

Removal of Cu Metals from Wastewater by Adsorption using Synthetic Zeolites from Rice Husk and Corncob

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ABSTRACT. Heavy metals, such as Cu, are hazardous components so that it needs to reduce their concentration due to their negative impact on the environment. One method that can be used to reduce heavy metals in waste is to use adsorbents (synthetic zeolites). Utilization of agricultural waste such as rice husks and corncobs as precursors of synthetic zeolites will add economic value because it is relatively cheap with a lot of availability. This research aimed to find out new variants of synthetic zeolites, which can reduce the concentration of Cu in the adsorption process. The study consisted of 3 stages, the first stage was zeolite synthesis by the sol-gel method with 3 zeolite variants (A, B and C), the second stage was characterization using XRD and SEM, and the third stage was zeolites optimization (variations in pH, weight, and concentration). According to the results of SEM, zeolite B had a larger and uniform pore size so as it produced a greater adsorption capacity (4.82 mg/g) to be compared with zeolites A and C. The results showed synthetic zeolite C was able to adsorb Cu waste by following the adsorption isotherm model of Langmuir.

Keywords: Corn Cobs, Heavy Metal, Rice Husk, Zeolites Adsorbent

INTRODUCTION

The issue of environmental pollution has recently become a great concern topic because it will have an impact on human health. One of the pollutions is the presence of heavy metals such as copper (Cu) metal. Heavy metals are pollutants that cannot be biodegradable because they are very difficult to remove naturally (Abas, Ismail, Kamal, & Izhari, 2013). Copper Metal (Cu) will cause damage to the liver and kidneys, even in high doses, can cause death.

Treatment that can be done to reduce the content of heavy metals is by deposition, membrane filters, ion exchange, and adsorption (Hegazi, 2013). One alternative method that can be developed is the adsorption method using synthetic zeolites. The use of synthetic zeolites is more than natural zeolites because synthetic zeolites have a higher level of purity and pore uniformity than natural zeolites. Based on research by Ghifari et al. (2017), zeolite synthesis produces greater adsorption efficiency compared to natural zeolites in the adsorption of dyes. The manufacture of synthetic zeolites requires a source of silicate and aluminate. Silicate is obtained from rice husks and corn cobs that have been made up while aluminate is obtained from sodium aluminate. Silica source plays an important role in the synthesis process and also

determines the morphology of the synthesized product (Zhang, Li, Liu, & Wang, 2019).

Agricultural wastes that can be used as sources of silica include rice husks (Islam, Liu, Shen, Ye, & Peng, 2018; Arneli, Solichah, Alfiansyah, Suseno, & Astuti, 2017), wheat husk ash (Shaikh et al., 2015) and teak sawdust (Saputro et al., 2017). Silica ash is widely used for various chemical processes, including desiccants, adsorbents, filter media, and catalyst components. According to Arneli, Pangestika, Fauziah, Wahyuningrum, & Astuti (2017), the silica content in rice husks is around 86.9-97.8% and in corncobs is 79,95% (Wardhani, Nurlela, & Azizah, 2017). Besides its high silica content, rice husks and corncobs can be obtained at a low cost. Their availability is abundant, and then they can be renewed so that they can be used as the new variant of synthetic zeolites. Existing research uses only one source of raw materials. The novelty of this research is to use 2 types of raw materials (a combination of rice husks and corncobs).

The zeolites synthesis method commonly used is the sol-gel method, hydrothermal method and microwave method. In this study, silica was isolated from rice husk ash and corncob ash using the sol-gel method due to the fact that it is simpler than the hydrothermal method, then the characterization was conducted with

XRD and SEM parameters, optimization was done by taking notice of the variations in pH, weight, and concentration. This research was important to do because it could find out new variants of synthetic zeolites that could reduce the concentration of metals in Cu waste in the adsorption process and add value to the use of rice husks and corncobs.

