EVALUATION OF LIQUID SMOKE-ACTIVATED PALM KERNEL SHELLS BIOCHAR FOR CADMIUM ADSORPTION

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ABSTRACT

This study aims at examining the cadmium metal adsorption using oil palm kernel shell biochar activated with liquid smoke. Charcoal was prepared through the pyrolysis of oil palm shells at a temperature of 380-400°C. In addition to producing charcoal, this process also produced liquid smoke from the vapor condensed in the condenser unit. Charcoal was crushed using a ball mill and was activated by immersing it in a liquid smoke solution for 24 hours to produce activated carbon, which was then characterized by Fourier Transform-Infrared (FTIR) spectroscopy. The activated carbon was used to adsorb cadmium at various initial concentrations (30 to 150 ppm), various contact time (from 30 to 180 minutes), and stirring speeds (100 and 150 rpm). The results show that adsorption efficiency was influenced by contact time and initial concentration. Maximum adsorption efficiency (95%) was obtained at 180 minutes of contact time and 60 ppm initial concentration. The results of the evaluation of the equilibrium models show that Langmuir isotherm was more suitable (constant correlation = 0.915) to describe cadmium adsorption, with maximum adsorption capacity (q_m) and Langmuir constants at 14.8 g/mg and 0.131 mg/g respectively.

Keywords: Liquid Smoke, Palm Kernel Shell, Biochar, Cadmium, Adsorption.

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INTRODUCTION

One indicator often used to detect water pollution is heavy metal contamination. A big problem for the environment, heavy metal contamination can be caused by uncontrolled industrial growth, vehicle emissions, agriculture, and domestic activities. Heavy metals are dangerous pollutants because they are toxic, especially when they get into the human body exceeding the tolerable limit. The presence of heavy metals in large quantities will affect various aspects of water, both biologically and ecologically. One of the dangerous heavy metals is cadmium, a metal in the form of silvery-white crystals. Cadmium can be found in industrial alloys, ceramics, soldering wastewater, Zn purification, pesticides, pigments, textiles and fertilizers.¹ The human body does not need cadmium to function and grow, as cadmium is very toxic and carcinogenic to humans, animals, and plants² and the World Health Organization has declared that the cadmium threshold in drinking water is 0.003 mg/L.³ Acute poisoning will cause gastrointestinal symptoms and kidney disease.⁴ For this reason, various studies have been carried out to find strategies to remove cadmium from contaminated water.

Many chemical and physical methods have been used to decontaminate metal cadmium from water including coagulation, complexation, electrochemistry, filtration, bioremediation, and adsorption⁵. The adsorption method offers various advantages to remove cadmium metal from waste including its high efficiency, low cost, and flexibility.^{6,7} Various biomass-derived adsorbents such as sunflower seeds⁸, grape seeds⁹, biochar from *Ipomoea fistulosa* have been used to treat cadmium-contained wastewater.

Before use, generally, adsorbents which are still in the form of charcoal are first activated with such chemical compounds as sodium hydroxide, hydrochloric acid, sulfuric acid, and phosphate compounds so that it becomes activated carbon. Activation is intended to enlarge the adsorbent pores for maximum adsorption. Thus, the activating compound also plays a role in the adsorption process. Among the activator candidates being promoted, liquid smoke can be an option due to its acid content. Liquid smoke

is produced from biomass pyrolysis at 300-400°C with little or no oxygen. Today, liquid smoke has been made from various agricultural waste or residues such as oil palm shells, palm fronds, coconut shells and durian skins.^{10,11} Liquid smoke from palm shells has a pH of around 3 and contains various phenolic acid and carboxylic compounds.^{12,13} Nevertheless, research on the use of liquid smoke as a carbon activator is still very limited that more researches and developments are needed. This study aims to evaluate the ability of the adsorbents from oil palm shell charcoal activated by liquid smoke to adsorb cadmium metal. The efficiency and adsorption capacity of cadmium, isotherm and the adsorption kinetics are then evaluated.

EXPERIMENTAL

Preparation of Activated Charcoal as an Adsorbent

Three kg of oil palm shells were put into a pyrolysis reactor (homemade, stainless steel, diameter= 32 cm, height = 50 cm), then heated at a temperature of 300-400°C for 3 hours. The vapor coming out of the reactor was condensed into the condensing unit to produce liquid smoke. After the pyrolysis process was completed, the reactor was cooled to room temperature and the resulting charcoal was removed from the reactor and was ground using a ball mill for 24 hours. The liquid smoke obtained was filtered to remove tar impurities. The procedure for preparing the liquid smoke and charcoal follows previous research^{12,13}. The activation process was carried out by soaking charcoal in liquid smoke for 24 hours. The activated carbon was then filtered, washed with distilled water to a constant pH (6-7). The activated carbon was finally dried at 105°C for about 12 hours to remove moisture. Then it was cooled in a desiccator at room temperature and put in an airtight container before being used for the adsorption process. The FTIR was used to characterize the activated carbon.

