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Research Article

Sorption of Toluidine Blue Dye Using *Sargassum tenerrimum* Brown Algae Powder in Batch Adsorption Studies

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Abstract
Discharge of synthetic dyes into water bodies is a persistent environmental concern because many dyes are toxic, stable, and difficult to remove by conventional treatment processes. This study evaluates the batch adsorption of Toluidine Blue (TB) from aqueous solution using dried *Sargassum tenerrimum* powder as a low-cost biosorbent. The effects of contact time (5–180 min), particle size (53–150 μm), and temperature (283–323 K) were investigated at an initial TB concentration of 20 mg/L. Adsorption increased rapidly during the initial period and approached equilibrium within 30 min for the conditions tested. Kinetic data were fitted using pseudo-first-order and pseudo-second-order models; the pseudo-first-order model gave the better fit (R^2 = 0.9903). Thermodynamic parameters were obtained from the Van't Hoff plot ($K_c = q_e/C_e$), giving $\Delta H°$ = +14.84 kJ mol^{-1} and $\Delta S°$ = +48.57 J mol^{-1} K^{-1}, indicating an endothermic process with increased randomness at the solid–solution interface. The calculated $\Delta G°$ values became negative at higher temperatures, confirming that adsorption becomes increasingly spontaneous as temperature increases. Overall, *Sargassum tenerrimum* powder is an efficient and sustainable biosorbent for TB removal from water.
Keywords: Toluidine Blue, *Sargassum tenerrimum*, Biosorption, Kinetics, Thermodynamics, Adsorption.

1. Introduction

The rapid expansion of textile, dyeing, and pharmaceutical industries has increased the discharge of dye-containing effluents into aquatic ecosystems. Synthetic dyes typically possess complex aromatic structures and high chemical stability, which make them resistant to biodegradation and difficult to remove using conventional treatment methods [11,14]. Even at low concentrations, dyes can reduce light penetration and may exert toxic effects on aquatic organisms.

Among available treatment technologies, adsorption is widely recognized as an effective and economically viable option due to its simplicity, high efficiency, and operational flexibility [1, 2, 10]. In recent years, biosorption using low-cost biomass materials has gained attention as a sustainable alternative to commercial activated carbon [4, 14]. Biopolymer-based adsorbents such as chitosan beads and composites have also been widely explored for dye capture [5, 12]. Agricultural wastes, algae, and bio-derived carbons have demonstrated promising adsorption capacities for the removal of diverse dyes from aqueous media [3, 6, 10].

Marine biomass is particularly attractive because its surface contains functional groups such as hydroxyl, carboxyl, amino, and sulfate groups, which can participate in electrostatic interactions and surface complexation with dye molecules [14]. Recent studies also highlight the development of composite biosorbents to improve adsorption performance and process stability [9, 13].

Toluidine Blue is a cationic dye widely used in textile and biological applications. Due to its positive charge, its adsorption behavior depends strongly on solution pH and the surface properties of the adsorbent [16]. Data on Toluidine Blue removal using locally abundant marine biomasses such as *Sargassum tenerrimum*, together with kinetic and thermodynamic parameters under standardized batch conditions, are still needed for process design and scale-up. Therefore, this work investigates the biosorption of Toluidine Blue onto *Sargassum tenerrimum* powder with emphasis on the effects of operating parameters, kinetic modeling, and thermodynamic assessment.

2. Materials and Methods

Toluidine Blue dye of analytical grade was used throughout the study. All other reagents were of analytical grade and used without further purification. Distilled water was used to prepare dye solutions and for all experimental procedures.

3. Experimental Procedure

The present investigation focuses on the removal of Toluidine Blue dye from aqueous media using *Sargassum tenerrimum* as a natural biosorbent. Batch biosorption experiments were carried out to examine the equilibrium behavior and to evaluate the influence of different operational parameters on dye removal efficiency.

The experimental work was conducted in the following stages:

3.1. Preparation of the Biosorbent

The marine algae *Sargassum tenerrimum* was collected from Jodugullapalem Beach (Visakhapatnam, India), washed thoroughly with tap and distilled water, and sun-dried for about two weeks until constant weight. The dried biomass was cut, ground, and sieved to obtain the required particle-size fractions. The powder was stored in airtight containers and used without chemical treatment.

3.2. Preparation of Dye Stock Solution

A Toluidine Blue stock solution (1000 mg/L) was prepared by dissolving 1.0 g of dye in 1000 mL of distilled water. Working solutions (20–200 mg/L) were prepared by appropriate dilution. The pH was adjusted using 0.1 N HCl or 0.1 N NaOH.

