Heavy Metal Reducing from Kotagede Silver Handicraft Waste Using Natural Zeolite and Synthetic Zeolite

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Abstract

In order to keep our environment healthy, spreading of heavy metals should be controlled. Adsorption of heavy metals using zeolite is an alternative to limit the metals. It is known that zeolites have an ability as heavy metal adsorbent. In this study, natural zeolite and synthetic zeolite were used for removing heavy metal from Kotagede metal craft waste. In this study, two adsorbents were used. First adsorbent which called mixed-adsorbent consist of mixture of natural zeolite - rice husk ash. Second adsorbent is synthetic zeolite which made from rice husk. The natural zeolite were supplied from Wonosari Yogyakarta and rice husk for synthetic zeolite supplied from Malang. Adsorption of heavy metals was carried out by mixing waste containing heavy metals with the adsorbent. Mixing was carried out for a certain time and observed changes in the content of heavy metals in the waste. The observations on waste after processing shows that pH of adsorbents do not influence the adsorption. Conversely, contact time affects the adsorption of heavy metal from the waste. Within first of 60 minutes the mixed-adsorbent can adsorb Ag metal by 56.92% while the synthetic zeolite is able to adsorb Ag metal as much as 51.28%. In the study of the effect of activator concentration, it is shown that 3.75 N of solution has effect on the Ag adsorption of 46.15% and synthetic zeolite reaches the Ag adsorption of 44.10%.

Keywords: Zeolite, Synthetic, Adsorption, Heavy Metal, Rice Husk Ash

1. Introduction

In general, industrial waste is detrimental to humans. The increasing number of people makes environmental issues develop into global problems that urgently need to be resolved. The existence of industrial waste that is increasingly accumulating can affect the quality of human life. Waste can accumulate on the ground or enter river.

One of the environmental pollution by industry is heavy metal pollution. This pollution condition can endanger human life. Physically, heavy metals are characterized by their specific gravity greater than 5 mg/cm^3. Metals which are categorized as heavy metal such as antimony (Sb), arsenic (As), beryllium (Be), cadmium (Cd), chromium (Cr), copper (Cu), lead ions (Pb), mercury (Hg), nickel (Ni), selenium (Se), cobalt (Co), silver (Ag), and zinc (Zn).

The presence of heavy metals in the open environment must be minimized so that humans avoid direct contact that endangers health. Several methods that can be used to reduce heavy metals from waste include neutralization, precipitation, ion exchange, biosorption, and adsorption. Heavy metal adsorption can be carried out using a variety of adsorbents. One of the adsorbents that can be used is zeolite.

In this study, the ability of synthetic zeolite to adsorb heavy metals was studied. To see the ability of synthetic zeolite, a comparison of the level of adsorption by synthetic zeolite and a mixture of natural zeolite and rice husk ash was carried out. The purpose of this study was to study the ability of synthetic zeolite to absorb heavy metals measured from the effect of contact time, activator concentration, and solution pH.

2. Literature Review

Zeolite is one of the adsorbents with high adsorption ability. The surface of the pores in zeolite is relatively wide and has a cation exchange capacity so that it can be applied over a wide temperature range. Zeolite is also called a molecular sieve or molecular mesh (molecular sieve) because zeolites have molecular-sized pores so that they are able to separate or filter molecules of a certain size. Zeolites have a negatively charged surface, internal pores, good chemical composition and physical properties, making them attractive for application in separation, filtration, ion exchange, catalysis and adsorption processes (Yoldi et al., 2019).

Some of the capabilities possessed by zeolites are as a dehydrating agent, adsorption, ion exchanger, catalyst and separator. The ability of dehydration in zeolites is caused by their structure which has open pores with an internal surface area that is able to absorb large amounts of water. In addition, zeolites are able to separate molecules of substances based on molecular size and polarity. The nature of zeolite as a molecular filter is possible because the zeolite cavity is so small that it is only able to absorb molecules whose size is smaller or equal to the size of the cavity.

