Comparison of the Effectiveness of Calcined Chicken and Duck Eggshells as Zn Metal Adsorbent Using Atomic Absorption Spectrophotometric

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Abstract: Zinc is a heavy metal that is often found in liquid waste and causes water pollution. Eggshells can be used as an adsorbent to reduce heavy metals in water because they have a lot of pores, CaCO₃, and mucopolysaccharide acid protein. This study aimed to determine the effectiveness of a comparison between calcined chicken and duck eggshells to adsorb Zn, by determining the optimum pH, contact time, optimum mass, and the characterization of adsorbents. The results of this study showed that calcined chicken eggshells adsorb Zn at an optimum pH of 6, with the required optimum contact of 75 min and a mass of 400 mg with adsorption effectiveness of 99.64%. Meanwhile, calcined duck eggshells have an optimum pH of 6, an optimum contact time of 60 min, and an optimum mass of 400 mg with adsorption effectiveness of 99.73%. Activated carbon from the market has an adsorption effectiveness of 99.53%. So, it can be concluded that calcined chicken and duck eggshells can be used as zinc metal adsorbent.

Keywords: calcined chicken eggshells; calcined duck eggshells; adsorbent; zinc metal

INTRODUCTION

Heavy metal contamination in water sources has emerged as a major global environmental concern, threatening both human health and aquatic ecosystems. Industrialization, climate change, and urbanization cause heavy metal pollution in the aquatic environment to increase [1]. Heavy metals are primarily found in objects that are produced by textile manufacturing, agriculture, household sewage, metallurgy, acid manufacturing, imaging industries, and ceramics [2]. Heavy metal ions are toxic, potentially carcinogenic, and can bioaccumulate in biological systems. Heavy metals can cause harm to various organs, including the neurological system, liver, lungs, kidneys, stomach, skin, and reproductive systems, even at low exposure levels [1]. The most popular heavy metals are zinc (Zn), lead (Pb), mercury (Hg), nickel (Ni), cadmium (Cd), copper (Cu), chromium (Cr), and arsenic (As) [3].

Zn is an essential trace metal required for the growth of living beings, with it being a cofactor of major proteins, and mediating the regulation of several immunomodulatory functions. However, its essentiality

also runs parallel to its toxicity, which is induced by various anthropogenic sources, constant exposure to polluted sites, and other natural phenomena. Several symptoms caused by Zn poisoning are fever, difficulty breathing, nausea, chest pain, and coughing. Excessive levels of Zn in these sources can alter the microbial diversity of soils and waters, thereby affecting the bioavailability and uptake of other metals as well [4].

Several methods that can be used to reduce the impact of heavy metal pollution on water are coagulation, filtration, foam flotation, ion exchange, advanced oxidation processes, electrolysis, activated sludge, microbial reduction, solvent extraction, aerobic and anaerobic processing, and adsorption [5]. The adsorption method is often used to remove heavy metals from aqueous solutions because of its simplicity [6]. Adsorption is a process that describes the attachment of dissolved substances in a liquid to a porous solid surface called an adsorbent [7]. Activated carbon, silica gel, and alumina are the most common industrial adsorbents. All these adsorbents are generally expensive, especially in developing countries of the world. As a result, there is a

need to create an avenue through which locally sourced materials from our environments are being converted into effective adsorbents for removing inorganic/organic solutes contained in wastewater [7].

Waste materials obtained from different sources have been used as potential adsorbents for the removal of inorganic and organic pollutants. Eggshell and eggshell membranes are waste materials produced in large amounts in the poultry and farm industries as well as restaurants, bakeries, or homes. Approximately 10% of the total mass of hen egg corresponds to eggshell byproduct, with an average weight of 60 g, and it is usually discarded in landfills without any pre-treatment [8]. Eggshells are composed of 85–95% calcium carbonate [9], which makes them an ideal adsorbent material for the treatment of soils and water contaminated by metallic ions [10]. In addition, eggshells have 7,000-17,000 pores and the porous nature of eggshells makes the residue a potential adsorbent to be used to remove various pollutants present in aqueous solutions [11-12]. Research on the potential of calcined chicken and duck eggshells as an adsorbent for Zn metal has not been carried out, therefore, this study was conducted to evaluate the effectiveness of calcined chicken and duck eggshells on the removal of Zn heavy metals from aqueous solution.

EXPERIMENTAL SECTION

Materials

Chicken eggshell and duck eggshell waste was obtained from *martabak* trader in Bandung, West Java, Indonesia. The analytical grade of H₃PO₄ (Pudak Scientific), methylene blue solution (polylab), iodine solution (polylab), sodium thiosulfate solution (polylab), starch indicator, aquadest (IPHA), HNO₃ (Pudak Scientific), NaOH (Pudak Scientific), HCl (polylab), Zn(NO₃)₂ solution (polylab), and market activated carbon were used in this research.

