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A Study of Compost as an Adsorbent for Congo Red Dye Removal Process

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Abstract

The human population continues to grow and so does the volume of textile products. Most of textile wastewaters contain synthetic dyes, which are mostly treated by less effective conventional wastewater treatment processes. Treatment using activated carbon is able to remove the dye from wastewater, but it is a high cost material. Rich organic carbon material, such as compost, might be an alternative solution. The objective of this study was to assess the capability of compost in treating dye wastewater by investigating the effect of compost dosage, particle size, and column height based on dye percentage removal and adsorption capacity data. A removal percentage of 20.49% and adsorption capacity of 5.33 mg/g were achieved when 200 ppm of Congo Red dye molecule was treated using 1-2 mm compost particles with dosage of 8 g/L. In addition, 90% dye removal and 0.38 mg/g adsorption capacity can be obtained when compost column height 60 cm was used. After a while, the dye molecule wore off the compost and fresh compost must be introduced into the system to maintain its percent removal. The Langmuir model successfully described the adsorption isotherm of Congo Red dye on compost particles.

Keywords: *adsorbent; compost; Congo Red Dye; textile wastewater*

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INTRODUCTION

As the human population continues to grow, so does the number of textile products. Alongside the products, wastewater is simultaneously produced. Since only 50% of dye is absorbed by the fiber during dyeing process, textile wastewater becomes one of the most polluting wastewater (Clarke and Anlicker, 1980; Harrelkas *et al*., 2009; Laxman, 2009). The synthetic dye can reduce light penetration to water, causing detrimental effect on the photosynthetic activity of aquatic flora, and therefore affecting the food source for aquatic organisms (Reddy *et al*., 2008; Upadhyay and Mahajan, 2014). It also forms chelated metal ions, which are toxic to aquatic organisms (Hunger, 2003; Toptas *et al*., 2013,).

The dyes that are commonly used in the textile industry can be classified into two categories: anionic and cationic (Ghaly *et al*., 2014). One of the anionic dyes oftenly used in textile manufacture is Congo Red, a synthetic diazo dye that is easily dissolved and is commonly found in the form of red crystal. This dye has strong adhesive nature on cellulose fiber, and hence it is widely used in textile industry. A high concentration of this dye can raise the biochemical oxygen demand level in water, and can cause water-borne diseases (Tunay *et al*., 1996).

The color contained in the wastewater can be removed by conventional treatment processes, such as filtration, coagulation, flotation, etc., but these methods are usually inefficient, expensive, and inapplicable to many color variations (Ghoreishi and Haghighi, 2003). One effective method of removing the substances is via adsorption (Webb, 2003; Toptas *et al*., 2013). Activated carbon is an efficient adsorbent due to its high adsorbent capacity (Reynolds and Richards, 1996; Banat *et al*., 2002). However, since activated carbon is expensive, many studies have been conducted to discover the alternatives. One of these alternatives is compost, which contains rich organic carbons and is believed to be able to remove pollutants from water and wastewater (Haug, 1993; EPA, 1998; Komosinska and Duewska, 2011).

The objective of this study was to assess the capability of compost in treating Congo Red dye, by determining the optimum compost dosage, particle size, and column height based on dye percentage removal and adsorption capacity data.

MATERIALS AND METHODS

The study was conducted using a laboratory scale batch reactor and serial columns. The batch reactor study aimed to determine the optimum compost dosage and particle size, whilst the serial column study was used to determine the optimum compost column height.

Adsorbent

As an adsorbent material, the compost was obtained from a municipal solid waste processing unit. It had pH 7.6; carbon/nitrogen (C/N) ratio 17; and water content 42%; which are the indication of matured compost according to the Indonesian National Standard of SNI: 19-7030-2004 for matured compost quality (National Standardization Agency of Indonesia, 2004). The maturity of the compost was necessary to ensure the compost was stable and would not undergo further biological changes; because such changes might have an inexplicable effect on the results. The compost was then sieved through mesh to obtain particle diameters from 0.85-1, 1-2, and 2-2.36 mm, and dried in an oven at 70°C for 2 hours.

Adsorbate

The adsorbate used was artificially made wastewater with a Congo Red dye concentration of 200 mg/L. The solution was made by dissolving Congo Red powder, which was weighed on electronic scales, into distilled water. The pH was then lowered to 3-3.5, using a solution of strong acid, which was 1 N hydrochloric acid.

Compost has carboxyl matrix on its surface. Under alkaline condition, the carboxyl matrix will become negatively charged anionic, leading to the inability to bind negatively charged Congo Red. Therefore, the absorption of Congo Red dye and compost should be carried out in acidic condition to optimize the adsorption process (Purkait *et al*., 2007; Sanada, 2014).

