# Alumina-Activated Carbon Composite as Adsorbent for Adsorption of Procion Red Dye from Wastewater Songket Industry

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## ABSTRACT

Alumina-activated carbon composite has been synthesized and studied for adsorption procion red dye. Composite was prepared by precipitation method aluminium hydroxide on the surface of activated carbon followed by calcinations. The Fourier transform Infra Red (FTIR), Scanning Electron Microscopy-Energy Dispersive X-Ray Spectroscopy (SEM-EDS) and Brunaeur Emmet Teller (BET) surface are being used to characterize the adsorbent. Batch adsorption experiments were carried out for the adsorption of procion red dye. Effect of the mass of composite, stirrer speed, contact times and pH of the solution on the adsorption capacity were studied. The obtained optimum conditions applied to adsorp of procion red dye from wastewater songket industry. The result showed that the adsorption optimum at mass of alumina-activated carbon composite 0.1 g, stirrer speed 150 rpm, contact times 2 hours at pH of the solution 9. The adsorption isotherm data according to Langmuir isotherm. The alumina-activated carbon composite can be removal of procion red dye from wastewater songket industry with effectiveness adsorption of 88.21 %.

Keywords: alumina, activated carbon, composite, procion red dye, adsorption

## INTRODUCTION

Water pollution by synthetic dye is a serious environmental and public problem. Many of the dies cause serious harm to aquatic life [1], causing allergic reaction and certain types of cancer and poisoning [2]. Procion red dye is one of the dye that is used in textile industrial, especially songket industry in Palembang, Indonesia. Procion red dye an cationic molecule and the dye having an aromatic structure. The dyes which have a complex aromatic structure are difficult to biodegrade [3]. The wastewater produced from dyeing process.

Adsorption methods is commonly used due to the biocompatibility, biodegradable and efficiency of these processes for the removal of azo-dyes [4]. Activated carbon shows the good adsorption characteristics towards pollutants both polar and non polar adsorbate molecule. The adsorption characteristic of activated carbon depend on the raw materials, methods, carbonization and activation process. Gelam tree *(Melaleucea leucodendronn* Linn.) is plant that has a hard texture and organic matter such as carbon, oxygen and hydrogen in the compound os cellulose, hemicellulose, lignin, resin and ash [5]. The plants grow in swamp area, South Sumatera. Gelam stem potentially used be as activated carbon because has a large surface area. The activated carbon from gelam stem with $ZnCl_2$ (25 % w/w) activator have surface area are 1213 $m^2$/g and low ash content [6].

In this study, the activated carbon from stem gelam was used to prepare activated carbon-alumina composite for adsorption of procion red dye. The composite material has excellent property because the material has dual pore size distribution characteristic. The other hand, alumina has a Lewis acid site (accept electrons) that $Al^{3+}$ in tetrahedral and octahedral positions. The other hand, alumina also has a Bronsted Lowry site i.e. $OH^-$ group (proton donating). The dye and composite interaction may occur by physics and chemistry mechanism. Some studies alumina-activated carbon composite ie, the use of alumina-activated carbon composite to adsorp formaldehyde. The activated carbon produced by Shaanxi Shenmu Co. Ltd. The adsorption capacity of alumina-activated carbon composite to adsorp formaldehide much better than of the pure activated carbon or alumina [7-8]. Another report, synthesize pores alumina gel and close pores activated carbon composite to adsorp acetone. The composite is a higher thermal resistance than activated carbon [9].

Several methods can be used to synthesize alumina, for example by precipitation, ball mill and solvo-thermal. In this study, alumina-activated carbon prepared by precipitation of aluminium hydroxide on the surface of activated carbon followed by calcinations. This method relatively simple and highly successful synthesis method. Characterization of the alumina-activated carbon composite by using FTIR, SEM-EDS and BET surface area analysis. The effect of various parameters such as mass of composite, stirrer speed, contact time and pH on the adsorption capacity was also studied. The interaction determination that occurred between procion red dye with alumina-activated carbon composite is determined by Langmuir and Freundlich isotherm. Futhermore, the composite is used to adsorp procion red dye from wastewater songket industrial sample.

