigeria, while type II anthill situated behind Works Department, ABUAD was harvested. The procedure used to prepare eggshell powder by Tan *et al.*[30] was adopted in this study. The waste chicken 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 24 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 kept in soft polythene bag and placed in sealed plastic container. The harvested anthill in lump form was manually pulverized into little pieces by mortar and pestle. The crushed anthill was then sieved through sieve mesh of 0.3 mm to obtain particle size less than 0.3 mm. Thereafter, the fine anthill powder was dried in an oven at 105°C for 4 h to remove moisture content. The dried anthill powder was then kept in sealed plastic container. The prepared eggshell and anthill powders were mixed in different proportion of eggshell to anthill (1-5) as suggested by central composite (CCD) illustrated in Table 1. Adequate amount of distilled water was added to the mixtures contained in the beaker to form suspension and stirred for 2 h on a hot plate to homogenize the mixtures. The mixtures were then filtered and the residue was placed in an oven to remove excess water at a temperature of 125°C for 2 h. The twenty different proportions of dried mixed anthill-eggshell powders were thus calcined in a muffle furnace at different temperature in the range of 700-900°C and different corresponding time in the range of 1-4 h with heating rate of 10°C min^{-1}.

Experimental design: The optimum preparation conditions of CAE adsorbent were obtained via Central Composite Design (CCD) of Response Surface Methodology (RSM) embedded in Design Expert 7.0.0. Three variables, that is, calcination temperature (x_1), calcination time (x_2) and mixing ratio of eggshell to anthill (x_3) were studied at axial and center runs levels with the required responses being the copper and zinc ions uptakes. Table 1 lists the range and levels of the three independent parameters considered. The ultimate goal in term of response was described as "maximization" i.e., the optimum preparation process parameters that would provide better adsorbent for the maximum heavy metals removal.

The response was obtained via adsorption process and used to develop mathematical relations which correlate the responses (heavy metals uptakes) to the CAE adsorbent preparation process variables studied through first order, second order and interaction terms according to the following polynomial equation[26]:

$$Y_i = \alpha_o + \sum_{j=1}^{3} \alpha_j x_J + \sum_{i,j=1}^{3} \alpha_{ij} x_i x_j + \sum_{j=1}^{3} \alpha_{jj} x_j^2 \quad (1)$$

where, Y is the predicted response, x_i and x_j represents the process variables, α_0 is the offset term, α_j is the regression coefficient for linear term, α_{ij} is the regression coefficient for first order interaction term and α_{jj} is the regression coefficient for quadratic effect.

Preparation of adsorbates: Copper nitrate trihydrate [$Cu(NO_3)_2.3H_2O$] and zinc nitrate haxahydrate [$Zn(NO_3)_2.6H_2O$] used as adsorbates in this current study were supplied by Topjay Chemical Industry, Ado-Ekiti, Nigeria. Simulated stock solutions of Cu(II) and Zn(II) salts having concentration of 350 mg L^{-1} were prepared in separate 500 mL conical flasks. In order to ensure that adsorption really takes place, the pH of the two salt solutions was adjusted to 5.0 with the aid of pH meter (model HI 2210).

Batch adsorption studies: Batch adsorption process was carried out by bringing each of CAE adsorbents prepared at different conditions together with 30 mL solution of Cu(II) and Zn(II) ions each in twenty set of 250 mL conical flasks in which 0.75 g of each of the prepared composite anthill-eggshell (CAE) adsorbent was charged into each flask. Thereafter, the set of flasks containing adsorbates and adsorbent were placed in a thermostatic water bath shaker (SearchTech Instrument) operating at constant temperature of 30°C and stirring speed of 150 rpm until adsorption process attained equilibrium contact time of 90 min. The concentration of cations remained un-adsorbed in the aqueous solution was analyzed with the

Table 1: Levels for the catalyst preparation process variables chosen for this study