EXPERIMENTAL SECTION

The research method consisted of 3 stages: the manufacturing of synthetic zeolites by the sol-gel method in 3 variations in composition between rice husk ash, corncob ash, and aluminate; then characterizing with XRD and SEM and zeolite optimizing with the variations in pH, weight, and concentration.

Materials

The material in this study used rice husks, corncobs, aluminum hydroxide, sodium hydroxide, distilled water, universal pH paper, filter paper, Cu(NO₃)₂ solution.

Instrumentation

AAS (Shimadzu 2010), X-ray Diffraction, Scanning Electron Microscope, Cu cathode lamp, analytical

balance (Shimadzu), shaker (Heidolf), furnace (Memert), pH meter (Agilent) and other glassware.

Synthesis and characterization of zeolites

Rice husks and corncobs were obtained from the Karawang area, West Java. Before synthesized, the raw material was made with a furnace and ground using a mortar to increase the surface area. 10 g of rice husk ash was dissolved in 6N NaOH solution for 24 hours (solution a), then corn cobs ash was treated in the same manner as in rice husk ash (solution b). Aluminate was made by weighing 25 g of aluminum hydroxide dissolved in 30.5 g of sodium hydroxide (solution c). Solutions a, b, and c were then put into a Duran bottle up to a volume of 100 mL with the composition of the formulation (A, B, and C), then all variations of the composition were heated in an oven at 105 °C for 24 hours. Furthermore, all of the treatments were filtered and washed with distilled water to a neutral pH using a universal pH, then roasted at 105 °C for 8 hours. The composition of synthetic zeolites can be seen in **Table 1**. Zeolite products were analyzed by XRD to determine crystallinity and SEM to determine solid morphology.

Table 1. Zeolite synthesis composition

The name zeolite synthesis	Composition (corn cobs: rice husk: sodium aluminate)
A	60:20:20
B	50:25:25
C	40:30:30

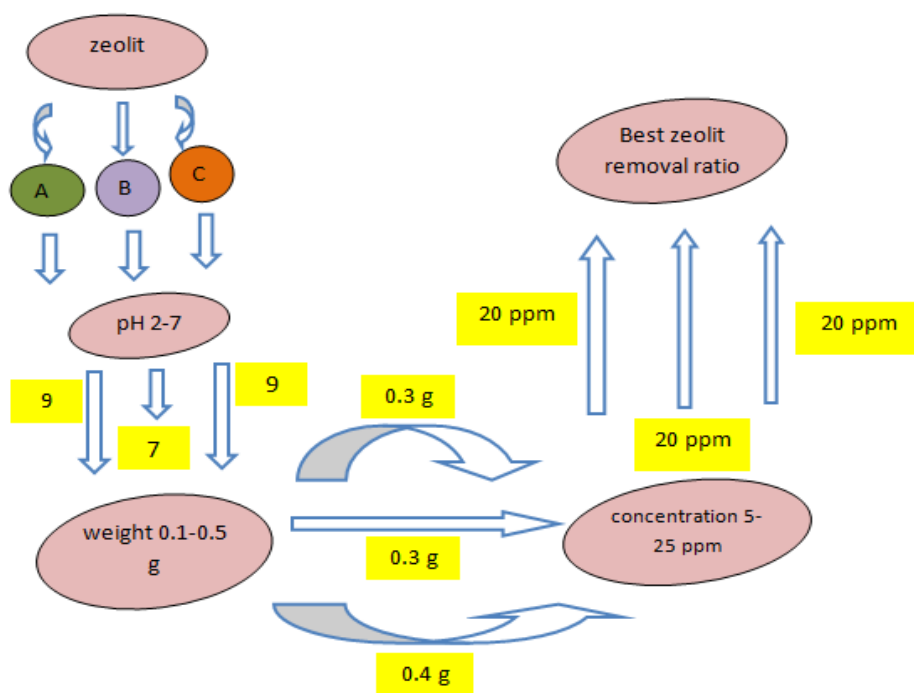


Figure 1. Experimental work optimization of synthetic zeolites adsorption with Cu metal

