

Banana Peel Activated Carbon in Removal of Dyes and Metals Ion in Textile Industrial Waste

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Abstract. Textile waste is produced in the starch process, a starch removal process, coloring, and printing. The use of banana peel (*Musa Paradisiaca*) was an alternative that was being developed as an absorbent to remove the color content and metal ions in textile waste. The purpose of this study was to analyze the workings and effectiveness of heavy metal adsorption and textile dyes with banana peel waste. Banana peel particles that were ready to be used as adsorbents were characterized using Scanning Electron Microscopy (SEM) to obtain particle morphology. Absorbance curve of Cu^{2+} dan Cr^{6+} can be obtained using spectrophotometric UV-Vis analysis with a wavelength of 635 nm for copper (Cu) and 469 nm for chromium (Cr). The activated carbon of banana peel was applied to 50 ml industrial waste solution and observed changes in absorbance for 120 minutes. The activated carbon was directly in contact with the solution of metal ions but the adsorption power was still not seen effectively so that the Atomic Absorption Spectroscopy (AAS) test was performed. The results of AAS analysis, namely activated carbon can reduce copper and chromium ion content respectively by 55.5% and 61%. If this activated carbon was used as an adsorbent for dyes in textile waste, the average absorption capacity of dye ion was 12.21% during the contact time of adsorption 120 minutes.

Introduction

Indonesia is a developing country that has thousands of companies in the industrial sector. From Sabang to Merauke every industry will not escape with the waste disposal. Waste may consist of solid, liquid, and gas wastes. Waste to be disposed of must be through serious processing because of a lot of dangerous contents that can pollute the environment and can damage the ecosystem. One of them is liquid waste that can kill life in water with the existence of waste containing hazardous and toxic substances (B3). Examples of B3 waste are heavy metals such as Al, Cr, Cd, Cu, Fe, Pb, Mn, Hg, and Zn. Heavy metals are generally toxic even in low concentrations [1]. Based on the chemical and physical properties, the level of toxicity of heavy metals to aquatic animals can be sorted (from high to low) as follows mercury (Hg), cadmium (Cd), zinc (Zn), lead (Pb), chrome (Cr), nickel (Ni), and cobalt (Co). According to [2] the list of the highest to lowest metal toxicity order for humans who consume fish is as follows $\text{Hg}^{2+} > \text{Cd}^{2+} > \text{Ag}^{2+} > \text{Ni}^{2+} > \text{Pb}^{2+} > \text{As}^{2+} > \text{Cr}^{2+} > \text{Sn}^{2+} > \text{Zn}^{2+}$. The properties of heavy metal toxicity can be grouped into 3 groups, are high toxic consisting of elements Hg, Cd, Pb, Cu, and Zn. Medium toxic is composed of Cr, Ni, and Co, while the low toxic is made up of elements Mn and Fe.

Apart from being free of heavy metals, discarded industrial wastewater is also kept from being contaminated by dyes. The coloring is a pollutant that can be identified by direct vision used in various industries such as textiles, food, paper, plastic, food, and cosmetics. The content of these pollutants can be prevented by removing one of the dyes namely methyl blue before liquid waste is discharged into the environment.

The toxic content contained in the water is very dangerous for the human body such as poisoning. Symptoms of acute poisoning include the feeling of metal in the patient's breathing and the presence of a burning sensation in the throat and vomiting. Symptoms of Wilson's disease is hepatic cirrhosis, for example, damage to the brain, as well as the decline in kidney activity and metals deposition in the cornea of the eye. Symptoms of Kinsky's disease is the formation of stiff and reddish hair in the patient.

