Calcined Duck Eggshells as Sustainable Adsorbents for Lead Removal from Laboratory Waste

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Abstract. Pb metal is a heavy metal that comes from wastewater and can cause very big problems for organisms and the environment because it has high toxicity and is non-biodegradability. One way to solve the problem of heavy metal pollution is using the adsorption process. Duck eggshells are household and commercial waste that have not been utilized to their full potential. This study aims to determine the effectiveness of the adsorption of duck eggshells that have been activated physically and chemically by determining the optimum pH, optimum contact time, and optimum mass as well as knowing the characteristics and content of the egg shell ducks. Duck eggshells were physically activated by being heated in a high temperature of 900 ^{0}C and chemically activated through immersion process using H3PO4 for 24 hours. Pb Metal was measured using the Atomic Absorption Spectrophotometry tool at wavelength of 283.3 nm. The characteristics and content of duck eggshells were analyzed using the SEM-EDS tool. The results showed that the optimum condition of the duck eggshells in adsorbing Pb metal was at pH 6, optimum time at 75 minutes, and optimum mass of 500 mg with adsorption effectiveness of 94.75%. The results of the examination using the SEM tool showed that the duck eggshells that had been physically and chemically activated had larger pores compared to the duck eggshells that have not undergo the activation process. EDS analysis showed that the elements contained in the shell of duck eggs are carbon elements (C), oxygen (O), calcium (Ca), and phosphorus (P).

Keywords: *Lead; laboratory waste; calcined duck eggshells; adsorption*

1 Introduction

Heavy metals are the natural components of the earth's crust. But human activities, geochemical and biochemical cycles upset the balance of these metals and cause their release into the environment [1]. Chemistry

Received ________, Revised _________, Accepted for publication __________
 ISSN: xxxx-xxxx, DOI: 10.5614/xxxx

laboratory wastewater contain much more heavy metals and other hazardous compounds than industrial waste. The content of heavy metals in chemical laboratory liquid waste comes from practicum and research activities of students and lecturers. Heavy metals that burden chemistry laboratory wastewater among others Cu, Fe, Cr, Mn, Al, Zn, Pb, Cd, Ni, Hg, and As [2].

Lead (Pb) is a highly dangerous element that poses a repulsive threat to human health and the environment. Once in the body, lead ions can cause cardiovascular and heart disease, mental impairment and other diseases. The WHO has identified lead as an element that poses significant risks to human health and limits the amount of lead in drinking water to 0.01 mg/L. Lead ions are very difficult to remove from the human body once it enters the body. Therefore, lead ions must be removed from the water environment [3]. Treatment methods for lead-containing wastewater include adsorption, chemical precipitation, electrolytic, membrane separation, ion exchange, and biological methods. The adsorption method has always attracted much attention due to its wide range of material sources, simple operation and low cost. The commonly used adsorbents include the activated carbon, mineral materials, chitosan, lignin, fly ash, carbon-based materials and silica [4].

Eggshells can be used as an adsorbent because the main components of eggshell are calcium carbonate (94%), organic matter (4%), and other minerals. Calcium carbonate can be converted into calcium oxide through calcination, which improves its adsorption ability. Therefore, eggshell waste could potentially be turned into valuable adsorbents through this process [5].

The large-scale production of eggs results in a substantial amount of eggshell residue, often considered as waste. These discarded shells naturally decompose in soil approximately within a year [6]. Eggshell waste has been ranked as the 15th major food industry pollution problem by the Environmental Protection Agency. They are considered as a major source of environmental pollution when not properly dumped off in specified locations, thus causing health hazards later due to fungal growth on these eggshells [7].

Several authors have shown that it is the calcium carbonate–based composition of chicken eggshells that has the property of adsorbing heavy metals, such as cadmium, chromium, nickel, lead, cobalt [8]. However, research on efficiency of biosorption the of duck egg shells on heavy metals is still rare.

This study investigates the feasibility of using a commonly accessible agricultural byproduct, duck eggshells, as a sustainable and cost-effective option for remediating heavy metal contamination in laboratory waste. The purpose of this study is to determine the efficiency of biosorption of duck egg shells that have been activated physically and chemically on lead (Pb) from laboratory waste by determining the optimal pH, contact time, and mass, as well as the characteristics and content of the duck egg shell.

