

Adsorption of procion red and congo red dyes using microalgae *Spirulina sp*

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ABSTRACT

Adsorption of procion red and congo red dyes using microalgae *Spirulina sp* was conducted. *Spirulina sp* was obtained by cultivation and production in laboratory scale. *Spirulina 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 *Spirulina sp*. On the other hand, thermodynamically procion red was stable than congo red on *Spirulina sp* which was indicated by adsorption capacity, enthalpy, and entropy.

Keywords: procion red, congo red, microalgae, *Spirulina 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 *Spirulina sp* has functional group such as carbonyl, hydroxyl, aliphatic chains, and ether. Carbonyl on *Spirulina sp* has strong IR vibration indicated that *Spirulina sp* can act ligand to bind with adsorbate (Zulkifli et.al, 2016). This preliminary information is useful to treat *Spirulina sp* as adsorbent for remove metal ions or dyes from aqueous solution.

In this research, microalgae *Spirulina 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® water purification system. Concentration of dyes was determined using Thermo Scientific spectrophotometer UV-Visible Genesys™ 20.

2.2. *Spirulina sp* Cultivation and Production (Zulkifli et.al, 2016)

Cultivation and production of *Spirulina 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 *Spirulina sp*

Article History:

Received 15 August 2017; revised 23 September 2017; accepted 25 September 2017

<http://doi.org/10.26554/sti.2017.2.4.102-104>

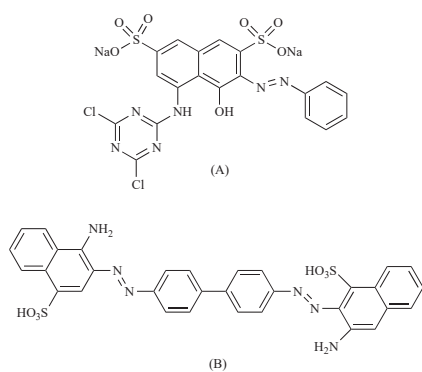


Figure 1. Structure of procion red (A) and congo red (B)

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.

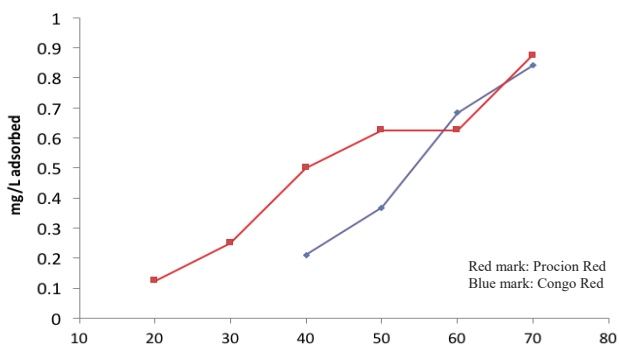


Figure 2. Adsorption time of procion red and congo red on *Spirulina* sp

Table 1. Kinetic adsorption of procion red and congo red on *Spirulina* sp

Kinetic Parameter	Procion Red	Congo Red
Adsorption rate (min ⁻¹)	5.4 x 10 ⁻⁴	1,63

Table 2. Thermodynamic adsorption parameter

Thermodynamic Parameter	Variables	Congo Red	Procion Red
Adsorption capacity (b) mg.g ⁻¹	25 °C	0.148	11.23
	28 °C	0.063	10.87
	33 °C	0	3.155
	5 mg/L	46.392	165.58
	10 mg/L	113.569	160.58
Enthalpy (DH) KJ.mol ⁻¹	15 mg/L	150.175	0
	20 mg/L	185.992	219.348
	25 mg/L	265.848	258.574
	5 mg/L	148	535
	10 mg/L	366	521
Entropy (DS) KJ	15 mg/L	485	0
	20 mg/L	601	711
	25 mg/L	859	839

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-

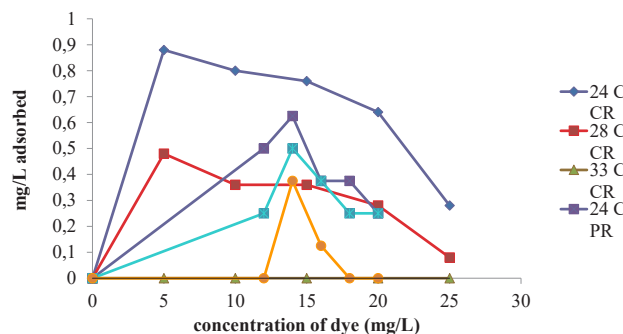


Figure 3. Effect of concentration and temperature of procion red and congo red

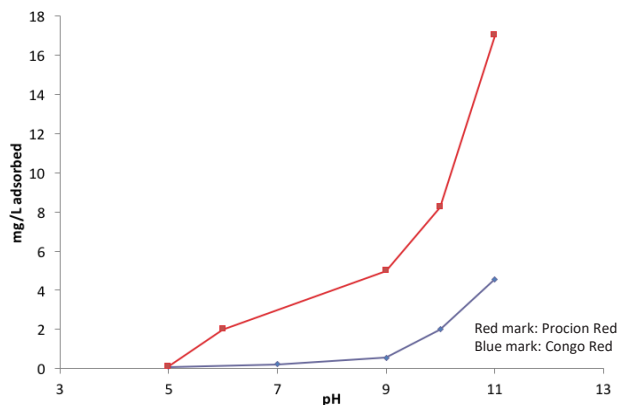


Figure 4. Effect of acidity

rous material. Interaction of adsorbent from algae with adsorbate is assumed as chemical interaction.

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 is 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 mention 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 con-

go 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 ($5.4 \times 10^{-4} \text{ min}^{-1}$) 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.*

ACKNOWLEDGEMENT

Authors thank Universitas Sriwijaya through "PNBP Hibah Pro-fesi 2017" contract number 987/UN9.3.1/PP/2017 for support this research to H.Z. Thank to Integrated Research Laboratory, Graduate School Universitas Sriwijaya for equipment and analysis.

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