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Biosorption chrome (Cr) and dyes using biosorbent in the modified tea bag

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Abstract

Biosorption has been known as a potential method in reducing heavy metals and dyes in wastewater, including chrome (Cr) and dyes contents of the wastewater from the batik industry. Straw and spent mushroom compost (SMC) are potential biosorbents due to cheap, abundant, and easily obtained. However, the effectivity of the biosorbents is not only depended upon the type of material but also their surface area. In this study, a modified tea bag was used to increase the surface area of the straw and spent mushroom compost to absorb Cr and dyes from the batik industry wastewater. The optimum of biosorbent ratio and pH in Cr absorption and dyes decolorization was measured. This experiment was conducted using Spilt Plot Design. The results showed that the highest Cr absorption was found at 0,0050 mg/g, and the percentage of decolorization was 68,92% in the biosorbent ratio of 3:1 and pH 5. Biosorbent packed in the tea bags modification was effective removes Cr and dyes in the batik industry wastewater.

Keywords: batik, dyes, heavy metals, natural biosorbent, wastewater

Introduction

Indonesia has been known for its various batik industries. However, inappropriate management of batik wastewater treatment causes pollution in water bodies around the batik industries in Indonesia. For example, Cr concentration in wastewater from the Sokaraja batik center in Banyumas Regency (Central Java) reaches 0.231 $mg.L^{-1}$ [1] (Lestari *et al.* 2015) of which exceeds the threshold set by the Indonesian government No. 82 of 2001 (< 0.05 $mg.L^{-1}$).

Among the available methods of wastewater treatment management, the biological method is one of the cheapest methods that can be used in batik wastewater treatment. In this method, the biosorption mechanism through the application of biosorbents has been reported effective in removing heavy metals and dyes from various wastewater (Okuo *et al.* 2006). Biosorption is sufficient to absorb heavy metals and dyes in wastewater due to their high absorption rate and broad spectrum (Veglio & Beolchini 1997, Azmat *et al.* 2007). Various types of biosorbent have been used to reduce various pollutants, particularly heavy metals. These include powdered *Triplochiton scleroxylon* (Akissi *et al.* 2013), activated carbon activated by Fe_3O_4 (Abdel-fattah *et al.* 2014), *Sargassum filipendula* alginate (Bertagnolli *et al.* 2014), *Spirulina platensis* (Kwak *et al.* 2015), peanut hull (Owalude & Tella 2016), *Nauclea diderrichii* seed (Omorogie *et al.* 2016), and *Sargassum hystrix* (Ghasemi *et al.* 2016).

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In the study of Cr absorption using biowaste, a combination of various biosorbents provides higher effectivity in Cr removal than using a single biosorbent. For example, the application of *S. cinereum* and SMC of *Pleurotus ostreatus* mixture (3:1) was reported more effective in absorbing Cr than individual application (Lestari 2016). A combination of *Annona squamosa* and *Aspergillus niger* seeds (Babu & Preetha 2014), apple seeds and *A. niger* (Taylor *et al.* 2015) as biosorbents were also more effective than a single application of biosorbent.

A straw of *Oryza sativa* and SMC of *P. ostreatus* contains lignin and cellulose compounds that have the potential to absorb Cr and dyes. A surface area (Joo *et al.* 2011) and the active group in lignin and cellulose in the form of O-H and C = O play a role in Cr binding (Lestari 2018). Placing biosorbents in a container is necessary to increase the surface area of the biosorbents. Among the containers, tea bags are useful because they have pores that can be passed by wastewater and are easily separated from wastewater. However, the tea bag method has weakness due to biosorbent clots formation (Lestari 2016); therefore, it is necessary to modify this method through various absorbents ratio experiment. The objective of this study is to examine the optimum pH and ratio of *O. sativa* straw and SMC of *P. ostreatus* mixture in the tea bag in Cr and dyes removal from batik wastewater.

Materials and methods

Samples and experimental design

Wastewater samples were collected from the batik industrial center in Kauman Sub Village, Sokaraja Kulon Village, Sokaraja Subdistrict, Banyumas Regency, Central Java. In the experiment, the initial pH of the wastewater was set to 5, 6, 7, 8, and 9.