2 Materials and Method

Materials

Eggshell trash from chickens and ducks was acquired from a Martabak trader in Bandung, West Java, Indonesia. The following analytical grade materials were used in this study: market activated carbon, methylene blue solution (polylab), iodine solution (polylab), sodium thiosulfate solution (polylab), starch indicator, aquadest (IPHA), HNO_3 (Pudak Scientific), NaOH (Pudak Scientific), HCl (polylab), and $Zn(NO_3)_2$ solution (polylab).

Method

a. Eggshell adsorbent preparation
The wasted chicken eggshells are collected, washed with clean water, dried in the oven, pulverized into tiny particles, and sieved through appropriate mesh sizes [9].
b. Calcination of duck Eggshell
200 g of powdered duck eggshell was placed in a crucible and heated to 900 °C for two hours in a furnace. The resulting duck eggshell is calcined and then let to cool. After that, it was sieved using a no. 100 mesh size [9].
c. The process of duck eggshells activation
150 g of calcined duck eggshells were soaked for 24 hours in a 4 N H_3PO_4 activator solution. Additionally, filter paper is used to filter the mixture, and distilled water is used to wash it until the pH is neutral, then dried in oven at 110 °C for 3 h and weighed to calculate the adsorbent yield [9].
d. Characterization of Duck eggshell

- Water content analysis
  One gram of calcined eggshell was put in a porcelain dish with a known mass. It was then dried in an oven set at 105°C until it reached a constant mass, then it was cooled. The values of water content are then determined using Equation (1).

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

- Adsorption to methylene blue
  The UV-vis spectrophotometer was used to detect the amount of methylene blue absorbed by calcined duck eggshell at 664 nm, which is the maximum absorption wavelength of methylene blue. Using Equation (2), the adsorption capacity (qe) was determined.

$$q_e = \frac{C_0 - C_e}{M} \times V \quad (2)$$

  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 [10].
- Iodine Number
  In an erlenmeyer flask, 1.0 g of adsorbent was added, followed by 25 mL of 0.125 N iodine solution. The solution was agitated for 15 minutes before closing the Erlenmeyer and storing it in a dark place for 2 hours. The solution is then filtered, and the filtrate is pipetted for 5 mL into an Erlenmeyer flask before being titrated with Na2S2O3 solution until it is light yellow. A total of 1.0 mL of the starch indicator was added to the filtrate, and the titration was continued until the blue hue faded. The titration is repeated three times. Calculate the result obtained from Eq uation (3).

$$\text{Iodine number} = \frac{\left(N_1V_1 - N_2V_2\right) \times 126.9 \times F_p}{W} \text{mg/g} \quad (3)$$

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

- Scanning electron microscopy – energy dispersive spectrometry (SEM-EDS)
  The samples were fixed to the SEM sample holders using carbon tape before being vacuum-coated with a 20-nm coating of platinum. SEM was carried out at 15 kV and room temperature. The average pore size was determined using image analysis software [11].

e. Preparation of Pb metal testing

- Creation of $Pb(NO_3)_2$ 100 ppm solution
  A total of 0.159 grams of $Pb(NO_3)_2$ was put into a 1000 mL beaker and dissolved with aquadest until the limit mark so that a 1000 ppm solution was obtained. After that, 100 mL was taken and put into a 100 mL measuring cup.
- Creation of $Pb(NO_3)_2$ Standard Solution
  The $Pb(NO_3)_2$ 100 ppm solution was then taken for 0.125; 0,25; 0,5; 1,25; and 2.5 mL and put into a 25 mL measuring flask so that a standard curve of 0.5; 1; 2; 5; and 10 ppm were obtained. After that, the standard curve equation was calculated.
- Creating a Pb standard curve
  The absorbance of the solution was measured using Atomic Absorption Spectrophotometry at a wavelength of 283.3 nm. The measurement was repeated three times in a standard series solution containing Pb 0.5, 1, 2, 5, and 10 ppm.

f. Method verification

- Accuracy Test
  A 3,588 mL of a 1 ppm liquid waste solution was transferred to a 25 mL measurement flask. Following that, it was added with three different concentration levels, namely 0.1 ppm, 1 ppm, and 10 ppm, by adding 0.025 mL, 0.25 mL, and 2.5 mL of 100 ppm raw solution, resulting in 1.1 ppm, 2 ppm, and 11 ppm respectively. Aquadest was then added to the solution until it reached the limit mark, and three absorbance measurements at a specified wavelength (Pb = 283.3) were taken. The accuracy was then computed using the method (85% to 115% is the optimum accuracy).

  $$\%\, Recovery = \frac{A - B\ x\ 100\%}{C}$$

  A = sample content after Pb standard addition
  B = sample content before Pb standard addition
  C = pb raw solution content added to the sample.
- Precision Test

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) [12].