Variable	Factor coding	Level -2	-1	0	+1	+2
Calcination temperature (°c)	x_1	668.39	700	800	900	931.61
Calcination time (h)	x_2	0.53	1	2.5	4.0	4.47
Mixing ratio of eggshell to anthill	x_3	0.37	1	3	5	5.63

aid of Atomic Absorption Spectrophotometer (Buck Scientific 210VGP, USA). Prior to cations concentration analysis, all aqueous samples were filtered in order to reduce the interference of adsorbent with the analysis[3]. The uptake of Cu(II) and Zn(II) ions was thus calculated by using Eq. 2 reported by Tan *et al.*[3]:

$$E_A = \frac{C_o - C_e}{C_o} \times 100\% \quad (2)$$

Where, C_o and C_e (mg L^{-1}) are the initial concentration and concentration at equilibrium, respectively. The E_A is the cation uptake (%).

Characterization of the synthesized composite anthill-eggshell adsorbent: The morphology and topography of the prepared CAE adsorbent prepared under optimum conditions were examined by scanning electron microscope (SEM-JEOL-JSM 7600F). Fourier transform infrared (FTIR) analysis was carried out on both raw and thermally treated adsorbents in order to identify various functional groups present on their surfaces and compared, by using FTIR spectrometer (FTIR- IR Affinity-1S Shimadzu, Japan). Moreover, the chemical composition analysis of raw and calcined CAE adsorbent at optimum temperature was carried out by X-ray fluorescence (XRF) machine (skyray model EOX3600B).

Statistical analysis: In this study, Central Composite Design (CCD) of Response Surface Methodology (RSM) in Design Expert 7.0.0 was used to quantify the correlation between the output variable (heavy metal uptake) and input variables, that is adsorbent preparation process variables (calcination temperature, calcination time and mixing proportion of eggshell to anthill). This experimental design was done at three levels in order to estimate the optimum preparation conditions of mixed anthill-eggshell adsorbent[18]. The fitness of the developed models were evaluated by analysis of variance (ANOVA-Type III)[3], with an assumption that the probability level ($p<0.05$) indicates significant model term.

RESULTS AND DISCUSSIONS

Development of model equation: The entire design matrix with corresponding values of the responses obtained from experimental studies is presented in Table 2. As recommended by the design expert software, the quadratic model was adopted for the three responses and used to develop correlation between composite anthill-eggshell adsorbent to the metal ions uptake. The final mathematical models in terms of coded factors for the Cu(II) ion uptake, (Y_1) and Zn(II) ion uptake, (Y_2) are depicted in Eq. 3 and 4, respectively:

Table 2: Experimental design matrix and responses

	CAE preparation variables			Experimental responses	
Adsorbent code	Calcination temperature, x_1 (°C)	Calcination time, x_2 (h)	Mixing ratio of eggshell to anthill, x_3	Cu(II) uptake, Y_1 (%)	Zn(II) uptake, Y_2 (%)
	-1	-1	-1	96.00	63.00
CAE01	-1	-1	-1	96.00	63.00
CAE02	+1	-1	-1	61.78	94.86
CAE03	-1	+1	-1	96.00	87.89
CAE04	+1	+1	-1	98.51	85.31
CAE05	-1	-1	+1	99.76	73.46
CAE06	+1	-1	+1	83.43	100.00
CAE07	-1	+1	+1	93.94	95.20
CAE08	+1	+1	+1	99.98	93.40
CAE09	-2	0	0	96.69	62.71
CAE10	+2	0	0	84.77	86.83
CAE11	0	-2	0	99.60	96.71
CAE12	0	+2	0	97.97	94.46
CAE13	0	0	-2	87.49	94.43
CAE14	0	0	+2	97.29	100.00
CAE15	0	0	0	99.29	95.20
CAE16	0	0	0	98.20	98.40
CAE17	0	0	0	90.83	100.00
CAE18	0	0	0	98.71	98.60
CAE19	0	0	0	88.31	99.17
CAE20	0	0	0	99.14	92.94

$$Y_1 = 96.0 - 5.03x_1 + 3.95x_2 + 3.29x_3 + 7.39x_1x_2 + 2.68x_1x_3 - 3.25x_2x_3 - 3.39x_1^2 + 1.26x_2^2 - 2.43x_3^2 \quad (3)$$

$$Y_2 = 96.80 + 7.48x_1 + 2.40x_2 + 3.34x_3 - 7.85x_1x_2 - 0.57x_1x_3 - 0.025x_2x_3 - 11.91x_1^2 + 0.11x_2^2 + 1.05x_3^2 \quad (4)$$

