Recycling of textile sludge for removing textile dye of reactive red 231 on aqueous solution

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Abstract: Carbonization treatment successfully converted textile sludge into potential adsorbent. The carbonization was performed at the range of 400 to 800 °C without oxygen involved. In order to investigate the adsorption performance of carbonized sludge then a series of adsorption tests was carried out. Adsorption experiments indicated that the highest adsorption capacity was obtained at the carbonization temperature of 400 °C. The maximum adsorption capacity for removal textile dye of reactive red 231 on aqueous solution was reached 49.1 mg/g. The pH of carbonized sludge played a significant role in the adsorption of reactive red 231 in the solution. Since the reactive red 231 is categorized as an anionic dyes, the lower pH was appropriate to accelerate adsorption process through charge neutralization by abundant H+ ions.

1. Introduction

The generation of textile sludge becomes complicated problems in the field of solid waste disposal due to weight and large amount of quantity. As an example It was reported by Balasubramanian et al. that more than 150 kg/day of textile sludge is released from a textile common effluent treatment plant in Tripur India [1]. In Bangladesh, the generation of textile sludge from water treatment plant reached 36 Mt in 2012 [2]. In textile wastewater treatment, various chemicals are added and some of chemicals are settled in the sediment tank. As a result, the sludge is contaminated by toxic and hazardous contaminations such as chromium, cadmium, lead, mercury and toxic organic chemical with high load of biochemical oxygen demand (BOD) and chemical oxygen demand (COD) [3]. Textile industry consumes large amount of water and various type of chemicals. Around 200 m³ of water is used by textile industry to produce one ton of textile products [4]. The textile wastewater contains large amount of dyes and chemicals including trace metals which is harmful to the environment and human
Problems faced by textile industry are not only coming from textile sludge. The problem most often faced by the textile industry is the colored wastewater coming from the dyestuff of dyeing and printing processes. In coloring process the dyes are classified as acid, direct, disperse, pigment, reactive, vat dyes, etc [2]. Among various types of dyes reactive dyes are often used for coloring of cellulose fibre [5]. Reactive red 231 or often called Procion Brilliant Red is one type of reactive dyes. During coloring process composed of dyeing and printing not all dyes attach to fibre or fabric. Some of them waste along with textile wastewater to be colored wastewater.

Recycling is a process to convert waste material into a new valuable product. According to the United States of Environmental Protection Agency there are many benefits of recycling application, such as reducing the amount of waste for final disposal, conserving natural resources, preventing pollution from the sources, etc [6]. The sludge and colored wastewater problems will be handled with one shot of treatment. The recycling of textile sludge into new product is the main idea in this research. New product called carbonized sludge will be used to remove textile dye of reactive red 231 on the solution through the adsorption treatment. The objective of this research is not only to investigate the possibility of textile sludge become carbon adsorbent but also to identify the capability of carbonized sludge for color removal treatment, especially for decolorization of reactive red 231 on the solution. In addition the finding of this research will contribute profitably for the development of textile waste management in the future.

2. Material and Method

2.1. Sludge and reactive red 231

Sludge was obtained from one of textile industry in Wakayama Prefecture, Japan. The physical form of sludge received is black, smelly (bad odor), soft, and has been dewatered before. Dewatered sludge and dried sludge are shown on the Figure 1. Heating at 105 °C and at 800 °C revealed that dewatered sludge has 77% of water content, 17% of organic content, and 6% of ash content (Figure 2). Based on the analysis with automatic high sensitive NC analyser type NCH-22F (Sumigraph, Japan), dried sludge has 31.4% of carbon content (Figure 2). While according to analysis with Energy dispersive X-Ray spectrometer type EDX-800HS (Shimadzu, Japan), the chemical composition of textile sludge (ash based) from the largest component consist of $\text{Al}_2\text{O}_3$ (45.6%), $\text{Na}_2\text{O}$ (12.4%), $\text{Fe}_2\text{O}_3$ (11.0%), $\text{SiO}_2$ (10.6%), $\text{TiO}_2$ (3.2%), $\text{P}_2\text{O}_5$ (3.0%), $\text{CaO}$ (2.8%), $\text{SO}_3$ (2.3%), $\text{MgO}$ (1.9%), $\text{K}_2\text{O}$ (1.0%), $\text{MnO}$ (0.1%).

Figure 1. Dewatered sludge (left) and dried sludge (right)
Figure 2. Carbon content (left) and water, organic matter, and ash content (right)

Reactive Red 231 with the commercial name of Procion Brilliant Red H-EGXL was obtained from DyStar Japan. Reactive red 231 has a chemical formula of \( \text{C}_{44}\text{H}_{24}\text{Cl}_{2}\text{N}_{14}\text{Na}_{6}\text{O}_{20}\text{S}_{6} \) and has a 1469.98 of molecular weight [7]. The chemical structure of reactive red 231 is shown on the Figure 3. For the adsorption preparation, reactive red 231 powder was dried in oven at 105 °C overnight to remove water content and to get constant of weight. Furthermore, stock solution was made by dissolving 1.00 g of reactive red 231 into 1 L of deionized water to 1000 mg/L of concentration. In order to get reactive red 231 solution with certain concentration, the stock solution was then diluted again with deionized water.

