# Biosorption of a Sulfur Dye from Aqueous Solutions by Dried Acid-Pretreated Activated Sludge

Thai Anh Nguyen, and Ruey-Shin Juang

***Abstract*—**Activated sludge (AS) is a low cost and available locally material in wastewater treatment plants. In this study, the adsorption of Sulfur Blue 15 (SB15) from aqueous solution by dried activated sludge (DAS) was investigated. The acid washing biomass was applied for the reuse. The isotherm data fitted both the Langmuir and Freundlich models with the correlation coefficient ($r^2$) of 0.9531 and 0.9953, respectively. The monolayer adsorption capacity was calculated as 11.19 mg/g. Besides, the kinetic data of sulfur dye to dried acid-pretreated activated sludge (DAAS) were well described by the pseudo second-order adsorption kinetics.

***Keywords*—**Activated sludge, Acid washing, Adsorption, Sulfur dye.

## I. Introduction

SULFUR dyes are used popularly with mass production due to their cheap price and good properties in washing and light fastness. These dyeing effluents cause harmful to environment seriously [1].

Sludge based carbon or AS is a natural carbon source. This material can be converted successfully into activated carbon with chemically pretreated methods [2]. Chemical activation agents were used to prepare activated carbon (AC) from AS such as sulfuric acid, sodium hydroxide [3], hydrogen peroxide [4]. Moreover, the biosorption of dyes by dried or live activated sludge was surveyed in much research [5-8]. They found that the adsorption properties of activated sludge is similar to activated carbon (AC) [8]. Furthermore, dried activated sludge can replace AC as well as costly adsorbent materials [6].

The present study focuses on the use of dried acid - pretreated biomass activated sludge to adsorb Sulfur Blue 15 (SB15). The adsorption characteristics of sulfur dye in relation to DAS were surveyed with adsorption kinetic and isotherm models. Besides, SEM images and BET results also were chosen for the investigation of adsorption ability of DAS.

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## II. Materials and methods

### A. Microorganisms

Activated sludge was taken from a municipal sewage treatment plant in Chiao Tung University, Hsinchu, Taiwan. AS was washed with 1% (v/v) hydrochloric acid (1200 ml acid per 25 g of DAS), and was washed 04 times with distilled water after acid treatment. Acid-pretreated AS was dried at 50°C to constant weight and sieved through a < 2 mm diameter.

### B. Sulfur dye and dyeing

Sulfur Blue 15, SB15 (Sky blue CV B-15, C.I. 53540, CAS 1327-69-1, dye content 95%) was purchased from Ningbo New Dragon International Co., Ltd. Sodium sulfide nonahydrate ($Na_2S.9H_2O$) used for reducing process was purchased from Alfa Aesar, a Johnson Matthey Co. With the weight ratio of SB15 to sodium sulfide was 0.4, SB15 was dissolved completely in sodium sulfide solution.

### C. Analytical methods

The absorbance spectrum of SB15 was assessed using an Ultrospec 2100 Pro UV/visible spectrophotometer over a broad concentration range. The concentration of SB15 was obtained through absorbance measurements at 298 nm. Color was monitored spectrophotometrically using a HACH DR/2000 direct reading spectrophotometer.

### D. Experiment method

Sulfur dye batch biosorption experiments were conducted by shaking 5 g of DAS or DAAS in 250 ml of dye solution in an incubator with a rotary shaker at 200 rpm at 30°C. After each biosorption process, the sample was separated by centrifugation (10,000 x g for 10 min) and supernatant was analyzed for remaining dye concentration using UV spectrophotometer by monitoring the absorbance at 298 nm. The amount of dye adsorbed on dried activated sludge at equilibrium, $q_e$ (mg/g), was calculated by the following equation:

$$q_e = \frac{(C_0 - C_e) \times V}{m} \quad (1)$$

where $C_0$ and $C_e$ are the initial and equilibrium liquid phase concentration of SB15 (mg/l), respectively, $V$ is the volume of the solution (l), and $m$ is the weight of adsorbent used (g).

