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Chromium contaminant uptake of Batik Industry effluent using adsorbent from Coconut Waste

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ABSTRACT

Batik is a heritage culture of Indonesia which gains high demand in market. Industry of Batik used a high amount of water and created environmental pollution due to its wastewater. The pollution arises from Batik-making process whereas the colouring material contains heavy metals such as chromium (Cr). Aim of this research was to determine the potency of coconut husk, which is a by-product of coconut, as activated carbon or adsorbent of Cr in Batik wastewater. An experimental study and was conducted to assess the effect of different adsorbent dosage and contacting time to Cr concentration in Batik wastewater. The results indicated that there were no different effect of adsorbent dosage to Cr removal. However, the contacting time showed that 30 minutes was the optimum level to reduce Cr content in Batik wastewater.

Key words *: Activated carbon, Coconut husk, Heavy metal, Pollution, Wastewater*

Introduction

Indonesia is an archipelago that is rich in resources and various cultural heritages (Felaza, 2015; Selamet, 2018). The wealth of resources and various cultural heritages in Indonesia are the basis for the country's development (Asfina and Ovilia, 2017). One of Indonesia's well-known cultural heritages is batik (Steelyana, 2012; Kusumasari, 2013). Batik is an artwork that has high value (Kusumawati and Hartowiyono, 2017; Dinata and Fan, 2019). In 2009, UNESCO had acknowledged Batik as a global cultural heritage (Jones, 2018; Sulistianingsih and Pujiono, 2018). This influences the level of demand for batik production which is increasing tremendously (Habib *et al.*, 2017). The rise in batik production has caused environmental pollution problems, especially rivers due to its wastewater (Tangahu *et al.*, 2019)

The environmental problems arise due to batik-making processes. It is appraised that the utilization of water in the batik-making process is around 25 - 50 m^3 per meter of batik cloth (Indrayani, 2018). Ministry of Industry data in 2017 shows that the production of batik in Indonesia averages 500 million meters per year, which is equivalent to 25 million m^3 of water annually (BBKB, 2020). Moreover, the batik coloring process usually uses naphthol and indigo colors which contain heavy metals such as chromium (Cr) (Desianna *et al.*, 2017; Hastuti *et al.*, 2018). Therefore, there would be high amount of polluted wastewater that will be discharged into waters as the results of Batik making and this may damage the water quality of adjacent rivers (Murniati *et al.*, 2015; Natalina and Firdaus, 2018)

The heavy metal Cr in waters with relatively high concentrations may damage aquatic organisms due to its toxicity (Huseen and Mohammed, 2019), while in relatively low concentrations, it will accumulate in the bodies of aquatic organisms such as plankton

(Burada *et al.*, 2006). The toxic power possessed by heavy metals will work as a barrier to enzymes, so that the body's metabolic processes are cut off (Jan *et al.*, 2015). Furthermore, this heavy metal will act as an allergen, mutagen, teratogen or carcinogen for humans (Tchounwou *et al.*, 2012).

The adsorption process is a waste treatment technique which is expected to be used to reduce excessive concentrations of heavy metals (Soliman and Moustafa, 2020). One of the adsorbents that are often used in the adsorption process is activated carbon (Ndi Nsami and Ketcha Mbadcam, 2013; Saleem *et al.*, 2019). However, commercially available activated carbon is very expensive and has high regeneration costs (Park *et al.*, 2019). Several studies have been conducted to find out the possibility of making activated carbon which is cheaper, one of which is from agricultural waste (Ukanwa *et al.*, 2019; Ani *et al.*, 2020). Waste from coconut trees is widely used to produce activated carbon, especially coconut shells (Gratuito *et al.*, 2008; Sanni *et al.*, 2017). Another part of coconut that is rarely used is coconut husk. Whereas coconut husk is a potential agricultural waste to be used as activated carbon because it contains lignin and cellulose (Suhas *et al.*, 2007; Wang and Sarkar, 2018). This study is aimed to determine the use of coconut husk as adsobent to diminish chromium content in batik industrial wastewater.