## EXPERIMENT
### Chemicals and instrumentation
The chemical used in this study had analytical grades and was supplied from Merck including KOH, $Al(NO_3)_3$, $NH_4OH$, $Al(OH)_3$, NaOH, HCl, procion red dye, and filter paper Whatman 42 and other materials such as aquadest, distilled water.

Instruments applied during research include FTIR spectrometer (Shimadzu 5400, sample was measured as a mixture on KBr pelleted samples were scanned over the wavenumber range 400-4000 $cm^{-1}$), SEM-EDS JEOL JMS 1400, BET surface area (NOVA 4000 quanta chrome), UV-Vis spectrophotometer (Shimadzu 1240), mechanical shaker (Edmund Buhler BC 25), pH meter (Schott Gerate CG 820), furnace (Neycraft JFF 2000), analytical balance (Metler AE 166) and oven (Fisher scientific 655 F).

### Synthesis of alumina-activated carbon composite
The activated carbon was prepared as following procedure from reference [10]. The stem of gelam plant with $\pm$ 10 cm in size is heated in a furnace at temperature of 500 $^o$C for 4 hour. The carbon produced were crushed and sieved to size of 80 mesh. About 50 g of carbon were impregnated with 45% KOH solution with a ratio of carbon: KOH solution = 1: 4 for 14 hour at room temperature. The mixture was then put in a furnace and heated in 600 $^o$C for 2 hours. The resulting activated carbon was washed with distilled water until neutral, and the activated carbon was further dried at temperature of 110 $^o$C.

Synthesis of alumina-activated carbon composite was used precipitation methods by adding 25 g of activated carbon into 100 mL of 0.1 N $Al(NO_3)_3$ and then 0.1 N $NH_4OH$ solution was added drop wise to mixture under vigorous stirring until pH of the solution $\pm$ 10. The solid precipitate was washed with distilled water, filtered and dried overnight at 120 $^o$C

in oven. The composite were calcined at 350 $^{\circ}$C for 3 hours, and the product was analyzed using FTIR spectrometer, SEM-EDS and BET surface area.

**The batch adsorptions experiments**

The procedure was carried out by preparing 5 solution of 50 mL of procion red dye solution with concentration 30 mg/L. The composite with variation 0.1; 0.2; 0.3; 0.4; and 0.5 g were added to the dye solution. After that, the mixture was stirred at a constant speed in 150 rpm at room temperature for 60 minutes. Then, the mixture was filtered using filter paper. The filtrate was measured using spectrophotometer Uv-Vis at 560 nm. The amount of procion red dye was calculated following equation.

$$q_e = \frac{C_0 - C_e}{W} \, x \, V$$

Where $q_e$ is the adsorption capacity of the composite (mg/g) at equilibrium, $C_0$ and $C_e$ are the initial and equilibrium procion red dye concentration (mg/L), V is volume of solution (L) and W is the mass of adsorbents (g).

The adsorption of procion red dye under different conditions including stirrer speed (50; 100; 150; 200 and 250 rpm), contact time (0.5; 1.0; 1.5,; 2.0 and 2.5 hours) and pH (5; 6; 7; 8; 9 and 10). The pH mixture was adjusted using 1.0 M HCl and 1.0 M NaOH. Adsorption isotherm studies were conducted by varying the initial concentration of procion red dye from 5.0 to 30 mg/L with interval 5.0 mg/L. Langmuir isotherm is expressed as the following equation [11].

$$\frac{C_e}{q_e} = \frac{1}{b \, q_m} + \frac{C_e}{q_m}$$

Where $C_e$ is the equilibrium concentration (mg/L), $q_e$ is the adsorption capacity (mg/g), $q_m$ is the complete monolayer adsorption capacity (mg/g) and b is the Langmuir constant (L/mg). Freundlich equation is presented as following [12].