Basically zeolites are categorized into two groups, namely natural zeolites and synthetic zeolites. Natural zeolites are found in lava rock holes, sedimentary rocks, especially fine-grained pyroclastic sediments. Synthetic zeolites are made for special purposes and can be distinguished based on their Al and Si components (Saputra, 2006). Synthetic zeolites can be grouped according to the ratio of the levels of Al and Si components in the zeolite into: Zeolite with low Si content (rich in Al), Zeolite with moderate Si content, Zeolite with high Si content, and high Si zeolite (Kurniawati, 2010). Synthetic zeolites are more often used because of the uniformity of particle size and higher levels of purity compared to natural zeolites. In addition, the synthetic zeolite structure can be made as desired (Reyes et al., 2011).

The use of zeolites for the adsorption of certain materials is common. The term commonly used in adsorption is adsorption which is the process of moving a material from one phase to the surface of another phase, especially the solid phase (Webber, 1972). According to Said, et al., (2008) the occurrence of adsorption in zeolite takes place in the zeolite crystal spaces which are filled with free water molecules. When the zeolite mineral is heated at a temperature of 300 °C to 400 °C, the water will come out so that the zeolite can function as a gas or liquid absorber. Besides being able to absorb gas or liquid, zeolite is also able to selectively separate molecules.

Process of making synthetic zeolite using rice husk ash. Rice husk ash is produced from the burning process of rice husk. In rice husk besides carbon there is relatively much silica. Usually rice husk ash is used on a limited basis for some simple purposes, for example for rubbing ash. Even in some areas, rice husks are discarded and considered as less useful materials. In fact, rice husk ash is a very potential material as an adsorbent for heavy metals in waste.

Rice husk is a by-product of abundant rice milling. The use of rice husks has been limited to efforts to increase economic value and reduce its impact as waste. Rice husks are used as a source of silica, fuel, growing media, and water purification (Putranto et al., 2015). As a source of silica, rice husk ash has a high percentage of silica content (85-98%). In addition, there are also other components such as Potassium, Calcium, Iron, Phosphate, and Magnesium (Hsu and Luh, 1980). Rice husks when burned will produce grayish white ash with the majority content of SiO_2. Rice husk ash with a high silica composition has great potential to be used as an adsorbent. The chemical content of rice husk consists of 50% cellulose, 25%-30% lignin, and 15%-20% silica (Ismail and Waliudin, 1996). The inorganic composition of rice husk ash is different, depending on the geographical conditions, the type of rice, and the type of fertilizer used (Shukla et al., 2011).

Adsorption is generally divided into two types, namely, physical and chemical adsorption. Physical adsorption is adsorption caused by the interaction between the adsorbent and the adsorbate on the surface which is only influenced by Van Der Waals forces or hydrogen bonds (Castellan, 1982). The physical adsorption process is reversible because it can be released again with a decrease in the concentration of the solution. The adsorbate is tightly bound to the adsorbent so that the adsorbate can move from the surface to other parts and can be replaced with other adsorbates (Larry et al., 1992). Chemical adsorption is an adsorption process that involves breaking and forming new bonds on the surface of the adsorbent. Adsorbates which are adsorbed in chemical processes are generally very difficult to regenerate, this adsorption is usually not reversible. To separate the adsorbate and adsorbent must be heated at high temperatures (Larry et al., 1992).

Adsorption is a surface phenomenon. In adsorption, the interaction between the adsorbent and the adsorbate occurs on the surface of the adsorbent. The larger the surface area, the more substances are adsorbed. However, the adsorption still depends on the nature of the adsorbent (Fatmawati, 2006). Adsorption can occur between solid-liquid, solid-gas, or gas-liquid phases. The molecule that is bound to the interface is called the adsorbate, while the surface that absorbs the adsorbate molecules is called the adsorbent.