Ppm vs Pt-Co Standard Curve

The measured Congo Red dye concentration data would be in Platinum-Cobalt (Pt-Co) based on ASTM D105-05 (ASTM, 2011): Standard Test Method for Color of Clear Liquids (Platinum-Cobalt Scale). Hence in order to convert Pt-Co to ppm, a standard curve was needed. Several Congo Red dye solutions (concentration in ppm) were made and analyzed for their Pt-Co. A standard curve and equation to convert Pt-Co to ppm could then be built. All collected Pt-Co data were converted into ppm units.

Batch Study

The solution of Congo Red dye was contacted with various of dosages of compost (in range 1-12 g/L) and various compost particle sizes (0.85-1, 1-2, and 2-2.36 mm) in 100 mL glass bottles. The glass bottles were then put on a shaker and they were shaken at 150 rpm for 2 hours and followed by centrifugation for 5 minutes.

A factorial design of experiment was used to determine the optimum dosage and particle size. It started from compost with particle size of 1-2 mm. The tested dosages were 2, 5, 8, and 11 g/L. The obtained optimum dosage from these four dosages was scale down to 1 g/L and scaled up to 12 g/L, so a wide dosage from 1-12 g/L was covered, from which a more precise optimum dosage could be obtained. The optimum compost dosage was then used to find the optimum particle size by varying compost particle size (0.85-1 mm and 2-2.36 mm). The samples were checked using DR 2000 spectrophotometry at 445 nm wave length to determine its Pt-Co. By using Pt-Co standard curve, the value converted into concentration ppm. Percent removal was determined relative to initial concentration of Congo Red Dye in ppm.

Serial Column Study

The optimum compost dosage and particle size obtained in the batch study were used in the serial column study to determine the optimum adsorbent height. Figure 1 shows the experiment set up. Every column had height of 20 cm and 3-inch diameter, and was set up as shown in Figure 1. The highest outlet represented a column height of 20 cm, the second highest represented a column height of 40 cm, the third highest represented a column height of 60 cm, and the last outlet represented a column height of 80 cm. Congo Red dye solution was pumped into the compost-containing columns. At the time the solution appeared at the last outlet, the first sample was collected - all outlets were sampled. The second sample was taken at 100 seconds after the first sample and the third sample was withdraw at 100 seconds after the second sample.

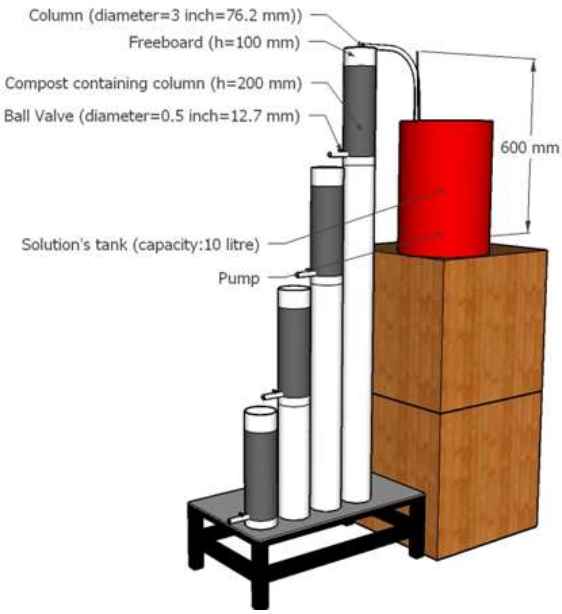

Figure 1. Serial of column reactor

Due to the compost nature to impose color to the water that bypasses it, Pt-Co of blank sample was needed. The Pt-Co of the blank sample was acquired by passing the distilled water pH 3.5 to the compost columns and tested using spectrophotometry. Finally, to obtain the Pt-Co of Congo Red from the effluent of the compost columns, the sample Pt-Co was subtracted by the blank Pt-Co.

Adsorption Capacity

Adsorption capacity expresses the amount of Congo Red dye absorbed by 1 g of compost. The adsorption capacity was determined using the equation below:

$$q_e = \frac{(C_o - C_e)}{m} V \quad (1)$$

where:

q_e = the amount of adsorbate adsorbed per adsorbent's mass (mg/g)
C_o = the dye concentration before adsorption (mg/L)
C_e = the dye concentration after adsorption (mg/L)
V = the solution volume (mL)
m = mass of compost/adsorbent (g)

Isotherm Study

An isotherm study is useful in identifying the behavior of an adsorbent in an adsorbing the target adsorbate molecules (Salihi *et al*., 2017). The common isotherm models which are mostly used for water and wastewater are the Langmuir and Freundlich isotherm models (Benjamin, 2009). The data from batch study was analyzed based on the linearization of the models.