$$\ln q_e = \ln K_F + \, 1/n \ln C_e$$

Where k and n are Freundlich constant. The value 1/n is a measure of adsorption intensity or surface heterogeneity. The optimum condition adsorption obtained to adsorp procion red dye from wastewater songket industry. The alumina-activated carbon composite was added to 50 mL wastewater songket industry, experiment regulated at optimum conditions. Then, the mixture was filtered using filter paper. The filtrate was measured using spectrophotometer UV-Vis at 560 nm.

**RESULT AND DISCUSSION**
**Characterization of alumina-activated carbon composites**

Reaction between $Al(NO_3)_3$ and $NH_4OH$ forms $Al(OH)_3$ occurs in activated carbon pores. Futhermore, changing the composition of the activated carbon surface. The $Al(OH)_3$ were produced under alkaline solution ($\pm10$). The reaction is shown as below:

$$Al(NO_3)_3 \; + 3NH_4OH \; \rightarrow \; Al(OH)_{3(s)} \; + 3NH_4NO_3$$
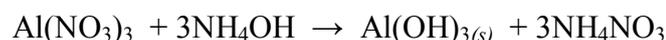
The aluminium hydroxide was precipitated in an amorphous state and on further ageing transformed to bohemite. The yield obtained in this synthesis of alumina-activated carbon composite is 72.41 %. Figure 1 is showed the structure of alumina.
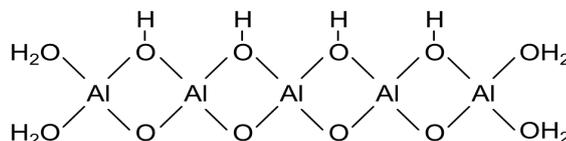
**Figure 1**. Structure of Alumina

The FTIR, SEM-EDS and BET surface area spectra of the alumina-activated carbon were recorded. The FTIR spectra activated carbon and alumina-activated carbon was shown in Figure 2. The characteristic band of activated carbon and alumina-activated carbon composite at 1569.9 and 1563.3 $cm^{-1}$ is the vibration of C=C aromatic and amplified C-H stretching at 2850.6 and 2920.1 $cm^{-1}$. The FTIR spectra of 1000-1300 $cm^{-1}$ showed C-O-C (ether) that is at 1161.1 and 1145.8 $cm^{-1}$. The other broad spectra at 3500-3200 $cm^{-1}$ is the peak for OH group. Meanwhile the remaining of C-H stretching for methyl or methylene group were recorded at 3317.8 $cm^{-1}$ for the activated carbon, and at 3328.9 $cm^{-1}$ for the resulted of alumina-activated carbon composite. The characteristic spectra FTIR for alumina, can be assigned 624-659 $cm^{-1}$ is the uptake group C-O-R$^+$, where R$^+$ is $Al^{3+}$ [13]. This peak appears at 611.4 $cm^{-1}$. The wave number of 1100 $cm^{-1}$ is the peak for Si-O and Al-O while the region of 900 $cm^{-1}$ indicates the absorption of Al-OH [14].
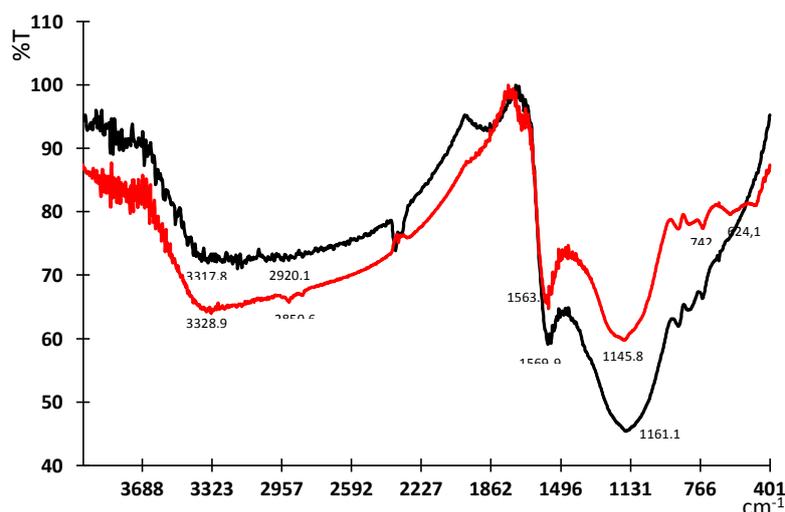
**Figure 2.** FTIR spectra of activated carbon (red line) and alumina-activated carbon composite (black line)