Instrumentation

The tools used in this research include analytical balance, 100 mesh sieve, furnace, oven, crucible, blender, stopwatch, beaker glass, Whatman 40 filter paper, porcelain cup, vacuum Buchner, magnetic stirrer, measuring pipette, measuring flask, universal pH, pH

meter, Erlenmeyer, UV-vis spectrophotometry, atomic absorption spectrophotometry (AAS), and Zn hollow cathode lamp. The morphological analysis of the powder samples was examined using scanning electron microscopy (SEM) Hitachi SU3500 with EDAX Octane Pro

Procedure

Eggshell adsorbent preparation

The discarded chicken eggshells are collected and washed with clean water, dried in the oven, pulverized into fine particles, and sieved with the appropriate mesh sizes [13]. This process is also done on duck eggshells.

Calcination of chicken and duck eggshell

A total of 200 g of chicken eggshell and duck eggshell powder was put into a crucible and heated in a furnace for 2 h at 900 °C. The resulting calcined chicken and duck eggshell is allowed to cool. Then it was sieved with a mesh size of no. 100 [13].

Activation process of chicken eggshell and duck eggshell

Calcined chicken and duck eggshells were weighed as much as 150 g, then soaked in a solution of 4 N H_3PO_4 activator for 24 h. Furthermore, the mixed solution is filtered by filter paper and washed with distilled water until the pH was neutral (pH = 7), then dried in oven at 110 °C for 3 h and weighed to calculate the adsorbent yield [13].

Chicken eggshell characterization

Water content analysis. A total of 1.0 g calcined eggshell was placed in a porcelain dish, then dried in an oven at 105 °C until a constant mass was obtained and then cooled. Then the water content levels are calculated according to the Eq. (1).

Water content (%) =
$$\frac{\text{initial weight} - \text{final weight}}{\text{initial weight}} \times 100\%$$
 (1)

Adsorption to methylene blue. The adsorbed amount of methylene blue by active carbon was measured using a UV-vis spectrophotometer at 664 nm, the maximum absorption wavelength of methylene blue. Adsorption capacity (q_e) was measured by the Eq. (2);

$$q_e = \frac{C_0 - C_e}{M} \times V \tag{2}$$

where C_0 and C_e are initial and final concentration, V is volume of the solution in L, and M is the mass of the adsorbent used in g [11].

lodine number. A total of 1.0 g of adsorbent was put into an Erlenmeyer flask, then 25 mL of 0.125 N iodine solution was added. The solution stirred for 15 min then the Erlenmeyer was closed and stored in a dark place for 2 h. Then the solution is filtered, then the filtrate is pipetted for 5 mL and put into an Erlenmeyer flask and titrated with $Na_2S_2O_3$ solution so that the solution is light yellow. A total of 1.0 mL of the starch indicator was added to the filtrate and the titration continued until the blue color just disappeared. The titration is performed 3 times. Calculate the result obtained by the Eq. (3);

Iodine number =
$$\frac{\left(N_1 V_1 - N_2 V_2\right) \times 126.9 \times F_p}{W} \text{mg/g}$$
 (3)

where N_1 is normality of iodine (N), V_1 is volume of analyzed iodine solution (mL), N_2 is normality of sodium thiosulfate (N), V_1 is volume of analyzed sodium thiosulfate solution (mL), 126.9 is atomic weight of iodine, F_p is dilution factor, and W is sample weight.

SEM - energy dispersive spectrometry (SEM-EDS). The samples were affixed *via* carbon tape to the SEM sample holders and vacuum-coated with a 20-nm layer of platinum. SEM was performed at 15 kV and room temperature. The average pore size was calculated with image analysis software [14].

Preparation of Zn metal testing

Preparation of standard series solutions $Zn(NO_3)_2$. Standard solution of $Zn(NO_3)_2$ 10 ppm was taken 0.5, 1.0, 1.5, 2.0, and 2.5 mL and put into different 25 mL measuring flasks. Then, each solution was diluted with aquadest to the mark and homogenized to obtain a concentration of a standard series solution of Zn 0.2, 0.4,

Calibration curve creation. The blank solution (Zn 0.0 ppm) was measured for absorbance using AAS at a suitable wavelength for Zn metal, which is 213.9 nm. The treatment was replicated 3 times. The same procedure is done for the standard series solution of $Zn(NO_3)_2$ with a concentration of 0.2, 0.4, 0.6, 0.8, and 1.0 ppm. Next, a calibration curve was made to get the regression line

equation, so that the value of r is obtained which is the correlation coefficient from the curve obtained.

Method verification

Accuracy. The Zn solution that had been diluted to 0.6 ppm was taken as much as 1.5 mL and put into a 25 mL measuring flask. The solution was added with three concentration levels, namely 0.4, 0.6, and 0.8 ppm with the addition of a standard 10 ppm solution of 1.0, 1.5, and 2.0 mL then all solutions were diluted with a diluent solution to the limit mark.

