Research Article

Continuous Sorption of Remazol Brilliant Orange 3R Using *Caulerpa scalpelliformis* Biochar

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An ever increase in the utilization of water for domestic and industrial activities resulted in the depletion of fresh water. Water is being used in huge quantities for manufacturing and other activities. The toxic pollutants used in the industries get mixed with water and result in the degradation of water quality. Textile industries are considered as one of the major industries that release a huge quantity of wastewater. The dye used in the textile industries is not completely utilized in the dyeing process and gets mixed with water and reaches the environment. *Caulerpa scalpelliformis*, a novel sorbent, was used for the preparation of biochar and successive removal of dyes in a continuous operation. The operating conditions, namely, biochar bed depth, dye flow rate, and initial dye concentration, were investigated, and the experimental result was validated with the mathematical models.

1. Introduction

Globally, emerging pollutants from industries had become the major challenge in recent years that cause an impact on the environment, human health, and aquatic fauna life. The major pollutants that are used in huge quantities are dyes [1]. Due to their complex nature and nonbiodegradable properties, they are difficult to remove once they are mixed with water [2]. Hence, wastewater has to be treated before discharging into water bodies [3]. If 1 mg/L of dyes is mixed in water, it acts as a thin trap on the surface of the water bodies [4, 5]. This will block the sunlight diffusion deep into the water bodies that affects photosynthesis activity. This results in the degradation of much aquatic life [6–8].

The most commonly adopted methods are precipitation, membrane filtration, oxidation, ion exchange, and adsorption process [9, 10]. Adsorption using activated carbon was considered as one of the prominent treatment methods [11]. Many adsorbents, namely, zeolite, silicate, lime, and activated carbon, were used. Among different adsorbents, activated

carbon is the most commonly used due to enhanced characteristics toward pollutant removal efficiency. However, due to its expensive nature and difficulties in regeneration, recent studies have focused on biosorption using waste materials [12]. Many biosorbents were successfully produced from agricultural waste, seaweeds, waste biomass, plant leaves, and fruit seeds. Several microorganisms, namely, bacteria, yeast, fungi, algae, and cyanobacteria, were also used in biosorption techniques, but using the live microorganism for biosorption has several disadvantages. Under moist conditions, proteinous materials of microbes will putrefy; maintaining and discarding microbes will result in additional cost. So, the development of alternate novel adsorbents for toxic pollutants' removal is emerging research.

Biochar is a carbonaceous material formed in the oxygen-limited environment under the thermal breakdown process. This biochar is rich in carbon, functional groups, and active binding sites, and several pores are present due to the pyrolysis process [13]. Many researchers proved that biochar produced from rice husk, coconut shell, peanut

shell, marine seaweeds, orange peel, date seeds, palm seeds, etc., can be successfully utilized for pollutant removal [14]. Energy from waste is considered one of the tools for reducing greenhouse gases in the atmosphere. The emerging techniques, namely, gasification, torrefaction, and pyrolysis, are used for converting waste into energy [15]. Among these methods, slow pyrolysis is considered as one of the promising techniques for converting waste into energy, resulting in solid residue called biochar, bio-oil, and synthetic gas [16].

Nearly 45% of textile dyes used worldwide are found to be reactive dyes [17] that are toxic and carcinogenic [18]. The presence of aromatic rings in the structural composition of dyes indicates nonbiodegradable properties. The reactive dyes will form covalent bonds between the fabric surface and the dye ions, resulting in strong binding. So, reactive dyes are a major challenge, and many batch studies were conducted. However, not many studies have demonstrated the remediation of reactive dyes in a continuous study. The present study focusses on the utilization of biochar produced from *Caulerpa scalpelliformis* for the decolorization of Remazol Brilliant Orange 3R (RBO3R).

2. Materials and Methods

2.1. Biosorbent Preparation. *Caulerpa scalpelliformis* is a marine seaweed that is available naturally in the seashore of South India. The required amount of seaweeds was collected and washed with deionized water. The washed seaweeds were sun-dried for 7 days to remove the moisture content naturally. The seaweeds were shredded into 7.5 mm and maintained in a hot air oven for 24 h at 103°C. Finally, the seaweeds were kept in the muffle furnace for 15 minutes at a temperature of 350°C. Remazol Brilliant Orange 3R (RBO3R) was obtained from Sigma-Aldrich, India.

2.2. Batch Study. The batch study was conducted in a controlled environment in an orbital shaker. 100 ml of the required initial dye concentration was used to investigate the sorption process. 150 rpm was maintained in the shaker for 6 h. After the required equilibrium time, 3 ml of the sample was taken and centrifuged at 3000 rpm for 5 min. The clear solution is taken for the measurement of the final dye concentration using a spectrophotometer at 490 nm. The partition coefficient is calculated to determine the optimum initial dye concentration for the sorption using biochar.