This experiment was conducted using Spilt Plot Design. The main plot was the mixture of *O. sativa* straw and SMC of *P. ostreatus*, and a subplot was pH. Five different ratios (1:0, 3:1, 1:1, 1:3, and 0:1) of mixed biosorbents were used in this study. A total of 300 mg of biosorbents was used in each tea bag (6 × 6 cm) with the ratio of mixture refers to the experimental treatment.

Cr and dyes adsorption assay

The absorption experiment was conducted in the Erlenmeyer 250 mL, of which each Erlenmeyer was filled 100 mL of batik wastewater, and one packed biosorbent in the tea bag with the composition and particle size according to treatment. All the Erlenmeyer were incubated in the shaker incubator at a 175 rpm and a temperature 25ºC for 1 hour.

Absorption capacity was calculated by the following formula:

$$q = \frac{V\ (C_0 - Ceq)}{m}$$

q = absorption capacity ($mg.g^{-1}$)
V = volume of solution (L)
m = biosorbent weigth (g)
C_o = initial concentration ($mg.L^{-1}$)
C_{eq} = final concentration ($mg.L^{-1}$)

A percentage of decolorization was measured at each interval treatment using the spectrophotometric method. A total of 5 mL of each treated wastewater was centrifuged at 5,000 rpm for 10 min. The supernatant was further measured by a spectrophotometer at 645 nm. The decolorization percentage was calculated using the following formula:

$$\% \text{ decolorization} = \left[\frac{(\text{the initial absorbance} - \text{the final absorbance})}{\text{the initial absorbance}}\right] \times 100\%$$

Data were analyzed using the ANOVA test at 5% significant level to determine the effect of treatment.

Results

The results showed that there was a decrease in the concentration of Cr in the batik wastewater (Fig. 1). The Cr concentration before being treated with *O. sativa* straw and SMC of *P. ostreatus* biosorbents range from 0.0179 $mg.L^{-1}$ to 0.0282 $mg.L^{-1}$ but after the biosorbents treatment range from 0.0012 $mg.L^{-1}$ to 0.0045 $mg.L^{-1}$. The highest Cr absorption capacity (0.0050 ± 0.003 $mg.g^{-1}$) was found in *O. sativa* straw and SMC of *P. ostreatus* (3:1) at pH 5 (Fig. 1) with 75.72% absorption efficiency from the initial concentration of 0.0219 to 0.0016 $mg.L^{-1}$. The lowest Cr absorption capacity (0.0029 ± 0.001 $mg.g^{-1}$) was found in *O. sativa* straw and SMC of *P. ostreatus* (3:1) at pH 9 (Fig 1.) with 62.00% of absorption efficiency from the initial concentration of 0.0219 to 0.0041 $mg.L^{-1}$.