Figure 3a and b are shown SEM image respectively to activated carbon and alumina-activated carbon composite with magnifications 10.000x. Activated carbon surface is more homogeneous and porous while after modification activated carbon with alumina into composite partially closed pores.
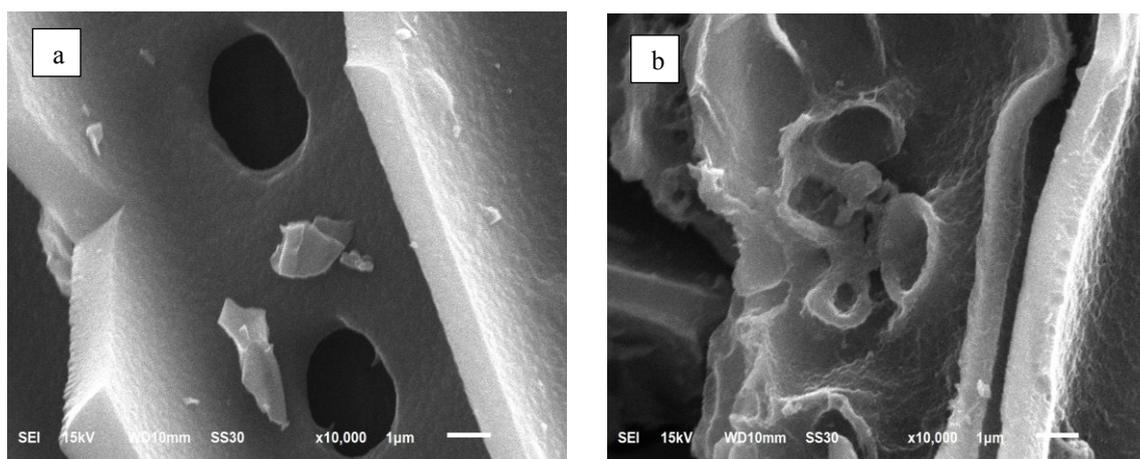
**Figure 3.** Morphology of (a) activated carbon and (b) alumina-activated carbon composite

The EDS spectra of the adsorbent is showed the presence of element in activated carbon and alumina-activated carbon composite (Table 1). The main element of the activated carbon is C (99.20%). Formation of alumina-activated carbon composite changes the composition of the elements. The presence of Al in the activated carbon demonstrated the adsorption Al onto activated carbon.

**Table 1**. Elemental analysis of the activated carbon and alumina-activated carbon composite

| Element | Activated carbon (%) | Alumina-activated carbon composite (%) |
|---------|----------------------|----------------------------------------|
| C | 99.20 | 84.80 |
| O | 0.8 | 13.36 |
| Al | - | 1.84 |

The surface area and total pore volume of activated carbon and alumina-activated carbon composite is summarized in Table 2. The activated carbon has a large specific surface area 535 ($m^2$/g). It is a typical for commercial activated carbon (minimum surface area 300 $m^2$/g). The presence of alumina in the activated carbon reduct of the surface area to 489 $m^2$/g. However, alumina has an active site which able to increase the adsorption capacities.

