Biosorption of Reactive azo dyes from Aqueous Solution using Chitosan

M. Lutfi Firdaus[1], Amelia Herlina[2], Wiwit Alwi[3], Agus Sundaryono[4], and Eko Swistoro[5]

***Abstract*—**A home-made chitosan from shrimp shells (*Penaeus merguiensis*) was used as biosorbent to remove reactive azo dyes, Remazol Violet dan Remazol Blue, from aqueous solution. The adsorption of the dye was investigated under different pH, adsorbate concentration, adsorbent dosage and contact time. Langmuir and Freundlich adsorption isotherm models were applied and thermodynamic parameters were calculated. Equilibrium data fitted well with the Langmuir model. The most ideal condition for adsorption of reactive azo dyes onto chitosan was found to be at pH 3. The optimized method removes more than 97% of Remazol Violet and more than 82% of Remazol Blue. The results indicate that home-made chitosan can be employed as a low cost alternative to commercial adsorbent in the removal of dyes from aqueous solution.

***Keywords*—**Adsorption, azo dye, chitosan, isotherms, kinetics.

I. Introduction

AZO dyes are the most frequently used synthetic dyes for colouring a variety of goods such as textiles, leather and clothes. Azo dyes can break down to form a class of chemical substances referred to as aromatic amines that are considered to be hazardous and carcinogens [1]-[2]. Moreover, azo dyes produce intense colour even in small concentration that result in the receiving water bodies to have unpleasant sight [3]. Therefore it is crucial to treat azo dyes wastewater before their disposal.

Numerous methods have been used to treat azo dyes effluents, including physical, chemical and biological methods such as photodegradation, coagulation, precipitation, oxidation, use of activated sludge, etc [4][5][6][7][8][9]. Biosorption is one of the most effective and economically practicable due to its fast chemical reduction and abundant amount of biosorbent in our surroundings.

One of candidate for biosorbent is chitosan. Chitosan is a natural polyaminosaccharide that synthesized from deacetylation of chitin (Fig. 1). In nature, chitin is the second most abundant polymer after cellulose. Chitin is found in crustacean shell such as shrimps, prawns and crabs. Chitosan can be used as adsorbent to remove azo dyes due to the presence of amino and hydroxyl groups, which can serve as the active sites [10][11]. This paper reports the biosorption of two types of azo dyes using a home-made chitosan extracted from shrimp shells.

II. Materials and Method

Chitosan was made from chitin extracted from shell of shrimp waste (*penaeus merguiensis*). The shell materials were dried at 50°C in oven for 24h and homogenized for further processing. Extraction of chitin involved deproteinization with 3.5% w/v sodium hydroxide solution under reflux at 65°C for 2 hours, demineralization with hydrochloric acid 1M (1:10 w/v) and finally deacetylation of chitin with sodium hydroxide 50% w/v to form chitosan (Figure 1). All reagents were pro-analysis grade and purchased from Merck and all solutions were prepared with distilled water. Azo dyes of Remazol Violet and Remazol Blue were used as adsorbates (Figure 2).

Batch adsorption experiments were performed on a thermostat shaker with a shaking of 150 rpm. An amount of 0.10 g of the chitosan and 10 mL of azo dyes solution (initial concentration 15 ppm) were used. The system was maintained under shaking at 30ºC for 12 h until adsorption equilibrium reached. The influence of pH on adsorbates removal was studied by adjusting solutions to different pH values (1–10) using a pH meter. The effect of contact time on azo dyes removal was also carried out from short time to 35 hours. After filtration, the aqueous sample was taken and analyzed with an UV/visible spectrophotometer (Thermo, Genesys 20). The wavelengths selected were 550 nm and 600 nm for Remazol Violet and Remazol Blue, respectively.

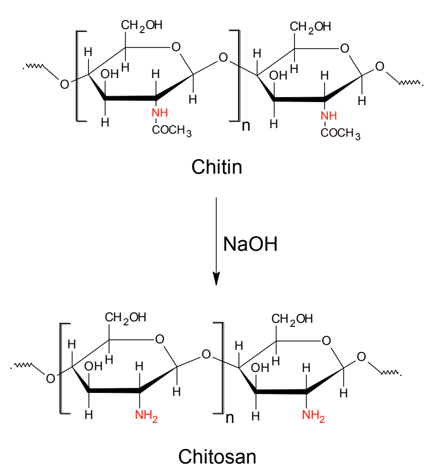

Fig. 1. Synthetic scheme of chitosan from chitin (deacetylation process).

