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Biosorption of Eriochrome Black T Using *Exserohilum rostratum* NMS1.5 Mycelia Biomass

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Abstract: The presence of eriochrome black T (EBT) dye in waste water causes a significant hazard to human health and ecology. In the current study, biosorption was employed to eliminate EBT from water. Thus, we utilized endophytic fungi strain *Exserohilum rostratum* NMS1.5 mycelia biomass as biosorbent agent. The process was carried out at room temperature by magnetic stirring. The results indicated that an increase in pH would decrease adsorption capacity and removal percentage. In addition, an increased EBT concentration would decrease the removal percentage and increase biosorption capacity. The equilibrium time indicated that after 300 min of mixing, the percentage removal and biosorption capacity were 80.5% and 100.61 mg/g, respectively. The biosorption isotherms and kinetics were compatible with the Freundlich model and the pseudo-second-order. This research indicates that *E. rostratum* NMS1.5 may be utilized as an environmentally friendly and affordable alternative biosorbent material for EBT removal.

Keywords: *Exserohilum rostratum* NMS1.5; eriochrome black T; dye; biosorption

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1. Introduction

Textile industry effluent is a considerable problem when dyes that are present in aquatic environments are toxic, carcinogenic and mutagenic [1,2]. Even at a low concentration (<1 mg/L), the colors are visible in water [3]. Eriochrome black T (EBT) is an azo dye containing sulphonate groups and aromatic rings discovered in wastewater [4]. Conventional methods such as coagulation, ion exchange, membrane filtration, adsorption and advanced oxidation processes have been investigated for dye removal [5–7]. Among these, adsorption is considered one of the famous and attractive technologies that use an adsorbent [8,9].

Numerous sorbent materials such as zeolite [8] and activated carbon [10] have been studied. However, these sorbents are still a little expensive. As a result of the above reasons, researchers have reported using biological materials such as algae, fungi and bacteria for dye removal from water, which are practical and economical [11]. On the other hand, these materials are not toxic since they do not require a supply of nutrients, which are referred to as biosorbents, and the process is called biosorption [12,13]. In this study, we used the endophytic fungi strain *Exserohilum rostratum* NMS1.5 mycelia biomass to remove eriochrome black T (EBT) from water.

2. Materials and Methods

2.1. Materials

Eriochrome black T (EBT), sodium hydroxide (NaOH), hydrochloric acid (HCl), sulfuric acid (H2SO4), and sodium chloride (NaCl) were purchased from Kanto Chemical Co.,

Inc. (Tokyo, Japan). A pH meter and magnetic stirrer were used LAQUA twin Horiba and REXIM RSH-4AN, respectively. The biosorbent of *Exserohilum rostratum* NMS1.5 mycelia biomass was derived from prior studies [14]. The fungal endophytes were cultivated in a PDB medium and incubated at 28 °C for seven days. Then, the medium was filtered, and mycelia were oven-dried at 60 °C for three days for further experiments.

2.2. Biosorption Experiments

All experiments were conducted on a magnetic stirrer at room temperature. After treatment process, the sorbent was filtered and supernatant put in cuvette (Quartz) to check absorbance (556 nm). We analyzed the effect of pH (2–10), initial EBT concentration (10–25 mg/L), and contact time (15–300 min). The biosorption removal rate and capacity were calculated using Equations (1) and (2), respectively.

$$\%R = \frac{C_o - C_e}{C_o} 100 \quad (1)$$

$$q\,(t) = \frac{C_o - C_e}{W} V \quad (2)$$

where %R: removal rate (%), q: adsorption capacity (mg/g) (t: time), C_o: initial concentration (mg/L), C_e: concentration at time (mg/L), W: biosorbent mass (g), V: volume (L).

2.3. Characterization

EBT concentration was measured using a UV–Vis spectrophotometer (Jasco V-530, Tokyo, Japan). The functional group of the biosorbent was determined using ATR-FTIR (Thermo Scientific Nicolet iS10, Thermo Fisher Scientific, Waltham, MA, USA).

3. Results and Discussion

3.1. FTIR Data before and after Adsorption

Figure 1 illustrates the FTIR spectra before and after biosorption. After the biosorption process, the peak shifted from 3273 to 3333 cm^{-1}, suggesting the formation of -OH. A peak between 2840 and 3000 cm^{-1} represents C-H stretching. After biosorption, an increased band peak from 1635 to 1647 cm^{-1} was assigned to N-H, which corresponded to the O-H groups. The bands at 1549 and 1532 cm^{-1} suggested that the N-O and C-H groups corresponded. A new band that formed at 1337 cm^{-1} after biosorption was probably dye to C-H bending [15].

