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FOREWORD

Compliment of the season to all our contributors, well-wishers and world of Academia in general. I respectfully appreciate and welcome you all to the volume 3 issue 2 of Federal Polytechnic – Journal of Pure and Applied Sciences (FEPI-JOPAS) which is a peer reviewed multi-disciplinary accredited Journal of International repute. It is imperative to re-affirm that FEPI-JOPAS publishes full length research work, short communications, critical reviews and other review articles. In this issue, readers will find a series of manuscripts of top-rated significance in pure and applied sciences, engineering and built environment. This issue is the last of its kind for 2021 calendar year which features findings from basic and applied researches of high societal impacts from the seasoned authors. These articles have been reviewed and packaged for wider readership through the collective efforts of our managing editor, publishing editors, our valuable reviewers and editorial board members.

In this particular issue, you will find that Ilelaboye and Jesusina evaluated the quality of biscuits and chin-chin made from okara enriched plantain-sorghum flour blends. Ojo and Ebisin utlilized convolutional neural network for gender classification through facial analysis. Omotayo and Fafioye investigated antimalarial potential of ethyl acetate fraction of Phyllanthus niruri while Olubodun and Adetona examined landscaping as a strategy for combating air pollution in Lagos megacity. Buoye and Ojuawo provided imperative dataset on Covid-19 crisis management in Nigeria and Brazil. Obun-Andy and Banjo investigated effective communication as a tool for good governance in Nigeria. Yusuff and co-workers conducted a field survey on fish hatcheries in Yewa South and Yewa North Local Government of Ogun State. Akinlade and co-workers meticulously expatiated on the effect of aqueous blend of three herbs on haemato-biochemical indices of broiler chicken at starter phase. Ajeigbe, Sangosina, Ogunseitan, Lawal, & Yusuff analysed the Effects of Neem Leaves (Azadirachta Indica) and Cassava Peels on the Performance of West African Dware Goat. Abdussalam & Adewole in their paper carefully explained the Formulation of Natural Products Repellents for the Control of Cockroaches (Periplaneta americana). Elesin & Obafunmiso gave as Assessment of Public Toilets Facilities Provision and Management in Tertiary Institutions in Nigeria- An Overview of The Federal Polytechnic, Ilaro, Ogun State. Ajayi and Adegbola Removal of Pb^{2+} And Zn^{2+} ^{f}rom Aqueous Solution using Eggshell Powder as Adsorbent: Kinetics and Equilibrium Studies

I would like to deeply appreciate and extend my profound gratitude to my co-editors, editorial board members, reviewers, members of FEPI-JOPAS, especially the Managing Editor, as well as all the contributing authors for making the production and publishing of this volume 3 issue 2 a reality. I will like to appreciate the authors in this issue for allowing their works to be subjected to our thorough and rigorous peer-review processes and for taking all the constructive criticism in good fate. The authors are solely responsible for the information, date and authenticity of data provided in their articles submitted for publication in the Federal Polytechnic Ilaro – Journal of Pure and Applied Sciences (FEPI-JOPAS). I am looking forward to receiving your manuscripts for the subsequent publications.

You can visit our website (https://fepi-jopas.federalpolyilaro.edu.ng) for more information, or contact us via e-mail us at fepi.jopas@federalpolyilaro.edu.ng.

Thank you and best regards.

Prof. Olayinka O. AJANI

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Removal of Pb^{2+} And Zn^{2+} from Aqueous Solution using Eggshell Powder as Adsorbent: Kinetics and Equilibrium Studies