## III. Results And Discussion

*Biosorption kinetics*

The pseudo-second-order kinetics model has been tested to describe the biosorption kinetics [9]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e}\right)t \tag{2}$$

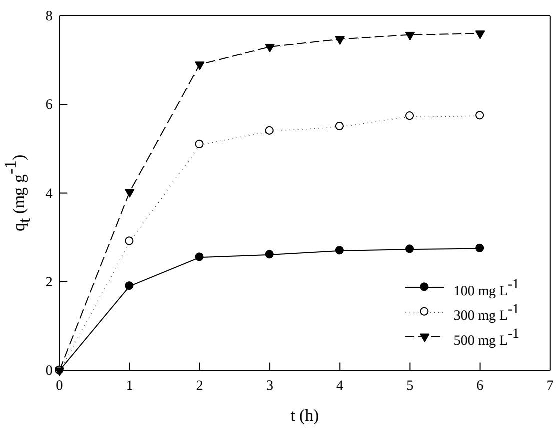
where $q_t$ is the amount of biosorption at time $t$ (mg/g) and $k_2$ is the pseudo-second-order rate constant (g/mg/min).

Fig. 1 shows the variations of the amounts of adsorption with time and the validity of pseudo-second-order model. The pseudo-second-order model reveals satisfactory fit ($r^2 > 0.97$).

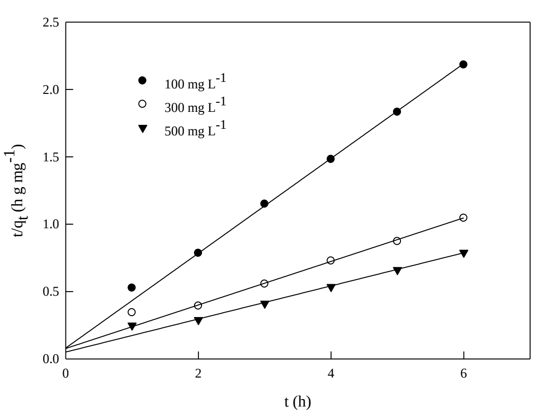
TABLE I
PARAMETERS OF THE PSEUDO-SECOND-ORDER KINETIC MODEL FOR THE ADSORPTION OF SB15 ON DAAS AT 30°C[a]

| $C_0$ | $k_2$ | Calculated $q_e$ | $r^2$ |
|---|---|---|---|
| 100 | 1.534 | 3 | 0.9955 |
| 300 | 0.338 | 6 | 0.9770 |
| 500 | 0.296 | 8 | 0.9805 |

[a]Unit: $C_0$ (mg/L); $k_2$ (g/mg/min); $q_e$ (mg/g)




(a)




(b)

Fig. 1 (a) Time changes of SB15 concentrations and (b) their pseudo-second-order kinetic plot during the adsorption of SB15 on DAAS at 30°C

*Biosorption isotherm*

The linearized form of the Langmuir and Freundlich models are given in Eqs. (3) and (5). These equations were selected to describe the biosorption mechanisms. The Langmuir theory indicates a homogeneous type of adsorption as well as once a dye molecule occupies a binding site, no further adsorption can occur at that site [10], while the Freundlich theory refers to a heterogeneous surface with a non-uniform distribution of enthalpy of adsorption [11] and can be applied to multilayer adsorption [12].

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} \times K_L} + \frac{C_e}{q_{\max}} \tag{3}$$