3.3. Batch Biosorption Studies

Batch biosorption experiments were performed by adding *Sargassum tenerrimum* powder (typically 1.5 g; 30 g/L) to 50 mL of Toluidine Blue solution in conical flasks. The flasks were agitated in an orbital shaker at 100 rpm. Unless otherwise stated, experiments were carried out at 303 K and the contact time was fixed at 30 min based on preliminary screening. After the desired contact time, the biosorbent was separated by filtration and the residual dye concentration (Ce, mg/L) was measured using a UV–Visible spectrophotometer at the maximum absorbance wavelength of TB (λmax = 630 nm).

Adsorption capacity at equilibrium (qe, mg/g) and percentage removal were calculated as:

$$qe = (C0 - Ce)\, V / m$$

$$\text{Removal (\%)} = [(C0 - Ce) / C0] \times 100$$

Where:
C0 is the initial dye concentration (mg/L), V is the solution volume (L), and m is the dry mass of biosorbent (g). All measurements were performed in duplicate or triplicate, and average values are reported (± standard deviation where available).

4. Results and Discussion

4.1. Effect of Agitation Time

The adsorption of Toluidine Blue onto *Sargassum tenerrimum* powder was studied as a function of contact time at room temperature. Experiments were performed with 50 mL of 20 mg/L dye solution using 53 µm particles and the selected biosorbent dose. Dye uptake increased rapidly at the beginning and then slowed as equilibrium was approached. The maximum removal of TB under these conditions was 75% at 30 min (Figure 1), corresponding to an adsorption capacity increase from 0.20 to 1.50 mg/g.

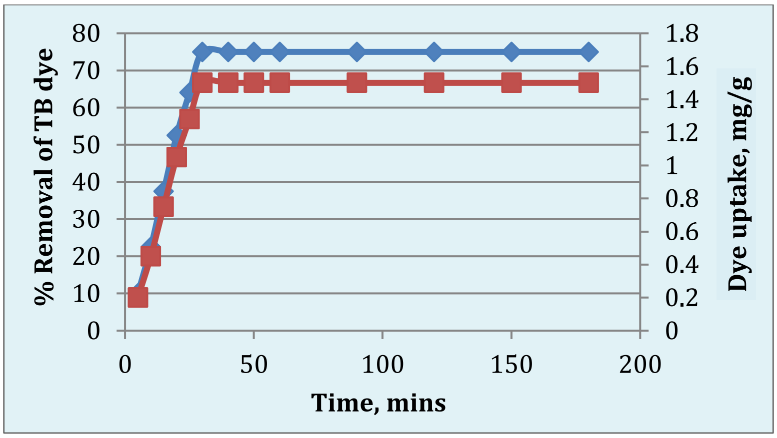

Figure 1. Effect of solution time on TB removal.

4.2. Effect of Particle Size

The effect of particle size on TB removal by *Sargassum tenerrimum* powder was studied using 50 mL of dye solution at an agitation time of 30 min and room temperature. As shown in Figure 2, the percentage removal decreased from 75% to 56% when particle size increased from 53 to 152 µm, and the adsorption capacity decreased from 1.50 to 1.12 mg/g. This behavior is attributed to a reduction in available surface area and accessible adsorption sites at larger particle sizes.

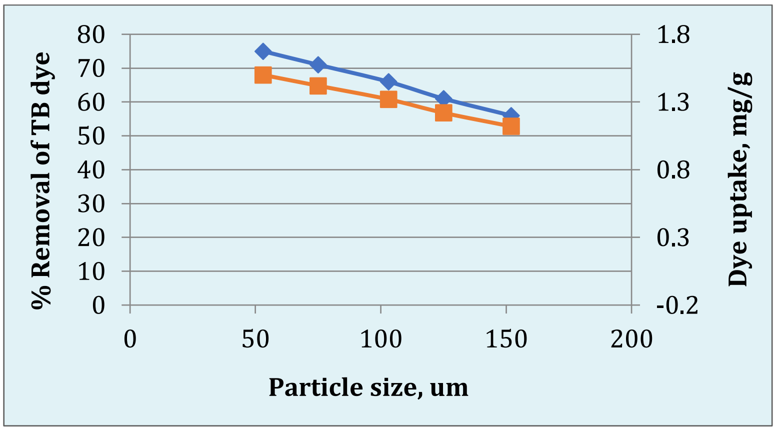

Figure 2. Effect of solution particle size on TB removal.