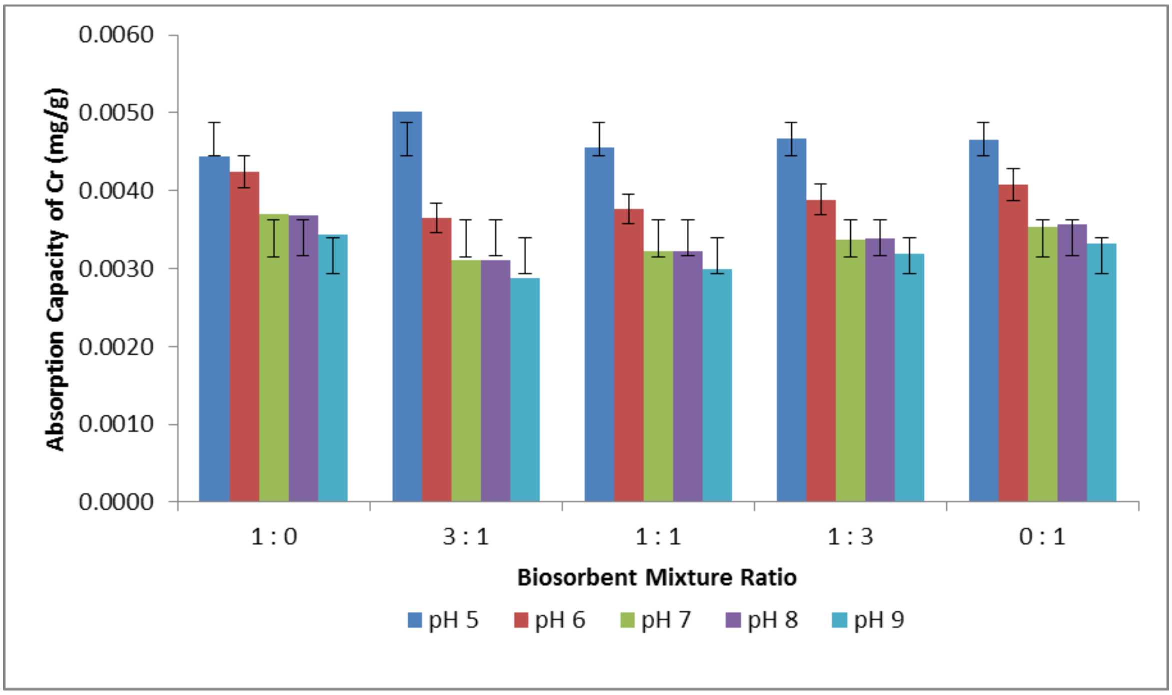

Figure 1. Absorption capacity of Cr by *O. sativa* straw and *P. ostreatus* SMC mixture in a modified tea bag

In the decolorization assay, the highest decolorization capacity (68.92%) was found in the ratio of *O. sativa* straw : SMC of *P. ostreatus* (3:1), and the lowest (44.81%) was found in the ratio of *O. sativa* straw : SMC of *P. ostreatus* (1:3) (Fig. 2).

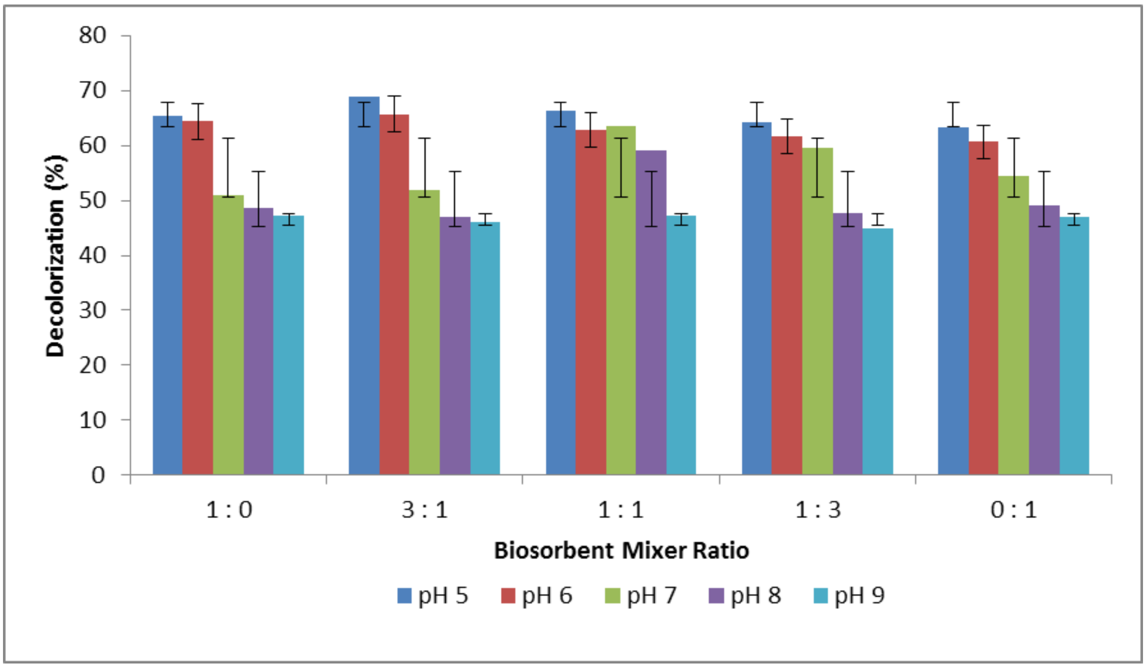

Figure 2. Decolorization capacity of mixture of *O. sativa* straw and SMC of *P. ostreatus* in a modified tea bag