3.2. The pH Effects

The pH is the most important in biosorption experiments, since it influences both the biosorption capacity and the color of the medium. Figure 2 illustrates the pH dependency of EBT biosorption effectiveness on the biosorbent. The findings suggested that pH 2 might be suitable for EBT biosorption, similar to Rezaee et al. and Chettri et al. [16,17]. This is owing due to the strong electrostatic interaction between the positively charged surface of *Exserohilum rostratum* NMS1.5 and EBT, which is created by absorbing H^+ ions.

3.3. Effects of Initial EBT Concentration

The initial EBT concentration ranged from 10 to 25 mg/L and a biosorbent dose of 0.01 g/50 mL of dye solution was used to evaluate EBT biosorption (Figure 3). The biosorption capacity increased as the concentration increased from 30.86 to 66.80 mg/g, but the percentage removal decreased from 61.7 to 12.2%. This is because increased EBT concentration would be an increased number of molecules. Then, an increase in the biosorption capacity. However, it would decrease the mass transfer resistance of the adsorbate. Consequently, the removal percentage decreases [8,18,19].

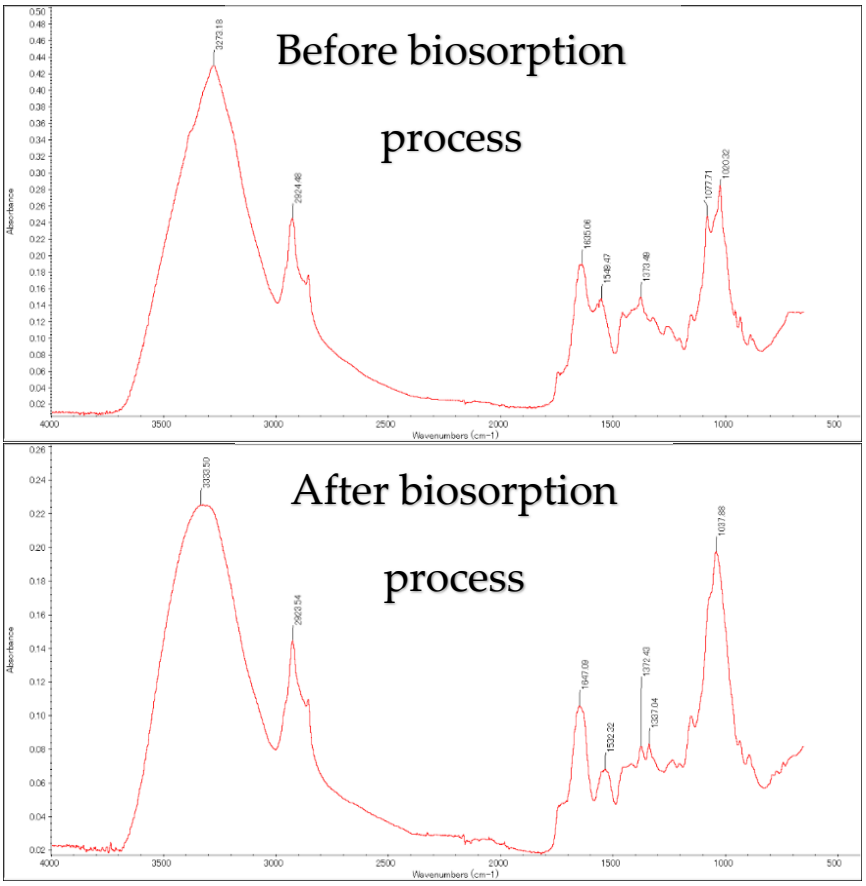


Figure 1. FTIR data before and after EBT biosorption.

