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COMBINATION OF CORN WASTE AND EGG SHELL AS Zn METAL ADSORBENT WITH BATCH SYSTEM

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ABSTRACT

This study aims to determine: the ability of corn cobs and eggshells as Zn metal adsorbents, functional groups of corn cobs and eggshells adsorbent, what isotherm patterns occur in the adsorbent corn cobs and eggshells in adsorbing Zn metal, the optimum ratio and optimum mass of the adsorbent composition of corn cobs and eggshells in Zn metal adsorption, the optimum contact time for adsorbent corn cobs and eggshell in adsorbing Zn metal, the optimum concentration of adsorbate to be adsorbed by corn cobs and eggshell adsorbents. This study used an experimental method in the laboratory. characterization includes functional groups using FTIR, and test the effectiveness of adsorbents using the AAS instrument. Kinetic analysis of adsorbent by adsorption isotherm with Langmuir isotherm, Freundlich isotherm, Temkin isotherm, and dubinin-radushkevivh isotherm. The results showed that: Corn cobs and eggshells can be used as zinc metal adsorbents; in the corn cobs adsorbent, there is a functional group -OH at wave number 3415,15 cm^{-1} and in the eggshell, there is a bent vibration of calcium carbonate at wave number 3400,65 cm^{-1}, the adsorption process of Zn metal by adsorbent corn cobs and egg shells follows the Langmuir isotherm pattern (chemical adsorption), the comparison of the optimum composition and mass of the adsorbent corn cobs and eggshells in Zn metal adsorption are 1:2 and 0,15 grams with Zn metal adsorbed by 80,4571%, the optimum contact time for the adsorbent corn cobs and eggshells in adsorbing Zn metal is 90 minutes with the percentage of absorbed Zn metal concentration is 75,5957%, and the optimum concentration of adsorbate for adsorbed by corn cob and eggshell adsorbents is 1 mg/L with adsorbed Zn percentage of 82,8377%.

Keywords: *Corn Cob, Egg Shell, Adsorption, Zn Metal*

INTRODUCTION

Pollution is the most serious problem facing Indonesia, especially the problem of industrial waste pollution. Industry produces a lot of waste containing heavy metals such as Cu, Zn, Cr, Cd, Ni, and Pb which are very dangerous for life. Waste treatment that is not carried out properly can threaten the life of the creatures around it. The characteristics of combustible waste include cancer-causing (carcinogenic), toxic

(toxic) and explosive [1]. Heavy metals are metal elements with a density of more than 5 g/cm^3.

Based on previous research, most of the sources of pollution that enter river water bodies contain Zn metal. The normal level of Zn in seawater according to WHO is 1.5 ppm, while according to the ministry of the environment it is 0.05 ppm [2]. Zn is toxic at high levels, but at low levels is needed by organisms as a coenzyme [3]. Another study stated that heavy metal levels in the Tondano river water in Sulawesi were also quite high, ranging from 0.01 to 1.12 mg/l. [4]. Zn metal pollution in water has far exceeded the threshold set by the Ministry of the Environment.

Adsorption is a separation process in which fluid components move to the surface of an adsorbent. Most adsorbents are porous materials, and adsorption occurs mainly on the pore walls [5]. One of the handling of environmental pollution of heavy metal Zn is to use corncob and eggshell waste as adsorbents, both materials are easy to obtain, and the cost is affordable. Agricultural waste products with high cellulose content can be used as alternative adsorbents, such as corn cobs [5]. Egg shell is one of the household waste which is quite a lot. About 10% of eggs are shells, so about 133,703 tons of eggshells are produced annually. Egg shell has a fairly high calcium carbonate content, around 85-95%, so that eggshell has the potential as an adsorbent [7]. Previous research using eggshell as an adsorbent has shown that eggshell adsorbent has a porous surface and a $CaCO_3$ content of 93% [8]. Therefore, eggshell particles can be used as an alternative to absorbent industrial wastewater containing certain metal solutions, such as Fe [9].