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Abstract
Pollution caused by human activity is a growing concern in today's world. Several contaminants from various companies are emitted into the environment. Heavy metals are non-biodegradable, poisonous, and persistent pollutants that have negative impacts on the ecological niche of all life forms, including humans. Therefore, the objective of this study was to use locally produced chicken eggshell powder to remove metal ions (Pb^{2+} and Zn^{2+}) from aqueous solutions using an adsorption technique. The sorption process is influenced by pH, contact time, initial metal ion concentration, and sorbent dose. The pH of 7.0 and contact time of 60 minutes is ideal for the uptake of metal ions. Pseudo-first order and pseudo-second order rate measures were utilized to examine the adsorption kinetics. Langmuir and Freundlich models were employed for the adsorption isotherm study. Equilibrium adsorption data of Pb^{2+} and Zn^{2+} followed the Langmuir and Freundlich isotherms with R^2 of 0.834 and 0.993 respectively. The kinetics data revealed pseudo-second order rate model to best describe the reaction while Freundlich isotherm model was a better model that best fit for Pb^{2+} and Zn^{2+} adsorption onto eggshells adsorbent. In conclusion, chicken eggshell powder may be employed as alternative, low cost and effective local adsorbent for Pb^{2+} and Zn^{2+} removal from aqueous solution.

Key words: Metal ion; Adsorption; Eggshell powder; Kinetics; Equilibrium

INTRODUCTION

Frequent discharge of heavy metal-containing wastes from agrochemicals such as herbicides and pesticides, as well as industrial activities such as mining, oil refining, pigments, and smelting, has resulted in a slew of environmental issues. The existence of heavy metals in the environment has potential health risks for humans and plants (Volesky, 2000; Garbisu & Alkorta, 2003). Lead is one of the most poisonous heavy metals that induce environmental pollution. Lead pollution comes from the coating of metals, pigments, the ceramic and glass industries, textile dyeing, refining and finishing of petroleum (Volesky, 2000; Aksu, 1998). In low concentrations, lead can cause a variety of adverse effects, including impaired behavior, damage to the nervous system, and even increased blood sugar. Lead is stored mainly in muscles, bones, the brain, and kidneys. Increased lead concentration can cause many serious illnesses, including gastrointestinal damage, anemia, liver disease, neurological disorders, and death (Lo et al., 1999). Zinc is one of the most abundant elements in the Earth's crust. In regions where zinc is naturally present or mined, it can easily contaminate the soil and water. When consumed in excess, whether willingly through supplements or involuntarily from contact with contaminated soil or water, zinc can result in serious health crises such as anemia, nausea, and stomach cramps. A high level of zinc can harm the pancreas, disrupt protein metabolism, and lead to arteriosclerosis. Chemical oxidation or reduction, electrochemical treatment, ion exchange, coagulation and precipitation, evaporation, membrane separation and electroplating adsorption are the traditional techniques of removing lead and zinc from aqueous solutions and industrial wastewater. However, these techniques have different drawbacks, such as toxic waste generation, being expensive to maintain, producing large quantities of secondary pollutants, sludge, high reagent and energy requirements, and are not always effective for low concentrations of metals (Pan, Cao, & Zhang, 2009). The most effective classical method is activated carbon adsorption, but it's production cost is extremely expensive and it cannot be regenerated (Farooq et al., 2010). Hence, it is essential to discover inexpensive and environmentally friendly methods to remove heavy metals from the environment (Juwarkar, Singh, & Mudhoo, 2010; Sahan et al., 2010). Adsorption is a process that uses agricultural materials as adsorbents to remove toxic heavy metals from aqueous solutions. Adsorption is among the most promising alternative strategies for the lessening of heavy metal ions, because it provides many benefits, such as the possibility of biosorbent regeneration and metal recovery, high metal binding capacity, low cost, environmentally friendly and more traditional efficient treatment wastewater dilution method. Hence, this study aims to determine the capacity of chicken eggshell powder as an alternative biomass for the removal of Pb^{2+} and Zn^{2+} ions in aqueous solution.

Sorbent Preparation

Chicken eggshells were obtained from Eleshin Poultry Farm in Ilaro. The eggshells were rinsed with tap water followed by distilled water two times each. Thereafter, the samples were dried under the sun for about six days and then in the oven at 80ºC for three hours. The dried eggshells were sieved after being grounded through a 100 micrometre sieve and stored in desiccators before use.

Reagents and Metal ions Solutions Preparation

All of the chemicals used in this study were analytical grade. The reagents used include $Pb(NO_3)_2$, HNO_3, NaOH and $ZnSO_4$. $Pb(NO_3)_2$ and $ZnSO_4$ were used to make stock solutions of the standardized Pb^{2+} and Zn^{2+} ions of 2.5 mg L^{-1} each. HNO_3 and NaOH (1 mol/L each) were prepared by sufficient dilution of concentrated HNO_3 and sufficient weighing of NaOH pellets, respectively.