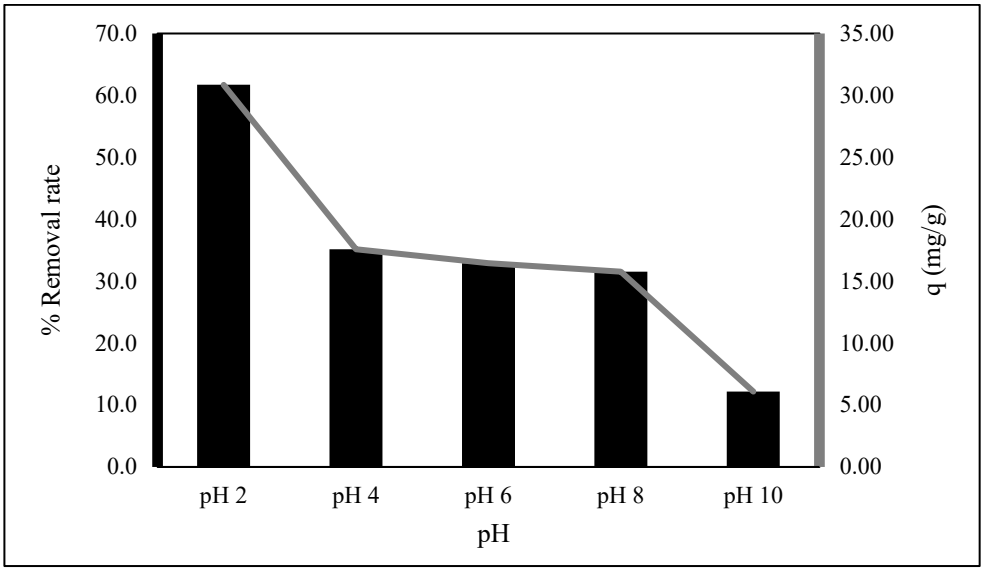


Figure 2. pH effects (0.01 g, 50 mL (EBT: 10 mg/L), time: 15 min).

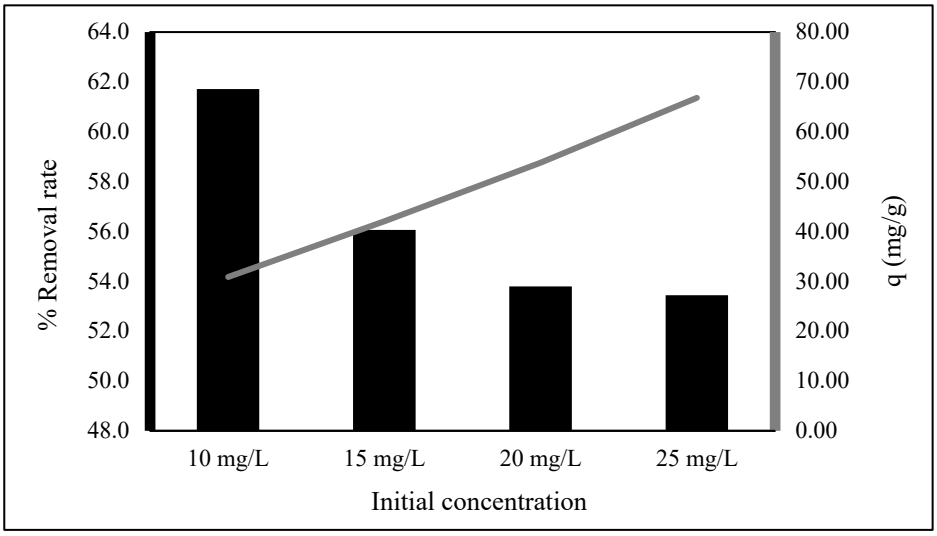


Figure 3. Initial EBT concentration effects on adsorption capacity and removal percentage (time: 15 min).

3.4. Isotherm Studies

The adsorption isotherm models depict the biosorbent with the biosorbate and describe the interaction between the biosorption capacity and the liquid phase concentration of biosorbate under equilibrium conditions at a constant temperature [20]. In this investigation, the Langmuir and Freundlich models were used [21–24]. Langmuir occurs on a homogeneous biosorbent surface, while Freundlich on the heterogeneous biosorbent surface [18,24]. The Langmuir, Langmuir separation factor and Freundlich are presented in Equations (3)–(5), respectively.

$$C_e/q = \left(\frac{C_e}{q_{max}}\right) + 1/(K_l q_{max}) \quad (3)$$

$$R_L = \left(\frac{1}{1 + bC_o}\right) \quad (4)$$

$$\ln_q = \ln K_f + \frac{1}{n} \times \ln C_e \quad (5)$$

where q is the adsorbent amount at time (mg/g), K_l is the interaction constant between adsorbate and adsorbent in Langmuir model (L/mg), q_{max} is the maximum biosorption capacity (mg/g), C_e is the adsorbate equilibrium concentration (mg/L). K_f is the biosorption capacity in the Freundlich model (mg/g), 1/n is the intensity of biosorption. R_L is the adsorbate and biosorbent interaction which it can be classified as favorable ($R_L < 1$), linear ($R_L = 1$), unfavorable ($R_L > 1$), and irreversible ($R_L = 0$) [25].