The amount of an adsorbate that is adsorbed on the surface of the adsorbent is influenced by several factors (Gaol, 2001). The first factor is the type of adsorbate. The size of the adsorbate molecule can determine the level of adsorption of the adsorbate. The molecules that can be adsorbed are molecules with a diameter equal to or smaller than the diameter of the adsorbent pores. The second factor is the polarity of the adsorbate molecule. Polar molecules are more strongly adsorbed than less polar molecules. So that the more polar molecules can replace the less polar molecules that have been adsorbed. The third factor is the purity of the adsorbent where the purer adsorbent has a better adsorption capacity. The fourth factor is the surface area, the larger the surface area of the adsorbent, the more adsorbate will be adsorbed. The fifth factor is temperature. Generally better adsorption takes place at low temperatures.

The amount of adsorbate on the adsorbent will increase as the temperature of the adsorbate decreases. Substantial physical adsorption is common at temperatures below the boiling point of the adsorbate, especially below 50 °C. On the other hand, in chemical adsorption, the amount adsorbed decreases with increasing the temperature of the adsorbate. The sixth factor is pressure. In physical adsorption, the increase in adsorbate pressure results in an increase in the amount of adsorbed substance.

3. Methods

In this research, several work steps were carried out starting with preparing an adsorbent or adsorbent. There are two types of adsorbents prepared, namely mixed adsorbents and synthetic zeolite. Mixed adsorbent is a combination of natural zeolite obtained from Wonosari Yogyakarta and rice husk ash. Natural zeolite is cleaned and activated before use. After the zeolite was activated, it was continued with heavy metal adsorption from Kotagede metal craft wastewater.

Rice husk as synthetic zeolite material was obtained from Malang, East Java. A total of 100 grams of rice husks were cleaned and then soaked in hot water for 2 hours and dried in an oven at 100°C. After that, the rice husks were mashed by pounding and then sieved through a 100 mesh sieve. Furthermore, the clean and dry rice husks were placed in a porcelain dish followed by ashing using a furnace at a temperature of 400 C for 10 hours. The results of the ashing obtained white rice husk ash which is ready to be converted into synthetic zeolite.

To obtain synthetic zeolite, as much as 20 grams of husk ash was put in a 500 ml beaker along with 120 ml of 6 M HCl and stirred using a magnetic stirrer. The solution was then filtered using whatman filter paper no. 42. Then the residue was neutralized with distilled water. The residue was dried in an oven at 120°C for 30 minutes. After drying, the residue was dissolved in 167 ml of 4 M NaOH and boiled until thickened in a furnace at 500°C for 30 minutes. The results of this heating produced crystalline solids which after cooling were added 200 ml of distilled water and allowed to stand overnight. After that, the solution was filtered using filter paper. The resulting filtrate is a sodium silicate solution. Sodium aluminate is prepared by dissolving 20 grams of NaOH in 100 mL of distilled water. The solution was heated at 100°C and then 21.6 grams of Al_2O_3 were added little by little with stirring and diluted to 250 mL. The result is a synthetic zeolite.

Prior to heavy metal entrapment, the liquid waste originating from Kotagede Yogyakarta was tested with pH parameters and metal ion levels which would later be used as initial concentrations in the sample. The liquid waste was homogenized with a magnetic stirrer then the pH of the solution was measured with a pH meter. A total of 100 mL was taken to be tested with AAS brand Perkin Elmer PinAAcle 900T to determine the initial concentration.

A total of 25 ml of the solution was put into a measuring flask and distilled water was added until the volume became 100 ml. Next, the solution was transferred to an Erlenmeyer and 2 grams of adsorbent was added to each solution. Then the solution was stirred using a magnetic stirrer at a speed of 150 rpm at various times of 20, 40, and 60 minutes. The solution was filtered using Whatman filter paper No. 42 to separate the filtrate and residue. Then the filtrate was analyzed using Atomic Adsorption Spectrophotometer (AAS) and calculated the heavy metal adsorption capacity. The same experiment was carried out on other waste samples. To study the effect of activator concentration and pH, the action steps are similar to the steps described but different treatments. In the study of the effect of activator concentration, the activator concentration was used for activation before adsorption was carried out. Likewise with the effect of the pH of the activator, before adsorption the pH of the activator was set at pH 6, 7, and 8.