Optimization of synthetic zeolites adsorption with Cu metal

Optimization was done to find out the optimum weight of zeolites to adsorb Cu metal at certain concentrations and pH. In this step, the first step was to optimize the pH of Cu solution in which zeolite was weighed 0.1 gram then added 25 mL of Cu solution 10 ppm with a variation of pH 2,4 7 and 9 using a pH meter then shaker for 30 minutes, and the filtrate was taken to measure the concentration of the remaining Cu by using AAS. The second stage was the optimization of zeolite weights with a variation of 0.1-0.5 grams and the third stage was the optimization of the concentration of Cu with a variation of 5,10,15 and 25 ppm. The optimization work step can be seen in **Figure 1**. Cu concentration after adsorption (residual) could be determined by calculating Cu concentration using the equation $y = a + bx$ with the condition: adsorbed concentration = initial concentration - residual concentration.

Determination of adsorption capacity was carried out under the optimum pH of Cu solution and zeolite weights, but the variation of concentration was carried out with fixed stirring speed (200 rpm) for 30 minutes and room temperature (Al-Senani & Al-Fawzan, 2018). The adsorption capacity was calculated from the Langmuir equation (1) or the Freundlich equation (2).

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \quad (1)$$

$$\log\left(\frac{x}{m}\right) = \log k + \frac{1}{n}(\log c) \quad (2)$$

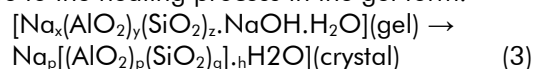
The determination of the adsorption isotherm model was done by changing the Langmuir or Freundlich isotherm equation into a straight line equilibrium curve. The determination of the equilibrium model depended on the determinant coefficient (R) with a high value.

RESULTS AND DISCUSSION

Synthesis of zeolites

Raw materials for making synthetic zeolites had to have a high silica content, one of which was contained in rice husks and corncobs. Information about rice husks and corncobs can be seen in **Table 2**. In this study, silica from rice husks and corncobs was isolated by the thermal method. After cleaning, rice husk and corn cobs were then made using stove furnaces and followed by ashes at 600 °C for 2 hours to produce corn cobs ash and rice husks as silica sources. The resulting powder was still slightly blackish color caused by other residues such as carbon and several other types of oxides that were still left behind. Besides the thermal method of silica isolation, silica can also be isolated by non-thermal methods, namely by using HCl solution. Research conducted by Wardhani, Nurlela, & Azizah (2017) produces silica from brown rice husk ash using non-thermal methods. Silica from rice husk ash and corncobs was dissolved with NaOH to produce sodium silicate. The reaction to the formation of sodium silicate is shown in **Figure 2**.

According to Kong et al. (2019) research, zeolite can be synthesized from sodium aluminate (a mixture of NaOH and $\text{Al}(\text{OH})_3$ in hot distilled water) and silica using temperature conditions of 100 °C. This heating aims to perfect the crystal growth between aluminate salts and silicate salts. The results of the mixture form a white gel that shows the interaction between the two because the polymerization process has occurred (Ojha et al., 2004). Furthermore, crystals are formed due to the heating process in the gel form.



The resulting crystalline solids are then washed with distilled water to a neutral pH to remove excess reagent from the adsorbent (Adeniyi et al., 2019). The next step is drying to evaporate the water trapped in the zeolite pores. Dehydrated zeolite will have an open pore structure with a large surface area so that it has a large adsorption ability. The chemical structure of zeolite can be seen in **Figure 3**.