The linearization equation for Langmuir is as follow (Salihi *et al*., 2017):

$$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{K_L . q_m} \quad (2)$$

And the linearization equation for Freundlich is as follow (Salihi *et al*., 2017):

$$log(q_e) = log(k_r) + \frac{1}{n} log(C_e) \quad (3)$$

where:

q_e = amount of adsorbed Congo Red dye per unit weight compost (mg/g)
C_e = amount of Congo Red dye remaining in the solution (mg/L)

The plot of C_e/q_e versus C_e was built from Langmuir linearization equation. Whereas the plot of log q_e versus log C_e was built from Freundlich linearization equation. Regression analysis was applied to the plots. The selection of the model was based on the largest R^2 value.

RESULTS AND DISCUSSION

Compost Characteristics

Figure 2 shows the surface condition of the compost before and after batch and column series adsorption studies. Close examination reveals that, before adsorption, the surface of the compost tended to have larger pores, of around 2,521 nm in diameter, whilst, after adsorption, the surface of the compost appeared to be more replete. Such morphological condition proves that Congo Red molecules filled the empty pores of the compost. A and B show that the surface of the compost is coated by a layer formed by the accumulation of Congo Red molecules. This indicates that compost can bind these molecules during the adsorption process.

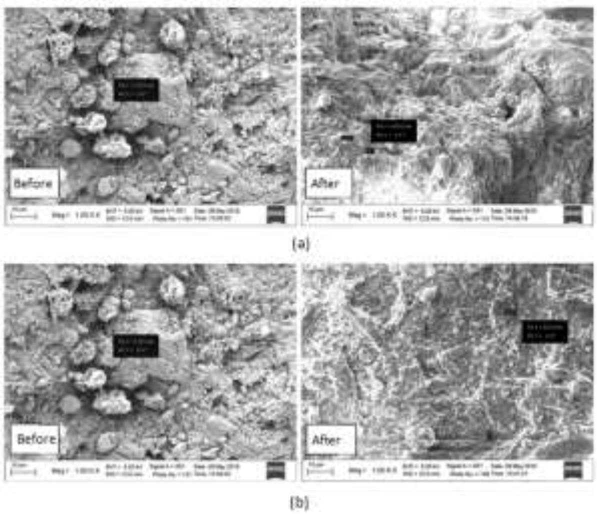

Figure 2. The surface of compost before and after adsorption in batch study (a) and column study (b)

Standard Curve: ppm vs Pt-Co

The concentration of Congo Red dye in 1, 2, 3, 4, and 5 ppm were analyzed to acquire their Pt-Co value, after which a standard curve (Figure 3) was built. The linear equation is:

$$y = 59.4x + 10.2$$

where:
y: Pt-Co value
x: Dye's concentration (ppm)

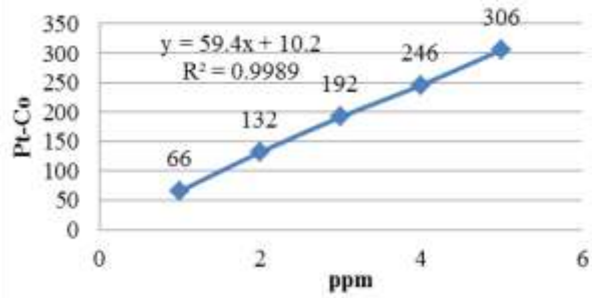

Figure 3. Standard curve

Effect of Compost's Dosage

The result of the batch study to determine the optimal dosage of compost is presented in Figure 4. Percent removal tended to increase until it reached around 20% removal at 8 g/L and 11 g/L. At first, adsorption capacity showed a similar trend to percentage removal, but it culminated at 5.33 mg/g with an 8 g/L dose, and then decreased. It was concluded that the optimum dosage of compost to adsorb Congo Red dye was 8 g/L. It reflects that the use of higher dosage had no effect on percent removal and that it decreased adsorption capacity, resulting in inefficient resource application.

Raising the adsorbent dosage to the adsorbate increased the number of bound dye molecule, due to the greater of surface area of the adsorbent, which increased the number of places where adsorbate molecules could bind (Pushpa *et al*., 2015). However, there was a point where the number of molecular bonds tended to decline, as shown in Figure 4. This was caused by the inability of the dye molecule to fill all exchangeable sites on the biosorbent due to the hindrance from crowded compound, which usually resulted in low uptake of the dye (Aksu and Cagatay, 2006).