Effect of pH

The pH of 2.5 mg L^{-1} metal ions solutions was adjusted with 1 $molL^{-1}$ HNO_3 and NaOH solution, which resulted in metal ions standards with pH ranging from 3 to 8. A considerable amount (2.0 g) of eggshell was slowly stirred for 60 minutes at 35ºC in a rotary shaker with 30 ml of each of the metal ion solutions. Previous research had shown that biosorption reached equilibrium within 60 minutes (Ayodele and Godswill, 2014). Before performing Atomic Absorption Spectrophotometry (AAS) measurements, samples were instantly filtered using 0.45 µm filter paper paper.

Effect of Contact Time

At room temperature, contact time impact was conducted in a rotary shaker containing 30 ml of stock solutions with 2g of the adsorbent using 250 ml Erlenmeyer flasks at 180 rpm. The contact time effect was studied between 15 - 105 minutes. The metal ion quantity in the filtrate was determined using AAS after filtering the adsorbent with 0.45 m filter paper. The equilibrium adsorption time was determined from the plot of adsorption capacity against time. The adsorption capacity, qe (mg/g) at equilibrium, is calculated using Equation (1), while the percentage of Pb^{2+} and Zn^{2+} ions uptake is calculated using Equation (2).

$$qe=(Co-Ce)\frac{V}{W} \qquad (1)$$

$$\%\,of\ metal\,ion\,uptake=\frac{Co-Ce}{Co}\times 100 \qquad (2)$$

Effect of Sorbent Dosage

A rotary shaker was used to stir precisely weighed volumes of eggshell varying from 0.5 g to 3 g with 30 ml of metal ion solutions at pH 7 for 1 hour. The mixture were then filtered through a Whatman filter paper. The concentrations of metal ions in the filtrates were determined.

Effect of Metal ion Concentration

Metal ion standards in the range of 2.5 to 15 mg L^{-1} were made. On a mechanical shaker, a measured quantity (2.0 g) of eggshell was stirred for 60 minutes at pH 7 with 30 ml of each set of metal ion standards. The compositions were filtered after 60 minutes of stirring at room temperature. The concentrations of metal ions in the filtrates were determined

RESULT AND DISCUSSION

Effect of pH

According to Ofomaja and Ho (2007), pH influences heavy metal ion dissociation, hydrolysis, complexation, precipitation, and other processes in an aqueous solution. Furthermore, pH has an influence on the availability and speciation of ions, which has a direct impact on sorption of metal ions from aqueous solutions. Figure 1 depicts the influence of pH on adsorption capability of eggshell for Pb^{2+} and Zn^{2+} ions. When the pH was increase from 3 to 7, the sorption of Pb^{2+} and Zn^{2+} by eggshell increases. Sorption rates were substantially higher at pH 7 than at other pH standards. The sorption effectiveness does not improve substantially beyond pH 7.

Similar results have been reported in the literature for a variety of sorbent systems (Ajaykumar, et al 2009; Sharma 2007). This means that when analyzing adsorption kinetics and equilibrium, adsorption at pH 7 is preferred. The ion-exchange mechanism, in which carbonate groups with cation-exchange properties play an important role in the effect of pH on metal ion sorption (Chojnacka, 2005). Pb^{2+} and Zn^{2+} sorption were reduced at lower pH because of competition between hydrogen and metal ions on sorption sites. More carbonate groups are linked with hydrogen at lower pH, leaving fewer carbonate groups available to metal ions.

The surface charge of eggshell is also affected by pH. Positively charged sites occur on the surface of eggshells under acidic conditions, causing metal ions to be poorly adsorbed on or repelled by it (Wang, Chen, Huang, & Cao, 2010).When the pH of a solution approaches 7, additional carbonate groups in the eggshell appear to have access to metal ions, which should allow them to better engage with binding sites of negatively charge. As a result, the optimum pH of 7 was chosen in further sorption tests.

