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Experimental and chemometric analysis of bioremediation of remazol dyes using biochar derived from green seaweeds

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ABSTRACT

The present study investigates the bioremediation of Remazol brilliant blue R (RBBR), Remazol brilliant orange 3R (RBO3R), Remazol brilliant violet 5R (RBV5R) and Remazol Black B (RBB) using biochar derived from three marine seaweeds such as *Ulva lactuca*, *Ulva reticulata* and *Caulerpa scalpelliformis.* The removal efficiency of different biochars was studied by varying the operating parameters such as biochar dosage, pH, temperature and initial concentration in batch experiments. The optimum values were attained at 2 g/L biochar dosage, 1.75 pH, 30°C temperature and 0.05 mmol/L initial concentrations. Among the different green seaweeds, *U. lactuca* derived biochar loaded with RBO3R showed that maximum removal efficiency in all the batch studies. The removal efficiency of biochar was in the order of *Ulva lactuca* > *Ulva reticulate* > *Caulerpa scalpelliformis* and for dyes it was in the order of RBO3R followed by RBBR, RBV5R and RBB. FT-IR and SEM images were used to study the binding matrix of the derived biochar. The result indicated that the derived biochar is suitable for the adsorption process since a lot of binding pores were seen over the surface of the biochar. In this work, the chemometric analysis was also carried out to classify and compare the dye removal capability of different green seaweeds derived biochar.

Keywords: Marine seaweeds; Biochar; Remazol dyes; Dye removal; Chemometric analysis

1. Introduction

The increase in water use has resulted in unimaginable wastewater generation in recent days. Before disposal to the environment, this wastewater needs proper treatment. If it is not treated properly, the entire aquatic ecosystem will be degraded [1]. Among different pollutants, dyes are the important pollutants that cause surface pollution and adversely affect drinking water quality [2]. Dyes are classified into synthetic dyes and natural dyes. Many industries including textile [3,4], leather [5,6], paint [7,8], paper [9], food [10,11] and agriculture [12] use synthetic dyes.

These dyes are poisonous in nature and affect human health if it is not treated properly [13]. Thus, the removal of dye is the biggest challenge in the current scenario and proper treatment method has to be adopted to avoid the pollution load to the environment since it has a high resistance to biodegradation in water [14]. A small dye concentration of about 1 mg/L in the freshwater source may result in noticeable color and thus rendering it unsuitable for human consumption. In contrast, high concentrations of coloring affect the water's self-purification capacity and, in turn, result in the depletion of dissolved oxygen and act as a barrier to sunlight penetration into water and thus affecting the photosynthesis of microorganisms and aquatic life in water bodies [15].

Treatment techniques currently available to remove dyes from wastewaters are generally categorized under chemical,

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biological and physical methods [3]. Many physical and chemical methods are used to remove the dyes [16,17]. But, in recent times, biological methods are preferred [18,19]. Among these methods, biomass-derived from agricultural wastes, seaweeds, etc., are recently used for the bioremediation of the dyes using methods such as biosorption, biodegradation, bioaccumulation, bioleaching, phytoremediation, bio-sparging, bio-augmentation, bioventing and bio-stimulation [2,20]. Of these different biological methods, recent research is concentrated on biochar for the remediation of heavy metals and dyes [21–23].

Based on the above actualities, biochar seems to be a suitable sorbent for the remediation of dyes. However, work done on the possibility and practicability of biochar as sorbent material for Remazol dyes are very limited. Hence, the current research investigates the potential of different biochars derived from marine green algae (*Ulva lactuca*, *Ulva reticulata*, and *Caulerpa scalpelliformis*) towards sorption of various Remazol dyes (Remazol Black B; Remazol Brilliant Violet 5R; Remazol Brilliant Orange 3R; Remazol Brilliant Blue R). To the best our knowledge, this is the first research that the biochar derived from green marine seaweeds is used for the adsorption of Remazol dyes. These marine seaweeds are produced in large quantity naturally in the seashores (south Tamilnadu, India) and it can obtain at minimum cost or nil cost. Therefore, it will reduce the treatment cost associated with the dye removal process.

2. Materials and methods

2.1. Dyes

Four Remazol dyes were employed in the current investigation, which includes Remazol Black B (RBB), Remazol brilliant orange 3R (RBO3R), Remazol brilliant violet 5R (RBV5R) and Remazol brilliant blue R (RBBR) were procured from Sigma-Aldrich (India). The properties of Remazol dyes are given in Table 1.

2.2. Biochar preparation

In the current research for the production of biochar, three green seaweeds (marine algae) namely *U. lactuca, Ulva reticulata* and *Caulerpa scalpelliformis* were used. These seaweeds are collected from the seashores of south Tamilnadu, India. The procedure for biochar preparation employed in this work is the same as the method employed in previous works [24,25]. The pyrolysis temperature was varied between 300°C and 500°C to find the best temperature for the maximum yield of biochar. After the pretreatment of the biochar, it is used for the adsorption studies. Elemental analyzer, SEM and FT-IR were carried out for biochar characterization.

