Modified Tea Bag Biosorbent as Cr (VI) Removal in Batik Wastewater

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Abstract. Batik wastewater contains heavy metals that are harmful to the environment. One of these metals is Cr (VI). Cr (VI) on batik wastewater has been removed by biosorption. Biosorption capacity depends on the biosorbent type and surface area. Abundant, cheap, and readily available biosorbent is straw and baglog waste. A modified tea bag can increase biosorben surface area. This research aimed to obtain the optimum biosorbent ratio and pH of Cr (VI) adsorption capacity. The experiments were conducted using a Split Plot design. The collected data were analyzed using F-test with a significance level of 5%. The results showed that the highest of Cr adsorbed was 0.0047 mg/g with efficiency decrease was 84.23% in the biosorbent ratio of 3:1 and pH 5. Modified teabag biosorbent was effective in removal Cr in batik wastewater.

1. Introduction

Sokaraja Batik Center is one of the small scale batik industries in Regency of Banyumas. It is common knowledge that small scale batik industries do not have a Waste Water Treatment Plant (WWTP). It is the case with Sokaraja Batik Center, which disposes wastewater straight into River Wangan. Pollutant compounds in batik wastewater can pollute the river. One of the heavy metals in batik wastewater is Cr (VI), where in River Wangan, it has exceeded the threshold concentration (0.231 mgL-1) of government regulation no. 82 of 2001[1].

Chromium in batik wastewater is very harmful to organisms in the River Wangan. Chromium might damage organs such as gills, liver, lungs, and kidneys, leading to death. The metal in batik wastewater can be removed by biosorption, a reduction of heavy metals through the adsorption process using dead or inactivated organisms [2]. Biosorption is significantly effective in heavy metal adsorption of wastewater due to its high absorption rate, relatively simple, selective, and inexpensive [3 - 5]. Biosorption can also degrade the dyes contained in batik wastewater.

As an alternative technology for wastewater treatment, biosorption must use biosorbent, which is relatively affordable and has been highly available. Straw and baglog waste meet these requirements. They contain lignin and cellulose, an active group to bind chromium through ion exchange. Lignin and cellulose contain hydroxyl and carboxyl, an efficient chromium ion exchanger [6]. The straw powder capable of reducing Pb in batik wastewater up to 50,35% [7]. P. ostreatus baglog waste can adsorb heavy metal and remove the odor [8].

Biosorption capacity is highly dependent on its surface area, contact time, and biomass [9]. The high biosorbent surface area and biomass can increase the number of active sites available to chromium binding, hence increase the adsorption capacity. Adsorption capacity can be increased by reducing the biosorbent surface area. Biosorbent, such as immobilized silica gel [10], biomass of 1-cm...
size [11], ash [12], pellet [13], and powder [14], has been widely applied to adsorb heavy metals in wastewater. All of them are effective but difficult to separate from the waste and might cause sedimentation. Biosorbent in the tea bag packaging quickly is separated from the wastewater but clotted [15]. Modified tea bags with the press can reduce clumping when it is dipped in batik wastewater. Another factor affecting the adsorption capacity is acidity. Acidity (pH) affects ion shape changes available for chrome binding. For this reason, this study was intended to obtain the optimum ratio of straw and baglog waste in modified tea bags as well as the optimum pH to adsorb Cr (VI) batik wastewater.

2. Methods

The experiments were based on Split Plot Design. The main plot was the mixture ratio of straw and baglog wastes, and the subplot was pH. The proportion of straw and baglog wastes was made up of five levels (1:0, 3:1, 1:1, 1:3, and 0:1) and five levels of pH (5, 6, 7, 8, and 9).

2.1 Biosorbent Production in Tea Bag

The biosorbent was weighted approximately 300 mg, with the composition according to the treatments. Biosorbent was wrapped in a tea bag paper, a size of 6 x 6 mm, and made into small columns by pressing. Then, it was packed in the tea bags and ready to use.

2.2 Batik Wastewater Preparation

The wastewater was obtained from the batik industrial center in Sokaraja Kulon Village, Sokaraja Subdistrict, Regency of Banyumas, Central Java. It was considered as the final waste of staining and dyeing residual. The initial pH of the waste was set to 5, 6, 7, 8, and 9.

2.3 Adsorption Experiments at Laboratory Scale

A 250-mL Erlenmeyer provided approximately 45 pieces of the bags. Each of the Erlenmeyer was filled with 100 mL of batik wastewater. Each of them was added with one pack of the tea bag biosorbent with the composition according to treatment. The Erlenmeyer was covered with paraffin, then homogenized in the incubator shaker at a speed of 175 rpm and temperature of 25ºC for 1 hour.