The three concentration levels were measured for absorbance at the selected wavelength (Zn metal at 213.9 nm) with three replications. Accuracy can be calculated using Eq. (4);

$$\%Accuracy = \frac{A - B}{C} \times 100\% \tag{4}$$

where A = measured metal content in the sample after standard addition of Zn, B = measured metal content in the sample before standard addition of Zn, and C = concentration of a standard solution of Zn added to the sample.

Precision. The precision demonstrates the closeness of agreement between a series of measurements obtained from multiple sampling of the same homogeneous sample under the prescribed conditions and is usually measured as relative standard deviation (%RSD) [15].

The Zn solution that had been diluted to 0.6 ppm was taken as much as 1.5 mL and put into a 25 mL measuring flask. The solution was added with the addition of a standard 10 ppm solution of 1.5 mL to obtain a solution concentration of 0.6 ppm, then the solution was diluted with a diluent solution to the limit mark. Then the absorbance was measured at the selected wavelength with 7 replications. The precision parameter is determined using a formula in Eq. (5);

$$\%RSD = \frac{SD}{\overline{x}} \times 100\% \tag{5}$$

where \bar{x} is average sample content (µg/mL) and SD is standard deviation.

Metal absorption effectiveness test

Measurement of Zn(NO₃)₂ solution. Zn standard solution 10 ppm was taken as much as 10 mL and placed

0.6, 0.8, and 1.0 ppm.

into a 100 mL measuring flask, then diluted with distilled water to the limit mark to obtain a solution concentration of 1 ppm. The absorbance of the solution was measured using AAS at a suitable wavelength for Zn metal. The treatment was replicated 3 times.

Determination of optimum pH of calcined chicken eggshell and duck eggshell. A total of 100 mg of calcined chicken and duck eggshells were put into each Erlenmeyer flask and 25 mL of sample solution was added with the addition of NaOH or HCl to reach 5 pH variations, namely at pH 2, 3, 4, 5 and 6. Stir using a magnetic stirrer for 30 min at room temperature. Then filtered by microfilter, the filtrate obtained was analyzed by AAS by replicating it 3 times [16].

Determination of optimum contact time of calcined chicken and duck eggshell. A total of 100 mg of calcined chicken eggshells was put into each Erlenmeyer and 25 mL of sample solution was added with the addition of NaOH or HCl until the optimum pH was obtained. Furthermore, stirring was carried out using a magnetic stirrer at 5 variations of mixing time, namely 15, 30, 45, 60, and 75 min [16]. Then filtered by microfilter, the filtrate obtained was analyzed by AAS by replicating each time variation 3 times. This method is repeated for calcined duck eggshells.

Determination of optimum dose of calcined chicken eggshell and duck eggshell. The sample solution of Zn(NO₃)₂ 25 mL was added with calcined chicken eggshells with 5 variations of each, namely 100, 200, 300, 400, and 500 mg then the solution was adjusted to the optimum pH obtained in the previous treatment. Then stirred using a magnetic stirrer during the resulting optimum contact time. Then filtered by microfilter, the filtrate obtained was analyzed by AAS by doing 3 times replication. This method is repeated for calcined duck eggshell.

Testing of activated carbon from the market. The sample solution of $Zn(NO_3)_2$ 25 mL was added with market activated carbon with the optimum mass obtained then the solution was adjusted to pH 7. Then stirred using a magnetic stirrer during the resulting optimum contact time. Then filtered by microfilter, the filtrate was analyzed by AAS by doing 3 times replication.

Zn metal adsorption effectiveness. The contaminant removal efficiency (E_f) was calculated under each of the analyzed conditions and used as a parameter to select the work mass, as shown in Eq. (6);

Ef (%) =
$$\frac{C_i - C_f}{C_i} \times 100$$
 (6)

where C_i and C_f (mg/L) are the pollutant concentration in the beginning and end of the process, respectively [17].

RESULTS AND DISCUSSION

Eggshell Adsorbent Preparation

After going through the process of biosorbent preparation from chicken eggshells and then obtaining into powder of chicken and duck eggshells, the results can be seen in Fig. 1. The chicken and duck eggshell powder that has passed is sieved with a mesh size of no. 100 and then 200 g is weighed, then it calcined. Before the calcination of eggshell waste, the sorbent contains about 95% CaCO₃ as a major inorganic compound in it. The results obtained after the calcination proved that the main constituent from eggshell was CaO. The calcination temperature influenced the sorption ability of the eggshell waste sorbent [18]. CaCO₃ completely decomposed at the temperature range of 500-900 °C [19]. Calcination was carried out by heating in a furnace at a temperature of 900 °C for 2 h. The cooled carbon is ground with a mortar and sieved to obtain a homogeneous size.