4. Results and Discussion

The natural zeolite used in this study has a surface area of 111,5069 m^2/g. The synthesis of zeolite from rice husk was made in two stages. The first stage of rice husk ash preparation and the second stage of making sodium silicate solution and sodium aluminate solution. Furthermore, the two ingredients are mixed to form a solution based on rice husk ash. After mixing, a solid is formed by the following reaction (reaction 1).

$$SiO_2 + 2NaOH \rightarrow Na_2SiO_3 + H_2O$$
$$Al_2O_3 + 2NaOH \rightarrow 2NaAlO_2 + H_2O \quad (1)$$

Observation of the synthetic zeolite surface area of 90.1319 m^2/g. Na_2SiO_3 and Al_2O_3 are sources of Si and Al which are major elements in zeolites.

- ***Effect of Contact Time***

  Effect of contact time is calculated from the start of the adsorption process when the effluent and adsorbent are stirred using a magnetic stirrer. The experimental results show that the adsorbent contact time has a significant effect on the adsorption of some heavy metals as presented in Table 4.1. The experimental conditions are the mass ratio of natural zeolite adsorbent and rice husk ash (1:1) = 2 grams; Stirring speed = 150 rpm; Temperature = 30˚C; with the initial content of heavy metals known Ag = 0.065 ppm; Cr = 0.909 ppm; Cu = 1.981 ppm; Zn = 1.318 ppm. Stirring time is 20 minutes, 40 minutes, 60 minutes.

  Based on Figure 1 it can be seen that with longer stirring time the amount of heavy metals contained in the waste decreased. This shows that the adsorption that occurs is getting bigger as the contact time gets longer. The greatest increase in adsorption was experienced by Ag metal. Qualitatively, the longer the stirring time the percentage of Ag metal adsorption increased from 12.31% to 56.92%. Generally the adsorption is directly proportional to the contact time.

- ***Effect of Activator Concentration***

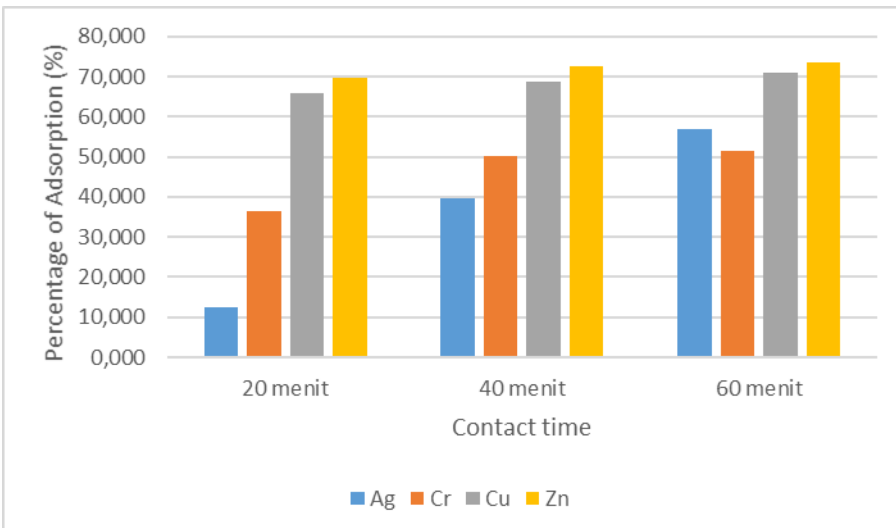
  Experimental results of the effect of activator concentration on heavy metal adsorption are shown in Figure 2. The adsorption time used was 60 minutes with an activator concentration of 1.25 N; 2.5 N; 3.75 N. The results show that the concentration of adsorbent activator has a positive effect on heavy metal adsorption. The greater the concentration, the more metal is adsorbed. Each metal is adsorbed by the adsorbent with different sizes.