Several techniques have been developed to remove metal ion content in industrial wastewater such as adsorption, flocculation, pyrolysis, and ion exchange. According Fong Moi study, polyaluminium chloride (PACl) coagulant is effective to adsorb heavy metal (Pb and Zn) more than 99% [3]. Pyrolysis process contacted cellulose/metal ion mixtures. The addition of metal ions to influence the pyrolysis of cellulose and with it the distribution of volatile and non-volatile products. Christian's study described that experiments focusing on the selective increase in yield for a specific pyrolysis product after the addition of salts and also phosphoric acid [4]. Ion exchange technique can remove traces of ion impurities from water and process streams and give a product of desired quality. Ion exchangers are widely used in large application in water treatment and pollution control the scale of operations is relatively small, for instance in the rare earth elements or noble metals, but the values of recovered metals are very high. Ion exchange process is particularly suitable for purification of metal ions with a high value and low processing [5]. Each method has advantages and disadvantages in terms of operation, cost, and design. In the adsorption process, an adsorbent is required such as activated carbon to absorb harmful compounds such as heavy metals and dyes. However, the use of activated carbon is high cost so that alternative natural adsorbent materials can be replaced [6].

Eco-friendly natural materials such as fruit and vegetable waste are being investigated to eliminate the dyes and heavy metal content found in water. As an example is the peel of a banana fruit. Banana peel as a vegetable material is believed to be an alternative to remove the heavy metal content contained in water by acting as an adsorbent. Purification and treatment of wastewater that is free of dyes and heavy metals make the survival of aquatic biota protected. In addition, banana peels have high adsorption power for organic compounds.

With the use of banana peels as an alternative to activated carbon, it can reduce the untapped banana waste. However, it is still unknown the effectiveness of banana peel adsorption in the absorption of other compounds. Therefore, further research is needed, to obtain a beneficial water treatment method because of its high effectiveness and adsorption capacity and low operational costs. In this study, we observed the adsorption capacity of banana peels including an adsorbent dosage that must be applied, waste color concentration, and waste pH for removal of textile dyes.

Materials and Methods

This research was conducted experimentally, the results of which will be analyzed regarding the effect of contaminant levels (metal dyes and ions), contact time, adsorbent content, and particle size of the adsorbent on adsorbent absorption. Material characterization and adsorption kinetics will be carried out to determine the efficiency of adsorption from banana peels.

Materials

The materials used in this study were banana peel, HCl, NaOH, textile industry waste, CuSO₄, K₂Cr₂O₇, and methyl blue. While the tools used are a set of adsorption devices, ovens to dry banana peels, vibrating screens to classify particle sizes of banana peels, magnetic stirrers for enlarging contact adsorbs, and UV-Vis Spectrophotometers to determine metal ion levels and textile dyes

Materials preparation

Banana peel that can be obtained from the local market is separated slowly from the fruit. Then it was washed using distilled water to avoid contaminants. Clean banana peel was dried in the sun for 2 consecutive days and continued with drying in the oven at 80°C for 18 hours until it was

completely dry. After that, dried banana peels are smoothed and classified according to the use of vibrating screens with the largest mesh size of 300 μm .

Analysis Characterization

Banana peel particles that are ready to be used as adsorbents were characterized using Scanning Electron Microscopy (SEM) to obtain particle morphology, Brunauer-Emmett-Teller (BET) to obtain particle porosity data, Atomic Absorption Spectroscopy (AAS) to determine the concentration of metal ion solutions which has been contacted with banana peel activated carbon and the Fourier Transform Infrared Spectrometer (FTIR) to analyze functional groups in banana peel particles. This characterization is carried out before and after the adsorption process.

Experiments

The experimental mechanism carried out was to contact 0.6 grams of activated carbon material in a 50 ml of 1:9 (v/v) batik waste solution. The contact time was carried out for 120 minutes, by observing the concentration of batik waste in the solution every 20 minutes using a UV-Vis spectrophotometric analysis. The isothermic adsorption method was used in this experiment so that there is no temperature change as seen in Fig. 1.

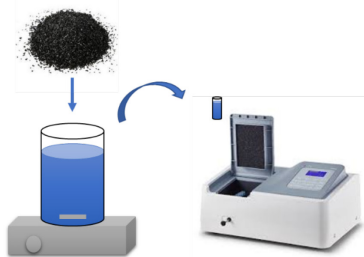


Fig. 1. Adsorption experiment.