Table 2. Information about adsorbent resources

Adsorbent	Main consistent	Primary source	Chemical characterization (%)		Primary uses
Rice husk (Chun, Gu, Hwang, Oh, & Lee, 2019)	The outer side of rice, obtained from rice grains stripping	Rice	SiO ₂	96.34	Wastewater treatment
			K ₂ O	2.3	
			MgO	0.45	
			Al ₂ O ₃	0.41	
			CaO	0.41	
			Fe ₂ O ₃	0.2	
Corn cob	Cotyledon forming sites and food storage	Corn	Contain a lot of rough fiber such as cellulose, hemicellulose, lignin and silica		Animal feed

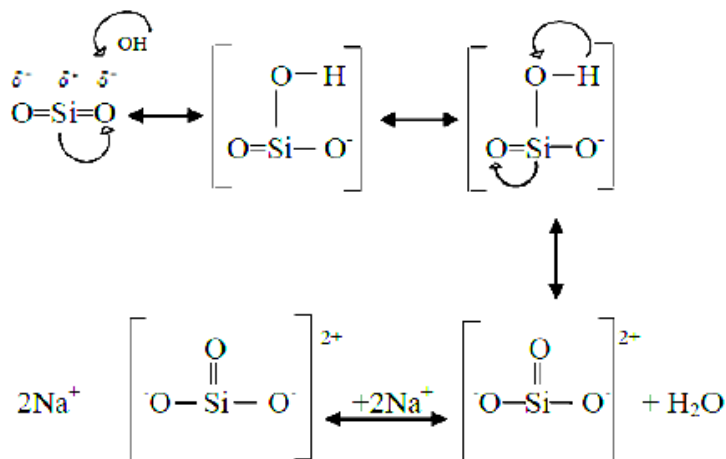


Figure 2. Reaction mechanism of sodium silicate formation (Mujiyanti, Nuryono, & Kunarti, 2010)

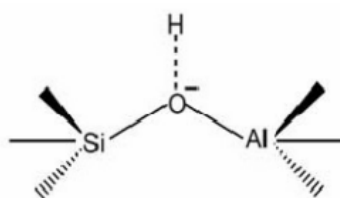


Figure 3. Chemical structure of zeolite (Mgbemere, Ekpe, & Lawal, 2017)

Characterization of zeolites

The third characterization of zeolites used XRD and SEM instruments. XRD was used to determine the type of crystals contained in zeolites, while SEM was used to determine the structure of zeolites. The results of XRD and SEM analysis can be seen in Figures 4 and 5. Characterization with XRD was carried out to determine the structure and types of minerals arranged in synthetic zeolites. From the XRD measurement, the peak for the three zeolites was at

24.3°, 13,9°, and 34,6° with the name zeolite sodium aluminum silica hydrate (S) (JCPDS no 42-0216). The crystallinity intensity of zeolite B (2318 CPS) was lower compared to zeolite A (2502 CPS) and C (3094 CPS) at 24.3°.

From the SEM results, it could be seen that the surface of the three zeolites was irregular and porous. Zeolite A had a smaller pore size (122.8-357.3 nm) compared to zeolite B (332.0-991.9 nm) and C (562.3-823.5 nm).