The authenticity of the developed models was examined based on their correlation coefficients (R^2) and values of standard deviations. As it is widely reported, the experimental response is assumed to be well predicted by the model, when the values of correlation coefficient and standard deviation are closer to unity and smaller, respectively[3]. In this current study, the values of R^2 for the model Eq. 3 and 4 were obtained to be 0.8386 and 0.9467, respectively. This implies that only 83.86% and 94.67% of the entire variation in the Cu(II) and Zn(II) ions uptake, respectively are attributed to the independent variables considered. However, the value of R^2 obtained for Eq. 3 was not as closed to unity compared to other one, but, it could still be considered as appropriate for the validation of the Cu(II) ion uptake model fitness. Meanwhile, the value of R^2 for Eq. 4 was considered relatively high, because it is closer to one. Thus, this implies that the experimental response agreed reasonably well with the predicted Zn(II) ion uptake from its model. The values of standard deviation for Eq. 3 and 4 were obtained to be 5.03 and 3.64, respectively. Amongst these values, the standard deviation for Eq. 4 is the smallest, which indicates that the predicted values for Zn(II) ion uptake are more accurate and also similar to actual response in terms of values. However, the standard deviation for Eq. 3 is larger compared to that of Eq. 4. This observation could possibly be that there are other preparation variables that influence adsorption of Cu(II) ion onto CAE adsorbent other than those considered for this current study. This calls for further research in order to identity other variables that affect CAE preparation process.

Furthermore, the fitness of the models were thorougly explained by analysis of variance (ANOVA-Type III). The ANOVA for Cu(II) and Zn(II) ions uptakes are presented in Table 3 and 4, respectively. As contained in Table 3 and 4, the model F-values for the Cu(II) and Zn(II) ions uptakes were found to be 5.77 and 19.74, respectively, which indicated that the two models were significant. According to ANOVA, values of $p<0.05$ indicate model terms were significant. However, the significant terms in the case of Cu(II) ion uptake were x_1, x_2 and x_1x_2 whereas x_1, x_2, x_3, x_1x_2 and x_1^2 were significant model terms in the case of Zn(II) ion uptake.

However, from the established statistical results, it can be observed that those two models were appropriate to predict the two responses (Cu(II) and Zn(II) ions uptakes) within the range of parameters considered in this study. Figure 1a and b depicted the graphs of the predicted values against the experimental values for Cu(II) and Zn(II) ions uptakes, respectively.

Table 3: Analysis of variance (ANOVA) ANOVA-Type III for response surface quadratic model for Cu(II) ion uptake

Source	Sum of squares	Degree of freedom	Mean square	F-value	Prob>F
Model	1315.77	9	146.20	5.77	0.0057
x_1	290.29	1	290.29	11.46	0.0069
x_2	179.12	1	179.12	7.07	0.0239
x_3	124.09	1	124.09	4.90	0.0512
x_1x_2	436.60	1	436.60	17.24	0.0020
x_1x_3	57.35	1	57.35	2.27	0.1632
x_2x_3	84.50	1	84.50	3.34	0.0977
x_1^2	80.14	1	80.14	3.17	0.1056
x_2^2	11.05	1	11.05	0.44	0.5238
x_3^2	41.25	1	41.25	1.63	0.2307
Residual	253.19	10	25.32	-	-

Table 4: Analysis of variance (ANOVA) ANOVA-Type III for response surface quadratic model for Zn(II) ion uptake

Source	Sum of squares	Degree of freedom	Mean square	F-value	Prob>F
Model	2354.46	9	261.61	19.74	<0.0001
x_1	641.60	1	641.60	48.42	<0.0001
x_2	66.06	1	66.06	4.99	0.0496
x_3	128.16	1	128.16	9.67	0.0111
x_1x_2	492.67	1	492.67	37.18	0.0001
x_1x_3	2.58	1	2.58	0.19	0.6686
x_2x_3	5.000E-003	1	5.000E-003	3.773E-004	0.9849
x_1^2	988.68	1	988.68	74.62	<0.0001
x_2^2	0.078	1	0.078	5.872E-003	0.9404
x_3^2	7.63	1	7.63	0.58	0.4653
Residual	132.50	10	13.25	-	-