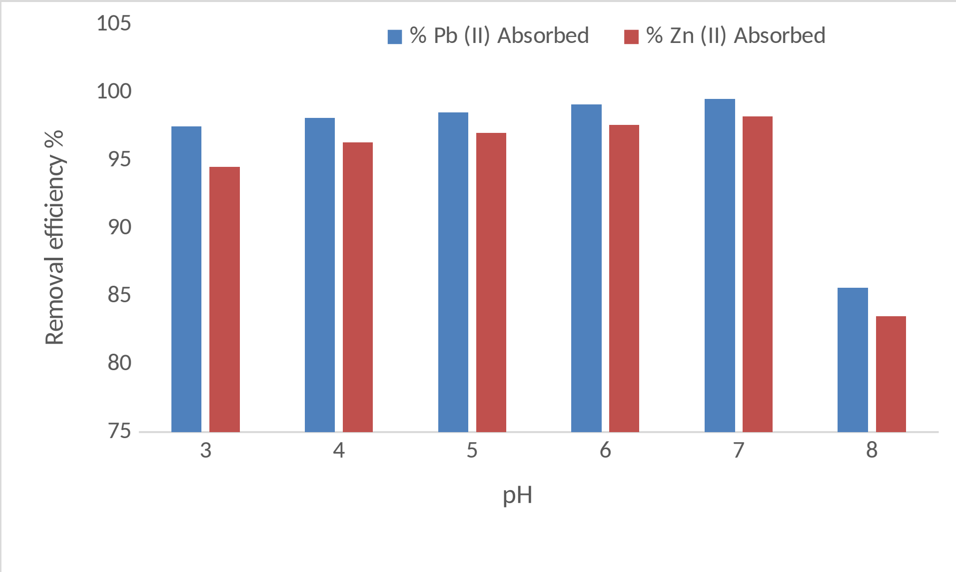

Figure 1 **Contact Time Effect**

The adsorption rate is crucial for designing batch adsorption studies. The influence of contact time was determined by adjusting the absorption of metal ions in the model solution within 105 minutes at room temperature. For these two metals, the percentage of metal absorption reached a maximum within 60 minutes (Figure 2). Thereafter, no substantial changes took place in the uptake efficiency of metal ions by the adsorbent after 1 hour. The short contact time determines the ability of the eggshell biomass as an ideal biosorbent to rapidly remove heavy metals from aqueous solution.