M. Lutfi Firdaus[1], Agus Sundaryono[4] and Eko Swistoro[5] are with Graduate School of Science Education, University of Bengkulu, Indonesia

Amelia Herlina[2] and Wiwit Alwi[3] are with Department of Chemical Education, University of Bengkulu, Indonesia

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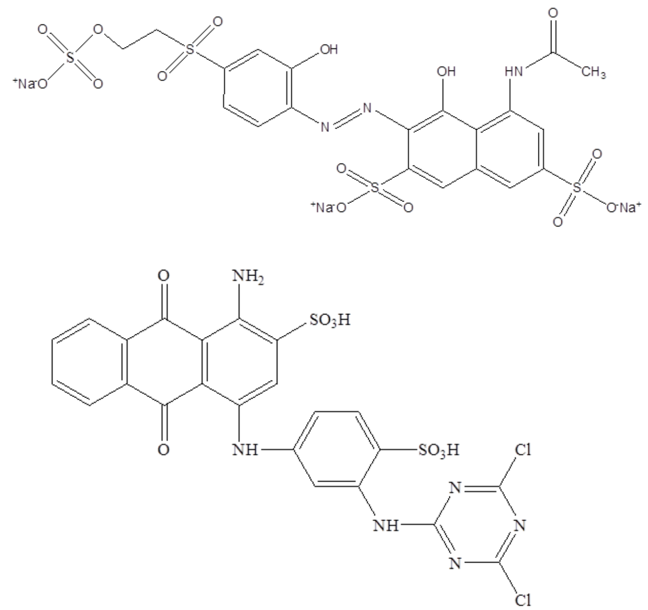


Fig. 2. Molecular structure of Remazol Violet (upper) and Remazol Blue (below).

III. Results and Discussion

Chitin was extracted from shrimp shell through deproteinization and demineralization processes. The yields for these two processes is shown in Table 1. Demineralization includes removal of calcium carbonate through reaction as follow

$$CaCO_3(s) + 2\ HCl(aq) \longrightarrow CaCl_2(l) + CO_2(g) + H_2(g)$$

Chitosan, the deacetylation product of chitin, is a polysaccharide composed by polymers of glucosamine and N-acetyl glucosamine. The functional amino group at the C-2 provides chitosan an outstanding capacity and high rate of adsorption. Percentage yield of chitosan from chitin is 55% or 18% if it is calculated from raw material of shrimp shell. Other characteristics of the home-made chitosan are shown in Table 1.

TABLE I
CHARACTERISTICS OF THE HOME-MADE CHITOSAN (N = 3)

Characteristic	Value (%)
Deproteinization yield	71,22 ± 2,08
Demineralization yield	45,57 ± 2,48
Water content	6,13 ± 0,21
Ash content	2,47 ± 0,31

Figure 3 shows adsorption pattern of Remazol Violet and Remazol Blue as a function of pH and contact time. The most ideal condition for adsorption of both reactive azo dyes onto chitosan was found to be at pH 3. The equilibrium of adsorption at optimmized pH 3 was achieved at short contact time. Therefore, there are no significant differences of dyes absorption on longer contact time as shown in Fig 3. By using the optimized adsorption condition, more than 97% of Remazol Violet and 82% of Remazol Blue adsorbed onto chitosan.

The linear form of the Langmuir isotherm model is given by

$$1/Q = 1/bqC + 1/q$$

where Q is the amount of azo dyes sorbed per unit mass of the chitosan (mg/g) at equilibrium, b is the adsorption coefficient, q is the amount of azo dyes sorbed per unit mass of the chitosan (mg/g) corresponding to complete coverage of available sites (i.e. monolayer saturation capacity), C is the residual metal ion concentration (ppm) at equilibrium. The values of b and q were evaluated from the slope and intercept of the linear plot, respectively [12].