2.3. Batch experiments

Batch experiments were carried out to find the optimum parameters. A 250 mL Erlenmeyer flask with 100 mL of the working volume is operated in a rotary incubated shaker at 160 rpm for a detention period of 6 h. After the batch experiment, it is centrifuged at 3,000 rpm for a period of 5 min. The experiments were carried out by varying different parameters such as biochar dosage (1, 2, 3, 4, 5, 7 and 10 g/L), pH (1.75–5.0), temperature (20°C–45°C), initial concentration (0.05–1 mmol/L) and contact time (10, 20, 30, 40, 50, 60, 90, 120, 180, 240, 300, 360 min). The percentage dye removal of biochar is calculated using Eq. (1).

$$\text{Removal efficiency} = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (1)$$

2.4. Thermodynamic studies

Thermodynamic parameters, that is, standard free energy ($\Delta G°$), standard enthalpy ($\Delta H°$) and standard entropy ($\Delta S°$) were calculated using Eqs. (2) and (3).

$$\Delta G° = -RT \ln K_L \quad (2)$$

$$\Delta G° = \Delta H° - T\,\Delta S° \quad (3)$$

where K_L or b_L is the Langmuir constant (L/mol), T is the temperature in K and R is the gas constant (kJ mol^{-1} K^{-1}). The value of $\Delta H°$ and $\Delta S°$ was calculated from the slope ($-\Delta H°/R$) and intercept ($\Delta S°/R$) of plot of ln K_L vs. $1/T$ [26].

2.5. Chemometric analysis

The removal efficiency of four different Remazol dyes using three different green seaweeds derived biochar under varied operating conditions (biochar dosage, pH, temperature and initial concentration) were used to perform the chemometrics using principal component analysis and cluster analysis with the aid of Minitab® (Ver. 16) software. This analysis was carried out to visually explore the bioremediation of remazol dyes using biochar derived from three different green seaweeds under varied operating conditions. The principle component analysis was performed by constructing a correlation matrix and finding the relative magnitudes of eigenvalues and scores

Table 1
Characteristics of Remazol dyes used in the current investigation

Dyes	Empirical formula	Color index	Molecular weight (g/mmol)	λ_{max} (nm)
Remazol brilliant blue R	$C_{22}H_{16}N_2Na_2O_{11}S_3$	61,200	626.54	595
Remazol brilliant orange 3R	$C_{20}H_{17}N_3Na_2O_{11}S_3$	17,757	617.54	490
Remazol brilliant violet 5R	$C_{20}H_{16}N_3Na_3O_{15}S_4$	18,097	735.58	577
Remazol black B	$C_{26}H_{21}N_5Na_4O_{19}S_6$	20,505	991.82	597

of first two principle components. The calculated eigen values and scores were graphically plotted using the Eigen profile plot or screen plot and score plot. On the other hand, the cluster analysis was performed by considering single linkage method and correlation distance measure to construct the dendrogram or tree diagram. This procedure is an agglomerative hierarchical method that starts separately with all variables, each forming its own cluster. The two variables closest to each other are joined in the first step. In the next step, either the first two are joined by a third variable, or two other variables are joined together into another cluster. This process will continue until all clusters become one.

3. Result and discussion

3.1. Influence of pyrolysis temperature on biochar yield

Pyrolysis temperature strongly influences the yield of biochar. Fig. 1 illustrates the influence of pyrolysis temperature on biochar yields for three green seaweeds. It was clear that the surge in pyrolysis temperature declines the biochar yield. This was due to the higher decomposition of seaweed constituents at elevated temperatures. Several investigators indicated that biochar yield decreases whereas other byproducts such as bio-oil and biogas increase with surge in pyrolysis temperature [27]. From Fig. 1, it is evident that the maximum biochar yield of 60%, 58% and 53% were obtained for *Ulva lactuca, Ulva reticulata* and *Caulerpa scalpelliformis* at 300°C, whereas at 500°C the biochar yield of 36%, 34% and 30% were obtained for *Ulva lactuca, Ulva reticulata* and *Caulerpa scalpelliformis*. So, after careful evaluation of results as presented in Fig. 1, biochar samples produced at pyrolysis temperature of 300°C were selected for further studies.

3.2. Influence of biochar dosage on % removal of Remazol dyes

The batch trails at different biochar dosages were carried out to predict the optimum dosage for the removal of dyes loaded with biochar. The experimental results showed that the maximum percentage removal of dye is achieved for *U. lactuca* loaded with RBO3R. The maximum removal efficiency of 98.20% is attained at a dosage of 10 g/L and a minimum of 47.40% is attained at dosage of 1 g/L. From results, it is evident that the increase in biochar dosage increases the removal efficiency. The maximum removal efficiency at high dosage is due to the presence of pores on the surface of biochar [28]. From Fig. 2 it is concluded that the maximum removal efficiency is achieved at a dosage of 10 g/L for all the biochars loaded with dyes. The maximum dye uptake capacity is achieved at a low biochar dosage of 1 g/L. This is due to that all the binding sites in the biochar are effectively utilized for dye binding. For example, the maximum dye uptake capacity for *Ulva lactuca* loaded RBB at a biochar dosage of 1 g/L is found to be 0.203 mmol/g (201.34 mg/g), with removal efficiency of 40.40%, whereas the dye uptake capacity for *U. lactuca* loaded RBB at a biochar dosage of 10 g/L is 0.0429 mmol/g (42.54 mg/g) with a removal efficiency of 85.80%. From the results, it is also evident that at a biochar dosage of 2 g/L, the dye uptake capacity is 0.1945 mmol/g (192.91 mg/g) with a removal efficiency of 77.80%. In comparison with a biochar dosage of 1 g/L, the biochar dosage of 2 g/L is found to be optimum in terms of dye uptake capacity and removal efficiency. So, the optimum biochar dosage for removal of dyes is fixed as 2 g/L.