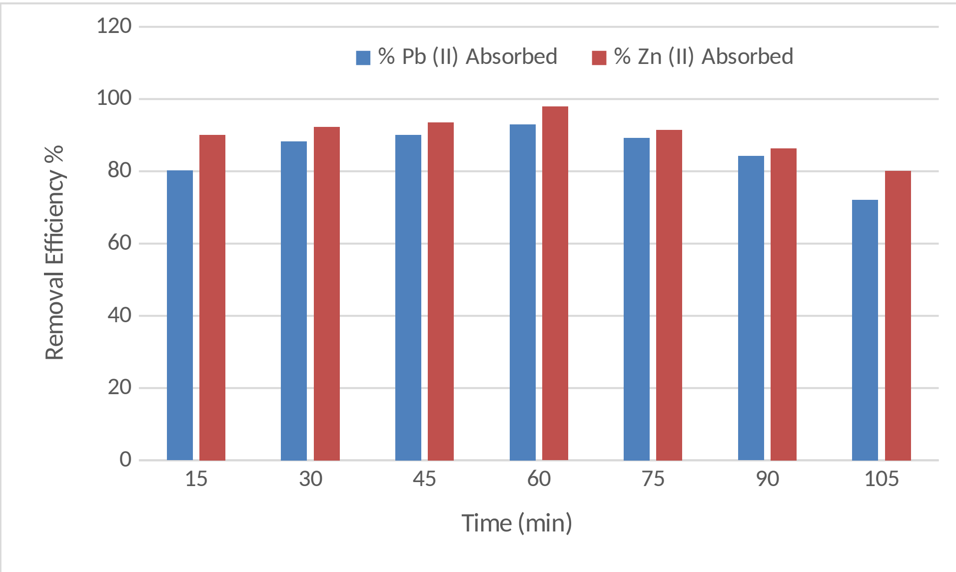

Figure 2. **Effect of Sorbent Dosage**

Figure 3 reveals a chart of the removal efficiency of metal ions against the adsorbent dosage used. At a preliminary metal ion concentration of 2.5 mg L^{-1}, the amount of metal uptake increases as the amount of eggshell increases from 0.5 g to 2.5 g. It means that the removal of Pb^{2+} increases from 93.1% to 99.2%, and the removal of Zn^{2+} increases from 81.6% to 96.8%. Because of the increased number of binding sites for the ions and sorbent surface region, these rises in the removal efficiency are noticeable. The available metal ions appear to be adequate to enclose all the substitutable sites on the eggshell at an enormous sorbent dosage, resulting in significant metal ion absorption (Ayodele and Godswill, 2014)

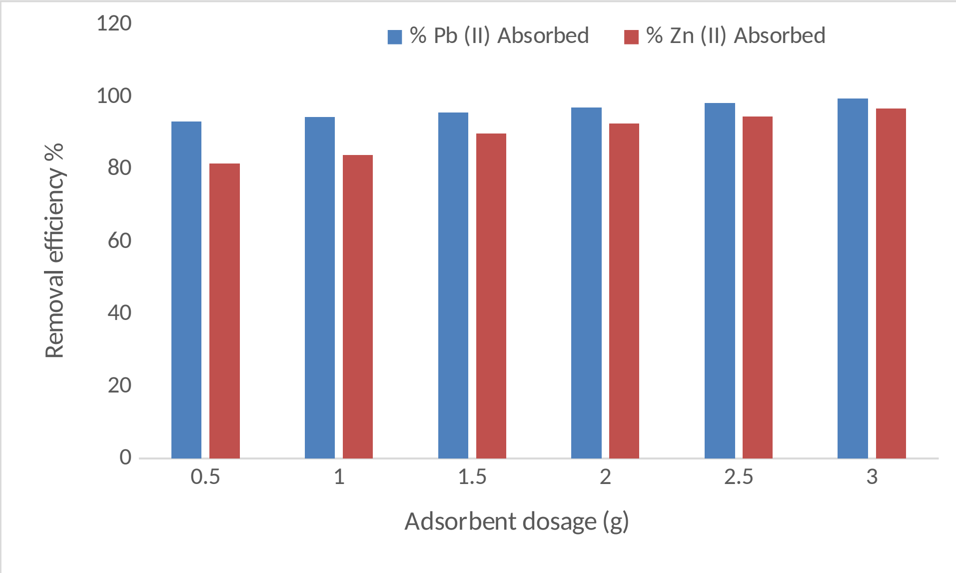

Figure 3: **Impact of Metal ion Concentration**

Metal ion concentration works as a powerful force that overcomes all barriers to metal ion mass transfer among the solid and liquid phases (Aksu & Akpinar, 2000). As the metal ion concentration increased from 2.5 to 15 mg L^{-1}, the metal uptake rate for Pb^{2+} decreased from 97.9% to 95.5% and for Zn^{2+} from 98.5% to 96.4% (Figure 4). All metal ions in solution interacted mostly with the active site at lower metal ion concentrations. Lower metal ion concentrations contributed to higher percentage adsorption as a result. Low percentage sorption at higher metal ion concentrations is due to clustering of the surface of the adsorbent (Ayodeji and Godswill, 2014). The overall surface area of the eggshell particles available for sorption reduces as a direct consequence of clustering, but the diffusion channel length rises (Yasemin & Tez, 2007). This discovery is consistent with the findings of Rao et al. and Chojnacka. Similar findings were also reported when sugar cane bagasse pith and wild cocoyam were employed as adsorbents (AjayKumar et al., 2009).