4.3. Effect of Temperature

The effect of temperature on TB adsorption was evaluated at 283–323 K using an initial dye concentration of 20 mg/L, particle size of 53 µm, biosorbent dose of 30 g/L (1.5 g), and contact time of 30 min (pH 5). The percentage removal increased from 86% to 93% as temperature increased, indicating that adsorption is favored at elevated temperature. The improved performance at higher temperature may be related to enhanced diffusion of dye molecules and increased accessibility of active sites on the biosorbent surface.

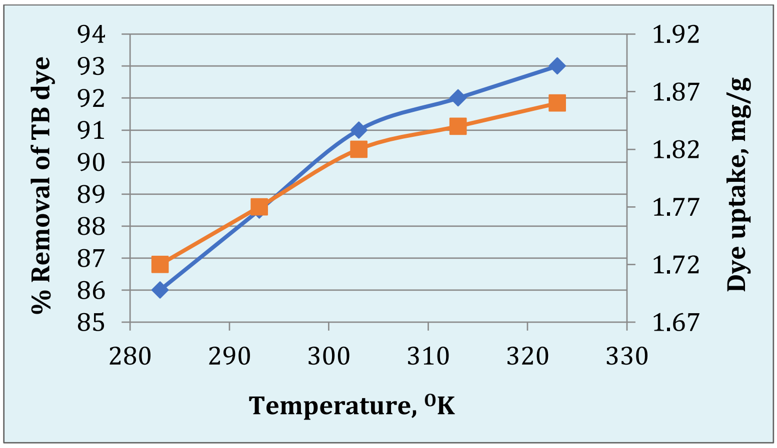

Figure 3. Effect of solution temperature on TB removal.

5. Kinetic Modelling

Adsorption kinetics were analyzed using the pseudo-first-order (PFO) and pseudo-second-order (PSO) models [7, 8]. The linearized PFO and PSO equations are:

$$\log(qe - qt) = \log(qe) - (k1/2.303)\, t \qquad (3)$$

$$t/qt = 1/(k2\, qe^2) + t/qe \qquad (4)$$

Where: qe (mg/g) and qt (mg/g) are the adsorption capacities at equilibrium and at time t (min), respectively; k1 (min^{-1}) is the PFO rate constant; and k2 ($g\ mg^{-1}\ min^{-1}$) is the PSO rate constant. For the present system, the PFO plot gave:

$$\log(qe - qt) = -0.0382\, t - 0.3745 \ (R^2 = 0.9509)$$

and the PSO plot yielded:

$$t/qt = 0.2822\, t + 25.394 \ (R^2 = 0.8184)$$

Based on the higher coefficient of determination, the pseudo-first-order model describes the adsorption kinetics more closely under the tested conditions. The magnitude of the rate constants and the short equilibrium time indicate rapid uptake on readily available sites, followed by a slower approach to equilibrium.

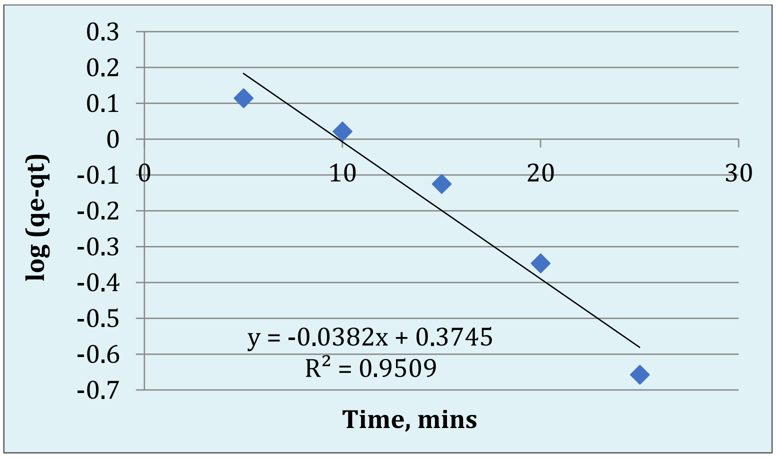

Figure 4. First order kinetics.

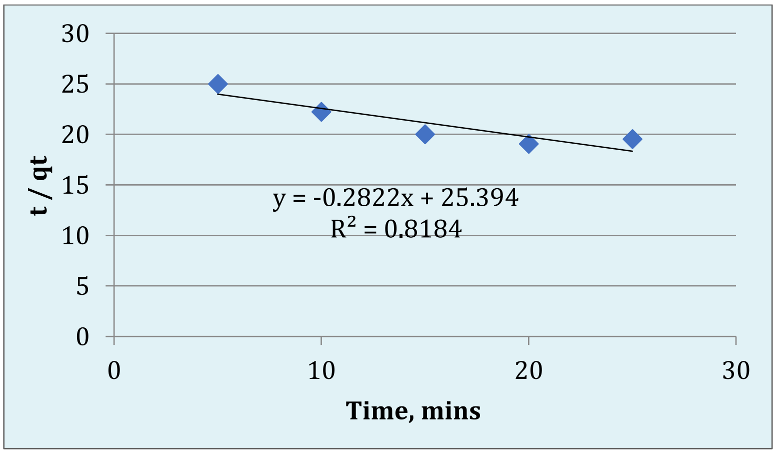

Figure 5. Second order kinetics.