Figure 3. Chemical structure of reactive red 231

2.2. Carbonization process

Carbonization is a conversion process of organic substances into carbon under absence of oxygen. The purpose of carbonization is to gain the carbon element by eliminating non-carbon element through thermal decomposition process [8]. In this experiment textile sludge was placed into iron box and was heated in the Muffle Furnace F0410 (Yamato, Japan) for 2 hours in the range of 400 to 800 °C of temperature to transform into carbonized sludge.
2.3. Adsorption test

Adsorption is a phase transfer process to eliminate substances (adsorbate) from gases or liquid phases by material called adsorbent [9]. Adsorption experiment was performed with batch series under difference series of time and dyes concentration. A carbonized sludge (heated by 400, 500, 600, 700 and 800 °C) with 100 mL dye solution were placed in a 300 mL conical flask, then were shaken with a shaking machine, series TB-9R-3F (Takasaki Scientific Instrument, Japan) at 150 rpm at 25 °C. Contact time was variated in the range of 10 to 5120 minutes for reactive red 231 removal. After that the solution was filtered and the supernatant was analyzed its wavelength with UV-2550 UV-Visible Spectrophotometer (Shimadzu, Japan) at the peak wavelength ($\lambda_{\text{max}}$: 535 nm for reactive red 231) to determine the residual concentration of dye on solution. The residual concentration of reactive red 231 was determined following the calibration curve of reactive red 231 on the equation (1)

$$
C = 39.6825A + 1.4762 \\
R^2 = 0.9973
$$

where: $A$ is the absorbance at the peak of wavelength (535 nm), $C$ is residual concentration (mg/L) and $R^2$ is the coefficient determination. Thus, the adsorption capacity of carbonize sludge for reactive red 231 removal was calculated following the equation (2) below [10].

$$
q_e = \frac{(C_0-C_e)V}{m}
$$

where: $q_e$ is the adsorption capacity, the amount of reactive red 231 adsorbed per unit weight of carbonized sludge (mg/g), $C_0$ is the initial concentration of reactive red 231 (mg/L), $C_e$ is the residual concentration of reactive red 231 after adsorption (mg/L), $V$ is the volume of solution (L) and $m$ is the weight of adsorbent (g).

3. Result and Discussion

3.1. Carbonized sludge

A scanning electron microscope (SEM) was used to identify the surface morphology of carbonized sludge. Carbonized sludge sample at 500 °C was scanned on the 10,000 magnification with a SEM series of JSM-6510 LV series (JEOL, Japan). Figure 4 shows the cavities on adsorbent structure as the result of carbonization. We thought that the porosity formed is a sign that the carbonization process was successful converting textile sludge into adsorbent. As show on the Figure 5 the carbon content on the carbonized sludge was slightly decreased when the temperature increased from 400 to 500 °C and then stable when the temperature reached over 500 °C, which was also supported by the loss of weight on the Figure 5. There was no further weight loss after 500°C of heat treatment. The presence of carbon from the carbonization process shows that the sludge-based adsorbent has been formed.
3.2. Adsorption capacity

In order to investigate the capability of carbonized sludge as a potential adsorbent, a series of adsorption tests was performed. Adsorption tests were carried out to identify the adsorption capacity of carbonized sludge for taking reactive red 231 from the solution. Adsorption experiments was conducted by triplicated. This research aims to explore the relation between adsorption capacity and the temperature of carbonization. First, adsorption experiment with time variation revealed that the reactive red 231 removal reached an equilibrium at 2560 minutes of contact time (Figure 6). It means that after 2560 minutes, no further adsorption was significantly occurred.

After we identified the equilibrium time, then adsorption experiments under different initial dye concentration were conducted. Initial dye concentrations were set up from 40 to 140 mg/L for carbonized sludge at 500 to 800 °C and from 200 to 300 mg/L for carbonized sludge at 400 °C. Adsorption isotherm was calculated to help for describing adsorption mechanism. Adsorption isotherm was expressed by Freundlich and Langmuir adsorption isotherm. The Langmuir adsorption isotherm is shown by the equation 3 [11]. Otherwise Freundlich adsorption isotherm is expressed by the equation 4 [12].
Figure 6. Adsorption capacity following time variation

\[ q_e = \frac{q_{\text{max}} K_L C_e}{1 + K_L C_e} \quad (3) \]

\[ q_e = K_f C_e^{1/n} \quad (4) \]

where: \( q_{\text{max}} \) is the maximum monolayer adsorption capacity of carbonized sludge for taking reactive red 231 (mg/g); \( K_L \) is the Langmuir capacity factor (L/mg). For the Freundlich adsorption isotherm \( K_f \) is the Freundlich capacity factor (mg/g)(L/mg)\(^{1/n}\), and \( 1/n \) is the Freundlich intensity parameter.

