Adsorption of procion red and congo red dyes using microalgae \textit{Spirulina} \textit{sp}

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ABSTRACT

Adsorption of procion red and congo red dyes using microalgae \textit{Spirulina} \textit{sp} was conducted. \textit{Spirulina} \textit{sp} was obtained by cultivation and production in laboratory scale. \textit{Spirulina} \textit{sp} was used as adsorbent for adsorption of dyes. Adsorption process was studied by kinetic and thermodynamic in order to know the adsorption phenomena. The results showed that kinetically congo red is reactive than procion red on \textit{Spirulina} \textit{sp}. On the other hand, thermodynamically procion red was stable than congo red on \textit{Spirulina} \textit{sp} which was indicated by adsorption capacity, enthalpy, and entropy.

Keywords: procion red, congo red, microalgae, \textit{Spirulina} \textit{sp}

1. INTRODUCTION

The dyes in industry is always used to create colorful fabrics. Dyes can be classified according to their solubility and chemical properties for fabrics i.e. acid dyes, basic dyes, direct dyes, mordant dyes, vat dyes, reactive dyes, disperse dyes, azoic and sulfuric dyes (Gilbert, 2017). Dyes such as procion red and congo red as shown in Figure 1, are intensively used in textile. These dyes are not degradable thus potential as pollutant in the environment. Several methods have been applied to remove dyes in aqueous medium such as adsorption and membrane filtration. Adsorption is commonly used to remove dyes from solution using adsorbent. This method is easy to operate, high efficiency, and also low cost (Bleam, 2017).

The successfully of this method is depending on quality of adsorbent. Inorganic adsorbents such as zeolites, clays, activated carbons and carbon nanotubes are commonly used to remove dyes from solution. On the other hand, organic adsorbents such as chitosan, lignin, cellulose, and algae are also efficient and renewable adsorbent to remove many kinds of dyes (Marzbali et.al, 2017). Among these adsorbents, organic adsorbents have advantages due to renewable source such as algae. Algae has been intensively used as adsorbent to remove heavy metal ion (Vafajoo et.al, 2018) and food dyes (Dikshit and Tallapragada, 2018) and textile dyes (Abd El-Rahim et.al, 2017). This ability is due to functional groups on algae such as hydroxyl, carboxyl, phosphate, sulfate, and other functional groups, which can act as ligand or nucleophilic to bind with metal ions or dyes.

Our previous experiment reported that microalgae \textit{Spirulina} \textit{sp} has functional group such as carbonyl, hydroxyl, aliphatic chains, and ether. Carbonyl on \textit{Spirulina} \textit{sp} has strong IR vibration indicated that \textit{Spirulina} \textit{sp} can act ligand to bind with absorbate (Zulkifli et.al, 2016). This preliminary information is useful to treat \textit{Spirulina} \textit{sp} as adsorbent for remove metal ions or dyes from aqueous solution.

In this research, microalgae \textit{Spirulina} \textit{sp} was used as adsorbent of procion red and congo red dyes. Procion red is reactive dyes with dichlorotriazine structure and congo red is dye with azo structure. Several factor that influencing the adsorption process such as kinetic and thermodynamic parameters were investigated.

2. EXPERIMENTAL SECTION

2.1. Chemical and Equipment

Chemicals were used after purchased directly without further purification. Water was supplied from Integrated Research Laboratory, Graduate School Sriwijaya University using Purite \textregistered water purification system. Concentration of dyes was determined using Thermo Scientific spectrophotometer UV-Visible Genesys™ 20.

2.2. \textit{Spirulina} \textit{sp} Cultivation and Production (Zulkifli et.al, 2016)

Cultivation and production of \textit{Spirulina} \textit{sp} was adopted from Zulkifli et al (2016) as follow: 10 mL of each component was added into 1 L of Erlenmeyer and the mixtures were stirred. The components are stock solution, trace elements, EDTA stock, iron solution, and boric solution. The components solution was added with deionized water to 1 L and solution was clear. Then solution was autoclave at 100 °C for 2.5 hours. The culture of \textit{Spirulina} \textit{sp}...
was added into Erlenmeyer after cooling the solution. The solution was continuously illuminated by four fluorescent lamps for 14 days together with aerator systems. A green solution was formed at 1 day. *Spirulina* sp was collected by centrifugation at 4000 rpm for 3 minutes. Dry *Spirulina* sp was obtained after dried at 45 °C overnight. The stock solution, trace elements, other constituents and also identification of *Spirulina* sp were referred to Zulkifli et al., 2016.

2.3. Adsorption of Procion Red and Congo Red Dyes on *Spirulina* sp

Adsorption of dyes was performed using batch system. The adsorption process was studied by two parameters i.e. kinetic and thermodynamic adsorption. Kinetic adsorption was investigated by adsorption time to obtain adsorption rate of dyes on *Spirulina* sp. Thermodynamic adsorption effect was studied by concentration of dyes and temperature of adsorption. The data of thermodynamic adsorption was capacity, energy, and entropy adsorption of dyes on *Spirulina* sp. The kinetic and thermodynamic adsorption data were obtained using Langmuir-Heinselwood and Langmuir Equations (Imron et al., 2017; Ginting and Mohadi, 2017).

2.4. Kinetic Adsorption of Dyes on *Spirulina* sp

*Spirulina* sp (0.5 g) was mixed with procion red 20 mg/L (10 mL) in 100 mL of Erlenmeyer. The mixtures were shaken at 50 rpm. Time of adsorption was varied at 10, 20, 30, 40, 50, 60, 70, 80, and 90 minutes. Solution and adsorbent was separated by filtration. Filtrate was analyzed by UV to determine concentration of procion red. Similar procedure was conducted using congo red as adsorbate.