2.4 Adsorption Capacity of Chromium

Adsorption capacity was calculated using the formula below:

\[
q = \frac{V(C_0 - C_{eq})}{m}
\]

- \( q \) = Adsorption capacity (mgg\(^{-1}\))
- \( V \) = volume of solution (L)
- \( M \) = biosorbent weight (g)
- \( C_0 \) = initial concentration (mgL\(^{-1}\))
- \( C_{eq} \) = final concentration (mgL\(^{-1}\))

2.5 Data Analysis

The results obtained were chromium adsorption, decolorization, and capacity. The data were analyzed using an ANOVA test on a 5% significant level to determine the treatment difference.

3. Results

The highest Cr(VI) adsorption capacity was in the straw and baglog waste in a ratio of 3:1 at pH 5 (0.0047 ± 0.003 mg g\(^{-1}\)) (Fig. 1) with adsorption efficiency of 84.23%. The lowest Cr adsorption capacity was in a 3:1 ratio at pH 9 (0.0026± 0.001 mg g\(^{-1}\)) (Fig 1.) with 66.04% adsorption efficiency.
The ratio of biosorbent mixer and pH based on the LSD test (Table 1) demonstrated that pH 5 and pH 9 have a different effect on Cr(VI) adsorption capacity than on other treatments.

Table 1. LSD value of pH to Cr adsorption capacity

| pH | Cr adsorption capacity (mgg\(^{-1}\)) |
|----|--------------------------------------|
| 5  | 0.0687a                              |
| 6  | 0.0521b                              |
| 7  | 0.0502b                              |
| 8  | 0.0500b                              |
| 9  | 0.0463c                              |

Note: numbers followed by the same letter doesn’t differ based on LSD at 95% confidence level

4. Discussion

The data revealed that the Cr(VI) concentration of batik wastewater before and after biosorption differed. Cr(VI) adsorption capacity was influenced by the ratio of biosorbent mixer and pH. Cr(VI) adsorption capacity in all composition ratios of the biosorbent was reduced from pH 5 to 9 (Fig. 1). It demonstrated that the optimal conditions of adsorption were at acidic pH. Metal adsorption has increased along with the reducing pH value but has decreased after passing the optimum at pH 6.53 [15]. Straw and baglog waste have some lignin with hydroxyl and carboxyl. These functional groups affect adsorption capacity. The adsorption capacity of \textit{S. cinereum} and \textit{P. ostreatus} baglog waste in the teabag with a ratio of 3:1 was 0.0042±0.0005 mg g\(^{-1}\) [16]. It shows that the packaging of modified pressing tea bags is higher in adsorping Cr since it provides more active sites than other forms of bioabsorbant.

The biosorption process is one of the mechanisms for the removal of heavy metal ions passively [17]. The process successfully occurs when heavy metal ions bind to the cell wall in two different ways. They produce complex formation between heavy metal ion with functional formations such as carbonyl, amino, hydroxyl, phosphate, and hydroxyl-carboxyl located on the cell wall. Also, ion exchange (in which monovalent and divalent ions, such as Na, Mg, and Ca in the cell wall) is replaced by a heavy metal ion. The active process coincides with the metal ion consumption and intracellular accumulation of metal ion. The presence of Cr(VI) reductase is the key to the enzymatic pathway. It reduces Cr(VI) to Cr(III) as soluble and membrane-bound enzymes. There are at least two steps in enzymatic Cr(VI) reduction. Firstly, Cr(VI) accepts one NADH molecule forming Cr(V) as intermediate and receives two more electrons from the same coenzyme forming Cr(III).
The ratio of the biosorbent mixer and the interaction of the biosorbent and pH showed no significant difference in chromium adsorption. However, pH significantly affects chromium absorption. It shows that the adsorption process of chromium is not affected by the mixed ratio but by the pH (Table 1). The adsorption difference is under the influence of compound concentration in biosorbent. Straw and baglog waste have known as potential adsorption material due to the high lignin content. Lignin has –OH and –COOH as its active binding site. Baglog waste also has cellulose as well as hemicellulose [18 - 19], which provide a more binding site.

5. Conclusion

The optimum ratio of straw and baglog waste in the modified tea bag to adsorb Cr(VI) in batik wastewater was 3:1 at pH 5. The respective biosorbent modified teabag was demonstrated more effectively than a teabag package in removing Cr(VI) in batik wastewater.

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