  Based on Figure 2, it is known that the concentration of activator is correlated with the amount of heavy metal adsorbed. In the mixed adsorbent, there is an increase in the percentage of all metal adsorption. The mixed adsorbent has a very strong effect on the adsorption of Ag metal compared to other metals. The highest adsorption occurred when the concentration of activator was made 3.75 N with a percentage of Ag sorption of 46.15%.

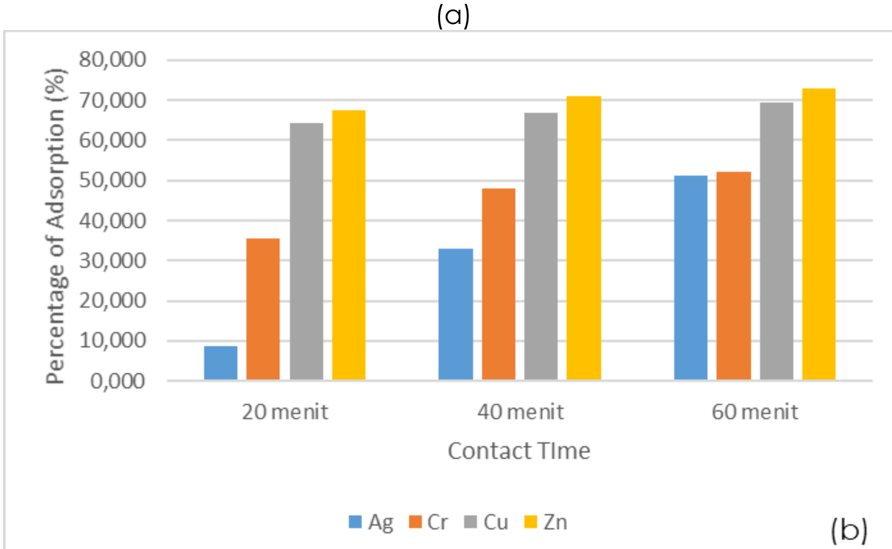
- ***Effect of pH***

  Experimental results are presented in Figure 3 with a time condition of 60 minutes and a solution pH of 6, 7, and 8. The results showed that there was a correlation between the pH of the percentage of heavy metal adsorption in the waste.

  From Figure 3 it can be seen that the pH of the solution affects the adsorption percentage. In this case the pH affects the charge of metal ions in solution. Under acidic conditions, the adsorbent will be easily protonated so that there is competition between metal ions and protons in interacting with the adsorbent. The percentage of heavy metal adsorption is relatively large at neutral pH experienced by Ag metal. At pH 8, metal adsorption decreased. This is because there is an increase in the concentration of OH- in the metal solution, resulting in metal ions binding to OH- more easily than binding to the adsorbent.



(a)



(b)

Figure 1. Influence of contact time against the percentage of adsorption (a) mixed adsorbent (b) synthetic zeolite adsorbent

Based on Figure 1 it can be seen that with a longer stirring time the number of heavy metals contained in the waste decreased. This shows that the adsorption that occurs is getting bigger as the contact time gets longer. The greatest increase in adsorption was experienced by Ag metal. Qualitatively, the longer the stirring time the percentage of Ag metal adsorption increased from 12.31% to 56.92%. Generally, the adsorption is directly proportional to the contact time.