The chemical activation process is then carried out using a $\rm H_3PO_4$ solution. The chemical activation process is the process of activating chicken eggshell carbon by adding certain chemicals to the sample to reduce the water

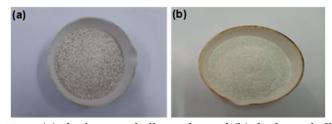


Fig 1. (a) chicken eggshell powder and (b) duck eggshell powder

content that is still left on the carbon surface so that the pores are more open and increase its absorption. H₃PO₄ is the most commonly used chemical activating agent because of its ease of recovery and low environmental impact [20]. H₃PO₄ promotes pyrolytic decomposition and the formation of cross-link structures in phosphate ester form, increasing porosity [21].

From Fig. 2, the calcination at temperature of 900 °C produced gray powder with little white powder. The resulting powder color changed from white to grey throughout the organic matter extrusion and subsequently into white. Therefore, snow-white powder obtained from the eggshells was CaO [22]. The CaCO₃ which is the main component of eggshells are known to have a decomposition temperature at 900 °C, perhaps at this temperature the CaCO₃ has been converted into CaO and CO₂ [23].

Characterization of Adsorbent

Water content

Water content is one of the requirements of adsorbent. High water content may reduce the quality of adsorbent. The water content of calcined chicken and duck eggshells can be seen in Table 1.

Methylene blue adsorption

The adsorption capacity of methylene blue can be used to determine the surface area of the adsorbent. The adsorption of methylene blue by carbon-based materials was studied by UV-vis spectrophotometry, monitoring the decrease in adsorption at 665 nm of an aqueous solution and converting the adsorption to concentration using a calibration curve [24]. Adsorption to methylene blue of calcined chicken and duck eggshells can be seen in Table 2. The data shows that calcined chicken eggshell has a higher adsorption capacity of methylene blue than calcined duck eggshell. The adsorption capacity of methylene blue could be an indication of the mesoporous nature because its molecule size is higher than 2 nm [25].

Iodine number

Iodine number is a number showing the ability of 1.0 g absorbent in absorbing iodine in mg. Data on the iodine number of calcined chicken and duck eggshell is presented in Table 3. The data shows that calcined

chicken eggshell has a higher iodine number than calcined duck eggshell. However, both of them have met the minimum requirement of 500 mg/g for water treatment applications [21].

SEM-EDS of calcined chicken dan duck eggshells

SEM is one of the fundamental techniques for membrane characterization as it gives the morphology and topography data of the prepared membranes. Furthermore, SEM can be used to determine the pore size in the case of a porous membrane [26]. EDS technique is mostly used for qualitative analysis of materials but can provide semi-quantitative results as well. Typically, SEM instrumentation is equipped with an EDS system to allow for the chemical analysis of features being observed in SEM monitor. Simultaneous SEM and EDS analysis is advantageous in failure analysis cases where spot analysis becomes extremely crucial in arriving at a valid conclusion [27]. Based on the results of the SEM test, the results are in the form of Fig. 3 and 4.

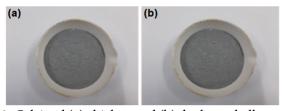


Fig 2. Calcined (a) chicken and (b) duck eggshells powder

Table 1. Water content of calcined chicken and duck eggshells

Samples	Water content (%)	
Chicken eggshell	0.022	
Duck eggshell	0.040	

Table 2. Methylene blue adsorption

Samples	Methylene blue adsorption (mg/g)	
Chicken eggshell	249.99	
Duck eggshell	243.09	

Table 3. Iodine number of calcined chicken and duck eggshells

Samples	Iodine number (mg/g)	
Chicken eggshell	1,475.50	
Duck eggshell	1,088.15	

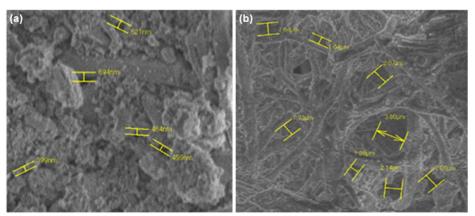


Fig 3. Results of SEM characterization of chicken eggshells with 3000 times magnification for (a) uncalcined and (b) calcined chicken eggshells

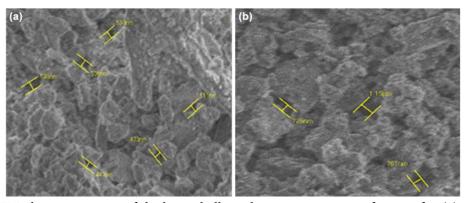


Fig 4. Results of SEM characterization of duck eggshells with 3000 times magnification for (a) uncalcined and (b) calcined duck eggshells

From Fig. 3 and 4, it can be seen that the calcined chicken and duck eggshells have pores. However, there is a difference, calcined chicken and duck eggshell have larger pores due to the calcination process. The porous nature may be attributed to the influence of activating agent H₃PO₄ on eggshell. The advantage of the porous structure was that it will allow electrolyte penetration which is favorable for ion diffusion, charge transfer, and capacitance increases [28]. During calcination, the CaCO₃ was thermally decomposed to CaO and CO₂. Calcination plays an important role in the morphology of chicken eggshell powder. They posited that calcined eggshell consists of small size particles and therefore larger total surface area [14,28].