Adsorption Test

The activated carbon was then used to adsorb cadmium metal obtained from $\text{Cd}(\text{NO}_3)_2$ solution. The adsorption process was carried out at various concentrations, namely 30, 60, 90, 120, and 150 mg/liter. 100 ml of $\text{Cd}(\text{NO}_3)_2$ solution was put into a 250 ml Erlenmeyer, into which 1 g of activated carbon was added, then stirred at the speed of 100 and 150 rpm. The contact time between activated carbon and cadmium metal varies in 30, 60, 90, 120, 150 and 180 minutes. The filtrate was then separated from the adsorbent by using a centrifuge. Cadmium concentration testing before and after adsorption was carried out using atomic absorption spectroscopy (JEOL-JSM 6510 LA, Shimadzu, Japan).

RESULTS AND DISCUSSION

Characteristics of Adsorbents Using FTIR Test

The functional groups found on the surface of activated carbon are strongly influenced by the type of raw material, the type of heating process and the activation process. Oxygen, nitrogen, halogen, and hydrogen are the main elements on the porous surface of activated carbon. These elements can have a significant influence on the surface morphology of activated carbon, the use of adsorbents and ion exchange during the adsorption process. Figure-1(a and b) shows the FTIR spectrum for the adsorbent of pyrolyzed oil palm shells before activation and after being activated using liquid smoke.

The peaks at 3743.83 and 3649.32 cm^{-1} wavelengths in oil palm shell samples before activation indicate the presence of hydroxyl (O-H) groups whose presence appears to be reduced in activated carbon samples after chemical activation. This confirms the previous research by Ma, et al.¹⁴ that identified the presence of O-H groups in the pyrolyzed palm oil shells with a wavelength range of 4000-3400 cm^{-1} . The presence of a peak at 3049, 46 cm^{-1} wavelength indicates the presence of a C-H group whose intensity also decreases after activation. The reduction of hydrogen bonds after chemical activation was caused using a dehydrated liquid smoke activator. The reduction of O-H and C-H groups indicates that the activation process removes large amounts of hydrogen and oxygen. Hesas et al.¹⁵ who analyzed pyrolyzed oil palm shells also found the presence of C-H groups in the wavelength range of 3000-2850 cm^{-1} . The presence of the C-H group has also been identified by Ma, et al. (2016) in the range 3000-2700 cm^{-1} . Aromatic groups in activated carbon samples before activation were observed at peaks with a wavelength of 1575.84 cm^{-1} . The presence of aromatic groups increases upon activation using liquid smoke. It was

noteworthy that in the activation of liquid smoke, a new peak emerges at a wavelength of 754.17 cm^{-1} , pointing the presence of aromatic groups originating from liquid smoke as an adsorbent activator.

Fig.-1: FTIR Spectrum for the Adsorbent (a=without activation, b=activated by liquid smoke)

Study of the Adsorption Process

Effects of Contact Time and Initial Concentration

The effect of contact time between adsorbent and cadmium metal ions was studied at various initial concentrations, stirring speeds (100 and 150 rpm), and contact time (30-180 min). The effect of contact time on cadmium removal at various initial concentrations is shown in Figures 2 (a-b). For all initial concentrations, cadmium removal increases with increasing contact time between adsorbent and adsorbate. As shown in Figure 2-a, at 100 rpm stirring and 30ppm initial concentration, removal efficiency increases from 59% at 30 minutes to 93% at 180 minutes of contact time. In the contact time range of 60-120 minutes, removal efficiency only increases 3% from the 30 min contact time, but a sharp increase occurs after 150-minute contact time. The same trend also occurs at an initial concentration of 60 ppm. At the higher initial concentrations (60-150 ppm), removal efficiency at 30 minutes contact time was slightly higher (62-67%), but it did not change much until 150 minutes of contact time, where removal efficiency ranges at 70%. At 180 minutes of contact time and 90 ppm initial concentration, removal efficiency increases significantly to 94%. This is likely because the contact surface of the adsorbent was still large that it can absorb more cadmium metal. However, at 150 ppm initial concentration, the efficiency drops to 83%, which indicates that at 100rpm stirring, cadmium metal adsorption was better at low concentrations. It has been reported that at low concentrations, there were more vacant positions of an adsorbent for absorption, thereby increasing concentration slope and increasing cadmium distribution into the adsorbent⁶.

Fig.-2: Effect of Contact Time on Cadmium Removal Efficiency (a=100 rpm, b=150 rpm)

Figure-2b shows the effect of contact time on cadmium removal efficiency at 150 rpm. As shown in Fig.-2b, the tendency for increased removal of efficiency was slightly different from Fig.-2a. Removal efficiency increases slowly until the 180-minute contact time. At 30 ppm initial concentration and 30, 60, 90, 120, 150 and 180 minutes of contact time, the removal efficiencies obtained were 51, 54, 55, 56, 68 and 90% respectively. This value was smaller than that of 100 rpm stirring. Removal efficiency in this study was almost the same as that in the previous studies using palm oil mill sludge biochar (93%), but using a longer contact time of 240 minutes. The metal removal rate is affected by the mass transfer from the solution to the binding sites. It has been reported that too low stirring prevents the adsorption from taking place thoroughly, whereas too fast stirring prevents a strong bonding between the metal ions and the adsorbent from forming⁶. Stirring facilitates the interaction between the adsorbent and the adsorbate which further increases the diffusion of mass transfer between the cadmium metal and the surface of the activated carbon. However, our results showed that the effect of stirring speed was not significant.