The experimental isotherm studies and linear correlation are shown in Figure 4 and Table 1, respectively. The biosorption process was found to be favorable ($R_L = 0.001$) and fitted the Freundlich isotherm model ($R^2 = 0.988$).

3.5. Adsorption Kinetics

The biosorption with the interaction time was evaluated in the range of 15–300 min with 25 mg/L of EBT concentration, and 0.01 g/50 mL of EBT solution was used. Figure 5 shows that in the first 15 min, a rapid increase in the biosorption capacity and percentage removal occurred. Then, they slowed at 120 min and gradually increased to 300 min. In the early phase of biosorption, the EBT dye particle to be absorbed was almost fully present in the solution with a high possibility of contacting the biosorbents' surface, and the active sites were unoccupied [26].

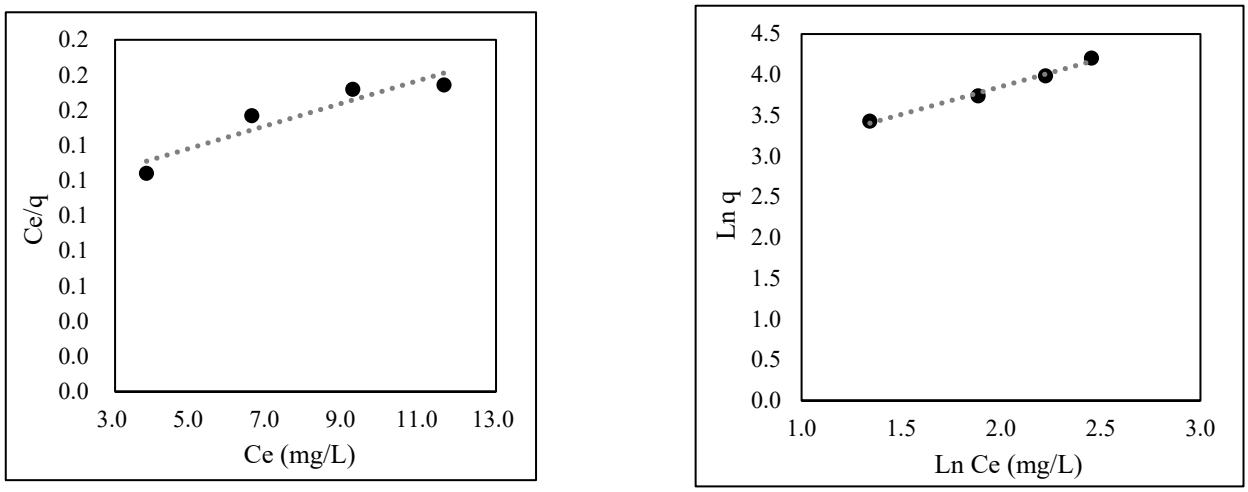


Figure 4. Adsorption isotherm model for EBT: (**a**) Langmuir; (**b**) Freundlich.

Table 1. Langmuir and Freundlich isotherm models of EBT adsorption.

q_{exp} (mg/g)	Langmuir Parameters				Freundlich Parameters		
	q_{max}	K_L	R^2	R_L	K_f	1/n	R^2
100.61	155.71	9.3906	0.877	0.001	307.38	0.68	0.988

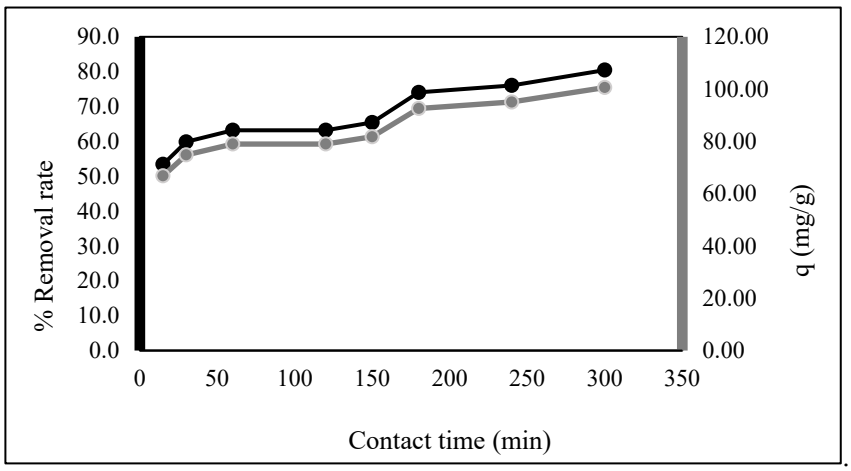


Figure 5. Contact time effects on EBT biosorption capacity and removal percentage (0.01 g, 50 mL (EBT: 25 mg/L), time: 15–300 min).