In both cases, it was revealed that the predicted response values agreed reasonably well with the corresponding actual values within the range of the operating parameters. However, Fig. 1b revealed that the predicted Zn(II) ion uptake values were nearly close to actual values, indicating that the relationship between the CAE preparation variables and Zn(II) ion was best described by the model developed. Meanwhile, Fig. 1a displayed that the model developed did not capture the correlation between independent variables to the Cu (II) ion uptake. This is because some of the values of predicted response are inaccurate. This was the reason why correlation coefficient (R^2) is low, as earlier explained.

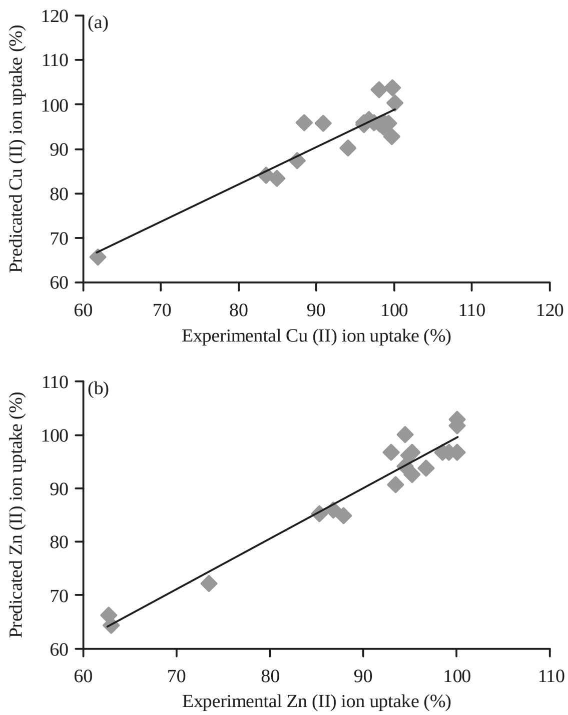

Fig. 1(a-b): Predicted vs. experimental (a) Cu (II) and (b) Zn(II) ion uptake (%)

Copper (II) ion uptake: As contained in Table 3, among the three preparation variables considered, only calcination temperature (x_1) and calcination time (x_2) exhibited the highest F-values of 17.46 and 7.07, respectively. This implies that they are the most influential factors on the Cu(II) ion uptake for the as-synthesized CAE adsorbent whereas mixing ratio of anthill-eggshell (x_3) showed no significant on the experimental response. Meanwhile, only the quadratic effect of calcination temperature on the Cu(II) ion uptake was significant. Figure 2 depicted the 3D surface graph of the interaction effect of the calcination temperature (x_1 and calcination time (x_2) on the Cu (II) ions uptake (Y_1).

For the construction of the plot depicted in Fig. 2, the mixing ratio of anthill to eggshell was fixed at center point (x_3 = 3.00). As shown in Fig. 3, the Cu(II) ion uptake (Y_1) increases as calcination temperature (x_1) and calcination time (x_2) increase. It could be deduced from Fig. 3 that to obtain 95.6% maximum Cu(II) ions uptake, the composite anthill-eggshell adsorbent will be thermally treated at 800°C for 4 h. The results obtained herein indicate that mixing proportion of eggshell to anthill has no significant effect on adsorption capacity and textural/morphological property of CAE adsorbent. However, thermal treatment of this composite