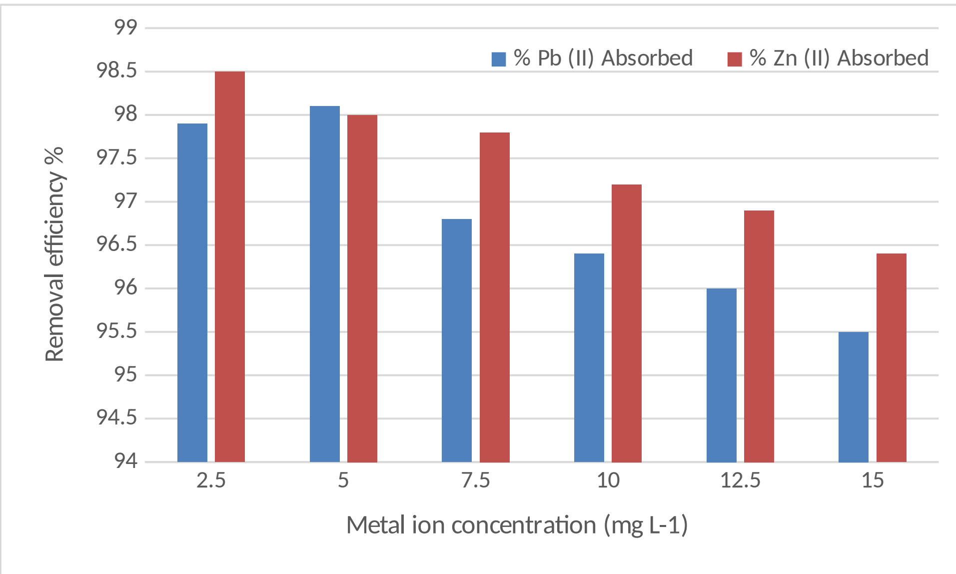

Figure 4: **Isotherm Studies**

Adsorption isotherms are essential in optimizing the usage of adsorbents for the removal of pollutants from aqueous solutions because they describe how pollutant concentrations interact with adsorbent surfaces (Emmanuel and Rao, 2008). The Langmuir and Freundlich adsorption isotherm model were used to facilitate the estimation of adsorption potentials of the eggshells. The linear form of these two models is stated as:

$$\frac{Ce}{qe} = \frac{1}{QzKb} + \frac{Ce}{Qz}, \tag{2}$$

$$\log(qe) = \log(Kf) + \frac{1}{n}\log(Ce) \tag{3}$$

where K_b is Langmuir constant defining affinity of binding regions and adsorption energy (mgL^{-1}), n is a constant which provides information on heterogeneity level, Q_z is adsorbent maximum monolayer capacity of adsorption (mgg^{-1}), K_F is Freundlich constant describe sorption capacity (g^{-1}) (mgL^{-1}).

Langmuir Isotherm

The regression coefficient (R^2) varying from 0.835 to 0.994 (Table 1) of Langmuir isotherm gives a satisfactory model for the adsorption system. Adsorption power (q_m) ranging from 0.9 to 1.0 (Table1) reveals an increase in adsorption affinity for metal ions in the order of Pb^{2+} > Zn^{2+}. Metals with high electronegativity show a remarkable tendency to adsorption than metals with low electronegativity. (Lim, Kang, Kim and Ko, 2008). Taking into account that the electronegativity of the Pb^{2+} and Zn^{2+} are 2.33 and 1.91, respectively, the observed adsorption affinity of the Pb^{2+} and Zn^{2+} affected by the q_m value is inconsistent with the order of electronegativity. This means that other factors, such as the initial concentration of Pb^{2+} and Zn^{2+}, will contribute to the adsorption affinity of Pb^{2+} and Zn^{2+} to eggshell. The acceptable adsorption energy order of metals is the Zn^{2+} greater than the Pb^{2+}, as indicated by the adsorption coefficient (K_a), which is connected to the apparent adsorption energy. Due to its higher K_a value, the adsorption strength of Zn^{2+} is more favorable than that of Pb^{2+}. Furthermore, K_R value can as well be utilized to predict whether adsorption is favorable or unfavorable (Venkata, Ramanaiah rajkumar, & sarma, 2007). Since K_R is greater than 0 and less than one (0.02 to 0.03), this indicated that adsorption of the two metal ions on egg shell is favourable.