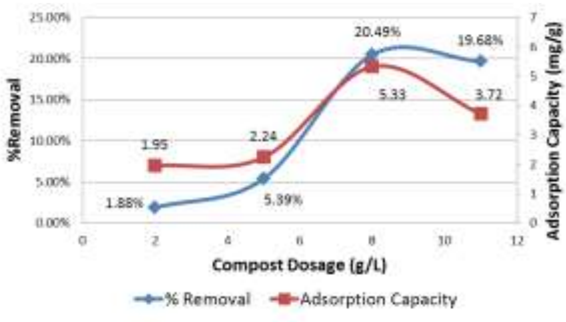

Figure 4. Percent removal of dye and adsorption capacity at particular compost dosages

Effect of Compost Particle Size

Figure 5 shows the result of the batch study in acquiring the optimum compost particle size to adsorb Congo Red dye. The optimum particle size was 1-2 mm.

Pushpa *et al*. (2015) stated that the smaller the particle size, the greater the surface contact area, providing more chances for the Congo Red dye molecule to bind, and therefore increase the uptake of Congo Red dye. However, if the particle is too small, it will undergo agglomeration, in which small particles adhere to each other, due to Van der Waals forces. This would decrease the surface contact area, thereby reducing the percentage removal of Congo Red dye. A weak electromagnetic force, such as Van der Waals forces, has no effect on large particles (Holdich, 2002).

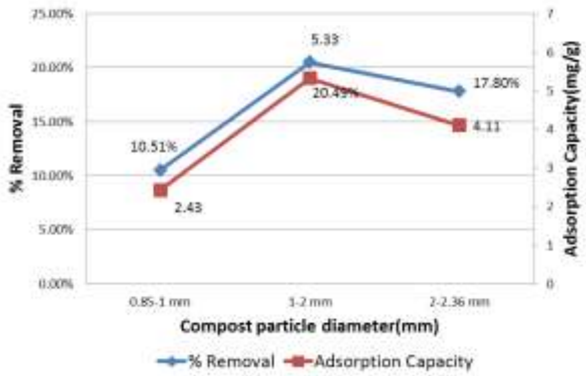

Figure 5. Percentage removal of dye and adsorption capacity of particular compost particle sizes

Effect of Compost Media's Height on Percent Removal

The result of the serial column study is presented in Figure 6. It shows that percent removal was increased for every column's height increase on every sampling. The increase was due to the extended surface area, providing more spaces for biosorption to occur; hence more dye was removed from the system (Metcalf, 2003).

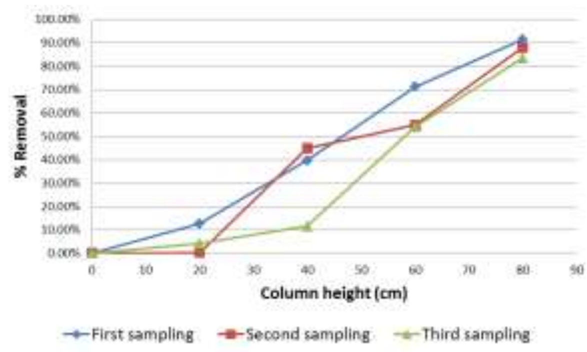

Figure 6. Percentage removal according to compost column height

The first sampling had the highest percent removal in almost all columns and was followed by the second sampling and then the third sampling. These findings pointed out that dye accumulation was taking place, diminishing the spaces provided by fresh compost to bind the dye molecules until it reached saturation. The first sampling had highest removal since the compost was still fresh; whilst the third sampling had the lowest removal since the compost was began to wear off.

The compost wearing off was indicated also by the difference of percent removal. In first sampling, the percent removal difference between 20 cm and 40 cm outlet was 27.06%, whilst the difference between 60 and 80 cm outlet was 20.27%. In the third sampling, the percent removal difference between 20 cm and 40 cm outlet was 7.53%, whilst the difference between 60 and 80 cm outlet was 29.45%. These explained that at the first, the columns at the upstream of the artificial waste adsorbed a lot of Congo Red dye and the downstream columns adsorbed the little remain of the upstream columns. But after some time, the upstream columns were saturated and adsorbed much less than the downstream columns. The downstream column could absorb more because it still had some spaces (absorbing less at the first). The downstream columns would finally be saturated also after some time. Therefore, in order to maintain the percent removal, fresh compost is needed to be introduced.