3.3. Influence of pH on % removal of Remazol dyes

During sorption, equilibrium pH plays an important role in the sorption capacity. The enhancement of Remazol dye sorption at low pH values (Fig. 3) was due

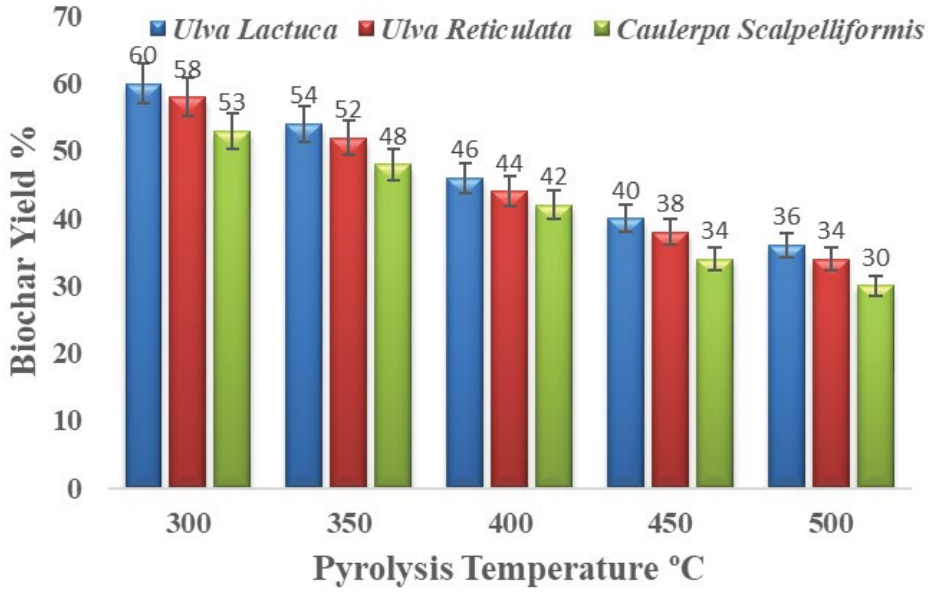

Fig. 1. Impact of pyrolysis temperature on the biochar yield for three green seaweed biomasses.

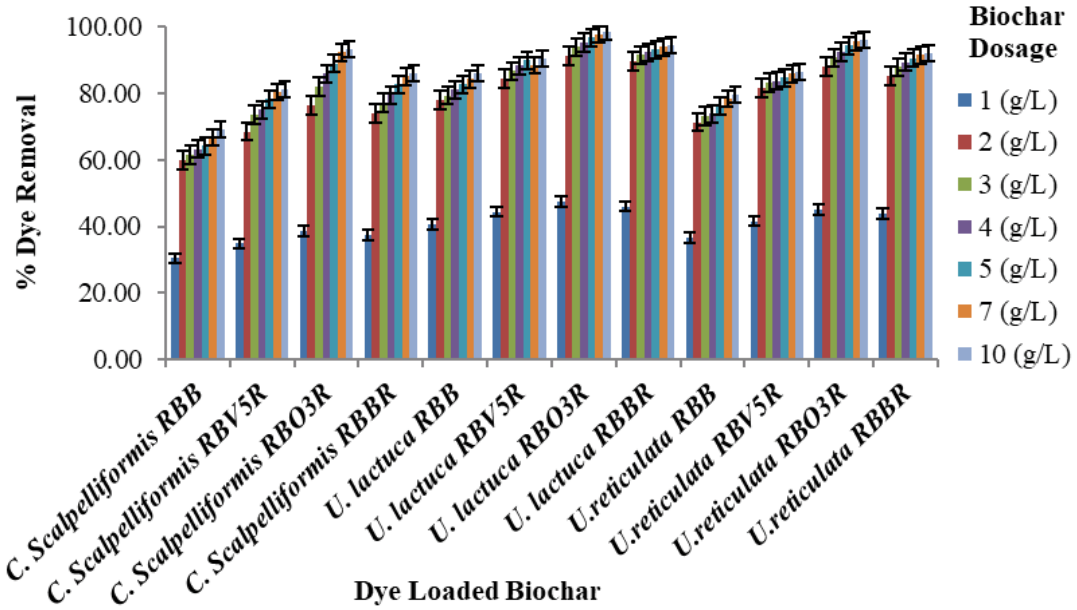

Fig. 2. Influence of biochar dosage in the % removal of RBB, RBV5R, RBO3R and RBBR loaded biochar.