**Table 2**. Data of BET surface area of activated carbon and alumina-activated carbon composite

| Adsorbent | Surface area ($m^2$/g) | Total pore volume ($cm^3$/g) |
|-----------|------------------------|------------------------------|
| Activated carbon | 535 | 0.56 |
| Alumina-activated carbon composite | 489 | 0.49 |

**Procion red dye adsorption**

The adsorption data obtained for the effect of different mass of alumina-activated carbon composite with 0.05; 0.1; 0.2; 0.3; 0.4 and 0.5 g. It can be seen from the results in figure 4 that the mass of composite significantly influenced the adsorption capacity. The more amount of alumina-activated carbon composite, the more amount of dye that can be adsorbed but due to the increase in the amount of dye adsorbed is not proportional to the increase in the amount of adsorbent, so the adsorption capacity has decreased. The number of

such sites per unit massa comes down resulting in comparatively less adsorption. The same results on the adsorption of the dye orange 16 and black 5 using activated carbon, the adsorption capacity are seen increase and then decreased [15]. In this study, composite mass of 0.1 g has the highest adsorption capacity.
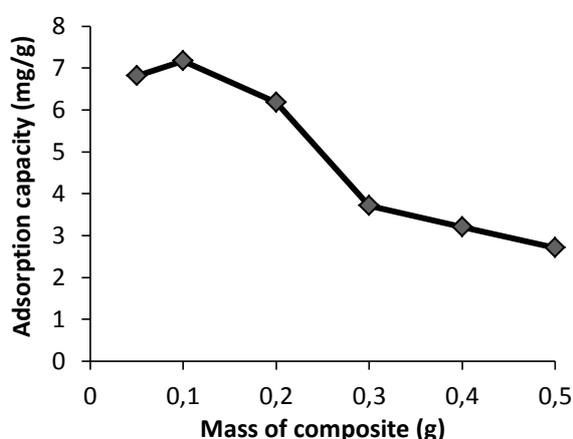


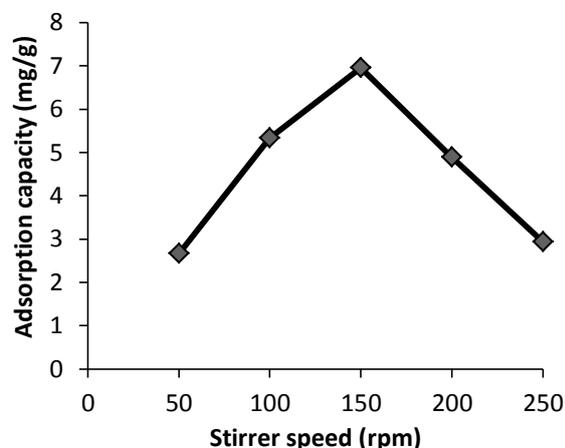**Figure 4**. Effect of mass of composite



**Figure 5**. Effect of stirrer speed

The effect of stirrer speed on the adsorption procion red dye onto composite that is presented in figure 3. At low stirrer speed, the effect of mass transfer for dye is increased the adsorption capacity. As the stirrer speed increases from 50 to 150 rpm, but at higher speed the adsorption capacity had lower. At high speeds, the number of collisions caused the release back the dye. In this study, the subsequent experiment are conducted at 150 rpm.
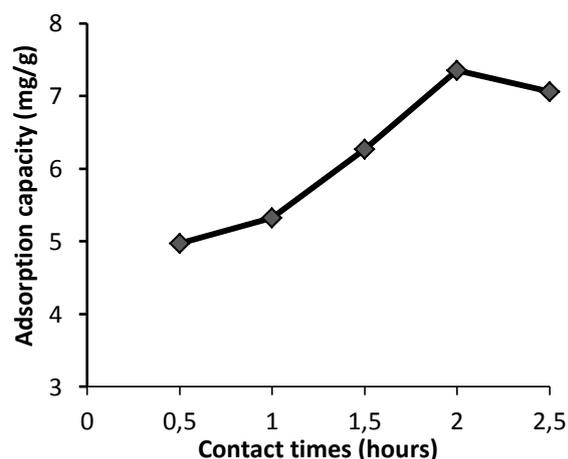