In this experiment, corn cobs and eggshells were combined, which in this case is a combination of organic and inorganic adsorbents. Organic adsorbents have good adsorption capabilities and are more economical, while inorganic adsorbents have good thermal power, are easy to modify, and are not easily brittle [10]. The combination of corn cobs and eggshells is expected to complement the two adsorbents so that the interaction between the adsorbent and adsorbate combination will be stronger. This study uses a batch system by immersing the adsorbent in an acid solution during the activation process. The use of a batch system because the process is simple and requires little supporting equipment [11]. The concentration of Zn metal in the Zn simulation solution was measured using the Atomic Absorption Spectroscopy (AAS) instrument. This research is expected to be one of the efforts to overcome environmental pollution, household waste, and agricultural waste.

METHODS

1. Adsorbent Preparation and Activation

The corncobs are washed and dried and crushed to produce a coarse corncob powder. Then blended and sieved through a 100 mesh sieve. Mixing aims to obtain finer corncob powder and sifting to obtain a uniform adsorbent size. The smaller the size of an adsorbent, the more surface area, so that the adsorbent absorbs more substances. Then the corn cobs were activated by soaking them in 0.1 M HCl for 3 hours. Then the adsorbent was neutralized using distilled water then filtered and dried in an oven overnight at 60 °C [12].

Egg shells are washed and dried in the sun. Then pounded using a mortar and pestle. Pounding aims to get eggshell powder, then sieved so that the powder size is uniform. Then the egg shell powder was baked in the oven for 1 hour at a temperature of 110 o C. Then the activation process was carried out using 0.1 M HCl for 24 hours. After the activation process, it was neutralized, filtered, and dried in an oven for 3 hours at 110°C [13].

2. Determination of Optimum Composition and Mass

Adding 0.15 gram of corncob adsorbent and eggshell using a ratio of 1:1, 1:2, and 2:1 with a weight ratio of respectively 0.075g:0.075g; 0.05g:0.10g; 0.10g:0.05g into a bottle containing 10 mL of Zn sample solution with a concentration of 2 ppm and stirred at 100 rpm for 30 minutes. Then filter with Whatman paper and put into a vial. The filtrate in the vial is then AAS tested. Entering adsorbents with mass variations of 0.1 g, 0.125 g, 0.15 g, 0.175 g, and 0.2 g using the optimum composition ratio into bottles stirred at 100 rpm for 30 minutes [14]. Then filter with Whatman paper, and the filtrate is then tested for AAS.

3. Optimum Timing

Entering the adsorbent with time variations of 15, 45, 60, 90, and 120 minutes using the optimum mass and composition into a bottle containing 10 mL of Zn sample solution with a concentration of 2 ppm and stirring at 100 rpm for 30 minutes. Then filter with Whatman paper, and the filtrate is then tested for AAS.

4. Determination of Optimum Concentration

Take 10 mL of Zn sample solution at a concentration of 0.5; 1; 1.5; 2; 2.5; 3 ppm is then put into the bottle. Put the adsorbent with optimum mass and composition into the bottle and stir at 100 rpm with optimum contact time. Then filter with Whatman paper, and the filtrate is then tested for AAS.

RESULTS AND DISCUSSION

1. Adsorbent Preparation and Activation

Corn cobs mostly comprise cellulose, hemicellulose, lignin, and extractives [12]. Cellulose has a great ability in the adsorption process due to the presence of OH groups. corn cobs to be used as heavy metal adsorbents [15]. The eggshell is the outermost part of the egg in the form of a hard layer. Each egg has 10,000–20,000 pores, so it is estimated that it can absorb solutes and be used as an adsorbent [15].

The purpose of activating the adsorbent is to lead to the activation of the hydroxyl groups on the cellulose so that the ability of the adsorbent to absorb metal ions increases [16]. HCl activator can enlarge the pores during the adsorption process [17]. The purpose of neutralization is to remove residual acid species and adhere impurities.

(2) Adsorbent Characterization

Functional group analysis was carried out on two treatments, adsorbent before and after activation of 0.1 M HCl.