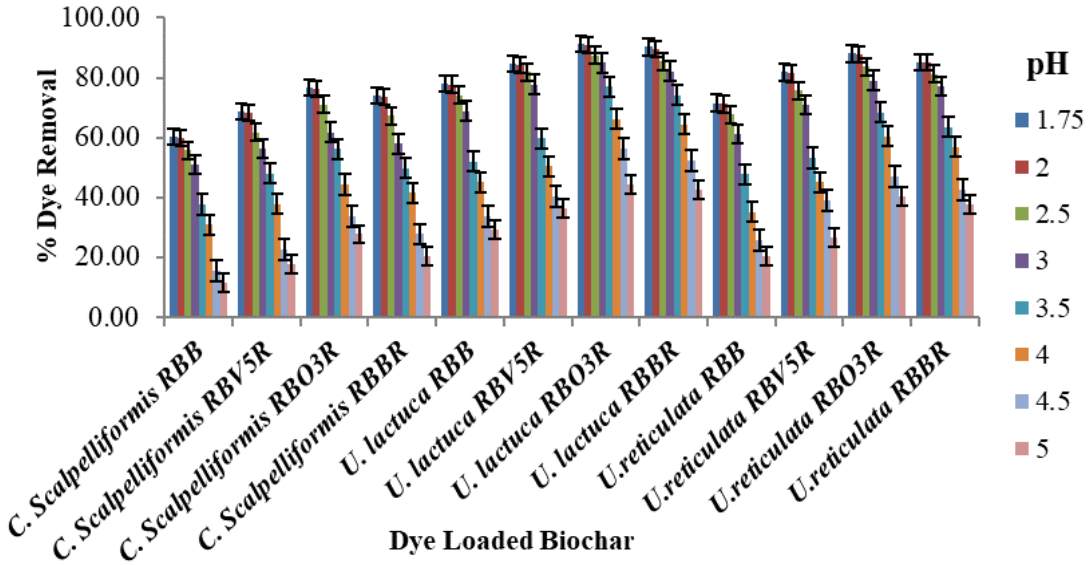

Fig. 3. Influence of pH in the % removal of RBB, RBV5R, RBO3R and RBBR loaded biochars.

to interactions (electrostatic) between biochar and reactive dye anions. Lignocellulosic constituents usually comprise of sulfate, carboxyl and amine groups [29]. Hence, under low pH scenarios, the functional groups existed on the biochar matrix would be expected to load with H^+ ions (protonated) and thus the surface attains overall positive charge. At the same time, reactive dyes exist in solution as negatively colored dye ions and thus react with positively charged surface of the sorbent [30]. Hence lower pH favors binding of dye molecules and this was reflected in the results. The removal efficiency is calculated by varying the pH between 1.75 and 5. The maximum removal efficiency of 91.20% with a dye uptake capacity of 140.80 mg/g at pH of 1.75 and a minimum of 44.60% with a dye uptake capacity of 68.85 mg/g at pH of 5 is attained for *U. lactuca* biochar loaded with RBO3R. So, from the investigation, it is evident that the increase in pH decreased dye removal efficiency. It is also concluded that the maximum removal efficiency for all the dyes loaded with different biochars is attained at pH of 1.75.

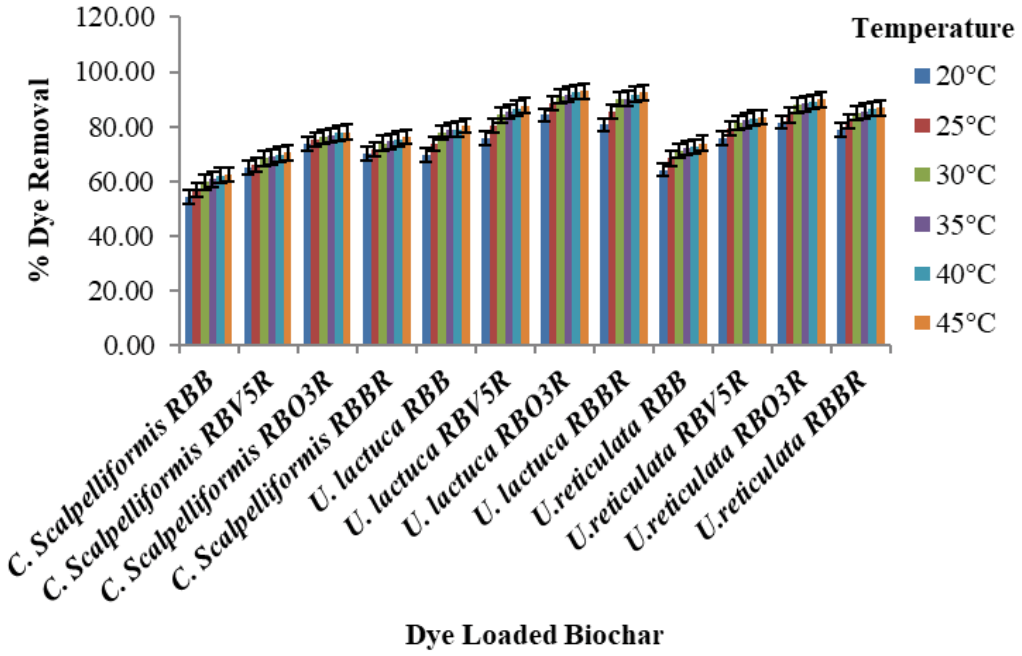

Fig. 4. Influence of temperature in the % removal of RBB, RBV5R, RBO3R and RBBR loaded biochars.

3.4. Influence of temperature on % removal of Remazol dyes

Many researchers have indicated that surge in temperature strongly influences the uptake potential and increases the removal efficiency of dyes [31,32]. The effect of temperature on the remazol dyes is studied by varying the temperature between (20°C–45°C) at a constant initial concentration of 0.5 mmol/L and pH of 1.75. The experiments revealed that the maximum removal efficiency of dyes was achieved at a temperature of 45°C. For example, a maximum dye removal efficiency of 93% with a dye uptake capacity of 143.58 mg/g is achieved for *U. lactuca* loaded with RBO3R at the temperature of 45°C. From Fig. 4, it is evident that an increase in temperature increased the removal efficiency. While considering the economy of the treatment, the removal efficiency of 91% with a dye uptake capacity of 140.49 mg/g is obtained at 30°C. The difference in removal efficiency between 30°C and 45°C is only 2%. The elevated temperature will increase the treatment cost. So, operating at room temperature will favor the economy of the treatment. Therefore, the optimum temperature for the removal of dyes is 30°C.