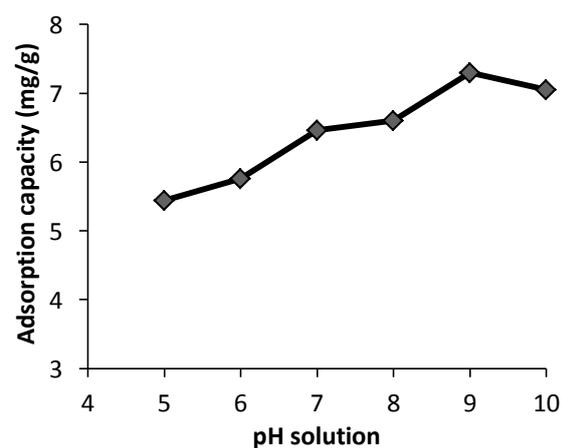**Figure 6**. Effect of contact times



**Figure 7**. Effect of pH solution

The effect of contact time on the adsorption of procion red dye by alumina-activated carbon composite was shown in figure 6. The adsorption process is influenced by the contact time. The contact time from 0.5 until 2 hours (interval 0.5 h) was increased the adsorption capacity and reached to equilibrium in 2 hours. The longer of the contact time, the more collisions between the dye and composite so adsorption capacity increases to reach equilibrium.

The pH a very significant effect on the adsorption process, pH solution influences the surface charge of the adsorbent. In the experiment, the effect of the pH varied from 5 to 10.

Figure 7 shown the effect of pH on the adsorption procion red dye onto alumina-activated carbon composite. It was observed that the procion red dye adsorption dependent on the pH of the solution. From pH solution 5, it was found that an increase in pH solution led to increase in adsorption capacity and maximum adsorption removal of dye was observed at pH solution 9 with adsorption capacity of 7.30 mg/g. The interactions occur as an electrostatic interaction. This could be explained by the fact that at lower pH, more protons will be available, positively charged alumina ($AlOH_2^+$). Therefore, ionic repulsion between the positively charged adsorbent surface and the procion red dye (cationic dye). At the high pH means decreasing of proton number, as an effect active side of alumina persist in negative charge ($AlO^-$). The was predicted increased the electrostatic interaction between negatively charged adsorbent and positive charged of procion red dye. The same result was obtained in the cationic dye adsorption process, for example adsorption methylene blue using pistachio in presence $CuFe_2O_4$ at pH 9 [16].

**Adsorption isotherm**

In order how the procion red dye with the alumina-activated carbon composite surface adsorption isotherm are used to analyze the experimental data. In this study, Langmuir and Freundlich models were used to describe the equilibrium adsorption. Langmuir isotherm is based the assumption that adsorption occurs at homogenous sites and monolayer coverage of the surface and Freundlich isotherm is describe heterogeneous and multilayer. The adsorption isotherm was studied by varying the initial concentration of procion red dye (5; 10; 15; 20; 25 dan 30 mg/L) at optimum conditions adsorption.
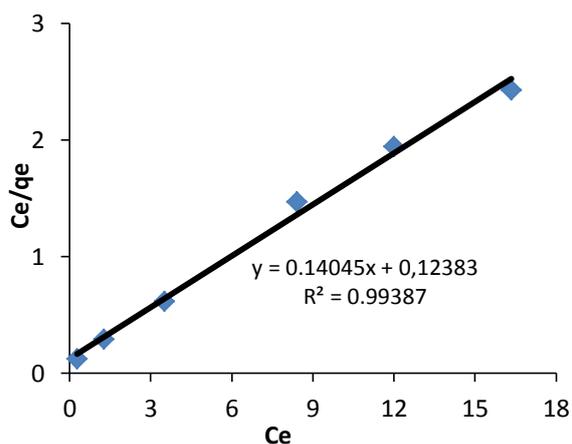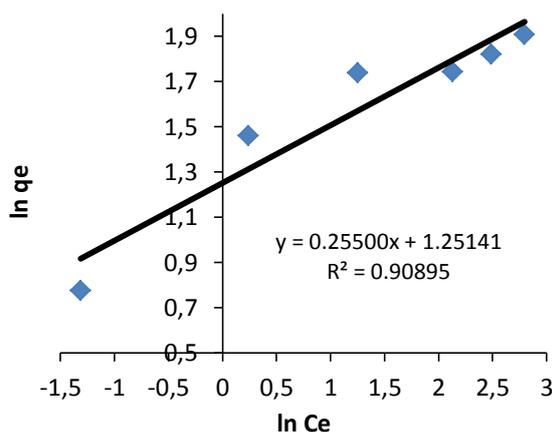