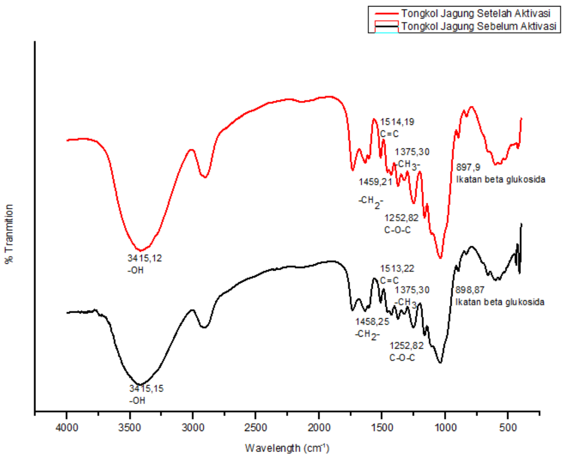

Figure 1. FTIR of corn cobs before and after activation

Table 1. Comparison of functional groups of corn cobs before and after activation

Before Activation		After Activation	
Functional groups	Wave number (cm^{-1})	Functional groups	Wave number (cm^{-1})
-OH	3415,15	-OH	3415,15
$-CH_2-$	1458,25	$-CH_2-$	1458,25
$-CH_3$	1375,30	$-CH_3$	1375,30
CO	1165.50	CO	1165.50
C=C lignin	1513.22	C=C lignin	1513.22
Beta-glucose bonds - d a	898.87	Beta-glucose bonds – d a	898.87
-COC- (eter)	1252.82	-COC- (eter)	1252.82

The functional group spectra from FTIR t showed that the functional groups present on corn cobs before and after activation were the -OH group shown at wave number 3415.15 cm^{-1} and CO at wave number 1165.50 cm^{-1}. The results of functional group analysis showed that with previous studies showing that in corn cobs, OH and carbonyl groups can play a role in the adsorption process [18].

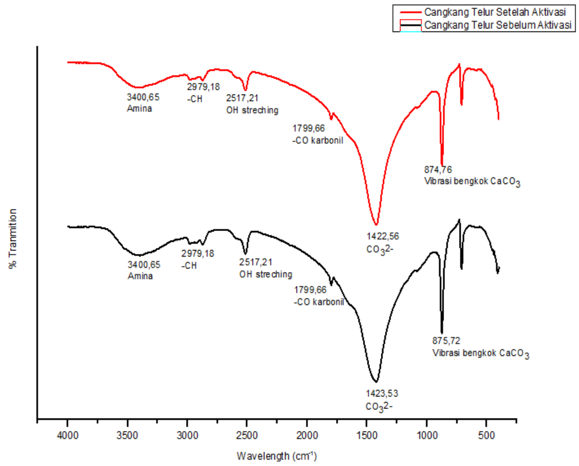

Figure 2. FTIR of eggshell before and after activation

Table 2. Comparison of eggshell functional groups before and after activation

Before Activation		After Activation	
Functional groups	Wave number (cm^{-1})	Functional groups	Wave number (cm^{-1})
Calcium carbonate bending vibration	875.72	Calcium carbonate bending vibration	875.76
CO_3^{2-}	1423.53	CO_3^{2-}	1422.56
-CO carbonyl	1799.66	-CO carbonyl	1799.66
-OH stretching	2517.21	-OH stretching	2517.21
-CH	2979.18	-CH	2979.18
Amine	3400.65	Amine	3400.65

Functional group analysis using FTIR on eggshell before and after activation showed that the organic compound content of eggshell changed shape and strain vibration [19]. FTIR spectra of eggshells indicate the potential of eggshells to be used as heavy metal adsorbents, especially Zn.

3) Determination of Optimum Composition and Mass

The experiment used variations in the composition of corncob and eggshell adsorbents 1:1, 1:2, and 2:1. with an adsorbate volume of 10 mL, an adsorbent mass of 0.15 g, and a contact time of 30 minutes.