A 1 ppm liquid waste solution was taken for 1 mL and put into a 25 mL measuring flask. After that, it was added with 1 ppm, so that a concentration of 2 ppm was obtained. A 1 ppm raw solution was taken for 0.25 mL from a 10 ppm raw solution. Solution was then added with aquadest until the limit mark and absorbance measurements were carried out at a predetermined wavelength (Pb = 283.3) for seven times. Then the precision was calculated with the formula (%RSD below 20%),

$$\%RSD = \frac{\mathrm{SD\ x\ 100\%}}{\mathrm{X}}$$

X = average sample content (μg/mL)
SD = Standard deviation

g. Metal absorption effectiveness test

- Measurement of $Pb(NO_3)_2$ solution

  Lead standard solution 10 ppm was taken up to 10 mL and placed in a 100 mL measuring flask, then diluted with distilled water to the limit mark to achieve a solution concentration of 1 ppm. The absorbance of the solution was measured with AAS at a wavelength appropriate for Zn metal. The procedure was repeated three times.

- Determination of optimum pH of Duck Eggshells
  A total of 100 mg of calcined duck eggshells were put into 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 [13].
- Determination of optimum contact time of calcined chicken and duck eggshell
  A total of 100 mg of calcined duck eggshells was placed in an Erlenmeyer, and 25 mL of sample solution was added with NaOH or HCl until the optimum pH was reached. Furthermore, stirring was performed using a magnetic stirrer at five different mixing times: 15, 30, 45, 60, and 75 minutes [13]. The filtrate was then filtered via a microfilter before

being examined using AAS three times for each time variation. This process is performed with calcined duck eggshells.

- Determining the optimal dosage of calcined duck eggshell

  The sample solution of $Pb(NO_3)_2$ in 25 mL was mixed with calcined duck eggshells in five different concentrations: 100, 200, 300, 400, and 500 mg, and the solution was adjusted to the optimal pH attained in the previous treatment. The mixture was then agitated with a magnetic stirrer for the optimum contact time. The filtrate was then filtered using a microfilter before being evaluated by AAS using three replications.

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

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

where Ci and Cf (mg/L) are the pollutant concentration int the beginning and end of the process, respectively [14].

3 Result and Discussion

Calcination and Activation of duck eggshell

After going through the process of making bioadsorbent from duck egg shells, duck egg shell powder was obtained, and the results can be seen in Figure 1.

(a) (b)

Figure 1 Duck Eggshell Powder (a) Before Calcination (b) After Calcination

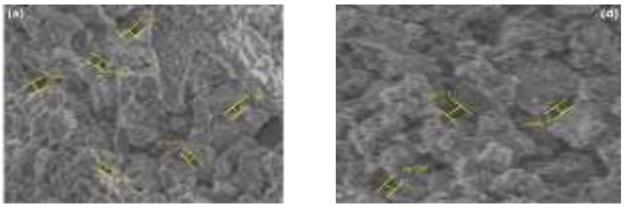
Figure 1 shows that the calcination process at 900 °C produces a dark colored powder. The resulting powder is initially white but turns dark during the extrusion process of the organic material. After that, the color returns to white. So, the snow-white powder obtained from egg shells turns out to be CaO [15]. $CaCO_3$, which is the main component of eggshells, is known to have a decomposition temperature of around 900 °C. At this temperature, it is likely that $CaCO_3$ has decomposed into CaO and CO_2 [16].

The calcination process not only affects the transformation of calcium, but also affects the color of the calcination product. Thermal treatment of calcium materials, such as shells, converts them to calcite (over 500°C) and calcium oxide (over 800°C) due to changes in the physical and chemical characteristics of the shell, including the decomposition of $CaCO_3$ to $Ca(OH)_2$ and CaO [17].