From Fig. 5(a) and 5(b), EDS analysis can identify the elements present in both samples. In calcined chicken eggshell and duck eggshell contain C, O, and Ca, while in calcined duck eggshell there are elements C, O, P, and Ca. Carbon content in calcined chicken eggshell is 6.37% whereas in calcined duck eggshell is 9.70%.

Calibration Curve of Zn(NO₃)₂

The calibration curve based on a standard solution of $Zn(NO_3)_2$, with concentrations of 0, 0.2, 0.4, 0.6, 0.8, and 1.0 ppm, was measured using AAS. The absorbance obtained is shown in Fig. 6.

From Fig. 6, the regression line equation for the standard solution $Zn(NO_3)_2$ is y=0.5516x+0.0144 with a correlation coefficient (R^2) of 0.9986. The R^2 was achieved in the linearity test for calculating the regression from the standard calibration curve. The R^2 value demonstrates a significant association between absorbance (x-axis) and solution concentration (y-axis) [29].

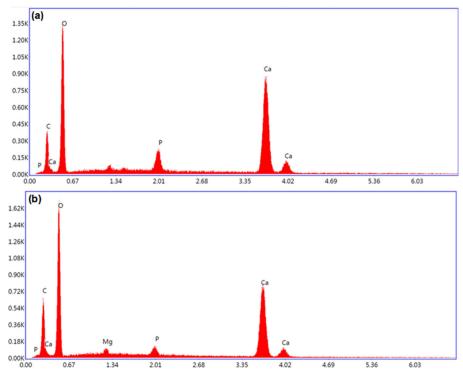


Fig 5. EDS result of (a) calcined chicken eggshell and (b) calcined duck eggshell

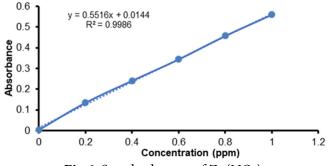


Fig 6. Standard curve of Zn(NO₃)₂

Method Verification

Accuracy

Parameter of accuracy aims to show the degree of closeness of the results of the analyst with the actual analyte levels. The Zn accuracy test using the addition method made 3 replications with the same treatment, each concentration was 0.4, 0.6, and 0.8 ppm. In Table 4, In the present study, it was found that the recovery range of samples analyzed ranged between 97.39–106.40%, the acceptable recovery range is 90.0–110.0%. So, the results of the accuracy-test above have met the requirements [30].

Precision

The precision parameter aimed to show the degree

Table 4. Accuracy parameter

Standard solution	Concentration	Accuracy
(ppm)	(ppm)	(%)
0.4	0.2492	106.40
0.4	0.2461	105.00
0.4	0.2443	104.18
0.6	0.3502	101.45
0.6	0.3493	101.18
0.6	0.3496	101.27
0.8	0.4530	99.39
0.8	0.4464	97.89
0.8	0.4466	97.94

of conformity between individual test results. The results of the analysis were shown from the RSD value. Sample precision test made 7 replications with one concentration of 0.6 ppm. A typical requirement for precision is RSD \leq 5.0% [31]. The results of the precision test in Table 5 have met the requirements.

Determination of Optimum pH of Calcined Chicken Eggshell and Duck Eggshell

The ability of adsorbent to adsorb also was affected by the acidity condition (pH) of the adsorbent surface. The pH effect on the adsorption of Zn is shown in Fig. 7.

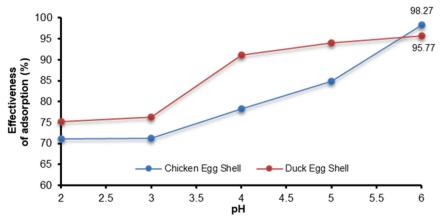


Fig 7. Effect of pH on Zn²⁺ adsorption

Table 5. Precision

Table 3. 1 recision				
Standard solution	Absorbance	Concentration		
(ppm)	Absorbance	(ppm)		
0.6	0.3459	0.6009		
0.6	0.3444	0.5982		
0.6	0.3442	0.5978		
0.6	0.3433	0.5962		
0.6	0.3409	0.5919		
0.6	0.3412	0.5924		
0.6	0.3429	0.5955		
SD		0.0032		
Average		0.5961		
%RSD		0.5390		

The change in initial pH affects the adsorptive process through the dissociation of functional groups on the active sites on the surface of the adsorbent. Fig. 7 shows the effect of pH on the removal of Zn²⁺ onto adsorbents from an aqueous solution. It was observed that with the increase of initial pH, the removal efficiency of Zn²⁺ increased. The highest removal was 98.27% (calcined chicken eggshell) and 95.77% (calcined duck eggshell) at pH 6. At low pH values, heavy metal removal was restricted with a strong dominance of hydrogen ions. This trend is possible because of the difficulty between metal ions and hydrogen on the adsorption site that limits the attraction of the metals. The increase in pH exposed the presence of carbonate groups in the eggshells to develop the negative charges on the surface of the eggshell particle and attract Zn²⁺ [32].