Table 3. Comparison of Optimum Composition on Zn. Adsorption

No	Adsorbent Composition	Zn metal adsorbed (%)
1	1:1	72.33
2	1:2	80.46
3	2:1	73.89

The variation of the ratio of adsorbent composition aims to determine the ratio of the optimum composition of corn cobs and egg shells needed to absorb Zn metal until a saturated condition is reached. The comparison of the optimum adsorbent composition can be determined by graphing the relationship between the ratio of the composition of the adsorbent to the concentration of Zn.

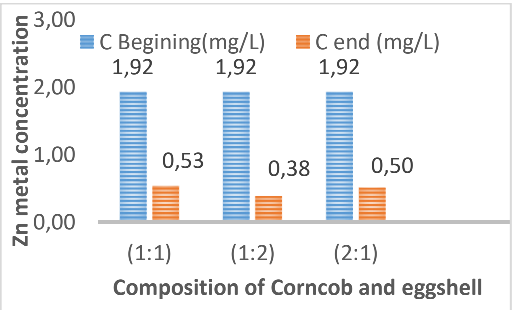

Figure 3. Graph of Optimum Composition

Figure 3 shows the optimum composition of the adsorbent is 1:2, the remaining Zn metal is 0.3754 mg/L so that the adsorbed Zn metal is 1.5455 mg/L or the percentage of Zn metal adsorbed is 80.4571%. While the composition ratio is the smallest at a ratio of 1:1 because the remaining concentration is 0.5316 mg/L, so that the adsorbed concentration is 1.3893 mg/L or 72.3255%, where the adsorbents of corn cobs and eggshells are the same. amount. The optimum ratio is 1:2, this means that the composition of the eggshell adsorbent is higher than that of corn cobs.

This experiment used variations in the mass of corncob and eggshell adsorbents, 0.100 g, 0.125 g, 0.150 g, 0.175 g and 0.200 g. The control variable used the optimum composition of corncob and eggshell adsorbent 1:2 with the same concentration, adsorbate volume, stirring speed and contact time in determining the optimum composition..

Table 4. Comparison of Optimum Mass on Zn Adsorption

No	Adsorbent Composition	Zn metal adsorbed (%)
1	0.100	36.60
2	0.125	58.71
3	0.150	80.46
4	0.175	75.52
5	0.200	64.79

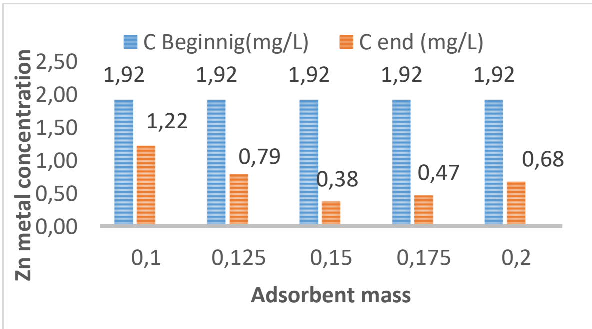

Figure 4. Mass Comparison Graph

Analysis is needed to determine the optimum mass of adsorbent needed to absorb Zn metal until it is saturated. The optimum mass of the adsorbent can be determined by graphing the relationship between the mass of the adsorbent and the concentration of Zn.

Table 5. Comparison of Optimum Time for Zn Adsorption

No	Contact Time (minutes)	Zn metal adsorbed (%)
1	15	55.68
2	30	56.27
3	45	64.36
4	60	70.02
5	90	75.60
6	120	70.86

Figure 4 shows that the concentration of Zn solution adsorbed by an adsorbent mass of 0.100 g to 0.150 g increased and decreased at a mass of 0.175 g to 0.200 g. Rojikhi (2014) states that increasing the mass of the dsorbent will cause the number of particles, surface area and space to be abundant from the pores so that it can absorb optimally [12]. The optimum adsorbent mass is 0.150 g, where the adsorbed Zn is 1.5455 mg/L or 80.4571%. The adsorbent mass that absorbs the least is 0.100 mg/L. When the adsorbent mass is 0.100 g to 0.150 g, the adsorbent has a high level of ability to absorb Zn metal and then decreases when the adsorbent mass is 0.175 g and 0.200 g; this indicates that the adsorbent has reached a saturation condition so that the absorption will decrease or undergo desorption.