2.3. Continuous Study. Figure 1 illustrates the experimental setup used for the investigation of the sorption process. A peristaltic pump is used to give the feed from the bottom of the column at varying flow rates. An adjustable plunger is provided at the top of the column to vary the biochar bed depth. Glass beads are provided at the bottom of the column to maintain a steady flow inside the column. The sample received at the outlet port is taken to a spectrophotometer for analysis at 490 nm. The column data analysis, namely, overall sorption zone (Δt), breakthrough time (t_b), exhaustion time (t_e), the total amount of dye sorbed (m_{total}), the volume of wastewater treated (V_{eff}), removal efficiency

(%), and sorption capacity (mmol/g), was calculated [6]. Furthermore, mathematical modeling, namely, modified dose-response (MDR) model and Yoon-Nelson (YN), was studied. As suggested by Sujatha et al. 2021 [19], the error analysis was calculated to find the accuracy of the models.

3. Results and Discussion

3.1. Batch Study. The batch adsorption study concluded that a maximum removal efficiency of 76.2% was obtained with 0.1905 mmol/g as uptake capacity. Furthermore, biochar was investigated for reusability potential. The result concluded that sodium hydroxide with an S/L ratio of 5 and desorption efficiency of 99.2% was obtained. Figure 2 illustrates the partition coefficient of biochar at different initial RBO3R concentrations. From Figure 2, it is concluded that the partition coefficient was decreasing with a surge in initial RBO3R concentration. For instance, the partition coefficient of 3.92, 3.18, 1.6, 0.6, and 0.37 L/g was observed for 0.1, 0.25, 0.5, 0.75, and 1 mmol/L, respectively. This indicates that biochar is having good potential at lower concentrations rather than at higher concentrations [20].

3.2. Continuous Study. Generally, the dye removal process was studied in batch operation, and this will not create a solution for a real-time wastewater treatment system. Since most of the treatment plants are operating continuously, a treatment method that favors the continuous removal of the toxic pollutants will be practically exploring a possible solution [19]. Figure 3 illustrates the overall performance of the column in RBO3R removal. The biochar bed depth (25, 20, and 15 cm), flow rate (0.6, 0.48, and 0.3 L/hr), and initial RBO3R concentration (0.1, 0.2, and 0.25 mmol/L) were studied.

3.3. Biochar Depth on RBO3R Sorption. Figure 4 illustrates the performance of the packed bed column by varying biochar bed depth. Table 1 summarizes the overall column parameters during sorption of RBO3R. It is observed that a surge in bed depth enhanced the volume of wastewater treated. For instance, at a biochar depth of 25 cm, the total volume of wastewater treated was 3.3 L, and the overall sorption zone reported was 11 hours. The removal efficiency of 74.53 and 72.69% was obtained for 20 and 25 cm bed depths. The sorption capacity of 0.084 and 0.087 mmol/g was obtained for 20 and 25 cm. Based on the sorption capacity, removal efficiency, and volume of effluent treated, a biochar depth of 25 cm was selected as the best condition for the maximum performance of the column. Table 2 summarizes the model constants for MDR and YN models. A correlation coefficient of 0.961 was observed for the MDR model. Tables 3 and 4 brief different error analyses. From Tables 3 and 4, it is concluded that the MDR model is superior to the YN model since the error was very less.

3.4. Flow Rate on RBO3R Sorption. Figure 5 illustrates the removal efficiency of RBO3R at varying flow rates. For instance, at a flow rate of 0.3, 0.48, and 0.6 L/hr, the sorption

FIGURE 1: Experimental setup for continuous removal of RBO3R [4].

FIGURE 2: Partition coefficient for sorption of RBO3R.

capacity of 0.087, 0.081, and 0.073 mmol/g was obtained. The removal efficiency of 72.69% was observed at a flow rate of 0.3 L/hr. The improved efficiency and sorption capacity at decreased flow rate were due to the increased overall sorption zone. For instance, the overall sorption zone for 0.3, 0.48, and 0.6 L/hr was attained as 11, 7.25, and 5.26 h, respectively. It is obvious that, at decreased flow rate, the time for biochar to interact with dye molecules will be high [21, 22]. This may result in increased interaction between the dye and biochar and resulted in increased binding capacity

of biochar [23, 24], whereas at the increased flow rate, the dye molecules will get washed out since the time for binding will be very less [25, 26]. So, it is concluded that a flow rate of 0.3 L/hr is optimum for RBO3R sorption.

3.5. Initial Concentration on RBO3R Sorption. From Figure 6, it was clear that removal efficiency was higher at a lower RBO3R concentration. For instance, the removal efficiency of 79.56% was obtained at 0.1 mmol/L, whereas at

FIGURE 3: Overall sorption of RBO3R.

FIGURE 4: Sorption of RBO3R by varying bed depth with mathematical modeling.

TABLE 1: Column parameters at varying conditions.