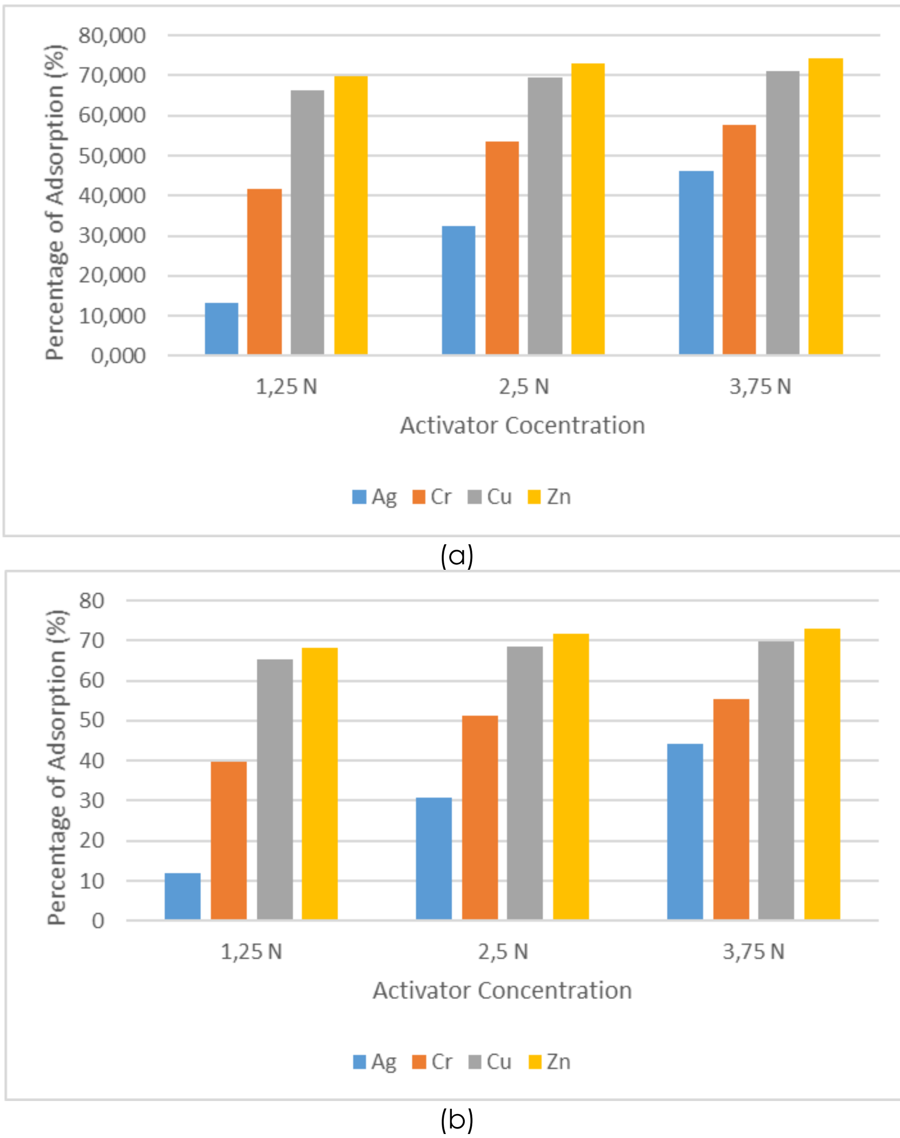
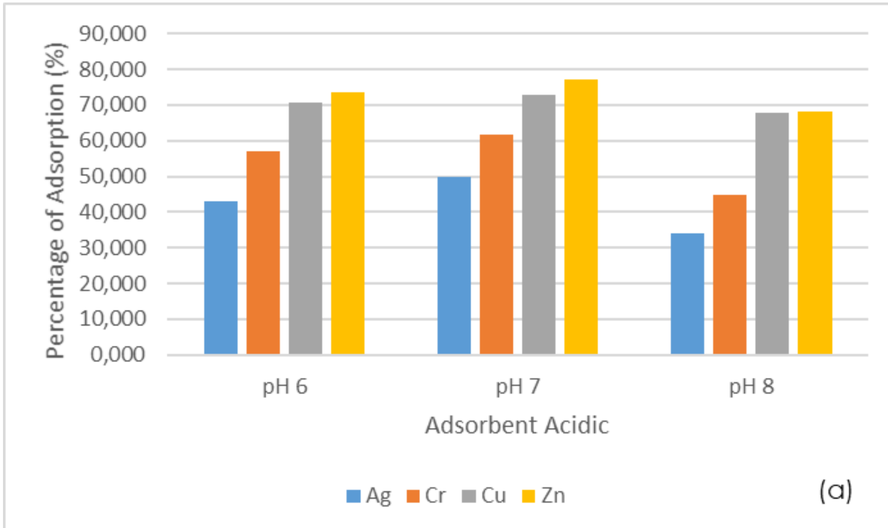
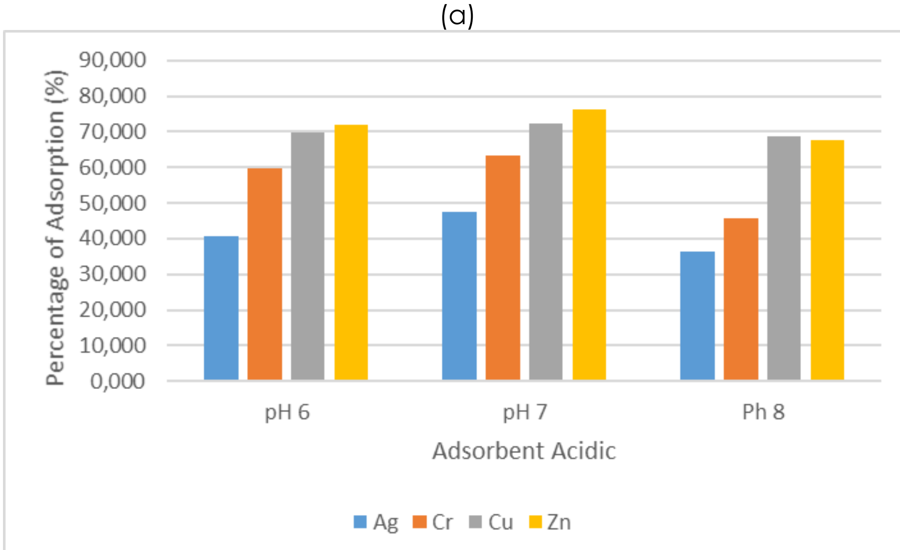