Effect of Compost Media's Height on Adsorption Capacity

Table 1 shows the adsorption capacity of the adsorbent in the batch study experiment. The artificial wastewater had around 200 ppm Congo Red dye, and the most efficient compost height was 60 cm. The column height of 20 cm showed the lowest adsorption capacity, compared to the columns of a greater height. The shorter the height, the briefer the contact time, meaning that there were fewer opportunities for free spaces compost to bind the molecule.

Table 1. The adsorption capacity in every column in the batch study experiment

Sampling outlet	1st samples (mg/g)	2nd samples (mg/g)	3rd samples (mg/g)	Total (mg/g)
20 cm	0.06	0	0.02	0.08
40 cm	0.12	0.20	0.03	0.35
60 cm	0.14	0.05	0.19	0.38
80 cm	0.09	0.15	0.13	0.37

The abundance of dye molecules also affected the adsorption capacity. Although there was more time for the adsorption to occur in the sample from column 4, the lack of dye molecule meant that the adsorption capacity was less than that of the sample taken from column 3.

Comparing the first samples and third samples in their upstream column (20 and 40 cm) and downstream column (60 and 80 cm) could support that compost bound fewer dye molecules due to saturation. At first, the upstream columns adsorbed a lot of Congo Red dye, the downstream columns only adsorbed the remains. But after some time, the upstream columns wear off and adsorbed little, whilst the downstream columns which still had spaces, could adsorb more.

Isotherm Model

The plotting and regression linear analysis was conducted to determine the isotherm model of Congo Red dye adsorption by compost particles. Figure 7 shows the plot for Langmuir model, while Figure 8 depicts the Freundlich model. The R^2 value of Langmuir model which is 0.981 is greater than R^2 of Freundlich model. Hence, the adsorption of Congo Red dye by compost had a better compatibility to Langmuir model.

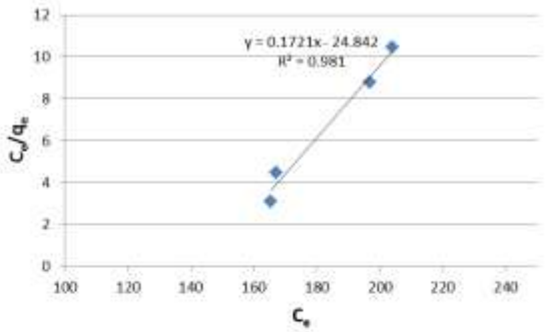

Figure 7. Langmuir model

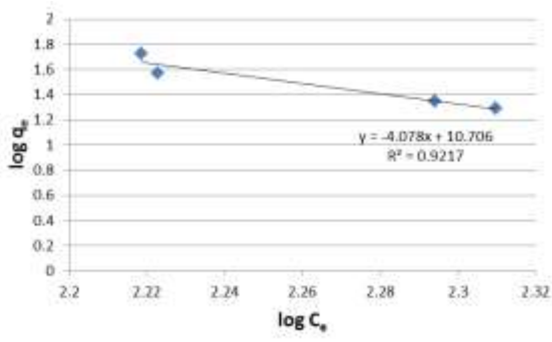

Figure 8. Freundlich model

Langmuir adsorption refers to monolayer and homogenous adsorption and monolayer adsorption (Foo and Hamed, 2010). Homogenous adsorption indicated that all compost surfaces have equal capability in adsorbing the Congo Red dye.

Monolayer adsorption indicates that only one layer molecule of Congo Red dye can be formed on compost surface. So if one Congo Red dye molecule has occupied the compost surface, the surface cannot adsorb another molecule anymore. The compost wearing off or saturation is the pragmatic explanation for the compatibility to Langmuir adsorption model.

CONCLUSION

Compost, which is rich in organic carbon, can be used as an alternative to remove Congo Red dye in wastewater. It is found that the optimum compost dosage to treat 200 ppm Congo Red dye in synthetic wastewater was 8 g/L. The higher the dosage, the more space was available to bind the dye molecules. However, an excessive compost dosage may not be inefficient, due to reduction of adsorption capacity. The optimum compost particle size was 1-2 mm, and the smaller the particle size, the greater the contact surface and the opportunities to contact and bind the dye molecule.

The most efficient compost column height was 60 cm, suggesting that the higher the compost column allow the higher percentage removal of dye due to the increase of contact surface and contact time. Saturation of compost by the dye molecules occurred, indicating that fresh compost must be introduced to the system to maintain the percentage removal at a certain level. The Langmuir adsorption model was suitable to represent the adsorption isotherm of Congo Red dye onto compost pore surfaces.

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