A significant number of linear kinetic models are utilized in the literature to examine the controlling mechanism of the biosorption process. Most researchers used pseudo-first-order and pseudo-second-order models [8,27]. The equations for pseudo-first Equation (6) and second Equation (7) models are shown below.

$$\log(q_e - q_t) = \log q_e - K_1 t \quad (6)$$

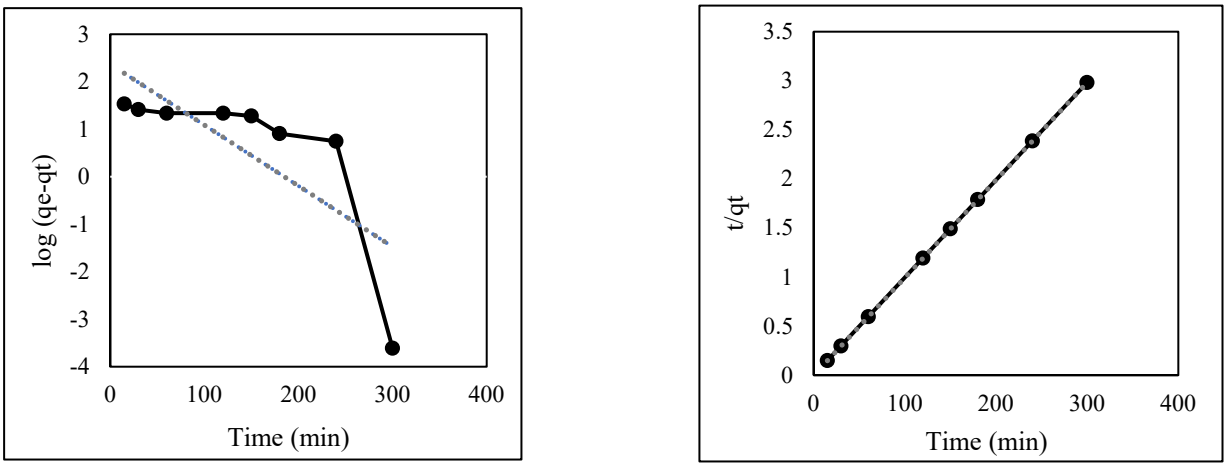
$$t/q_t = 1/(K_2 q^2 q_e) + t/q_e \quad (7)$$

The linear correlation and experimental data of EBT biosorption onto *Exserohilum rostratum* NMS1.5 are shown in Table 2 and Figure 6, respectively. We can see that the R^2

value of pseudo-second-order models was better than pseudo-first-order models. This indicated the pseudo-second-order kinetic model was fit for the biosorption process.

Table 2. Comparison between pseudo-first-order and pseudo-second order kinetics models for the biosorption of EBT.

Pseudo-First-Order			Pseudo-Second-Order		
q_e (mg/g)	K_1 (mg min/g)	R^2	q_e (mg/g)	K_2 (mg min/g)	R^2
10.68	-4.267×10^{-5}	0.563	101.01	1.23×10^{11}	1



(**a**) (**b**)

Figure 6. Adsorption kinetics model of EBT: (**a**) pseudo-first order; (**b**) pseudo-second order.

4. Conclusions

In the present study, we made the first report for the use of affordable and non-toxic mycelia biomass of *Exserohilum rostratum* NMS1.5 to remove EBT dye from water. We studied the effect of pH, initial EBT concentration and contact time. The results obtained showed that the optimum conditions were at pH 2 with a removal percentage and sorption capacity of 80.5% and 100.61 mg/g, respectively, for 300 min of equilibrium time. Increases in the initial EBT concentration would decrease the removal percentage and increase sorption capacity. The isotherm and kinetic model were fitted to the Freundlich and pseudo-second-order, respectively. The results indicated that *Exserohilum rostratum* NMS1.5 mycelia biomass could effectively remove EBT dye from water.

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