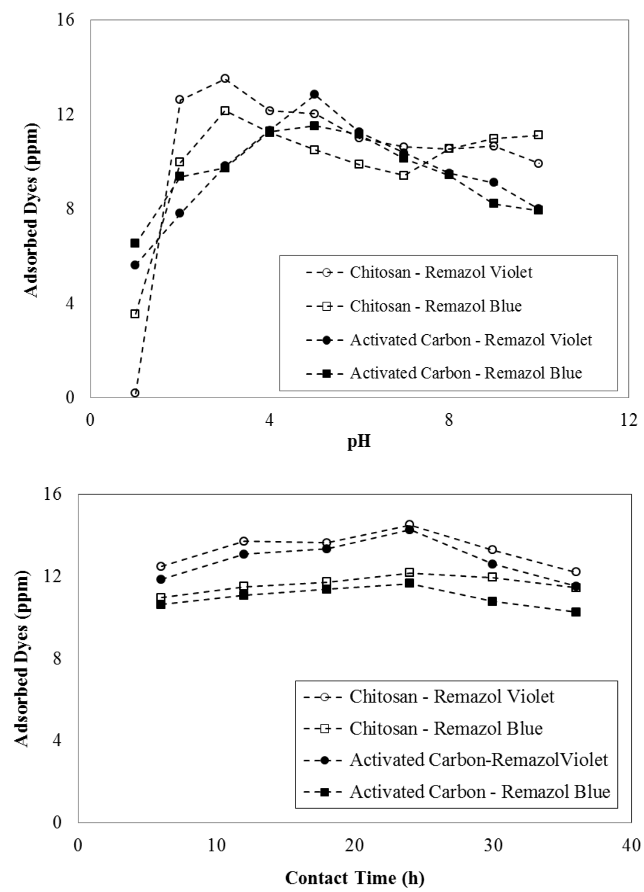
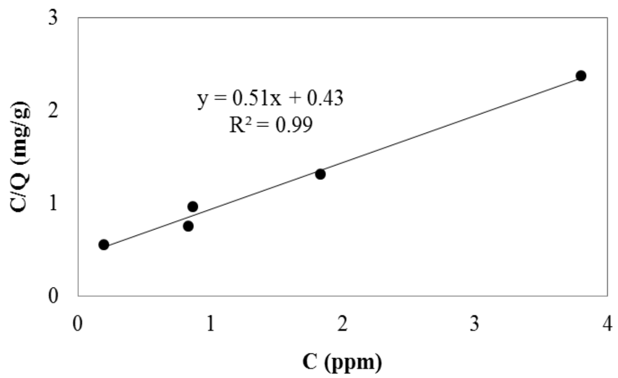


Fig. 3. Effect of pH (upper) and contact time (below) on the azo dyes adsorption. Activated carbon was used as references.

The Freundlich isotherm model is expressed as

$$\log Q = \log k + 1/n \log C$$

where k and n are the constants related to adsorption capacity and adsorption intensity, respectively. These constants were determined from the intercept and slope of the linear plot of ln Q versus ln C, respectively. Adsorption isotherms for Remazol Violet are shown in Fig 4. The experimental data were fitted to both Langmuir and Freundlich isotherms. However Langmuir isotherm gives higher R^2 than Freundlich isotherms that implies chemisorption is more favourable than physisorption. Adsorption isotherms for Remazol Blue are also similar to those of Remazol Violet.



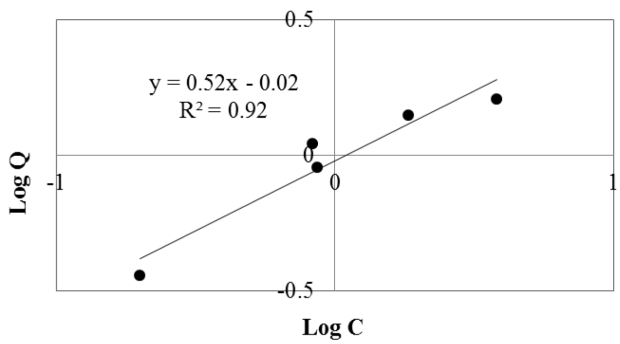


Fig. 4. Linearised Langmuir (upper) and Freundlich (below) isotherms for the adsorption of Remazol Violet onto chitosan.

IV. Conclussion

Chitosan is a good alternative as adsorbent to remove azo dyes in wastewater. It is environmentally benign and has a comparable adsorption ability as with activated carbon. Using the optimized adsorption condition, chitosan removed more than 97% and 82% of Remazol Violet and Remazol Blue, respectively. Furthermore, since it is produced from shrimp waste, chitosan is cheaper than other adsorbents.

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