3.5. Influence of initial concentration on % removal of Remazol dyes

The initial concentration of the dye also plays an important role in fixing the dye uptake capacity of the biochar. The experimental trials were conducted at a different initial concentration ranging from 0.05 to 1 mmol/L to find the optimum concentration for the dye removal. For all the dyes, the maximum removal efficiency is achieved at an initial concentration of 0.05 mmol/L. The maximum of 93.20% of removal efficiency is achieved at an initial concentration of 0.05 mmol/L whereas for the same dye removal efficiency of 60.16% is achieved at 1 mmol/L. From Fig. 5 it is concluded that the increase in initial concentration decreased the removal efficiency. So, the optimum concentration for the maximum removal efficiency is found to be 0.05 mmol/L.

3.6. Influence of contact time on % removal of Remazol dyes

Fig. 6 shows the impact of contact time on the bioremediation of dyes using biochar derived from green marine algae. The effect of contact time was studied at different time intervals. From Fig. 6, it is revealed that a maximum removal percentage for all dyes is attained at a contact time of 120 min and further increase in contact time (300 min) increased only a maximum of 2.6% of all dyes. For instances, a removal of 89.6% with a dye uptake capacity of 138.32 mg/g is attained at a contact time of 120 min and a maximum of 91% with a dye uptake capacity of 140.49 mg/g is attained at a contact time of 300 min for RBO3R of *U. lactuca* derived biochar. So, from the study, it is concluded that the contact time of 120 min is considered as the optimum time for the remediation of dyes.

3.7. Adsorption isotherm

The adsorption isotherm is crucial to comprehend the complete sorptional capacity of adsorbent and also the affinity of specific adsorbate towards the adsorbent. The sorption isotherm is a plot of equilibrium dye concentration left in the solution after sorption plotted against the sorptional uptake of adsorbent at fixed condition (generally constant temperature or pH). For the present study, isotherm was generated by changing the initial Remazol dye concentrations from 0.05 to 1 mmol/L at temperature 30°C and pH 2.0. The

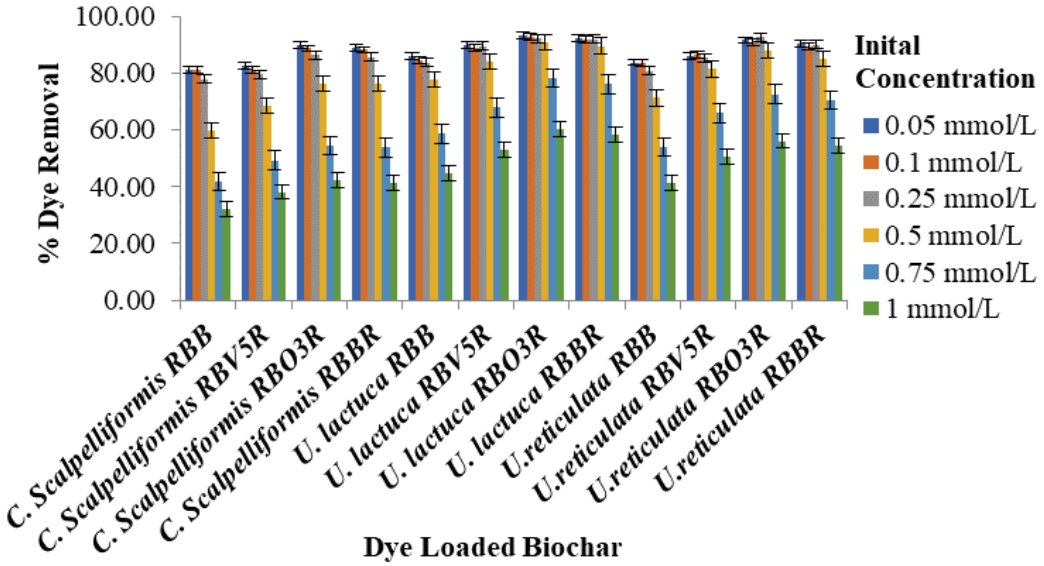

Fig. 5. Influence of initial concentration on the % removal of RBB, RBV5R, RBO3R and RBBR loaded biochars.