Results and Discussion

Adsorption is the process of accumulating adsorbate on the surface of the adsorbent caused by the attraction between molecules or a result of a force field on the surface of the solid (adsorbent) that attracts molecules of gas, steam or liquid. Waste of banana peel is used as an adsorbent of activated carbon for removing metal ions and dye ions in textile waste. The area of activated carbon is a very important parameter in determining the performance of activated carbon absorptivity. The area of activated carbon was measured using the Brunauer Emmet Teller (BET) Analysis, the adsorption of N_2 gas to fill the entire surface of the activated carbon, including in its pores, was recorded in units of volume which can then be analyzed using the equation (Eq. 1):

$$\frac{z}{(1-z)V} = \frac{(c-1)z}{c V_{\text{mono}}} + \frac{1}{c V_{\text{mono}}} \quad (\text{Eq. 1})$$

Where z is ratio of operating pressure/saturation pressure, V is the volume of gas that fills the surface on an activated carbon, V_{mono} is the volume of gas that forms 1 layer on the surface of the activated carbon, and c is a constant. From this equation, it can be obtained the value of the area owned by activated carbon in the unity of grams of activated carbon from slope and intercept value. The slope value of banana peel activated carbon, banana peel activated carbon by KOH solution, and commercial activated carbon are respectively 47.54, 22.7, and 35.1; while the intercept value are 33.79, 13.76, and 0.93.

Table 1 shows a comparison between banana peel carbon before and after activation using KOH alkaline solution. The area of banana peel carbon increased by more than 2 times after activation, from 42.814 m^2/g to 95.271 m^2/g in which the area of commercial activated carbon is 96.74 m^2/g . The size of this active carbon area shows a significant difference compared to commercial activated carbon. This shows that the activated carbon from banana peel can be used as a substitute for commercial activated carbon for the adsorption process supported by almost the same surface area.

Table 1. Comparison of banana peel activated carbon.

Banana peel activated carbon		Banana peel activated carbon by KOH solution		Commercial activated carbon	
z [P/P*]	V [cc/g]	z [P/P*]	V [cc/g]	z [P/P*]	V [cc/g]
0.095	2.234	0.103	5.644	0.1	19.77
0.15	3.463	0.151	8.335	0.152	22.861
0.203	4.656	0.201	11.09	0.201	25.531
0.252	5.844	0.251	13.97	0.253	27.742
0.308	7.327	0.301	16.48	0.303	29.892

Activated carbon that has been activated first uses an activator to increase the porosity value and specific surface area because the carbonization results are absorbent materials that are less active without further activation. The activator substances used are 0.5 N and 0.1 N NaOH solutions. Fig. 2 and 3 are the result of SEM analysis to determine the morphology of activated carbon particles. In the picture, there are small pores formed after the banana peel passes through the process of carbonization and activation of alkaline solutions. Activator NaOH 0.5 N has smaller pore than activator NaOH 0.1 N which is indicated from BET analysis about 9.34 nm and 13.94 nm respectively. An adsorbent must have a high specific surface area, which has small diameter pores so that the adsorbate retention process by the adsorbent is more effective.

Specifically, the pore size also determines the adsorption of a particular compound in solution. If the adsorbent's pore size gets smaller, the adsorption capacity is greater, assuming that the adsorbed component can enter the porous cavity. The greater number of adsorbents will provide a larger surface area for the adsorbate to be desorbed. In addition, the more the amount of adsorbent, the greater contact opportunities with the adsorbate molecules.

According to the analysis of SEM-EDX on 0.5 N NaOH activator contained 37.88% (w/w) of carbon, 36.01% (w/w) of oxygen, and the other component such as Na, Mg, and Si. While at 0.1 N NaOH activator has similar components in the result which is contained 45.94% (w/w) of carbon and 32.33% (w/w) of oxygen. The presence of other components is caused by incompletely dissolved in water washing process. Khu Le Van study obtained characterization and adsorption of rice husk as a supercapacitor. From that study the composition of carbon (C) atom is 83.04% (w/w) while oxygen atom is 16.96% (w/w) [8].

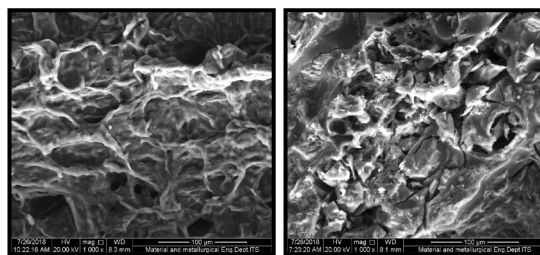


Fig. 2. Morphology of banana peel activated carbon using NaOH activator (a) 0.5 N, (b) 0.1 N.