Isotherm Studies

The adsorption isotherm is a mathematical model that illustrates the interaction between the adsorbate concentration and the adsorbent capacity obtained from the adsorption equilibrium study at a certain temperature. The adsorption isotherm plays a role in determining the maximum conditions to produce optimal adsorption. In this study, the Langmuir and Freundlich models were used to predict the equilibrium distribution of cadmium adsorption in activated carbon biochar from palm oil shells.

Langmuir Isotherm Model

In the Langmuir model, it is assumed that the monomolecular layer is formed during the adsorption event. All sites are equivalent and there are no interactions between adsorbed species. Adsorption takes place only on specific homogeneous sites in the adsorbent. When a specific site is occupied by an adsorbate molecule, further adsorption will not take place at that site.^{5,17}

Table-1: Maximum Adsorption Capacity of Various Adsorbents for Cadmium Adsorption

Adsorbent	Maximum Adsorption Capacity (mg/g)	Reference
Palm kernel shells (Liquid smoke activated)	14.81	Present study
Palm kernel shells (NaOH activated)	22.37	Ref.6
Bio-nanocomposite of chitosan	344.00	Ref. 18
Sugarcane bagasse	14.80	Ref.19
Cocoa pod husk biomass	13.43	Ref.20
Microwave induced oil palm shell activated carbon (phosphoric acid-impregnated)	227.27	Ref.21
Grape lex activated carbon	58.20	Ref.22
Commercial activated carbon (HCL activated)	25.10	Ref.23

Fig.-3: Langmuir Isotherm Model at 100 rpm

Figure-3 shows the equilibrium graph for the Langmuir isotherm model. The intercept shows the adsorption intensity, while the maximum adsorption capacity ($q_{\max}$) was calculated from the slope. The results of the analysis show that the value of the correlation coefficients (R^2) for the Langmuir equation was 0.905. At 100rpm stirring speed, the values of $q_{\max} = 14.81$ m/mg and $K_L = 0.16$ L/g were obtained. This value of the maximum adsorption capacity obtained was lower than in previous studies using activated coconut shell charcoal with NaOH activator, which was 22.37⁶. Table 1 shows $q_{\max}$ from some previous studies.

Fig.-4: Relationship between the Separation Factor Constants and Initial Concentration at 100 rpm

Important characteristics in the Langmuir isotherm can be expressed in the form of constant separation factor (R_L). This value predicts whether the isotherm takes place irreversibly ($R_L = 0$), favorable ($0 < R_L < 1$) or unfavorable ($R_L > 1$). Figure 4 shows the relationship between the separation factor constants and the initial concentration at 100 rpm stirring. The R_L value at an initial concentration of 30 mg/L was 0.169 and decreases to 0.039 at an initial concentration of 150 mg/L. It can be seen that the R_L value was less than 1 (for all initial concentrations), indicating that the adsorption of cadmium in activated carbon of oil palm shell biochar was favorable.

Freundlich Isotherm Model

This model describes a heterogeneous system, used to show non-ideal and reversible adsorption forms and not restricts with monolayer formation. This isotherm is widely used to explain the adsorption process of aqueous solutions. The Freundlich isotherm model for cadmium adsorption in this study was presented in Fig.-5. The isotherm constant values (K_f and n) of the Freundlich were 2.779 and 2.009, with $R^2 = 0.745$. The R^2 value of the Freundlich was smaller than Langmuir, which shows that the Langmuir model was more suitable to explain the cadmium adsorption equilibrium system with liquid smoke-activated carbon from palm kernel shells. This indicates that cadmium adsorption was more of monolayer adsorption with minimal interaction between adsorbed ions rather than surface adsorption with heterogeneous energy distribution.^{21,24} The results were different from those in the previous studies using NaOH activator, whose results show that both isotherm models were compatible.⁶

Fig.-5: Freundlich Isotherm Model at 100 rpm

CONCLUSION

In this research, liquid smoke can be an alternative activator to produce activated charcoal from biomass for the adsorption of heavy metals such as cadmium. The maximum adsorption capacity obtained was 14.8 g/mg with adsorption efficiency reaching 95%. At the contact time of 30-90 min, adsorption efficiency ranges at 60% and increases sharply along with the increasing contact time. The Langmuir model was more suitable to describe the isotherms with $R^2 = 0.9054$, suggesting that monolayer adsorption occurs between adsorbents and cadmium. The kinetics value of the study indicates that the adsorption behavior was better described as the first-order reaction with an R^2 greater than 0.99. At 100 rpm stirring, the values of K_1 and Q_e obtained were 1,045.46 g/mg.min and 103.09 mg/g respectively. The value of constant separation factor for cadmium was less than 1 for all initial concentrations and stirring speed, indicating that the cadmium absorption process was going well.

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