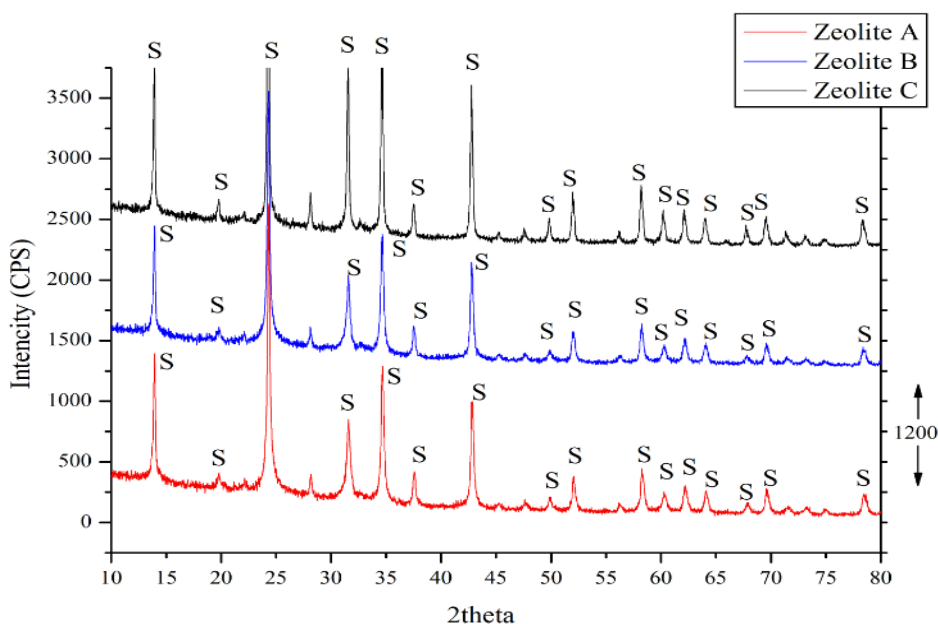


Figure 4. The XRD pattern of zeolite A, zeolite B, and Zeolite C

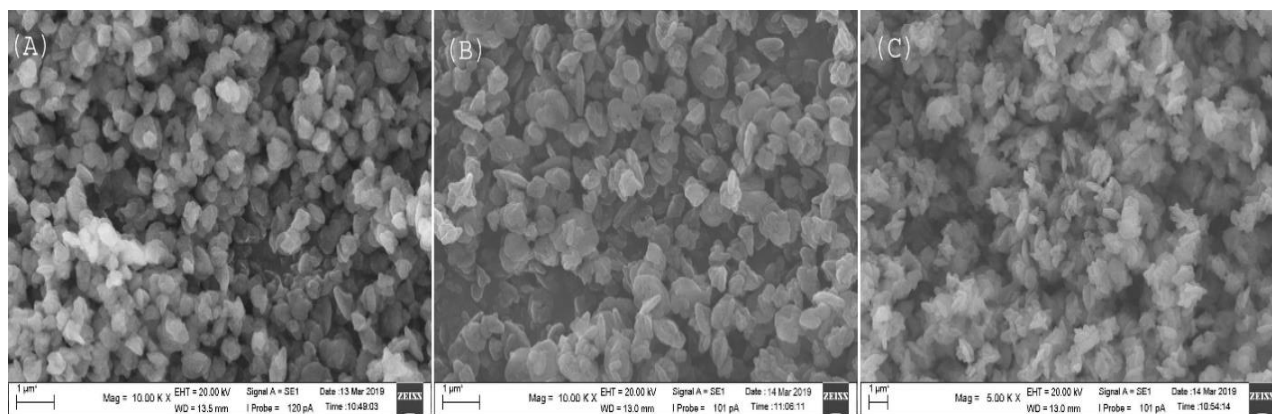


Figure 5. The SEM images of zeolite A (A), Zeolite B (B) and Zeolite C (C)

Optimization of zeolites

Adsorption is a mass transfer process that involves the accumulation of substances between two phases, such as the liquid-liquid, gas-liquid, gas-solid, or liquid-liquid phase (Gisi et al., 2016). In this study, a batch system was used. Adsorption batch experiment used several bottles containing different weights of the adsorbent. Furthermore, they were added with a Cu solution with a certain concentration at a certain pH and shaken for 30 minutes at a speed of 200 rpm.

The effect of adding zeolite weight (0.1-0.5 grams) to the reduction of Cu ions can be seen in Figure 6. Based on Figure 6, it was known that the adsorption efficiency increased from 20 to 80% at a Cu concentration of 10 ppm. The optimum condition for zeolites B and C was 0.3 grams, while for zeolites A was 0.4 grams. The greater the weight, the lower the % efficiency. This is caused by the fact that the higher weight has passed the supercritical point so that the dissolved concentration of zeolite decreases (Khuluk, Rahmat, Buhani, & Suharso, 2019). Based on Salleh, Mahmoud, Karim, & Idris

(2011), It can be done at one concentration point to see the effect of adding zeolite weight.