Determination of Optimum Contact Time of Calcined Chicken Eggshell and Duck Eggshell

Another important factor that influences the adsorption process is contact time. Contact time allows the diffusion and adhesion of adsorbate molecules to take place. To determine the optimum contact time this study was carried out in 5-time variations namely 15, 30, 45, 60, and 75 min with pH 6. In Fig. 8, the optimum contact time of calcined chicken eggshell occurs at 75 min with the percentage removal of Zn²+ was 98.75%, whereas the optimum contact time of calcined duck eggshell occurs at 60 min with the percentage removal of Zn²+ was 97.56%. Adsorption effectivity of calcined duck eggshell after 60 min decreased, this is due to active sites that bind beginning to release the Zn²+ ions back into the solution, so that the addition of time no longer increases the adsorption [32].

Determination of Optimum Adsorbent Dose of Calcined Chicken Eggshell and Duck Eggshell

The effect of adsorbent dosage on the effectiveness of Zn^{2+} removal can be seen in Fig. 9. The optimum dose of calcined chicken eggshell carbon is 100 mg with effective removal of 99.64%, whereas calcined duck eggshell is 125 mg with effective removal of 99.73%. It was observed that the removal efficiency of Zn^{2+} was increased with an increase in the calcined eggshell dosage. The increase in %removal may be due to the enhancement of the surface of adsorbent as well as

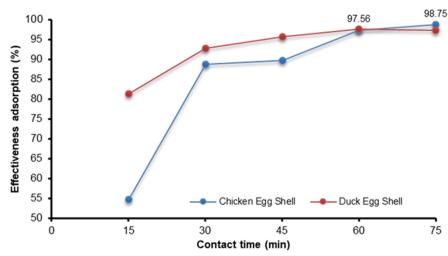


Fig 8. Effect of contact time on Zn adsorption

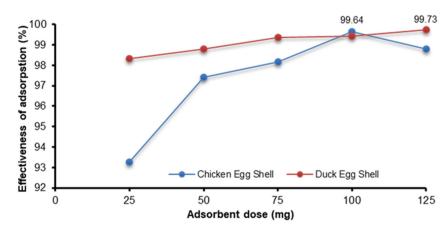


Fig 9. Effect of adsorbent dose on Zn adsorption

number of adsorption sites for Zn²⁺ [11], but after a certain concentration of further increase in biomass concentration does not affect removal percentage because no metal ions were left to be adsorbed on the empty actives sites after equilibrium point is achieved [33].

Comparison of the Effectiveness of Calcined Chicken and Duck Eggshell with Market Activated Carbon

After obtaining the results of the optimum pH, optimum contact time and optimum dose from the above research, then a comparison was made with synthetic adsorbents, namely, market-activated carbon. The purpose of this comparison is to use as a standard/reference for the quality of adsorbent that has been circulating in adsorption with adsorbent from chicken and duck eggshells made in this study. Fig. 10 shows that calcined

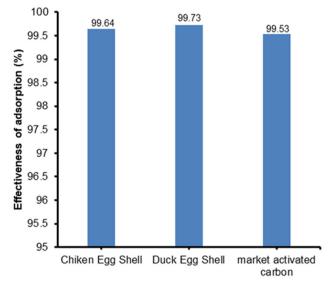


Fig 10. Comparison of effectiveness between calcined chicken eggshell and duck eggshell

duck eggshell has the highest effectiveness, which is 99.73%. This is because the calcined duck eggshells have a higher carbon content than calcined chicken eggshells. The adsorption effectiveness of calcined chicken eggshell and duck eggshell has a greater value than activated carbon from the market, this shows that both can be used as alternative adsorbent.

CONCLUSION

The results of this study showed that calcined chicken eggshells adsorb Zn at optimum pH of 6, with the required an optimum contact of 75 min and a mass of 400 mg with an adsorption effectiveness of 99.64%. While, calcined duck eggshells have an optimum pH of 6, an optimum contact time of 60 min, and an optimum mass of 400 mg with adsorption effectiveness of 99.73%. Activated carbon from the market has an adsorption effectiveness of 99.53%. So, it can be concluded that the calcined duck eggshell has the highest adsorption effectiveness.

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■ CONFLICT OF INTEREST

The corresponding author states that there is no conflict of interest on behalf of all authors.

AUTHOR CONTRIBUTIONS

The idea was conceived by Hesty Nuur Hanifah and Ginayanti Hadisoebroto. Cucun Cunayah and Diyanti Alma Kusuma Dani conducted the experiment and calculations. Hesty Nuur Hanifah and Ginayanti Hadisoebroto wrote and revised the manuscript. All authors agreed to the final version of this manuscript.