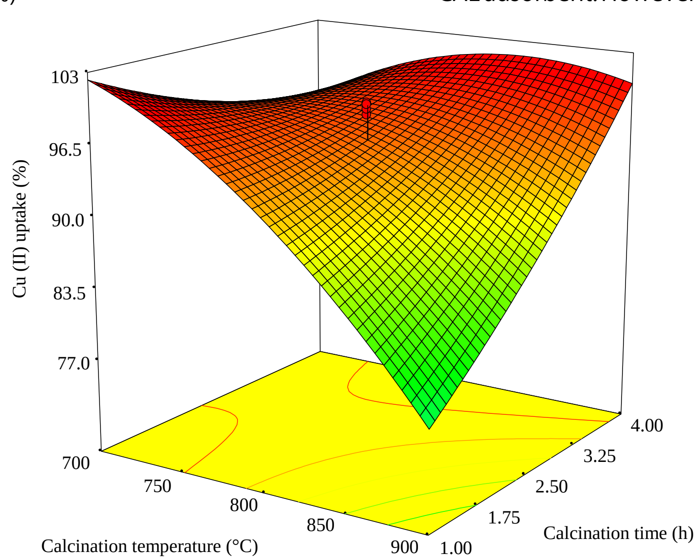

Fig. 2: Three-dimensional response surface plot of Cu (II) ions uptake (effect of calcination temperature and time)

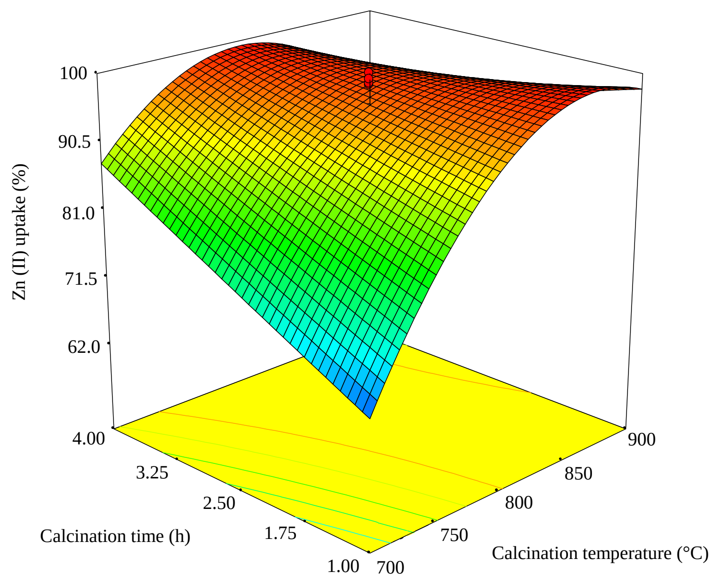

Fig. 3: Three-dimensional response surface plot of Zn (II) ions uptake (effect of calcination temperature and time)

adsorbent brought change to its chemical composition, functional groups and pore characteristics. A similar observation has been reported by Tan *et al*.[3] in the optimization of preparation of activated carbon derived from coconut husk. Calcination of raw adsorbent at elevated temperature and time resulted in complete removal of adsorbed gases and creates cavities on its surface which pave way for the adsorption of adsorbates. This is corroborated by the XRF and SEM analyses.

Zinc (II) ion uptake: In this case, the three preparation variables were found to have significant effect on zinc (II) ion uptake. However, calcination temperature has greatest effect on it, because it has the highest F-value of 48.42, compared to other two variables. Moreover, the quadratic effect of calcination temperature (x_1) on zinc (II) ion uptake was relatively large compared to those of calcination time (x_2) and mixing ratio of eggshell to anthill (x_3). Only the combined effect of calcination temperature and time on the response was significant. Figure 3 shows the 3-dimesnsional response surface of zinc (II) ions uptake which was plotted to express the combined effect of calcination temperature and time on the response. For this plot, mixing ratio of anthill to eggshell was held constant at 3.00 (center point). As seen in Fig. 3, the zinc (II) ions uptake increases with increase in calcination temperature and time.