Optimization results for the pH variation from 2 to 9 can be seen in Figure 7. It is important to vary the pH to determine the efficiency of zeolite adsorption on Cu metal. At low pH, the positively charged zeolite surface tends not to adsorb cations. In addition, when the pH increases, the surface of the zeolite is negatively charged so that an electrostatic attraction occurs between the positive charge on the Cu metal and the negatively charged zeolite (Abd El-Latif & Ibrahim, 2009).

The effect of variations in concentration on zeolites can be seen in Figure 8. Efficiency increases with the increase of solution concentration. In addition, the optimum adsorption capacity is determined under optimum pH and zeolite weight. The adsorption capacity tends to increase with the increasing of adsorbate concentration due to increased competition among adsorbates with the active side, which will shift towards the metal complex of the active side (Gupta & Bhattacharayya, 2008). The curve relationship between adsorption capacity and concentration variations can be seen in Figure 9.

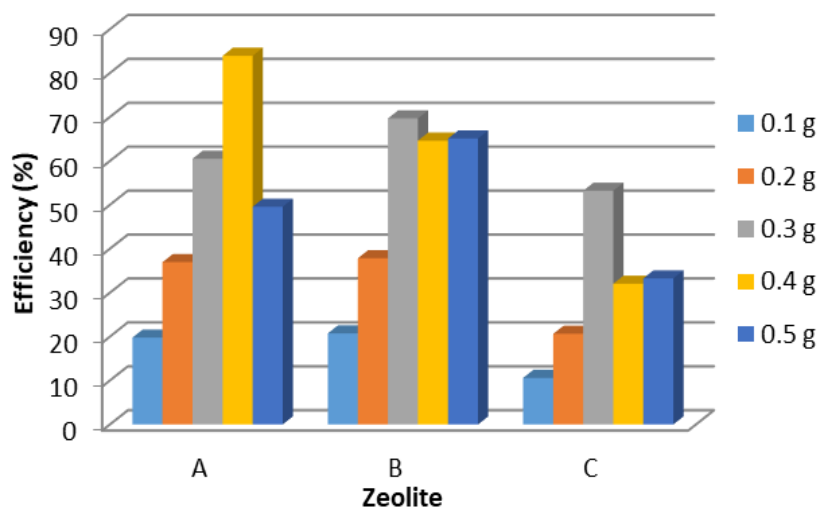


Figure 6. The removal efficiency of various zeolites with different weight

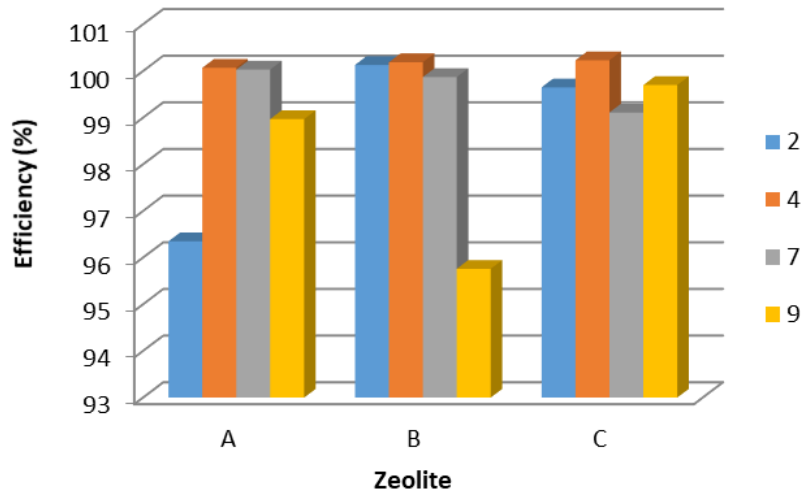


Figure 7. The removal efficiency of various zeolites with different pH

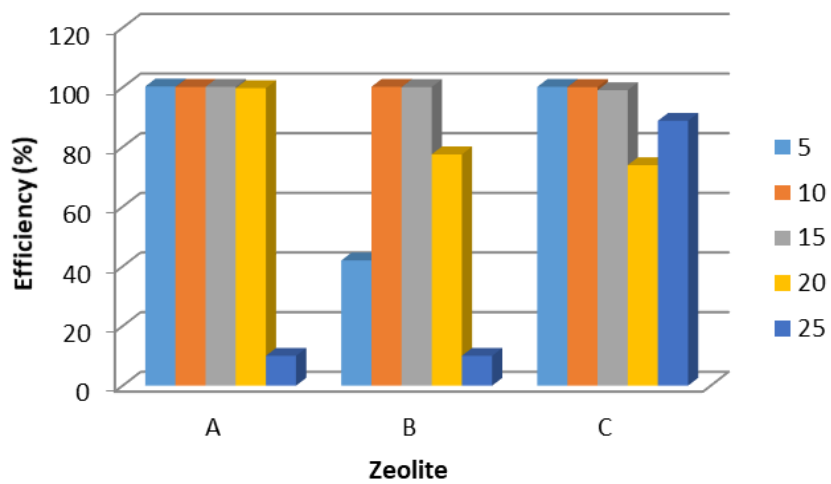


Figure 8. The removal efficiency of various zeolites with different concentration (ppm)

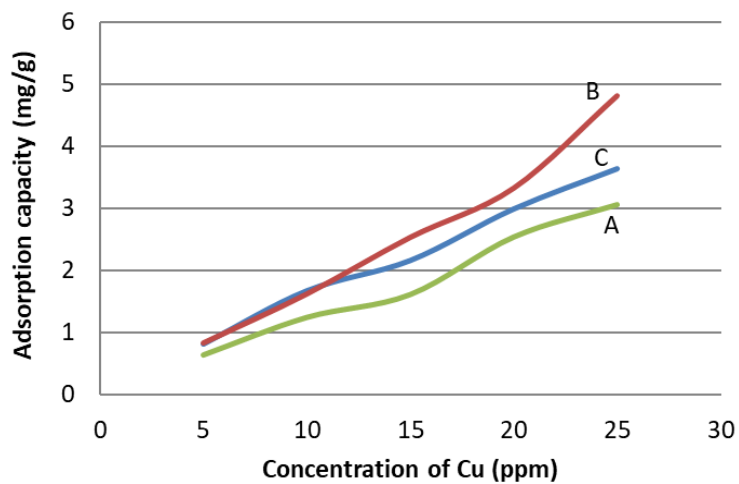


Figure 9. Graph of the relationship between adsorption capacity and concentration variations