Freundlich isotherm

This isotherm show a linear connection between the plotted parameters and the charts were not contained in this article. For the equilibrium unit concentration, the general capacity of the metal ions adsorbed to the eggshell is represented by K_f and 1/n, the values of K_f and 1/n collected from the Freundlich isotherms varying from 1.17 -1.26 and 0.39 - 0.50, respectively. The K_f adsorption capacity obtained for the two metal ions indicates that Zn^{2+} is greater than Pb^{2+}. The n value in this research is between 1.99 and 2.55. Therefore, Checken eggshell powder is a productive biomass for the absorption of metal ions. The value obtained for 1/n is less than 1, indicating that significant adsorption occurs at low concentrations of metal ions. It is worth noting that as the concentration increases, the increase in the amount of metal ion adsorption becomes less remarkable at higher concentrations and vice versa (Makata, sajidu, Masambal and Mwatseteza, 2010)

Table 1: Langmuir and Freundlich Isotherm Parameters for the Metal Ions by Eggshell

	Langmuir isotherm parameters				Freundlich isotherm parameter			
	K_a	Q_m	K_R	R^2	N	1/n	K_f	R^2
Pb	6.6	1.1	0.03	0.835	1.99	0.50	1.17	0.970
Zn	27.8	0.9	0.02	0.994	2.55	0.39	1.26	0.949

Kinetics of Metal Ions Adsorption

Table 2 and 3. shows the pseudo first and pseudo second order parameters k_1, q_e (calculated) and regression coefficient (R^2). The obtained R^2 value indicates that the first-order model is not suitable for explaining the adsorption system. The experimental rate constant k_1 of Pb^{2+} is the highest. The q_e calculated for the two metal ions is significantly varied from the Q_Z in the experiment. This is what is expected, because the pseudo-level is not suitable for defining the adsorption process. This result is invariant with the view of (Rao et al., 2010), that in most circumstances, the pseudo first-order equation of the liquid\solid system does not apply to the entire contact time range, and usually applies to the first 20-30 minutes adsorption process. On the other hand, the correlation coefficient (R^2) of pseudo-second-order kinetics is between 0.999 and 1.000, and is higher than the complementary coefficient of the first-order kinetic model. Therefore, calculated q_e value using the pseudo-second-order kinetic model is approximate to the corresponding value of the q_e (experimental) in Table 2 and 3. Hence, the kinetics of metal ion adsorption is best described by a pseudo-second-order kinetic model instead of a pseudo-first-order. The magnitude of h and k_2 is that Zn^{2+} is greater than Pb^{2+}. This means that Zn^{2+} is better absorbed by eggshells than Pb^{2+} in solution, which is similar to the outcomes in the literature. (Ayodele & Godswill, 2014).

Table 2: Pseudo-First Parameters for the Adsorption Metal of Ions by Eggshells

Metals	q_e (exp) / (mg g^{-1})	q_e (cal) / (mg g^{-1})	k_1 (min^{-1})	R^2
Pb	0.1246	3.49E*10^{-5}	-0.07	0.260
Zn	0.1260	7.47E*10^{-5}	-0.08	0.439

Pseudo second-order parameters for the Adsorption Metal of Ions by Eggshells

Metals	q_e(exp) / (mg g^{-1})	h / (mg g^{-1} min)	k_2 / (mg g^{-1} min)	R^2
Pb	0.1249	0.61	34.00	0.999
Zn	0.1259	2.59	157.32	1.000

CONCLUSION

Chicken eggshell powder was found to be an effective, environmentally acceptable, and low-cost adsorbent for removing Pb^{2+} and Zn^{2+} from aqueous solutions in this investigation. pH had a significant impact on the adsorption efficacy of eggshell for the removal of heavy metals, with a pH of 7 being shown to be ideal. The adsorption of heavy metal ions by eggshell was extremely fast in the first 30 minutes, with an equilibrium lasting 60 minutes. The ability of eggshell to adsorb metal ions decreased as the initial metal ion concentrations increased. Kinetic studies have demonstrated that the pseudo-second-order rate model better describes the reaction, while the Freundlich isotherm model is a better model, which better fits the adsorption of Pb^{2+} and Zn^{2+} in Chicken egg shells powder. In short, Chicken egg shells powder can be utilized as an alternative and effective local biomass for the lessening of Pb^{2+} and Zn^{2+} from aqueous solutions.

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