(4) Determination of Optimum Contact Time

In this research, the variation of contact time between corncob and eggshell adsorbents and samples was 15, 30, 45, 60, 90 and 120 minutes. The control variable used the Composition of the corncob and eggshell adsorbent 1:2, the corncob and eggshell adsorbent mass was 0.15 g, with the same concentration, adsorbate volume, and stirring speed when determining the optimum composition**.** The optimum contact time determines the time required between the adsorbent and the adsorbate, where the adsorbent will absorb maximum Zn metal until it is saturated.

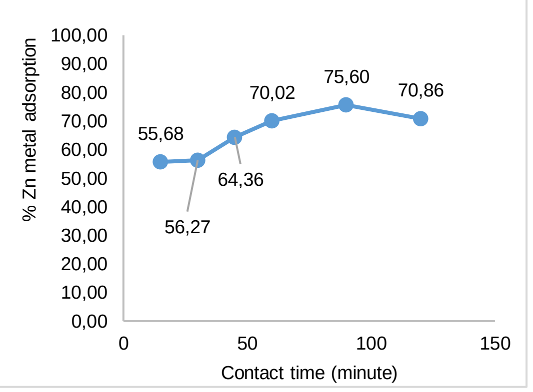

Figure 5. Graph of Optimum Time

Based on Figure 5, it is known that the percentage concentration of the adsorbed Zn solution continues to increase until it reaches the optimum condition, which is 90 minutes with an absorption percentage of 75.5957%, after passing through 90 minutes, the percentage of Zn metal adsorbed decreases. The decrease in the percentage of Zn metal adsorption is probably because the adsorbent is already saturated, so the absorption will decrease or desorption [6]. Contact time that is too long can reduce the effectiveness of the adsorbent during adsorption because it is already in a saturated condition, so desorption occurs, which can increase the content that has been absorbed [21].

(5) Determination of Optimum Adsorbate Concentration

This experiment used variations in the concentration of adsorbate, namely 0.5 mg/L, 1 mg/L, 1.5 mg/L, 2 mg/L, 2.5 mg/L, and 3 mg/L, the control variable used adsorbent composition 1:2, adsorbent mass 0.15 g, contact time 90 minutes with the same concentration, the volume of adsorbate, and stirring speed when determining the optimum composition.

Table 6. Comparison of the optimum concentration on Zn adsorption

No	Adsorbate Concentration (mg/L)	Zn metal adsorbed (%)
1	0.5	64.38
2	1	82.84
3	1.5	67,24
4	2	61.16
5	2.5	68.03
6	3	69,20

The optimum adsorbate concentration determines the optimum concentration absorbed by mass, composition, and optimum time.

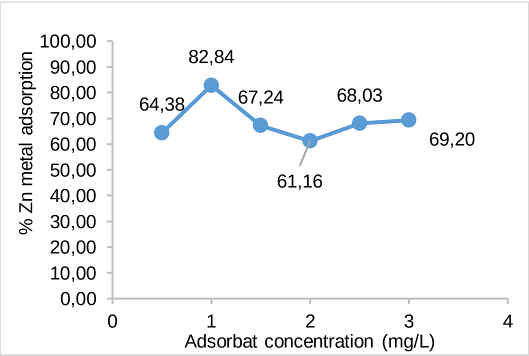

Figure 6. Graph of Optimum Concentration

Based on Figure 6, it is known that the adsorbate concentration of 1.0593 mg/L is the optimum concentration. The contact between the adsorbate and the surface of the adsorbent causes the adsorbate molecules to be adsorbed onto the surface in an amount that depends on the concentration. The biosorbent has a limited number of active sites and then becomes saturated at a certain concentration [20]. The decrease in the percentage of Zn metal concentration adsorbed on the adsorbent was due to the saturated adsorbent causing desorption or re-release between the adsorbent and the adsorbate. However, in this study, when the concentration of 1.9633 mg/L to 2.5969 mg/L continued to increase, the adsorbent ability increased again. Increase and decrease in the percentage of Zn adsorbed related to the desorption ability of the adsorbent as a form of self-defense [21].