The results obtained in this present study agreed with most of the works reported previously[3,6,31]. Generally, thermal treatment of solid materials at an elevated temperature and prolong time completely eliminates moisture content, organic contents and adsorbed gases, resulting in solid rearrangement and creation of pores on the material surface. Higher adsorption capacity exhibited by CAE adsorbent is attributed to the fact an elevated temperature and longer time were adopted, which resulted in opening and enlargement of the pores. This is corroborated by the SEM analysis and is attributed to why thermally treated CAE exhibited better performance in adsorption of heavy metals. A similar observation has been reported by Chowdhury *et al*.[6] in the removal of heavy metals onto kenaf fiber based activated carbon where the calcination of the adsorbent at different temperatures and times provided higher heavy metals uptake for samples treated at elevated temperatures[6]. The high adsorption capacity exhibited by CAE adsorbent was also attributed to the presence of active ingredients which include CaO from eggshell[1,18] and SiO_2, Fe_2O_3 as well as Al_2O_3 from anthill clay[2,32]. This is in accordance with XRF analysis.

Process variables optimization: The composite anthill-eggshell (CAE) adsorbent was prepared under the experimental conditions given in Table 5, which includes the predicted and experimental values for both Cu(II) (Y_1) and Zn(II) (Y_2) ions uptakes.

The optimum adsorbent preparation condition was obtained as: 863.78°C calcination temperature, 4 h calcination time and 1.86 mixing ratio of eggshell to anthill, which led to 97.89% of Cu(II) ion uptake and 99.34% of Zn(II) ion uptake. It was found that the experimental values obtained were closed

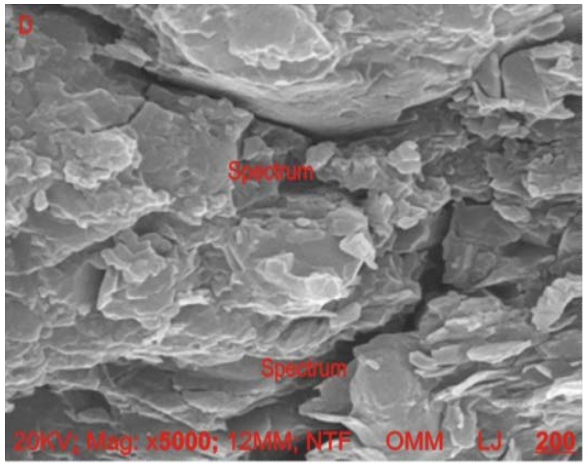

Fig. 4: SEM image of composite CAE adsorbent prepared under optimum conditions

Table 5: Central composite design predicted and experimental values for the responses

	Predicted values (model)		Experimental values	
Process parameters	Y_1 (%)	Y_2 (%)	Y_1 (%)	Y_2 (%)
x_1 (863.78°C)	96.63	97.28	97.89	99.34
x_2 (4.00 h)				
x_3 (1.86)				

x_1: Calcination temperature, x_2: Calcination time, x_3: Mixing ratio of eggshell to anthill

to those values predicted by the models, with relatively slight errors between the predicted and the experimental values, which was estimated as 1.29 and 2.07% for Cu(II) and Zn(II) ions respectively. The performance of the self-synthesized CAE adsorbent for the removal of Copper and Zinc ions was quite satisfactory, with the maximum percentage uptake closed to 100%, for Cu(II) and Zn(II) solutions concentration of 350 mg L^{-1} each. As reflected in literature, Chowdhury *et al.*[6] reported that only 96.54% of Cu(II) ion could be removed by kenaf fiber based activated carbon. Elham *et al.*[33] in their own study found that 70% of Zn (II) ions contained in industrial wastewater could only be adsorbed onto thermally treated rice husk. This implies that the composite CAE adsorbent developed in this study was effective to be employed to remove heavy metals from stock solution, with Cu(II) and Zn(II) ions nearly removed completely. The process/method adopted to develop CAE adsorbent was considered to be cost effective and practicable as both anthill and waste chicken eggshell were available in abundance, yet effective composite adsorbent with high adsorption capacity was able to be derived from their combinations.

Characterization of CAE adsorbent prepared under optimum conditions: The SEM image of CAE adsorbent prepared under optimum conditions (863.78°C calcination temperature, 4 h calcination time and 1.86 mixing ratio of eggshell to anthill) is shown in Fig. 4. From the SEM image, wide cavities were clearly observed on the surface of the adsorbent. This observation is attributed to the calcination process, which eliminates the adsorbed gases that occupy and fill up the available pores for adsorption[34] and also, transform the composite material into active mixed metal oxides as confirmed by XRF analysis. However, this is attributed to why thermally treated CAE adsorbent exhibited better performance in adsorption process.