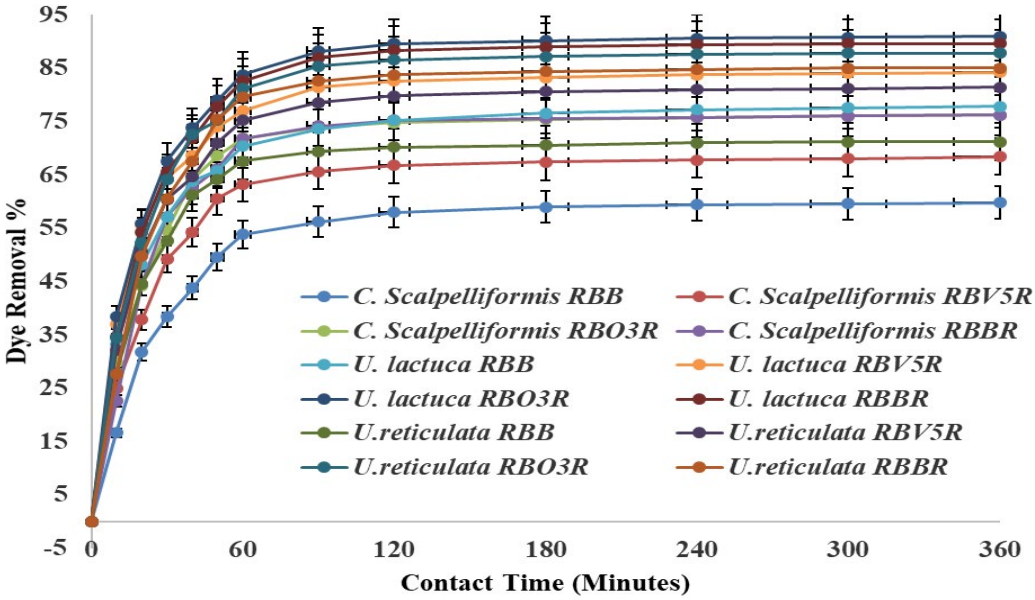

Fig. 6. Influence of contact time on the % removal of RBB, RBV5R, RBO3R and RBBR loaded biochars.

Freundlich, Langmuir, Sips and Toth models were used to plot and define the Remazol dye isotherms. The Freundlich and Langmuir models involve two-parameter, whereas Sips and Toth models comprises of three parameters. Of the four-isotherm investigated, Toth model is found to be best fit model with R^2 value of 0.999, 0.999, 0.999, 0.999 for RBB, RBV5R, RBO3R and RBBR for *U. lactuca* derived Biochar. For instances *U. reticulata* and *C. scalpelliformis* derived biochar also best fitted with the toth model with an R^2 value of 0.999 for all Remazol dyes. The detailed study about the adsorption isotherm is discussed in our previous study [25,33]. Table 2 summarizes the uptake capacity of Remazol dyes using different sorbents.

3.8. Thermodynamic studies

Table 3 summarizes the standard free energy ($\Delta G°$), standard enthalpy ($\Delta H°$) and standard entropy ($\Delta S°$) at temperatures of 293, 303 and 313 K for *U. lactuca* derived biochar in the remediation of all four Remazol dyes. From the

Table 2
Remazol dye uptake capacity of different sorbents

Sorbent	Dye	Uptake capacity	Reference
Coffee-husk based activated carbon	Remazol Brilliant Orange 3 R	66.76 mg/g	[34]
U. lactuca derived biochar	Remazol Brilliant Orange 3 R	185.72 mg/g	Present study
U. reticulata derived biochar	Remazol Brilliant Orange 3 R	173.22 mg/g	Present study
C. scalpelliformis derived biochar	Remazol Brilliant Orange 3 R	130.30 mg/g	Present study
Activated sludge	Remazol Black B	134.8 mg/g	[35]
Pine fruit shell	Remazol Black B	74.6 mg/g	[36]
Cotton plant waste stalk	Remazol Black B	35.7 mg/g	[37]
Cotton plant waste hull	Remazol Black B	50.9 mg/g	[37]
Rhizopus arrhizus	Remazol Black B	588.2 mg/g	[38]
U. lactuca derived biochar	Remazol Black B	221.67 mg/g	Present study
U. reticulata derived biochar	Remazol Black B	201.31 mg/g	Present study
C. scalpelliformis derived biochar	Remazol Black B	159.10 mg/g	Present study
Trametes pubescens	Remazol Brilliant Blue R	133.33 mg/g	[39]
Bone char	Remazol Brilliant Blue R	20.66 mg/g	[40]
Activated carbon from industrial laundry sewage sludge	Remazol Brilliant Blue R	33.47 mg/g	[41]
Immobilized active *Scenedesmus quadricauda*	Remazol Brilliant Blue R	68 mg/g	[42]
Inactivated *Scenedesmus quadricauda*	Remazol Brilliant Blue R	95.2 mg/g	[42]
U. lactuca derived biochar	Remazol Brilliant Blue R	182.85 mg/g	Present study
U. reticulata derived biochar	Remazol Brilliant Blue R	170.73 mg/g	Present study
C. scalpelliformis derived biochar	Remazol Brilliant Blue R	129.18 mg/g	Present study
U. lactuca derived biochar	Remazol Brilliant Violet 5R	194.56 mg/g	Present study
U. reticulata derived biochar	Remazol Brilliant Violet 5R	186.32 mg/g	Present study
C. scalpelliformis derived biochar	Remazol Brilliant Violet 5R	140.12 mg/g	Present study

Table 3
Thermodynamic study for the adsorption of remazol dyes by *U. lactuca* at different temperatures