The chemical activation process is carried out using a phosphoric acid solution. This activation aims to process carbon from duck egg shells by adding certain chemicals to the sample, so that the remaining water content on the carbon surface can be reduced. This will open the pores wider and increase their absorption capacity. Phosphoric acid was chosen as the activating chemical because it is easy to obtain and has minimal environmental impact [15].

Characterization of Duck Egg Shell Bioadsorbent using Scanning Electron Microscope – Energy Dispersive Spectrometry (SEM-EDS)

This test was carried out using an electron microscope which aims to determine the 3-dimensional shape of duck eggshell powder.



(a) **(b)**

Figure 2 Results of SEM Characterization of Duck Eggshells with the magnification of 3000 times (a)Before activation, and (b) After activation

The examination of the surface morphology of the adsorbent particles, as depicted in the image, reveals that the synthesized particles are smaller in size, leading to increased surface porosity of the adsorbent at a magnification of 3000x. In Figure 2, it can be seen that the duck eggshells after calcination and activation have larger pores compared to those that have not been calcinated and activated. The image indicates that CaO particles exhibit a regular morphology with a consistent size [18].

Additionally, the crystal structures of the CaO particles appear interconnected and skeletal rather than irregular, a result of the calcination process. The porosity observed in CaO particles is attributed to the release of CO_2 and H_2O from their internal structure during the calcination of Ca $(OH)_2$. The presence of these developed pores in the CaO microspheres enhances their ability to effectively remove heavy metals from wastewater. This efficient separation is facilitated by the high surface area, uniformity, and porosity of CaO [18].

SEM Analysis was also completed with EDS analysis which can show the chemical composition of the sample. The results of the EDS analysis identified the elements contained in the two samples. In the inactivated eggshell powder samples, there were elements of carbon (C), Oxygen (O), and calcium (Ca), while in the duck eggshells that had been activated, there were elements of carbon (C), Oxygen (O), Phosphorus (P), and Calcium (Ca). In this study, what distinguishes the duck eggshells before and after being activated is the phosphorus element (P) due to the immersion process of activated carbon that has been activated H_3PO_4 (phosphoric acid).

$Pb(NO_3)_2$ Calibration Curve Results

Calibration curves was created based on standard solutions $Pb(NO_3)_2$, with concentrations of 0.5; 1; 2; 5; and 10 ppm. The solution was analyzed three times each using SSA at a wavelength of 273 nm.

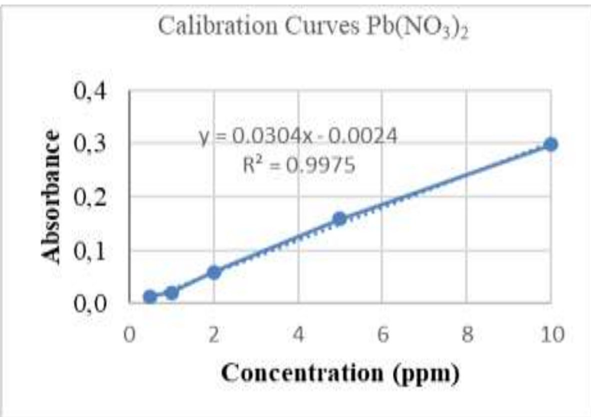


Figure 3. Calibration Curve of Standard Solution $Pb(NO_3)_2$

From the data in figure 3 above, the regression line equation was obtained, which is y = 0.0304x - 0.0024, with the result of correlation coefficient, namely r = 0.9975. (y) expresses the absorbance value and (x) represents the metal content. The value of r obtained in this study is in the range of 0.95 – 0.99, so the curve is said to have good linearity. The correlation coefficient value shows that the line formed is almost straight, so it can be said that the curve forms an ideal linear relationship.

Method Verification

Accuracy Test

The accuracy test aimed to show the degree of proximity of the analysis results to the actual analyte levels. In the accuracy test, the waste was made into 1 ppm, after which it was made into three different variations, namely 1.1 ppm, 2 ppm, and 11 ppm.

In this test, from the results shown by table 1, the % of the recovery calculated were in the range of 88.88% - 112%. Therefore, the accuracy test results above have met the requirements, where the recovery acceptance value must be between 85% to 115% [19].