[6] Determination of the Adsorption Isotherm Equation

Determination of the adsorption isotherm equation was carried out by measuring the adsorption of Zn metal which was adsorbed with time variations. The aim is to determine the isotherm pattern in the corncob and shell adsorbents. This study used four isotherm patterns: Langmuir, Freundlich, temkim, and dubinin-radushkevich adsorption isotherms. Langmuir equation by comparing the value of Ce with Ce/qe. The Freundlich equation by comparing the value of log Ce with log qe. The Temkin equation by comparing the value of ln Ce with qe. The dubininraduschevich equation by comparing the value of 2 with ln qe . Here is a graph of the equation:

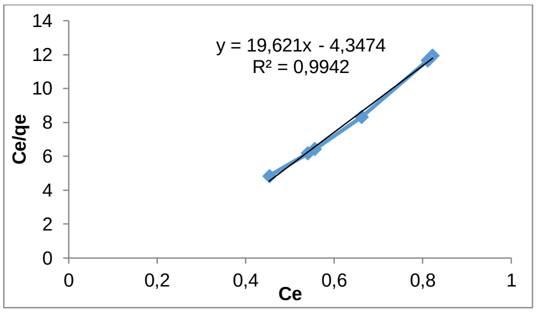

Figure 7. Graph of the Langmuir Isoterm

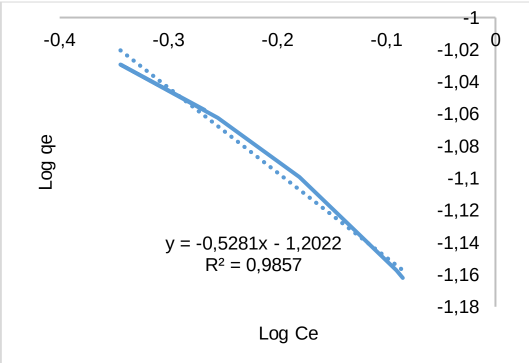

Figure 8. Graph of the Freundlich Isoterm

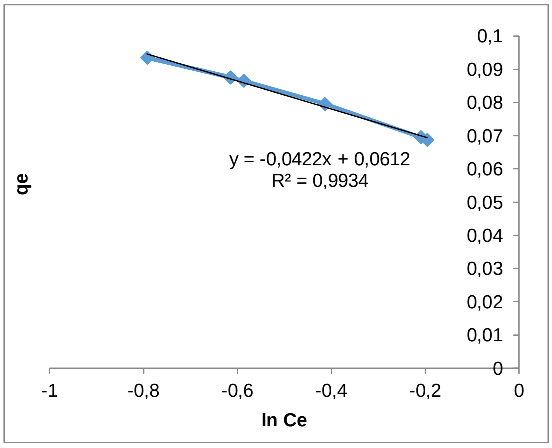

Figure 9. Graph of the Temkin Isoterm

Based on the comparison of the value of R 2, the adsorption of a combination of corn cobs and eggshell to metals Zn (II) is to follow the Langmuir isotherm. Fourth isotherm models demonstrate the value of R 2 > 0.9, which means the process of adsorption isotherm can follow the four models but is superior to the Langmuir isotherm. The Langmuir isotherm has a value of R 2 of 0.9942, Freundlich isotherms have a value of R 2 of 0.9857, isotherms temkin has a value of R 2 of 0.9934, and the isotherms Dubinin-radushkevich has a value of R 2 of 0.9575. In the Langmuir isotherm, the adsorption process occurs in a monolayer (single layer) onto a surface containing a limited number of identical groups. The Langmuir isotherm shows that the adsorption energy is uniform to the surface, and there is no transmigration of the adsorbate in the surface plane [22]. The Langmuir isotherm is used to describe the chemisorption process (chemical adsorption) so in this study, the adsorption process took place chemically. In the chemical adsorption process, the bond between the adsorbent and the adsorbate is quite strong. Still, sometimes the absorption is not maximal, or the absorption percentage is small. This chemical adsorption process is slow and reversible and includes an irreversible ion exchange or complexation reaction [23].