Material and Method

Activated Carbon Preparation

In general, there are three stages of making activated carbon (Mistar *et al.*, 2020) from coconut husk, namely dehydration, carbonization, and contact with waste . The coconut husk (Figure 1a) was taken from coconut sellers in Blimbing market, Malang. This material was considered as waste by the seller and farmer. The first step is to separate the coconut husk from the outer layer or coconut skin. After that, proceed with the process of dehydration by drying the coconut husks in the sun for 2 days to dry. This process aims to remove the water content in coconut husks. Furthermore, the carbonization process by burning coconut husk. The process aims to decompose the organic material and remove the dirt on the coconut husks. After that, the activation process is done by heating coconut husk which has turned into carbon (Figure 1b) at a temperature of 200 ^{0}C. Then it is into powder. After being powdered, it is sieved with a sieve measuring 500 microns. Then, it is weighed using a digital scale to achieve the designated dosage.

Industrial Batik Effluent Sample

Batik industrial wastewater that used for this research was obtained from Batik craftsmen in Malang City, Indonesia. The wastewater was resulting from batik colouring which contained a lot of dye and colour enhancer. It was observed that the wastewater had temperature of 21^0C, pH of 9.8, and Cr content of 0.144 mg/l. The concentration of chromium in this wastewater was greater than the standard set by Ministry of Environment Indonesia (<0.05 mg/l). Therefore, Batik wastewater should not be immediately discharged into adjacent waters or rivers since it will create pollution.

Design of Experiment and Statistical Analysis

The research used completely randomised factorial design (Figure 2) to analyse the effect of activated carbon from coconut husk doses and contacting time to the Cr removal from Batik wastewater. The doses were A1:0.5, A2:1.5, and A3:2.5 g, while the contact-

(a) (b)

Fig. 1. (a) Coconut husk; (b) Activated carbon of coconut husk

ing time were B1:30, B2:60, B3:90, B4:120, and B5:150 minutes. The activated carbon was applied to 1 L of Batik wastewater that placed in a jar with different doses and two replications. Therefore, this study utilized 30 experimental units. (jars). Then, temperature, pH, and Cr concentration of the wastewater were measured for every contacting time. Cr concentration was analysed using AAS. The measurement results then statistically analyse using R software.

A2B1	A1B2	A3B4	A2B4	A3B1
A3B3	A1B4	A3B5	A1B1	A1B3
A3B5	A1B2	A2B2	A1B3	A2B5
A3B2	A3B3	A2B5	A1B5	A3B1
A2B1	A1B4	A2B3	A2B3	A2B2
A2B4	A3B2	A3B4	A1B1	A1B5

Fig. 2. Experimental layout of the research

Results and Discussion

Cr Concentration and Water Quality of Batik Wastewater

It can be seen from Figure 3, the general trend of Cr concentration in Batik wastewater after the application of activated carbon was decreased along to the increasing of contacting time. However, there were few fluctuations of it. Lowest Cr concentrations were observed at contacting time of 150 minutes at all doses. However, at doses of 0.5 and 1.5 mg/l, the highest Cr concentration recorded at 60 minutes of contacting time, while for dose 1 mg/l was 30 minutes. For shorter contacting time, the gaps of Cr concentration at each activated carbon's dosage were wider than those of longer contacting time. Acceptable level of Cr concentration for every dose achieved at contacting time more than 90 minutes. Compared to the initial Cr concentration of Batik

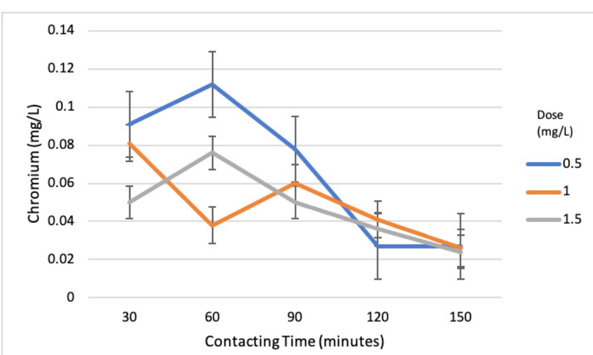
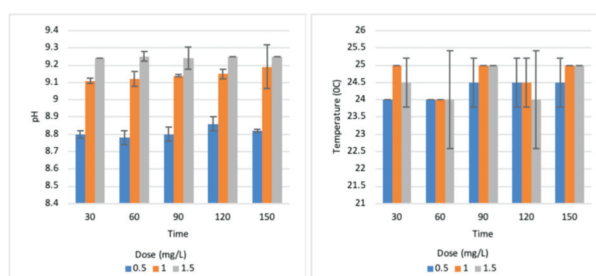