Table 1. Accuracy Test

Initial concentration	SSA-readable concentration (ppm)	Absorbansi	% Recovery
1.1 ppm	0,9210	0,0256	108
1.1 ppm	0,9276	0,0258	115
1.1 ppm	0,9013	0,025	88,88
2 ppm	1,9177	0,0559	110
2 ppm	1,9013	0,0554	109
2 ppm	1,9342	0,0564	112,17
11 ppm	10,5230	0.3175	97,10
11 ppm	10,5328	0.3178	97,20
11 ppm	10,4342	0.3148	97,21

Precision Test

Precision tests of the standard solution were carried out using a concentration of 2 ppm. Precision tests were performed seven times for each concentration in the analyzed sample. This precision test aims to prove the accuracy of a tool based on the level of individual accuracy of the analysis results shown from the *Standard Deviation* (SD) value or *the Relative Standard Deviation* (RSD) value.

Table 2. Precision Test

Repetition	Absorbansi	Concentration (ppm)
1	0.0593	2,0296
2	0.0583	1,9967
3	0.0585	2,0032
4	0.0589	2,0164
5	0.0587	2,0098
6	0.0571	1,9572
7	0.0473	1,6348
Average	**0.0569**	**1,94967**
SD = 0,140674	%RSD less than equals 20%	
%RSD= 7,21%		

In this precision test result shown by table 2, the %RSD value obtained from Pb waste is 7.21% with an SD value of 0.140674. The precision value obtained is suitable for use because it meets the requirements according to the Handbook of Pharmaceuticals, namely the acceptance limit for precision values in determining metal contamination levels is less than 20.0% [19].

Determination of optimum pH of Duck Eggshells

The determination of optimum pH was variated at pH 2, 3, 4, 5, and 6. After that, 3 tests were carried out. In this test, the values obtained were shown in figure 4 as follows.

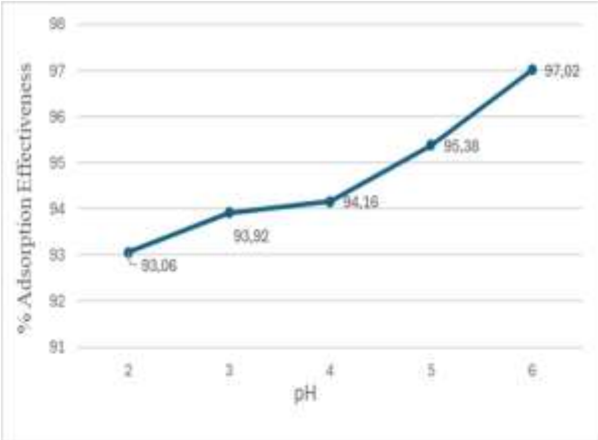


Figure 4. Data Results of Optimum pH Variations in Duck Eggshells

The results of determining the optimum pH show that the optimum pH value for duck shells is at pH 6. At pH 6, the effectiveness of adsorption showed the greatest value of 97.02%. The optimum pH value is the pH of the adsorbent in which it has the highest ability to absorb adsorbate. The adsorbent's ability to absorb is also influenced by the acidity (pH) on the surface of the adsorbent. Figure 4 shows the effect of pH on Pb absorption. The relationship between metal uptake and pH is associated with the ionization state of the functional groups in the sorbent and the chemistry of the metal in solution [18].

Analysis to determine the optimal pH shows that the ideal value for duck shells is pH 6, where the adsorption effectiveness reaches its peak at 97.02%. This optimal pH indicates conditions where the adsorbent shows its highest capacity to absorb adsorbate. Then at pH 2, the lowest effectiveness is 93.06%. At lower pH levels, H_3O^+ ions compete with Pb (II) ions for binding sites on the adsorbent, and the presence of hydronium ions (H^+) prevents metal ions from accessing these sites, resulting in reduced adsorption capacity [18].

Determination of the Optimum Time of Duck Eggshells

Another factor that affects the adsorption process is contact time. Determination of the optimum contact time on Pb metal adsorption using calcined duck eggshell was carried out at the optimum pH obtained and time variations of 15, 30, 45, 60, and 75 minutes. The results were shown in figure 5.