The activated carbon of banana peel was applied as an adsorbent in textile waste with a ratio of concentrations between textile waste and aquadest at 1: 9 (v / v) in a mixed volume of 50 mL. The volume ratio of 1:9 means that 5.5 mL the textile waste solution mixed with 44.5 mL aquadest. Table 2 is the result of the absorbance analysis using a UV-Vis spectrophotometer with a maximum wavelength of 663 nm. The analysis results using 0.3 grams of Banana Peel Activated Carbon (BPAC) have an average adsorption power of 12.21%. The higher the concentration of NaOH activation solution, the higher the adsorption power.

The activated carbon of banana peel is then tested in a textile waste solution where the waste contains Cu and Cr metal ions with the same method steps. The results of 120 minutes of adsorption were carried out by AAS to determine the concentration of metal ions contained. Table 3 is the AAS results and turbidity test on textile waste, which states that the longer the adsorption time of metal

ion concentration and turbidity level of the solution decreases [9]. This indicates that banana peel activated carbon can be used as an alternative to environmentally friendly adsorbents to reduce metal ion content in textile industry waste.

Table 2. Results of analysis of absorbance of textile waste solutions.

Time [minutes]	Alkaline Activator NaOH 0.1 N	Alkaline Activator NaOH 0.5 N
	1 : 9	1 : 9
0	0.562	0.977
20	0.555	0.908
40	0.533	0.865
60	0.551	0.849
80	0.543	0.844
100	0.542	0.792
120	0.538	0.78
% Adsorption	4.27	20.16
% Average of Adsorption	12.21	

Table 3. The results of the AAS analysis and the turbidity of the textile industry waste.

Time of Adsorption [minutes]	Solution sample		Turbidity [FTU]
	Cu Ion [ppm]	Cr Ion [ppm]	
0	0.09	0.95	556
40	0.07	0.62	541
120	0.04	0.37	523
K ₁ Lagergren Adsorption Kinetics [min ⁻¹]	0.037	0.026	-
K ₂ McKay Adsorption Kinetics [g min/mg]	1.159	0.298	-

Adsorption kinetics study is needed to determine the value of the adsorption rate constant indicated by the value k . The value of k_1 is the kinetics data analyzed in pseudo-first-order while k_2 is the kinetics data in the pseudo second order. Pseudo-first-orders use Lagergren equations and pseudo second orders using the McKay equation [10]. In this case, the Lagergren adsorption kinetics model was also used for the liquid-solid system. The sample used is the adsorption of methylene blue in textile waste with activated carbon. This model has been widely applied to adsorb pollutants in the solution system. According to Debora study [11] the maximum capacity of adsorption is 178 mg/g for reducing methyl blue content in solution system. The second order pseudo adsorption kinetics model developed by McKay was also carried out in this study. The results of the BPAC adsorption kinetics equation for methylene blue in textile waste with pseudo-first-order and pseudo-second-order are shown in Table 4.

Table 4. Results of Adsorption Kinetics.

Pseudo-first-order	Alkaline activator NaOH 0.1 N	Alkaline activator NaOH 0.5 N
	1 : 9 (v/v)	1 : 9 (v/v)
q_e [mg/g]	0.0004	0.0033
k_1 [1/min]	0.0051	0.0087
Pseudo-second-order	Alkaline activator NaOH 0.1 N	Alkaline activator NaOH 0.5 N
	1 : 9 (v/v)	1 : 9 (v/v)
q_e [mg/g]	0.0004	0.0033
k_2 [g min/mg]	1.4449	1.8928

Conclusion

Banana Peel Activated Carbon (BPAC) can be applied as an adsorbent of metal ions (copper and chromium) and dyes in textile waste, with adsorption power in textile waste solutions for dye ion removal of 4 - 20%. Although this adsorbent has relatively low carbon content based on SEM-EDX, BPAC could reduce metal ions about 55 – 61%.

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