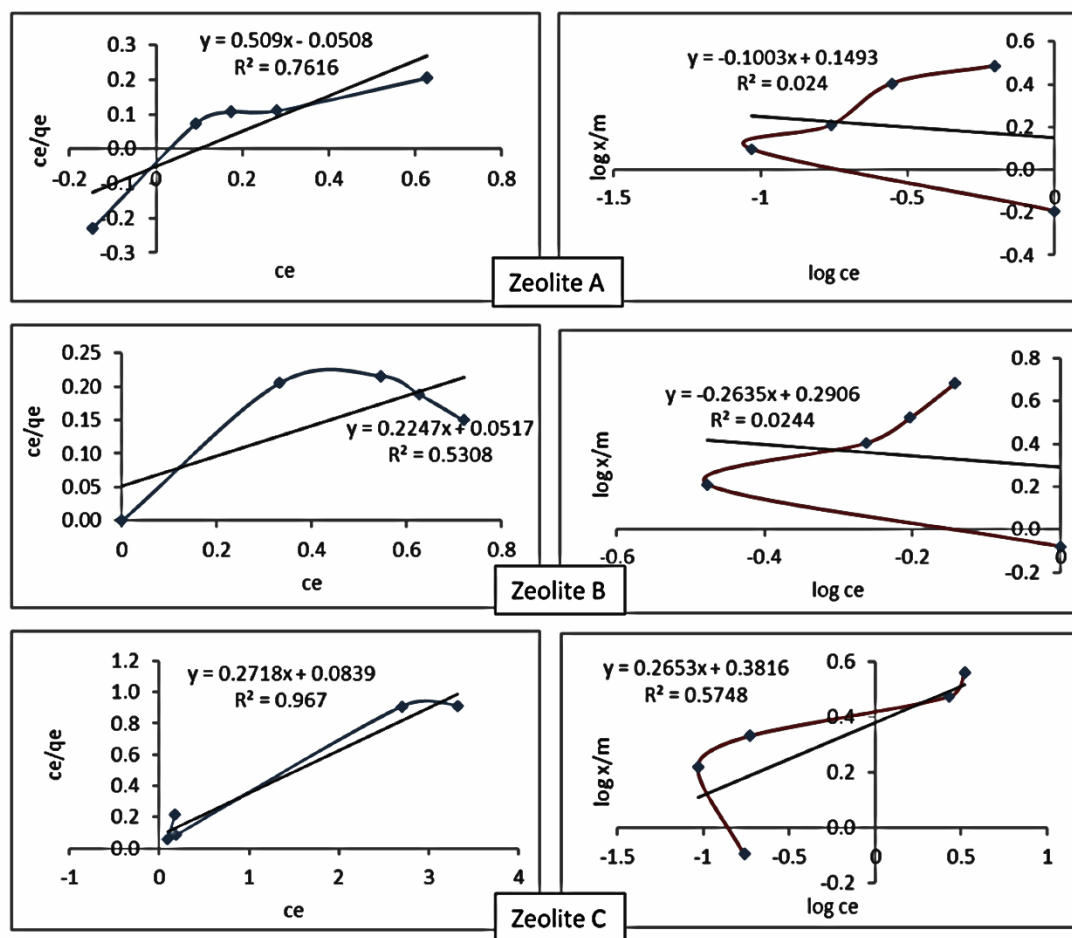


Figure 10. The adsorption isotherm of zeolite [Langmuir (left) and Freundlich (right)]

The adsorption capacity of zeolite A and C was 3.63 mg / g at a concentration of 25 ppm, while the adsorption capacity of zeolite B was greater that was 4.80 mg/g. This is caused by the fact that the adsorption ability of zeolite B was higher than zeolite A and C as evidenced by the results of SEM characteristics in which zeolite B had a greater surface area capability so that the adsorption power is better (Charles & Odoemelam, 2010).

Determination of isotherm adsorption is carried out to determine the molecular distribution between the liquid and solid phase when the adsorption process reaches a balance point (Farghali, Bahgat, & Khedr, 2013). Common isotherm adsorption models are Langmuir and Freundlich. The application of the isotherm equation is used by comparing the correlation value (R^2). The Langmuir and Freundlich adsorption isotherm model can be seen in Figure 10.

Based on Figure 10, zeolite C follows the Langmuir adsorption isotherm in which the Cu metal adsorption process occurs monolayer on a homogeneous surface, and after that, adsorption does not occur again (Al-anber, 2011). Zeolite A and B cannot determine the type of isotherm because the R^2 values in both were very low. However, further analysis needs to be done

with different methods to determine the specific adsorption mechanism for zeolites A and B.

CONCLUSIONS

The composition of rice husks and corncobs can be used as a new variant of synthetic zeolites containing sodium aluminum silica hydrate. The optimum conditions of zeolite A, B, and C adsorption were obtained at pH 7-9, with the zeolite weights of 0.3 and 0.4 grams at Cu concentration of 20 ppm. SEM characterization results showed that zeolite B had a particle shape with larger and more uniform surface area compared to zeolite A and C, in which zeolite C follows the Langmuir adsorption isotherm.

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