$$R_L = \frac{1}{1 + K_L C_0} \tag{4}$$

$$\ln q_e = \ln K_F + \left(\frac{1}{n}\right)\ln C_e \tag{5}$$

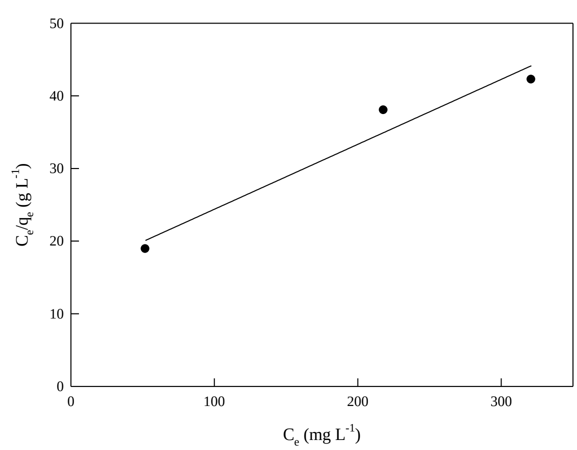
where $q_{\max}$ is the maximum capacity corresponding to complete monolayer coverage (mg/g), $K_L$ is the Langmuir constant (l/mg), $K_F$ is the Freundlich constant (mg$^{1-(1/n)}$ L$^{1/n}$ g$^{-1}$) related to adsorption capacity, the constant $n$ relates to the adsorption intensity, $R_L$ value (4) defined by Webber and Chakkravorti [12] is a dimensionless constant, commonly known as separation factor, $R_L$ value indicates the adsorption nature to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$).

Table II and Fig. 2 show high correlation coefficients (> 0.95) of the Langmuir and Freundlich equations. The value of $n > 1$ indicates that SB15 is favorably adsorbed on DAAS [11]. Moreover, $0 < R_L < 1$ indicates favorable adsorption nature.

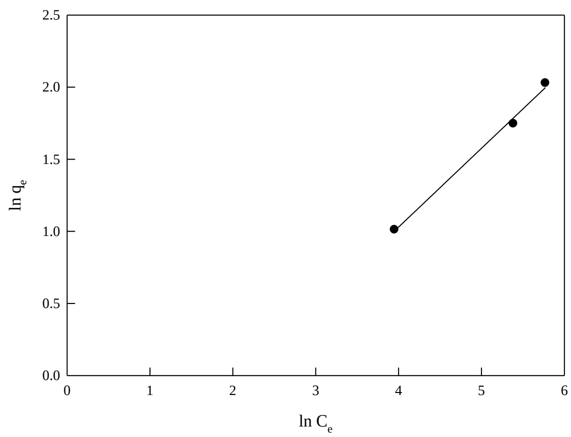
TABLE II
ISOTHERM CONSTANTS FOR THE BIOSORPTION OF SB15 ON DAAS AT 30°C[b]

| Langmuir equation | | | Freundlich equation | | |
|---|---|---|---|---|---|
| $K_L$ | $q_{max}$ | $r^2$ | $K_F$ | $n$ | $r^2$ |
| 0.0058 | 11.19 | 0.9531 | 0.3152 | 1.83 | 0.9953 |

[b]Unit: $K_L$ (l/mg); $q_{max}$ (mg/g); $K_F$ (mg$^{1-(1/n)}$ L$^{1/n}$ g$^{-1}$)




(a)

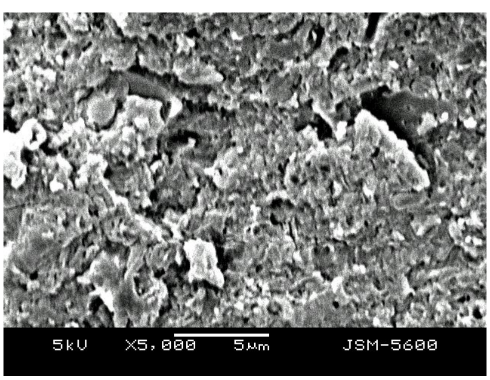



(b)

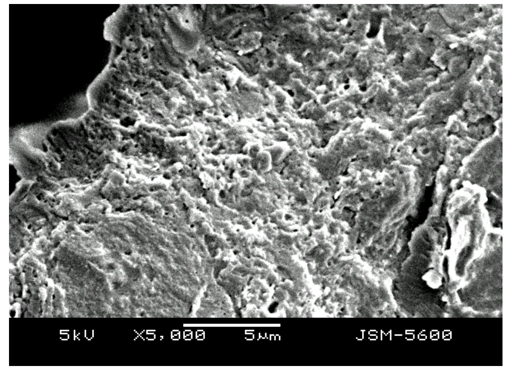
Fig. 2 The linear plots of (a) Langmuir, (b) Freundlich equations