Dye	Temperature (K)	K_L (L/mol)	$\Delta G°$ (kJ/mol)	$\Delta H°$ (kJ/mol)	$\Delta S°$ (J/mol/K)
RBB	293	11,848.96	–22.85	7.65	70.75
	303	17,938.52	–24.68		
	313	14,385.21	–24.92		
RBV5R	293	13,766.85	–23.22	19.24	88.18
	303	23,074.31	–25.31		
	313	22,679.46	–26.10		
RBO3R	293	16,627.8	–23.68	33.91	139.59
	303	31,693.89	–26.11		
	313	40,306.53	–27.60		
RBBR	293	14,321.65	–23.31	7.65	76.57
	303	29,551.05	–25.93		
	313	21,288.36	–25.94		

results, it is evident that the negative value of $\Delta G°$ indicates that the reaction is spontaneous. The positive value of $\Delta H°$ indicates that the reaction is endothermic. A positive value of $\Delta S°$ reflects the adsorbent's affinity to the adsorbed species. Additionally, the positive value of $\Delta S°$ suggests increased randomness at the solid/liquid interface with some adsorbent and adsorbent structural changes. The adsorbed solvent molecules, which are displaced by the adsorbed species, gain more translational entropy than the adsorbed ions/molecules are lost, thus enabling the prevalence of random thermodynamics in the system. A positive value of $\Delta S°$ suggests that the adsorption process involves a dissociative mechanism [26]. From the results, it evident that the reactions are spontaneous at all the temperatures. Similarly, for *Ulva reticulata* and *Caulerpa scalpelliformis* reactions are spontaneous at all temperatures [25,33].

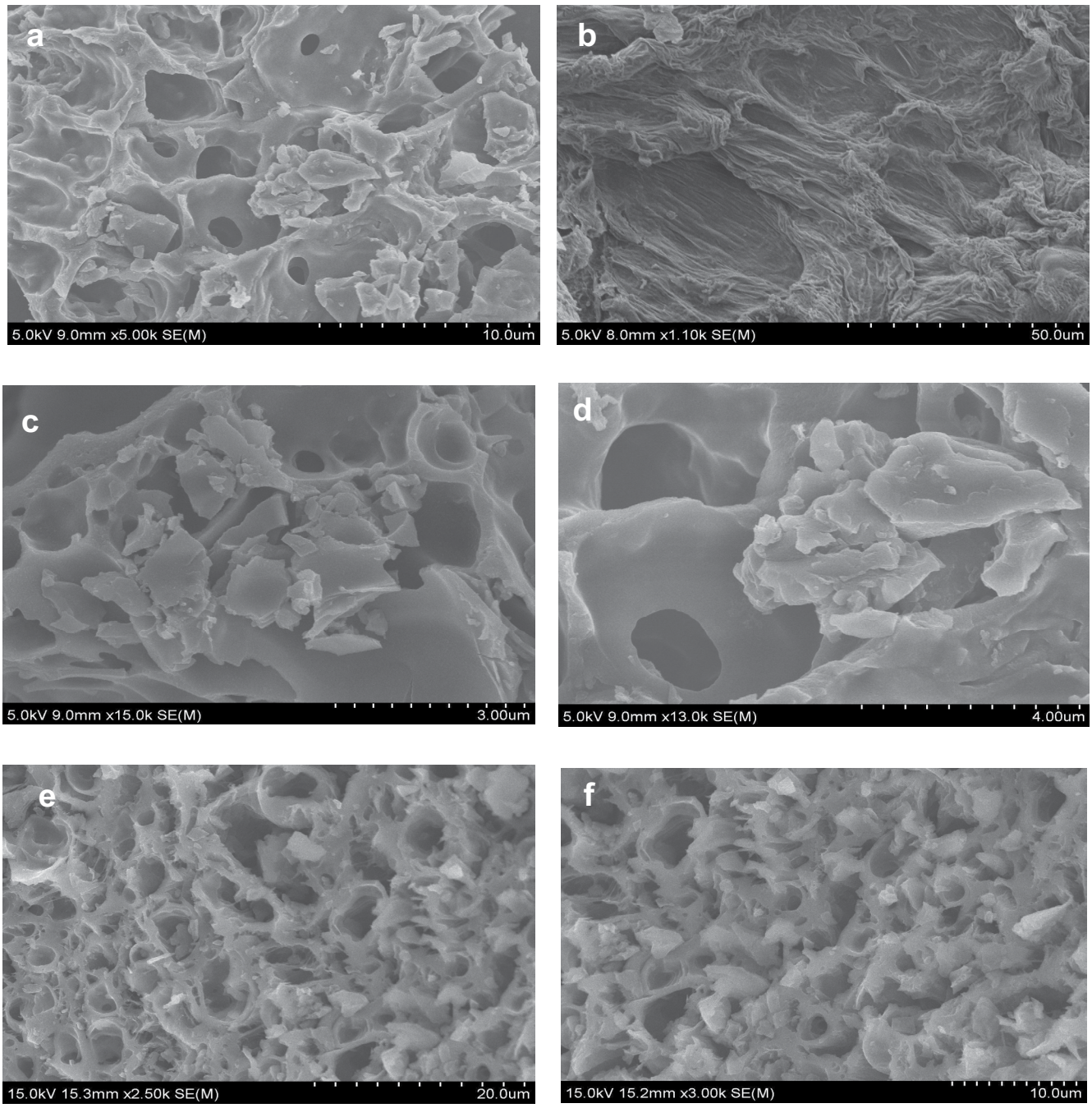

Fig. 7. Scanning electron micrographs of *U. lactuca* (a), *U. lactuca* derived biochar (b), RBB loaded biochar (c), RBV5R loaded biochar (d), RBO3R loaded biochar (e) and RBBR loaded biochar (f) [43].