Fig. 3. Cr concentration of Batik wastewater for each contacting time and dose of activated carbon from coconut husk

wastewater (0.144 mg/l), it can be said that the addition of activated carbon resulted to the Cr removal of this wastewater.

Coconut husk can be used as a substitute activated carbon because it contains the element carbon (C) and its hard structure. The content of coconut husk is lignin (29.4%), cellulose (26.6%), nitrogen (0.1%), water (8%), and ash (0.5%) (Abdullah *et al.*, 2014). Cr removal in this study is the result of metal adsorption ability of activated carbon (Abbas *et al.*, 2016). Activated carbon is a good adsorbent for metal ion because it has a high affinity with nonpolar molecules and is used for organic compounds to be isolated and extracted (Gratuito *et al.*, 2008). This material has promising character such as a large area of surface, large volume of pore, and chemical resistance (Ndi Nsami and Ketcha Mbadcam, 2013). In a wide range of sectors, it is used because it is relatively inexpensive (Saleem *et al.*, 2019). In addition, since it has a hydrophobic surface, activated carbon is less affected by water (Kuang *et al.*, 2020).

Figure 4(a) depicted the results of pH measurement in this study. Lowest pH of Batik wastewater (8.8 – 8.82) was observed at dose of 0.5 mg/l. Meanwhile, activated carbon at dose 1.5 mg/l resulted the highest level of pH (9.24-9.25). However, the patterns of pH were quite similar at all contacting time for each dosage. This level of pH had lower values than that of the initial Batik wastewater material (9.8), but the still out of the acceptable level set by Ministry of Environment which is ranged between 6-8 (Musa *et al.*, 2019). In addition, pH is one of major determinants of heavy metal absorption since it defines the adsorbent's surface charge as well as the level of ionization and speciation of the adsorbate (Li *et al.*, 2018). Previous studies suggested that optimum metal adsorption occurred at pH 6 and 7 (Abdel Salam *et al.*, 2011; Ouyang and Guo, 2016).



(a) (b)

Fig. 4. Water quality results of experimental study (a) pH; (b) Temperature

According to Figure 4(b), the temperature of Batik wastewater during experiment study were larger than the initial wastewater (21 °C). The values were ranging from 24 to 25 °C with high variation between adsorbent dosages and contacting time. This observed temperature is still safe for aquatic biota that tolerance at level 18-30 °C (Shindu, 2005). The adsorption process of activated carbon will increase along with the rise of temperature, and vice versa (Rilyanti and Fitriyah, 2007). High level of temperature (>30 °C) may cause destruction of the present functional groups in biomass since it surpassed the tolerance level (Mahmudi *et al.*, 2020).

Optimum Dosage of Activated Carbon and Contacting Time on Cr Removal

Prior analysis of ANOVA was performed by checking assumption such as normality and homogeneity. Normality was assessed by QQ plot as depicted in Figure 5(a), while homogeneity was observed by plotting residuals against fitted values (Figure 5(b)). In Figure 5(a), a large number of data points fell along the reference line. Therefore, it can be assumed the normality of the data. On the other hand, there are no obvious relationship between residuals and the fitted values (Figure 5(b)). Thus, presume the homogeneity of variances. Since both assumption were fulfilled, a complete randomized factorial ANOVA can be performed.

The ANOVA results suggested that the interaction effect of activated carbon dosage and contacting time (F-value=2.515, p=0.125) as well as the main effect of the dosage (F-value=3.436, p=0.075) were not statistically significant to Cr removal. Therefore all dosage used in this experimental research is considered to have similar effect to Cr concentration of Batik wastewater and it cannot be decided the optimum level of dosage. Meanwhile, the main effect of contacting time was significant (F-value=19.859, p=0.000). Hence, post hoc test such as Tukey test (Figure 6) conducted to determine the optimum contacting time in Cr removal.