Figure 7. Adsorption capacity following variation of dye concentration

The coefficient of determination \( (R^2) \) shown in Table 1 shows that the adsorption mechanism was fitted to the both of Freundlich and Langmuir isotherms. It shows that the adsorption mechanism can be approximately expressed by a monolayer model. As shown on Table 1 the highest maximum adsorption capacity \( (q_{\text{max}}) \) was reached by carbonized sludge at 400 °C for 49.1 mg/g. Otherwise there was no significant difference of adsorption capacity between carbonized sludge of 500, 600, 700, and 800 °C. The adsorption capacities were average for around 21.7 mg/g.
Table 1. Isotherm parameter of carbonized sludge for reactive red 231 removal

| Carbonization temperature (°C) | Freundlich isotherm | Langmuir isotherm |
|-------------------------------|---------------------|------------------|
|                               | $1/n$  | $K_f$ (mg/g)(L/mg)$^{1/n}$ | $R^2$  | $q_{max}$ (mg/g) | $K_L$ (L/mg) | $R^2$  |
| 400                           | 0.07   | 36.8                                    | 0.84   | 49.1 ± 1.9       | 0.66         | 1.00   |
| 500                           | 0.27   | 6.3                                     | 0.99   | 19.3 ± 0.1       | 0.16         | 0.99   |
| 600                           | 0.35   | 5.0                                     | 0.99   | 21.4 ± 0.3       | 0.12         | 0.99   |
| 700                           | 0.41   | 3.9                                     | 0.99   | 22.5 ± 0.6       | 0.08         | 0.98   |
| 800                           | 0.40   | 4.4                                     | 0.99   | 23.6 ± 0.8       | 0.09         | 0.99   |

Figure 8 shows the relation of carbonization temperature with surface area and pH of adsorbent. The surface area of adsorbent was calculated according to the Brunauer-Emmett-Teller (BET) N$_2$ adsorption method. While the pH of carbonized sludge was measured based on Japan Industrial Standard test method for activated carbon, JIS K1474 [14]. Specific surface plays an important role in the adsorption process. Activated carbon is often called a good adsorbent because it has a large specific surface area [13]. Figure 8 shows that surface area increased with the increasing of temperature, however after 500 °C there was no significant change of surface area. The pH also shows the same pattern with surface area. The pH increased with increasing temperature due to the decrease of carboxyl group on the sludge [15]. The pH increased until the temperature reached 600 °C then stable at temperature of 700 and 800 °C.

If we refer to the adsorption capacity result, the maximum capacity of reactive red 231 was reached when the carbonization was performed at lower temperature (400 °C). At that condition the surface area was 76.3 m$^2$/g (lowest) with pH of 5.8 (lowest). Reactive red 231 is categorized as an anionic dye type. It can be seen on the presence of the sulfonic group (SO$_3^-$) on their structure (Figure 3). Typically dyes containing -SO$_3^-$, -COO$^-$ and/or -O- groups are categorized as acid (anionic) dyes [16]. Anionic dyes carrying negative charge and they are proton acceptor. Carbonized sludge at 400 °C has the lowest pH than other carbonized sludge adsorbents. On the lower pH (acidic condition), H$^+$ ions are
more abundant than OH− ions. Since reactive red 231 is anionic dyes, negative charges are neutralized by abundant H+ ions under acidic condition, which is better for occurring adsorption process. The characteristic of anionic dye, which prefers acidic condition to alkaline condition for adsorption, was also suggested by the higher adsorption capacity of carbonized sludge at 400 °C. Thus, in this research the adsorption of reactive red 231 was controlled by pH value rather than surface area and/or carbon content. This research was also supported by Geethakarti and Phanikumar who showed that the adsorption capacity of tannery sludge-based activated carbon for removing reactive red 31 and reactive red 2 was higher on the lower pH condition [17]. Moreover, similar result was obtained by Al-Degs et al. which mentioned that the adsorption of reactive blue 2, reactive red 4 and reactive yellow 2 was more effective on the acidic condition [18].

4. Conclusion

The utilization of textile sludge into potential adsorbent was successfully performed through carbonization process. Heat treatment on carbonization process converts textile sludge into porous material of adsorbent. The carbonized sludge at 400 °C was able to remove Reactive Red 231 from aqueous solution with the maximum adsorption capacity of 49.1 mg/g. Carbonization temperature at 400 °C created textile sludge-based adsorbent with the highest adsorption capacity in comparison with higher carbonization temperatures. In this research, we deduced that adsorption mechanism of reactive red 231 was controlled by pH value than specific surface area. The lower pH of carbonized sludge at 400 °C was suitable for removing reactive red 231 which is categorized as an anionic dye. The recycling concept of textile sludge may be promising to handle the sludge and colored wastewater problem in the future of textile waste management. The selection of carbonization temperature for adsorbent production from textile sludge should be able to consider the type of dyestuff in the effluent to be more effective in removing dyes from the water body.

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