Figure 2. Correlation between activator concentration and percentage of metal adsorbed (a) mixed-adsorbent (b) synthetic-zeolite adsorbent

Based on Figure 2, it is known that the concentration of the activator correlates with the amount of heavy metal adsorbed. In the mixed adsorbent, there is an increase in the percentage of all metal adsorption. The mixed adsorbent has a very strong effect on the adsorption of Ag metal compared to other metals. The highest adsorption occurred when the concentration of activator was made at 3.75 N with a percentage of Ag sorption of 46.15%.



(a)



(b)

Figure 3. The influence of adsorbent acidic against percentage of adsorption (a) mixed-adsorbent (b) synthetic zeolite adsorbent

From Figure 3 it can be seen that the pH of the solution affects the adsorption percentage. In this case, the pH affects the charge of metal ions in the solution. Under acidic conditions, the adsorbent will be easily protonated so that there is competition between metal ions and protons in interacting with the adsorbent. The percentage of heavy metal adsorption is relatively large at neutral pH experienced by Ag metal. At pH 8, metal adsorption decreased. This is because there is an increase in the concentration of OH- in the metal solution, resulting in metal ions binding to OH- more easily than binding to the adsorbent.

5. Conclusion

Based on the results of experiments that have been carried out, it can be concluded that the time and concentration of the activator affect the amount of heavy metal entrapment. At the contact time tested, for 60 minutes the mixed adsorbent was able to adsorb 56.92% Ag metal, and the synthetic adsorbent reached 51.28%. The activator concentration which was relatively good for the adsorbent mixture of natural zeolite and rice husk ash was 3.75 N with Ag adsorption of 46.15% and for synthetic zeolite the concentration of activator was 3.75 N with a maximum adsorption of 44.10%. In the study of pH, it was found that pH did not have a significant effect on the adsorption of heavy metals.

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