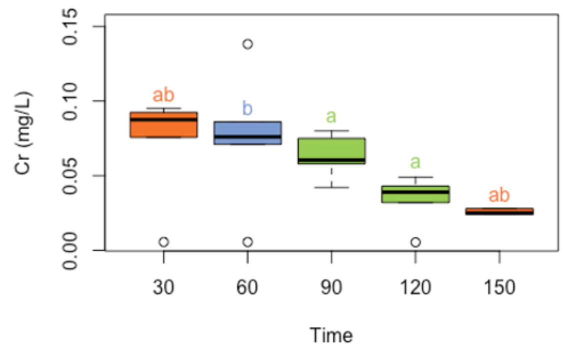
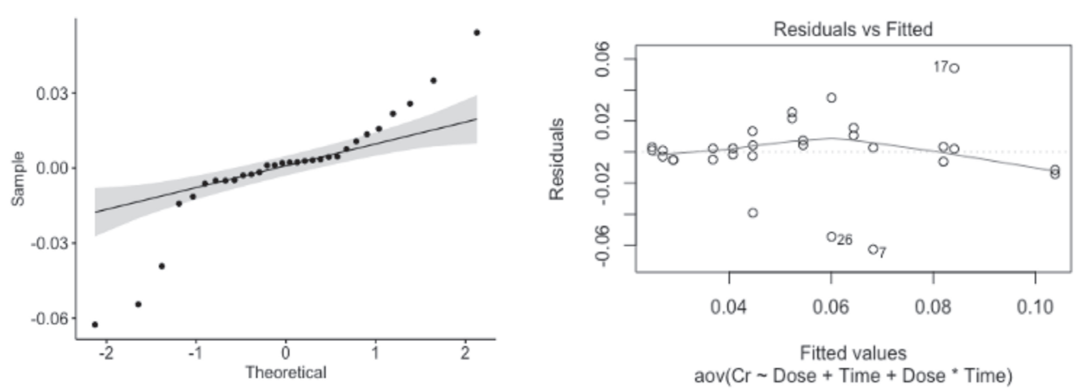


Fig. 6. Post hoc test (Tukey Test) for pairwise comparison of contacting time to Cr concentration

Boxplots with similar colour in Figure 6 indicates the levels of contacting time has no different effect to Cr concentration in Batik wastewater. Contacting time is an important factors governing metal adsorption process (Alghamdi *et al.*, 2019). The lowest Cr concentration occurred at 150 minutes of contacting time. However, the boxplot of this level of contacting time has the same colour and notation as in level 30 minutes. Therefore, it can be said that the contacting time of 150 and 30 minutes has the same adsorption ability to Cr in Batik wastewater. Nevertheless, the Cr content median of 30 minutes contacting time was above 0.05 mg/l which is the standard



(a) (b)

Fig. 5. Assumption checking results (a) Normality; (b) Homogeneity

set by Ministry of Environment. There were two contacting time which resulting Cr residue less than 0.05 mg/L. They were 120 and 150 minutes. Both contacting time contain notation “a”, meaning that their Cr concentration was equal. Thus, the optimum contacting time for Cr removal in Batik effluent is 120 minutes. This result aligned with Zn removal by using water hyacinth which showed adsorption progressively increases at initial stage but then decreased afterwards (Ariyani *et al.*, 2018). The high vacancy of empty adsorption hole in the first stage of adsorption can be attributed to this phenomenon, accompanied by the increasing of a rise in offensive forces due to the appearance of the adsorbed ions, making it more difficult for the remaining sites to enter (Alghamdi *et al.*, 2019; Guo *et al.*, 2019).

Conclusion

The untreated Batik wastewater in this research showed remarkable high concentration of Cr (0.114 mg/l) which surpassed the standard set by Ministry of Environment (0.05 mg/l). This research indicated that coconut husk can be used as adsorbent for Cr removal in this effluent. While the dosages did not showed significant different of Cr concentration in the wastewater, 120 minutes was suggested as the contacting time for optimum Cr reduction.

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