2.5. Adsorption of Dyes on *Spirulina* sp

Thermodynamic adsorption was studied by variation of concentration of dyes and temperature adsorption. Concentration of procion red was 12, 14, 16, 18, and 20 mg/L. Concentration of congo red as adsorbate was 5, 10, 15, 20, and 25 mg/L. Adsorption was conducted at 30 minutes for both procion red and congo red as adsorbates and filtrate was analyzed using UV.

Variation of adsorption temperature was 23, 28, 33 °C for both procion red and congo red. Adsorption was carried out at 30 minutes, amount of dyes 10 mL. After process finished, filtrate was analyzed using UV.

3. RESULTS AND DISCUSSION

The functional groups of *Spirulina* sp as our preliminary results are carbonyl, hydroxyl, aliphatic chains, and ether. These functional groups are important for dyes to bind because algae are nonpo-
The first adsorption process was investigated through adsorption time. Time adsorption of procion red and congo red using *Spirulina sp* was conducted at 20-70 minutes and the results are presented in Figure 2.

Figure 2 showed that procion red was more slightly adsorbed than congo red initial time. There is no adsorption process at initial time for congo red until adsorption time reached 40 minutes. On the other hand, adsorption of congo red is largely faster than procion red. Adsorption at 60 minutes showed that the amount of congo red adsorbed is higher than procion red.

The data in Figure 2 is calculated using Langmuir-Heinselwood equation in the assumption that process was chemical adsorption and reaction was quite well with order one kinetic model. The data was obtained and presented in Table 1. Data in Table 1 showed that adsorption rate of congo red was faster than procion red on *Spirulina sp*. Data in Table 1 showed that congo red is reactive dyes than procion red.

Another parameter is Thermodynamic adsorption. These data were investigated by variation of concentration and temperature adsorption. The results of concentration of dyes and temperature adsorption were presented in Figure 3.

Figure 3 showed that by increasing concentration and temperature adsorption of dyes can decrease the adsorption of dyes both for procion red and congo red. Probably due to chemical interaction between adsorbent-adsorbate can create opposite charges of system and adsorption amount will decrease. Thermodynamic adsorption data can be calculated from data in Figure 3 using Langmuir isotherm adsorption equation. The results of thermodynamic data is shown in Table 2.

Table 2 showed that adsorption capacity, enthalpy, and entropy of procion red is higher than congo red for all temperatures. Stability of procion red is higher as adsorbate than congo red. As mentioned above, congo red is labile adsorbate for *Spirulina sp* while procion red is stable adsorbate in this system.

Further investigation was the effect of acidity in the adsorption of procion red and congo red on *Spirulina sp*. The results of acidity of adsorption process are shown in Figure 4.

Figure 4 showed that by increasing pH of adsorption system will increase the adsorption amount for both procion red and congo red. These phenomena is totally different with adsorption of metal ions in which adsorption amount will decrease by increase pH system. At lower pH, there was no adsorption process of dyes. Adsorption significantly occurred at pH more than 7. Basic system is appropriate for adsorption of dyes on *Spirulina sp*.

**4. CONCLUSION**

Adsorption rate of congo red (1.63 min⁻¹) was faster than procion red (5.4x10⁻⁴ min⁻¹) on *Spirulina sp*. Adsorption capacity, enthalpy, and entropy of procion red were higher than congo red on several temperatures. This results indicated that congo red was labile adsorbate and procion red was stable adsorbate on *Spirulina sp*.

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**REFERENCES**

Abd El-Rahim, W.M., Moawad, H., Abdel Aziz, A.Z., Sadowsky, M.J. (2017). Optimization of Conditions for Decolorization of Azo-Based Textile Dyes by Multiple Fungal Species, Journal of Biotechnology, 260, 11-17.

Bleam, W. (2017). Chapter 8-Surface Chemistry and Adsorption, Soil and Environmental Chemistry (2nd Edition). Academic Press, 385-443.

Dikshit, R., Tallapragada, R. (2018). Chapter 3-Comparative Study of Natural and Artificial Flavoring Agents and Dyes. Natural and Artificial Flavoring Agents and Food Dyes (A HAND Book of Food Bioengineering), Academic Press, 83-111.

Gilbert, K.G. (2017). Dyes. Encyclopedia of Applied Plant Sciences (2nd Edition). Vol. 2. Elsevier, 368-373.

Ginting S.O., Mohadi. R. (2017). Adsorption of Congo Red Using Kaolinite-Cellulose Adsorbent. Science and Technology Indonesia, 2(2), 29-36.

Imron, M., Said, M., Lesbani, A. (2017). Adsorption of Procion Red Using Layer Double Hydroxide Mg/Al. Science and Technology Indonesia, 2(3), 64-67.

Marzabi, M.H., Mir, A.A., Pazoki, M., Pourjanshadzian, R., Tabeshnia, M. (2017). Removal of Direct Yellow 12 From Aqueous Solution by Adsorption Onto Spirulina algae as a High-Efficiency Adsorbent, Journal of Environmental Chemical Engineering, 5(2), 1946-1956.

Vafajoo, L., Cheraghi, R., Dabbagh, R., McKay, G. (2018). Removal of Cobalt[II] Ions From Aqueous Solutions Utilizing the pre-treated 2-Hypnea Valentiae Algae: Equilibrium, Thermodynamic, and Dynamic Studies. Chemical Engineering Journal, 331(1), 39-47.

Zulkifli, H., Hanafiah, Z., Jasatnri D., Lesbani, A. (2016). The Relationship of Culture Media and Chemical Composition on *Spirulina sp* for Metal Ion Adsorbent. Sriwijaya Journal of Environment, 1(5), 68-71.