■ REFERENCES

- [1] Hama Aziz, K.H., Mustafa, F.S., Omer, K.M., Hama, S., Hamarawf, R.F., and Rahman, K.O., 2023, Heavy metal pollution in the aquatic environment: Efficient and low-cost removal approaches to eliminate their toxicity: A review, *RSC Adv.*, 13 (26), 17595–17610.
- [2] Tran, H.N., Nguyen, H.C., Woo, S.H., Nguyen, T.V., Vigneswaran, S., Hosseini-Bandegharaei, A.,

- Rinklebe, J., Kumar Sarmah, A., Ivanets, A., Dotto, G.L., Bui, T.T., Juang, R.S., and Chao, H.P., 2019, Removal of various contaminants from water by renewable lignocellulose-derived biosorbents: A comprehensive and critical review, *Crit. Rev. Environ. Sci. Technol.*, 49 (23), 2155–2219.
- [3] Qasem, N.A.A., Mohammed, R.H., and Lawal, D.U., 2021, Removal of heavy metal ions from wastewater: A comprehensive and critical review, *npj Clean Water*, 4 (1), 36.
- [4] Hussain, S., Khan, M., Sheikh, T.M.M., Mumtaz, M.Z., Chohan, T.A., Shamim, S., and Liu, Y., 2022, Zinc essentiality, toxicity, and its bacterial bioremediation: A comprehensive insight, *Front. Microbiol.*, 13, 900740.
- [5] Bakka, A., Mamouni, R., Saffaj, N., Laknifli, A., Benlhachemi, A., Bakiz, B., El Haddad, M., Ait Taleb, M., Roudani, A., and Faouzi, A., 2016, The treated eggshells as a new biosorbent for elimination of carbaryl pesticide from aqueous solutions: Kinetics, thermodynamics and isotherms, *Sci. Study Res.: Chem. Chem. Eng., Biotechnol., Food Ind.*, 17 (3), 271–284.
- [6] Mohamed, Z., Abdelkarim, A., Ziat, K., and Mohamed, S., 2016, Adsorption of Cu(II) onto natural clay: Equilibrium and thermodynamic studies, *J. Mater. Environ. Sci.*, 7 (2), 566–570.
- [7] Yusuff, A.S., 2017, Preparation and characterization of composite anthill-chicken eggshell adsorbent: Optimization study on heavy metals adsorption using response surface methodology, *J. Environ. Sci. Technol.*, 10 (3), 120–130.
- [8] Murcia-Salvador, A., Pellicer, J.A., Rodríguez-López, M., Gómez-López, V., Núñez-Delicado, E., and Gabaldon, J., 2020, Egg by-products as a tool to remove direct blue desorption properties, *Materials*, 13 (6), 1262.
- [9] Bhaumik, R., Mondal, N.K., Das, B., Roy, P., Pal, K.C., Das, C., Banerjee, A., and Datta, J.K., 2012, Eggshell powder as an adsorbent for removal of fluoride from aqueous solution: Equilibrium, kinetic and thermodynamic studies, *E-J. Chem.*, 9 (3), 1457–1480.

- [10] Tamang, M., and Paul, K.K., 2022, Adsorptive treatment of phenol from aqueous solution using chitosan/calcined eggshell adsorbent: Optimization of preparation process using Taguchi statistical analysis, *J. Indian Chem. Soc.*, 99 (1), 100251.
- [11] Rajoriya, S., Saharan, V.K., Pundir, A.S., Nigam, M., and Roy, K., 2021, Adsorption of methyl red dye from aqueous solution onto eggshell waste material: Kinetics, isotherms and thermodynamic studies, *Curr. Res. Green Sustainable Chem.*, 4, 100180.
- [12] Awogbemi, O., Von Kallon, D.V., and Aigbodion, V.S., 2022, Pathways for sustainable utilization of waste chicken eggshell, *J. Renewable Mater.*, 10 (8), 2217–2246.
- [13] Demiral, I., and Şamdan, C.A., 2016, Preparation and characterisation of activated carbon from pumpkin seed shell using H₃PO₄, *Anadolu Univ. J. Sci. Technol.*, *A*, 17 (1), 125–138.
- [14] Awogbemi, O., Inambao, F., and Onuh, E.I., 2020, Modification and characterization of chicken eggshell for possible catalytic applications, *Heliyon*, 6 (10), e05283.
- [15] Ullah, A.K.M.A., Maksud, M.A., Khan, S.R., Lutfa, L.N., and Quraishi, S.B., 2017, Development and validation of a GF-AAS method and its application for the trace level determination of Pb, Cd, and Cr in fish feed samples commonly used in the hatcheries of Bangladesh, *J. Anal. Sci. Technol.*, 8 (1), 15.
- [16] Ravindran, G., Madhavi, M.R., and Abusahmin, B.S., 2018, Optimization of zinc(II) adsorption using agricultural waste, *Int. J. Eng. Technol.*, 7 (3.34), 300–304.
- [17] Zonato, R.O., Estevam, B.R., Perez, I.D., Aparecida dos Santos Ribeiro, V., and Boina, R.F., 2022, Eggshell as an adsorbent for removing dyes and metallic ions in aqueous solutions, *Cleaner Chem. Eng.*, 2, 100023.
- [18] Mrosso, R., Mecha, A.C., and Kiplagat, J., 2023, Carbon dioxide removal using a novel adsorbent derived from calcined eggshell waste for biogas upgrading, S. Afr. J. Chem. Eng., 47, 150–158.
- [19] Razali, N., Jumadi, N., Jalani, A.Y., Kamarulzaman, N.Z., and Pa'ee, K.F., 2022, Thermal decomposition