6. Thermodynamic Analysis

Thermodynamic parameters were evaluated from adsorption equilibrium data collected at different temperatures (283–323 K) at Co = 20 mg/L, biosorbent dose = 30 g/L (1.5 g), particle size = 53 μm, pH 5, and contact time = 30 min. The Van't Hoff plot is shown in Figure 6.

Kc = qe/Ce

The standard Gibbs free energy change was estimated using:

ΔG° = −RT ln (Kc)

The standard enthalpy (ΔH°) and entropy (ΔS°) changes were obtained from the Van't Hoff relationship:

- Log (Kc) = (−ΔH°/(2.303R)) (1/T) + (ΔS°/ (2.303R))
- A plot of log(Kc) versus 1000/T (Figure 6) produced a straight line described by:
- Log (Kc) = −0.7752(1000/T) + 2.5369 (R^2 = 0.9865)

From the slope and intercept, the thermodynamic parameters were calculated as ΔH° = +14.84 kJ mol^{-1} and ΔS° = +48.57 J mol^{-1} K^{-1}. The positive ΔH° indicates that adsorption is endothermic, consistent with the observed increase in removal with temperature. The positive ΔS° suggests increased randomness at the solid–solution interface, which can occur when hydrated water molecules are displaced from the biosorbent surface during dye uptake [12,15].

Using ΔG° = −RT ln(Kc), ΔG° decreased from +1.15 kJ mol^{-1} (283 K) and +0.64 kJ mol^{-1} (293 K) to −0.03 kJ mol^{-1} (303 K), −0.36 kJ mol^{-1} (313 K), and −0.76 kJ mol^{-1} (323 K). This trend shows that adsorption becomes thermodynamically more favorable at higher temperatures. The relatively low ΔH° value (14.84 kJ mol^{-1}) is consistent with predominantly physical adsorption interactions rather than strong chemisorption [16].

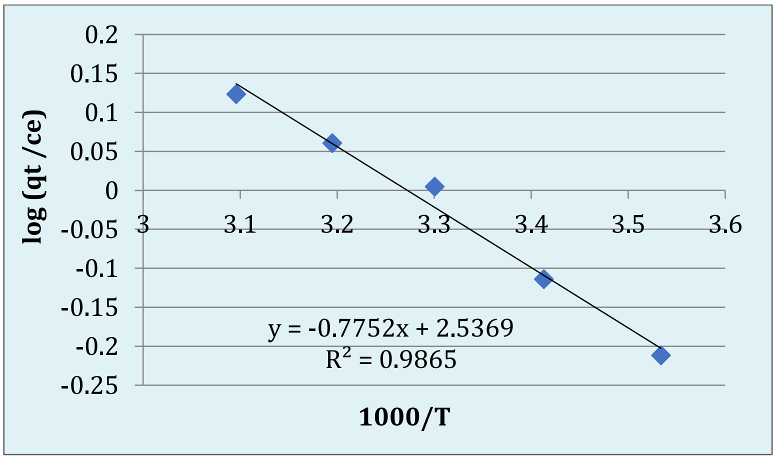

Figure 6. Vant Hoff's plot.

7. Conclusion

Batch adsorption experiments show that *Sargassum tenerrimum* powder can effectively remove Toluidine Blue from water. Adsorption approached equilibrium within 30 min, and smaller particles (53 μm) improved uptake. Removal increased with temperature, and thermodynamic analysis confirmed an endothermic, increasingly spontaneous adsorption process at higher temperature.

The high removal efficiency in a short time under mild conditions suggests strong practical promise. In particular, the rapid equilibrium (30 min) and optimal performance near ambient temperature imply that *Sargassum tenerrimum* powder could be used as a low-cost, sustainable adsorbent in wastewater treatment. Its efficacy against TB and likely other cationic dyes underscores its potential for mitigating dye pollution. Future work may explore scale-up and regeneration, but the current results clearly indicate that *Sargassum tenerrimum* biomass offers a viable route for eco-friendly dye remediation in industrial effluents.

Declarations

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