The displayed bands of FTIR spectra obtained for both raw and calcined adsorbent prepared under the optimum conditions are presented in Table 6. Table 6 shows that after calcination, some of the peaks in raw adsorbent varnished or shifted and also, new peaks were formed. These observations implied that transformation had occurred after thermal treatment of the raw adsorbent and also, indicated that the functional groups present on the surface of the optimal CAE adsorbent were actively involved in adsorption process.

Table 7 depicts the composition of raw and activated composite anthill-eggshell adsorbents. As can be seen from the XRF analysis, the content of CaO increased after calcination. This is attributed to liberation of CO_2 from $CaCO_3$ contained in chicken eggshell at an elevated temperature. This observation agreed with the result reported by Eletta *et al.*[18]

Table 6: FTIR of CAE adsorbent

IR band	Wavenumber (cm^{-1}) Raw CAE	Calcined CAE	Assignment/Vibration mode
1	3695.73; 3620.51	3643.65	Bonded O-H stretching
2	2980.12	-	Asymmetric stretching of the C-H bonds
3	2874.03	-	C-H symmetric stretching
4	2515.26	2513.33	C-H bonds in the methylene groups
5	1799.65	1799.65	C=O stretching of aldehydes
6	1622.19	1614.47	C=O stretching
7	1423.51	1417.73	C-O asymmetric stretching
8	1105.25	1087.89	Si-O-Si stretching
9	1031.95	1055.10	Al-Al-OH vibration of anthill clay
10	1008.80	-	C-O stretching
11	912.36	-	C-H out-of- plane bend of alkenes
12	875.71	875.71	C-O out- of- plane bending
13	711.76	713.69	C-O in- plane bending
14	538.16	-	Al-OH stretching
15	468.72	-	Si-O-Al vibration of anthill clay
16	-	412.78	CaO vibration mode

Table 7: XRF analysis result for the raw and calcined CAE

Material	Conditions	Chemical composition (wt%) Al_2O_3	SiO_2	P_2O_5	SO_3	K_2O	CaO	F_2O_3	MgO	Others
Raw	Oven dried at 125°C, 2 h	5.01	13.21	0.52	1.00	0.02	77.68	2.63	0.12	2.44
Calcined	Activated at 863.78°C, 4 h	1.62	4.83	0.49	0.76	-	86.57	2.45	0.14	3.13

The result also showed that the adsorbent contained F_2O_3, SiO_2 and Al_2O_3 and according to Fisli *et al.*[32], SiO_2 is an inorganic adsorbent and its presence in CAE enhances adsorption process. Moreover, the existence of SiO_2 layer with Fe_2O_3 serves as the adsorption site in the composite anthill-eggshell adsorbent[32]. Thus, it can be concluded that the close interaction among all these metal oxides is attributed to why thermally treated composite anthill-eggshell exhibited high adsorption capacity in the removal of heavy metals.

CONCLUSION

In this present study, Composite Anthill Eggshell (CAE) adsorbent was successfully developed from locally source waste and naturally occurring materials. The preparation process variables of the adsorbent were optimized by using Central Composite Design (CCD) and their effects on heavy metals adsorption were investigated. The obtained data showed that at 863.78°C calcination temperature, 4 h calcination time and eggshell/anthill mixing ratio of 1.86, the percentages of Cu(II) and Zn(II) ions removed from aqueous solution by optimal CAE adsorbent were 97.89 and 99.34% respectively. The results of SEM, FTIR and XRF analyses revealed that CAE adsorbent was porous, possessed active functional groups on its surface and made up of active mixed metal oxides with close interaction.

SIGNIFICANCE STATEMENT

This study discovers the possible interaction among the metal oxides contained in mixed anthill-eggshell that can be beneficial for water/wastewater treatment. This study will help the researcher to uncover the usefulness of anthill which has not been explored in wastewater treatment process. Thus, a new theory on the development and characterization of mixed anthill-chicken eggshell as a composite adsorbent for water/wastewater treatment may be achieved and documented.

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