Discussion

This study showed that a mixture of *O. sativa* straw and SMC of *P. ostreatus* could absorb about 0.0167 to 0.0237 $mg.L^{-1}$ of Cr from the batik wastewater (Fig. 1). The Cr absorption capacity in all *O. sativa* straw and *P. ostreatus* SMC mixture ratios of the biosorbent decreased when the wastewater acidity increased (from pH of 5 to 9) (Fig. 1). This data indicates that the biosorbent mixture activity is useful in acidic conditions. A previous study using a mixture *S. cinereum* and SMC of *P. ostreatus* also showed that metal absorption increased along with the decreasing of pH value (Lestari 2016). Although the absorption capacity is primarily related to the hydroxyl and carboxyl functional groups (active sites in the metal absorption capacity) in the straw and SMC mixture, however, the acid condition is probably related to the mycelium activity in absorbing Cr. Fungi usually produce organic acids when absorbing heavy metals, and the heavy metals oxidation process is more stable in acidic condition (Fomina *et al.* 2007). For example, *Penicillium janthinellum* F-13 was reported producing citric acid during aluminum toxicity reduction (Zhang *et al.* 2002), and *P. simplicissimum* (current name: *P. janthinellum*) produced citric acid during adsorption of Zn(II) (Franz *et al.* 1991).

Biosorption process is one of the passive removal mechanisms of heavy metal ions (Gupta 2015). The process occurs when heavy metal ions bind to the cell wall in two different ways, i.e. (1) ion exchange in which monovalent and divalent ions such as Na^{+}, Mg^{++} and Ca^{++} in the cell wall replaced by heavy metal ion, and (2) complex formation between heavy metal ion with functional formations such as carbonyl, amino, hydroxyl, phosphate, and hydroxyl-carboxyl located on the cell wall. The active process coincides in line with the metal ion consumption and intracellular accumulation of the metal ion.

The ANOVA analysis showed that there was no significant difference between Cr absorption with the ratio of biosorbents mixture and the wastewater pH, or the interaction between the two biosorbents to the Cr absorption. It showed that the Cr absorption by the biosorbents mixture was not affected by the ratio of the biosorbent mixture and wastewater pH. However, the absorption capacity influenced by the volume of biosorbent mixture in the tea bag. It is probably related to the number of the active binding site. The more volume of biosorbents in the tea bag increase the number of –OH and –COOH of the active binding sites. The SMC of *P. ostreatus* also contains cellulose and hemicellulose (Kartikasari *et al.* 2012, Sorta *et al.* 2012) of which provides more binding sites to absorb Cr from the wastewater.

Dyes decolorization activity by the mixture of *O. sativa* straw and SMC of *P. ostreatus* also showed a significant result (Fig. 2). The current decolorization activity (44.81-68.92%) showed that a mixture of *O. sativa* straw and SMC of *P. ostreatus* is more effective than a previous study that employed a mixture *S. cinereum* and SMC of *P. ostreatus* (39.92%) in the decolorization of the batik wastewater (Lestari 2018). It is also related to the activity of the mycelium of *P. ostreatus* in the SMC. The presence of mycelium was significant increases the decolorization of dyes in the batik wastewater because the fungal mycelium is natural dyes absorbent. The mechanism of fungal mycelium in absorbing dyes is usually through enzymatic and non-enzymatic mechanisms (Murugesan & Kalaichelvan 2003). The enzymatic process generally through laccase, lignin peroxidase, and manganese peroxidase enzymes activity, while non-enzymatic process via cell wall binding sites of fungi which contains glycoproteins, chitin, and glucans (Lu *et al.* 2017).

Conclusion

The optimum ratio of *O. sativa* straw and the SMC of *P. ostreatus* packaged in the modified tea bag to absorb Cr in the batik wastewater was 3 : 1 at pH 5.

Conflict of Interest

The authors state no conflict of interest from this manuscript.

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