**Figure 8**. Langmuir isotherm



**Figure 9**. Freundlich isotherm

The two adsorption isotherms shows in figure 8 and 9 and table 3 shows the Langmuir and Freundlich parameters. The values of correlation coefficients ($R^2$) for Langmuir and Freundlich models are 0.99387 and 0.90895 respectively. From the $R^2$ value, indicated the Langmuir isotherm describes the adsorption of procion red dye on the alumina-activated carbon composite very well and the dye tend to form an adsorbed solute monolayer. Also the calculated value of qm adsorption obtained from Langmuir model are 7.12 mg/g which close to the experimental value 7.30 mg/g. In addition, the slope of 1/n ranging between 0 and 1 at the Freundlich isotherm is measure of adsorption intensity or surface heterogeneity [17]. The value for 1/n less than one is indicates a Langmuir isotherm. In this study, the 1/n values calculated are 0.255 which means the adsorption process followed a normal Langmuir isotherm [18]. The results are in table 3.

**Table 3**. Kinetic parameters of isotherm adsorption

| Isotherm Model | Parameters |
|---|---|
| Langmuir | $R^2 = 0.14045$ |
| | qm = 7.12 |
| Freundlich | $R^2 = 0.90895$ |
| | 1/n = 0.225 |
| | k = 50.47957 |

**Adsorption of procion red dye from waster industrial songket**

Adsorption procion red dye from wastewater songket industry performed at the optimum conditions. The concentration procion red dye in wastewater songket industry as high as 978.840 mg/L. The alumina-activated carbon composite as adsorbent composite are used according to the color concentration in the wastewater (calculation by experiment adsorption capacity), stirrer speed 150 rpm, contact time 2 hours and pH of the solution 9. After adsorption process, the procion red dye concentration is 115.405 mg/L. Effectiveness of adsorption of 88.21 %. In the wastewater songket industry, besides procion red dye there are also other substances such as starch residual for bleaching process, additives and others so that there is competition between these substances to be adsorbed on the adsorbent. The result obtained is larger than adsorption procion red dye using rice husk and $Fe_3O_4$ obtained effectiveness adsorption of 80.83 nad 24.40 %, respectively [19, 20].

**CONCLUSION**

Synthesis of alumina-activated carbon composite has been successfully carried out. Activated carbon prepared from stem gelam and alumina synthesis by precipitation from reaction of $Al(NO_3)_3$ and $NH_4OH$. The FTIR characterization results showed Al-O bond appears at wave number at 611.4 cm$^{-1}$. These data are supported by the results of SEM-EDS in the presence of Al in the composite. The result of batch experiments for adsorption procion red dye showed that optimum condition obtained at mass of composite 0.1 g, stirring speed 150 rpm, contact time 2 hours at pH 9. Adsorption equilibrium data was fitted to Langmuir isotherm with adsorption capacity 7.12 mg/g not much different from the experimental of 7.30 mg/g. The adsorbent can be removal of procion red dye from wastewater songket industry with effectiveness adsorption of 88.21 %.

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