Initial RBO3R concentration (mmol/L)	Flow rate (L/hr)	Bed height (cm)	Sorption capacity (mg/g)	t_b (h)	t_e (h)	Δt (h)	V_{eff} (L)	Removal efficiency (%)
0.25	0.3	15	0.093	0.5	10	10.5	3.15	67.37
0.25	0.3	20	0.084	1.75	7.75	9.5	2.85	74.53
0.25	0.3	25	0.087	2	9	11	3.3	72.69
0.25	0.48	25	0.081	0.5	6.75	7.25	3.48	58.53
0.25	0.6	25	0.073	0.25	5.01	5.26	3.15	64.64
0.2	0.3	25	0.088	2	14	16	4.8	63.64
0.1	0.3	25	0.055	5.5	18.5	24	4.8	79.56

TABLE 2: Mathematical model constants for RBO3R sorption.

Initial RBO3R concentration (mmol/L)	Flow rate (L/hr)	Bed height (cm)	MDR model			YN model		
			a_{mdr}	b_{mdr}	R^2	t	k_{YN}	R^2
0.25	0.3	15	4.890	2.162	0.973	8.188	0.477	0.986
0.25	0.3	20	5.615	2.182	0.965	8.025	0.571	0.983
0.25	0.3	25	7.584	2.275	0.987	10.129	0.456	0.879
0.25	0.48	25	4.026	2.354	0.967	5.116	0.742	0.984
0.25	0.6	25	5.026	2.122	0.984	3.611	1.402	0.989
0.2	0.3	25	5.301	2.973	0.992	10.190	0.538	0.992
0.1	0.3	25	5.899	3.219	0.961	12.667	0.327	0.882

TABLE 3: Statistical error analysis for the MDR model.

Initial RBO3R concentration	Flow rate	Bed depth (cm)	MDR model						
			AARE	HYBRID	ARE	MPSED	RMSE	Adj R^2	R^2
0.25	0.3	15	0.004	0.463	0.409	2.397	0.023	0.969	0.973
0.25	0.3	20	0.004	0.366	0.441	2.505	0.024	0.969	0.965
0.25	0.3	25	0.004	0.274	0.402	2.287	0.022	0.969	0.987
0.25	0.48	25	0.003	0.271	0.301	1.684	0.016	0.961	0.967
0.25	0.6	25	0.003	0.155	0.291	1.439	0.013	0.980	0.984
0.2	0.3	25	0.003	0.178	0.285	1.568	0.015	0.991	0.992
0.1	0.3	25	0.005	0.421	0.456	2.555	0.024	0.954	0.961

TABLE 4: Statistical error analysis for the YN model.

Initial RBO3R concentration	Flow rate	Bed depth (cm)	YN model						
			AARE	HYBRID	ARE	MPSED	RMSE	Adj R^2	R^2
0.25	0.3	15	0.005	0.642	0.482	2.823	0.027	0.984	0.986
0.25	0.3	20	0.005	0.394	0.457	2.600	0.025	0.980	0.983
0.25	0.3	25	0.005	0.454	0.517	2.942	0.028	0.859	0.879
0.25	0.48	25	0.002	0.081	0.164	0.920	0.009	0.981	0.984
0.25	0.6	25	0.001	0.029	0.126	0.622	0.006	0.986	0.989
0.2	0.3	25	0.001	0.019	0.093	0.510	0.005	0.991	0.992
0.1	0.3	25	0.006	0.773	0.618	3.461	0.033	0.861	0.882

AARE: absolute average relative error; HYBRID: hybrid fractional error function; ARE: average relative error; MPSED: Marquardt's percent standard error deviation (MPSED); RMSE: root mean square error; Adj R^2 : adjusted R^2 .

FIGURE 5: Sorption of RBO3R by varying flow rate with mathematical modeling.

FIGURE 6: Sorption of RBO3R by varying initial concentration with mathematical modeling.

0.25 mmol/L, 72.69% was attained. The increased efficiency at reduced initial RBO3R concentration may have occurred because of the availability of abundant binding sites toward very few dye molecules [27, 28]. This may result in maximum sorption, whereas at higher concentration, the availability of the dye molecules was very high, and this may result in decreased removal efficiency [29, 30]. The overall sorption zone time was increased with a reduction in initial RBO3R concentration. For instance, a sorption zone of 11, 16, and 24 h was obtained for 0.25, 0.2, and 0.1 mmol/L. The overall sorption zone was found to be less for a practical application. Based on the overall column performance, 0.25 mmol/L was selected as an optimum initial RBO3R concentration for RBO3R sorption.

4. Conclusion

Biochar synthesized from *Caulerpa scalpelliformis* can be effectively used in continuous operation. The maximum removal efficiency of 72.69% and sorption capacity of 0.087 mmol/g were obtained at a biochar depth of 25 cm, a flow rate of 0.3 L/hr, and an initial RBO3R concentration of 0.25 mmol/L. The mathematical model study concluded that the MDR model was superior. Future research can be explored on assessing the potential of biochar by investing in regeneration studies. Possible assessments need to be conducted to suggest the solution to overcome the secondary pollutants to the environment.

Data Availability

The data used to support the findings of this study are included within the article.

Disclosure

This study was performed as a part of the employment of Addis Ababa Science and Technology University, Ethiopia.

Conflicts of Interest

The authors declare that they have no conflicts of interest regarding the publication of this paper.

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