Duck eggshells showed the highest absorption at 60 minutes. This indicates that the longer the contact time required, the higher the adsorption of an adsorbent to adsorb the metal until it reaches the optimal time. But at 75 minutes, it experienced a decrease in adsorption. This shows that a longer contact time will increase the ability of the adsorbent to absorb metal until the optimal time is reached. In general, increasing the adsorbent dosage will increase the adsorption efficiency, this is due to the increasing number of binding sites available on the adsorbent [18].

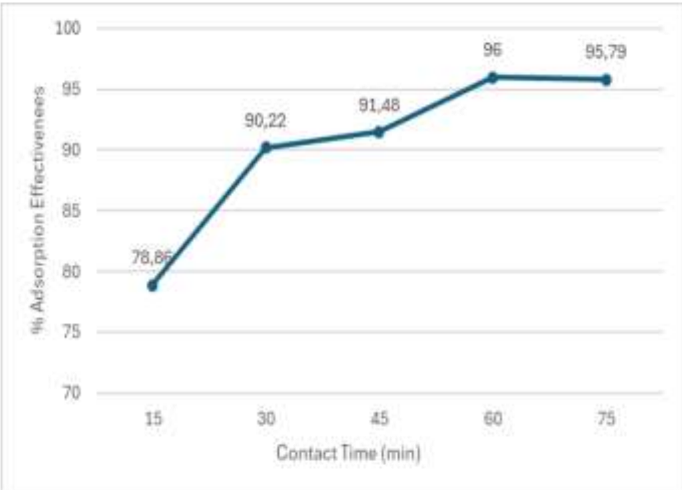


Figure 5. Data Results of Optimum Contact Time Variation of Duck Eggshells

Determination of the Optimum Mass of Duck Eggshells

In addition to the influence of pH and contact time, the mass of the adsorbent is also an important part of the adsorption process because it is one of the factors that determine the adsorption ability. Determination of the optimum mass in Pb adsorption using duck eggshell bioadsorbent was carried out at the optimum pH and optimum contact time obtained then varied the adsorbent masses of 100, 200, 300, 400, and 500 mg.

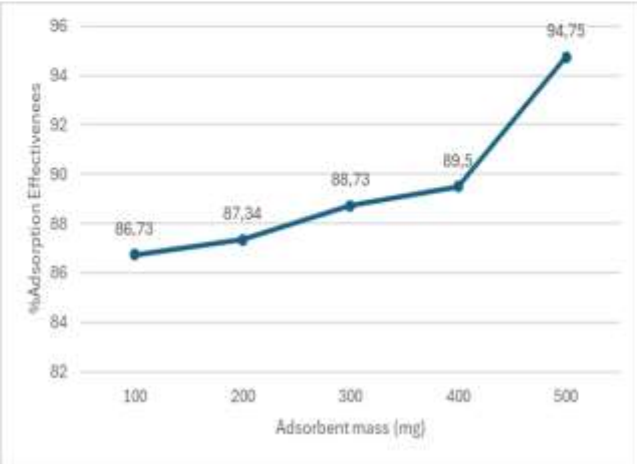


Figure 6. Data Results of Optimum Mass Variation of Duck Eggshells

The result from figure 6 shows that the largest absorption of duck eggshells against Pb Metal occurs at a mass of 500 mg. This shows that the higher the mass of the adsorbent used, the adsorption power of the metal is getting increased. Increasing the amount of adsorbent increases the adsorption capacity. This is most likely owing to the increased surface area offered by a larger amount of adsorbent, which improves interactions between the adsorbate molecules and the adsorbent surface. More active sites enable faster adsorption. Larger adsorbent masses resulted in higher uptake because the increased surface area provides more binding sites for absorption [20].

CONCLUSION

From the results of the research obtained, it can be concluded that:

1. The results of the examination using the SEM tool showed that duck eggshells that have been physically and chemically activated have larger pores compared to those that have not undergone an activation process, and the results of the EDS analysis show that the elements

contained in the duck eggshells are carbon (C), oxygen (O), calcium (Ca), and phosphorus (P).

2. Duck eggshells used for adsorption of Pb metal have an optimum pH at pH 6, optimum time at the 60 minutes, and an optimum mass of 500 mg with adsorption effectiveness of 94.75%.

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