- of calcium carbonate in chicken eggshells: Study on temperature and contact time, *Malays. J. Anal. Sci.*, 26 (2), 347–359.
- [20] Neme, I., Gonfa, G., and Masi, C., 2022, Activated carbon from biomass precursors using phosphoric acid: A review, *Heliyon*, 8 (12), e11940.
- [21] Spencer, W., Senanayake, G., Altarawneh, M., Ibana, D., and. Nikoloski, A.N., 2024, Review of the effects of coal properties and activation parameters on activated carbon production and quality, *Miner. Eng.*, 212, 108712.
- [22] Alhasan, H.S., Alahmadi, N., Yasin, S.A., Khalaf, M.Y., and Ali, G.A.M., 2022, Low-cost and ecofriendly hydroxyapatite nanoparticles derived from eggshell waste for cephalexin removal, *Separations*, 9 (10), 10.
- [23] Mohadi, R., Anggraini, K., Riyanti, F., and Lesbani, A., 2016, Preparation calcium oxide from chicken eggshells, *Sriwijaya J. Environ.*, 1 (2), 32–35.
- [24] Li, H., Budarin, V.L., Clark, J.H., North, M., and Wu, X., 2022, Rapid and efficient adsorption of methylene blue dye from aqueous solution by hierarchically porous, activated starbons*: Mechanism and porosity dependence, *J. Hazard. Mater.*, 436, 129174.
- [25] El-Bery, H.M., Saleh, M., El-Gendy, R.A., Saleh, M.R., and Thabet, S.M., 2022, High adsorption capacity of phenol and methylene blue using activated carbon derived from lignocellulosic agriculture wastes, *Sci. Rep.*, 12 (1), 5499.
- [26] Alqaheem, Y., and Alomair, A.A., 2020, Microscopy and spectroscopy techniques for characterization of polymeric membranes, *Membranes*, 10 (2), 33.
- [27] Nasrazadani, S., and Hassani, S., 2016, "Chapter 2 Modern analytical techniques in failure analysis of aerospace, chemical, and oil and gas industries" in *Handbook of Materials Failure Analysis with Case Studies from the Oil and Gas Industry*, Eds. Makhlouf, A.S.H., and Aliofkhazraei, M., Butterworth-Heinemann, UK, 39–54.
- [28] Balasubramanian, V., Daniel, T., Henry, J., Sivakumar, G., and Mohanraj, K., 2020, Electrochemical performances of activated carbon

- prepared using eggshell waste, SN Appl. Sci., 2 (1), 127.
- [29] Lutfi, N.N.H., and Rizal, F., 2022, Analysis of the heavy metal content of Zinc (Zn) in tofu using atomic absorption spectrophotometer (AAS), *Asian J. Health Appl. Sci.*, 1 (3), 30–34.
- [30] Aquisman, A.E., Bin Assim, Z., Binti Wahi, R., Kwabena, D.E., and Festus, W., 2019, Validation of the atomic absorption spectroscopy (AAS) for heavy metal analysis and geochemical exploration of sediment samples from the Sebangan river, *Adv. Anal. Chem.*, 9 (2), 23–33.
- [31] Epshtein, N.A., 2019, Validation of analytical

- procedures: Graphic and calculated criteria for assessment of methods linearity in practice, *Drug Dev. Regist.*, 8 (2), 122–130.
- [32] Abatan, O.G., Alaba, P.A., Oni, B.A., Akpojevwe, K., Efeovbokhan, V., and Abnisa, F., 2020, Performance of eggshells powder as an adsorbent for adsorption of hexavalent chromium and cadmium from wastewater, *SN Appl. Sci.*, 2 (12), 1996.
- [33] Badrealam, S., Roslan, F.S., Dollah, Z., Bakar, A.A.A., and Handan, R., 2018, Exploring the eggshell from household waste as alternative adsorbent for heavy metal removal from wastewater, *AIP Conf. Proc.*, 2020 (1), 020077.