*DAAS adsorption properties*

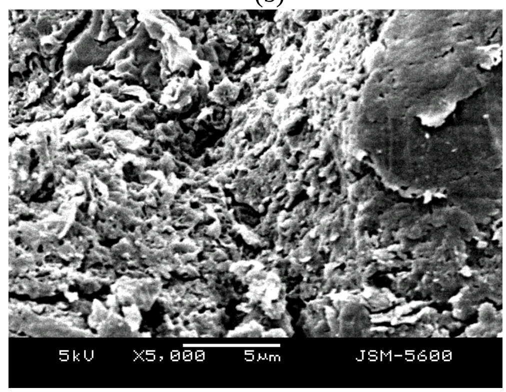
DAS and DAAS samples were examined to identify the change in surface morphology after acid activation via using scanning electron microscope (SEM). After acid washing without distilled water, the surface and pore of DAS was coated with a color layer from impurities causing smoother surface and smaller pore size (Fig. 3b). However, by adding distilled water to wash, the highly pore structure, rough and heterogeneous surface are created (Fig. 3c). The BET surface area of the DAS and the DAAS clean as measured by nitrogen adsorption at 77 K were 0.8735 and 1.1409 $m^2/g$, respectively (Table III). The DAAS clean have higher BET surface area. These results indicate that there is a good possibility for dye to be trapped and adsorbed after water washing of DAAS. Fig.4 also showed that decolorization of SB15 solution after adsorption with DAAS clean (with water washing) better than the others. On the other hand, the surface area of DAS and DAAS clean in this study is so smaller than the surface area of the produced AC from AS [3], the hydrogen peroxide-pretreated DAS [4] and live AS [13]. They have a specific surface area of 580, 183, 40 – 140 $m^2/g$, respectively.




(a)




(b)




(c)

Fig. 3 SEM images: (a) DAS without pretreatment, (b) DAAS without water washing; (c) DAAS with water washing

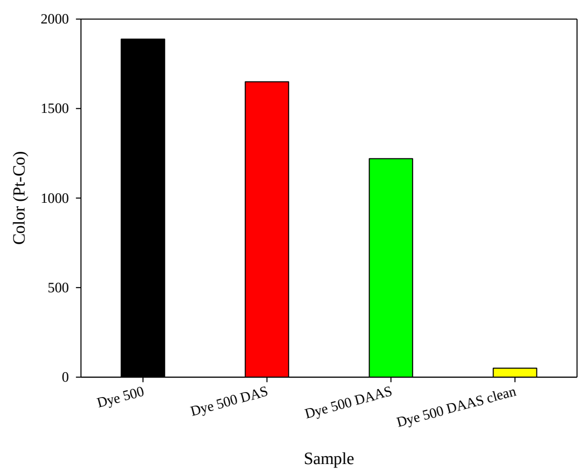



Fig. 4 Decolorization of 500-mg/l SB15 solution after the adsorption by DAS, DAAS and DAAS clean (water washing)

TABLE III
BET RESULTS OF DAS AND DAAS CLEAN[c]

| Sample | Surface area | Pore volume | Pore size |
|---|---|---|---|
| DAS | 0.8735 | 0.000596 | 27.3114 |
| DAAS (clean) | 1.1409 | 0.000203 | 7.1236 |

[c]Unit: Surface area ($m^2/g$); Pore volume ($cm^3/g$); Pore size (nm)

## IV. CONCLUSIONS

Activated sludge, which is discarded as a waste material from wastewater treatment plant, is a potential adsorbent for the removal of sulfur dye from aqueous solutions. Sulfur Blue 15 is not well adsorbed by dried activated sludge without acid pretreated step. However, this dye is well adsorbed by dried activated sludge with acid washing. The heterogeneous, rough and porous structure was observed by SEM technique. Equilibrium data fitted well with the Langmuir and Freundlich isotherm models. The adsorption kinetics of SB15 to DAAS followed pseudo-second-order kinetic. The pretreated method of DAS with the combination between clean water washing follow acid washing is cheaper than another pretreated DAS methods.

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