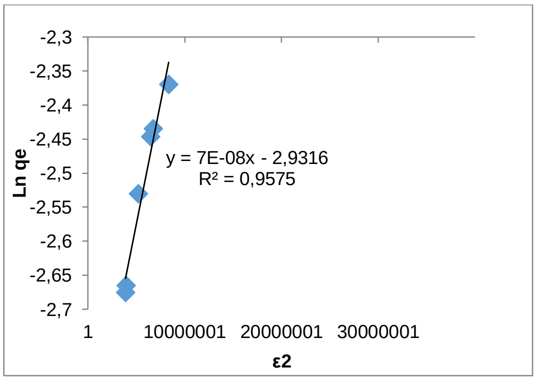

Figure 10. Graph of theDubinin-radushkevich Isotherm

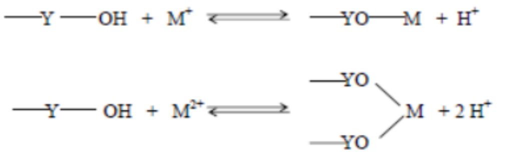

Figure 11. Alleged Ion Exchange Mechanism in Corncob Adsorbent and Zn(II) Metal Ions.

The adsorption, reaction occurs between cellulose (OH group) on corn cobs and a reaction between the $CaCO_3$ on eggshells with Zn metal. In the corncob adsorbent, the adsorption mechanism that occurs between the –OH group bound to the surface with positively charged metal ions (cations) is an ion exchange mechanism [24].

In skin, eggs are not calcined, and $CaCO_3$ in the eggs will undergo a displacement reaction to form calcium hydroxide (reaction 1). It is known that egg shells contain $CaCO_3$ as the main component. This indicates that the eggshell powder reacted in equation (reaction 2) precipitated as metal hydroxide [20] .

$CaCO_3 + 2H_2O \rightarrow H_2O + CO_2 + Ca(OH)_2$ (reaction1)

$H_2O + CO_2 + Ca(OH)_2 + X^{2+} \Longrightarrow H_2O + CO_2 + Ca^{2+} + X(OH)_2$ (reaction 2)

In addition, protonation and deproto nation mechanisms can also occur from cal cite , the main constituent of egg shells. Protonation (reaction 3) and deprotonation (reaction 4) can occur due to the hydrolysis and hydration processes of calcite [24].

$CaOH + H^+ \rightarrow CaOH^{2+}$ (reaction 3)

$CaCO_3H \rightarrow CaCO_3^- + H^+$ (reaction 4)

The protonation and deprotonation of calcite affect the surface charge of the eggshell, resulting in an electrostatic force that can either attract or repel the adsorbate. This can affect its performance as an adsorbent.

CONCLUSION

On the corncob adsorbent, there is a -OH functional group at a wave number of 3415.15 cm -1; on the egg shell, there is a bent vibration of calcium carbonate at a wave number of 3400.65 cm -1 , so that corn cobs and eggshells can be used as metal adsorbents. Zn. The adsorption process of Zn metal by combined adsorbent is more dominant following the Langmuir isotherm pattern, where the adsorption process takes place chemically. The ratio of composition and optimum mass of combined adsorbent is 1:2 with an absorption percentage of 80.4571%. The optimum contact time of the combined adsorbent in the adsorption of Zn metal is 90 minutes with an absorption percentage of 75.5957 %. Therefore, the optimum adsorbate concentration to be adsorbed by the combined adsorbent is 82.8377%.

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