3.9. Characterization of biochar

From Figs. 7–9 the biochar surface is found to have uneven pores. The green seaweeds which have been used for the study consist of Ulva which is rich in carboxyl, sulfate and phosphate sites. This will increase the binding nature of the biochar since it is an anionic polyelectrolyte. From the SEM image, it is evident that the biochar surface after the batch experiments is found to be smooth and which indicates that the impurities present on the surface are deteriorated.

In addition to the SEM analysis, FT-IR is carried out to know the nature of the binding sites. Fig. 10 shows the different spectra of three marine seaweeds. For example, the FT-IR spectra of biochar derived from *U. lactuca* pointed out the presence of strong bands at 1,072 (C–O [alcohol] band), 1,411 (C=O, symmetric), 1,628 (C=O stretch of COOH, asymmetric), 2,914 (C–H stretch) and 3,427 (–NH, –OH stretching). For instance, the FT-IR spectrum of RBB sorbed biochar exhibited major shifts of bands at 1,079 (C–O [alcohol] band),

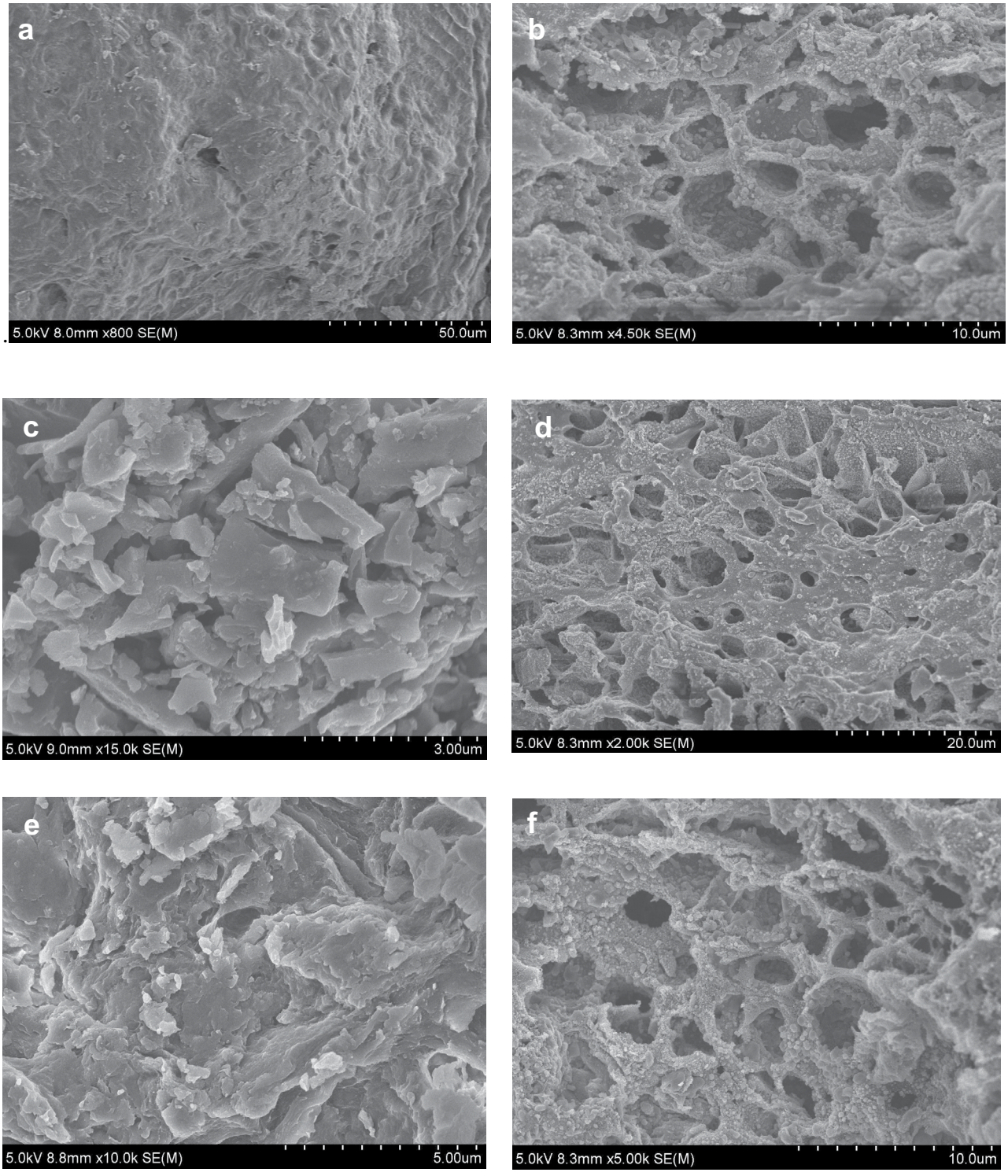

Fig. 8. Scanning electron micrographs of *U. reticulata* (a), *U. reticulata* derived biochar (b), RBB loaded biochar (c), RBV5R loaded biochar (d), RBO3R loaded biochar (e) and RBBR loaded biochar (f) [43].

1,417 (C=O, symmetric), 1,624 (C=O stretch of COOH, asymmetric), 2,927 (C–H stretch) and 3,474 (–NH, –OH stretching). So, there is a change in the biochar when it is loaded with the remazol dyes. This may be due to the exchange of the ions between the remazol dyes and the biochar. Hence, the FT-IR data revealed the involvement of numerous functional groups on the biochar matrix for the binding of remazol dyes.

Analyzing the elementary profile of green marine seaweeds based biochar (ultimate analysis), it is revealed that

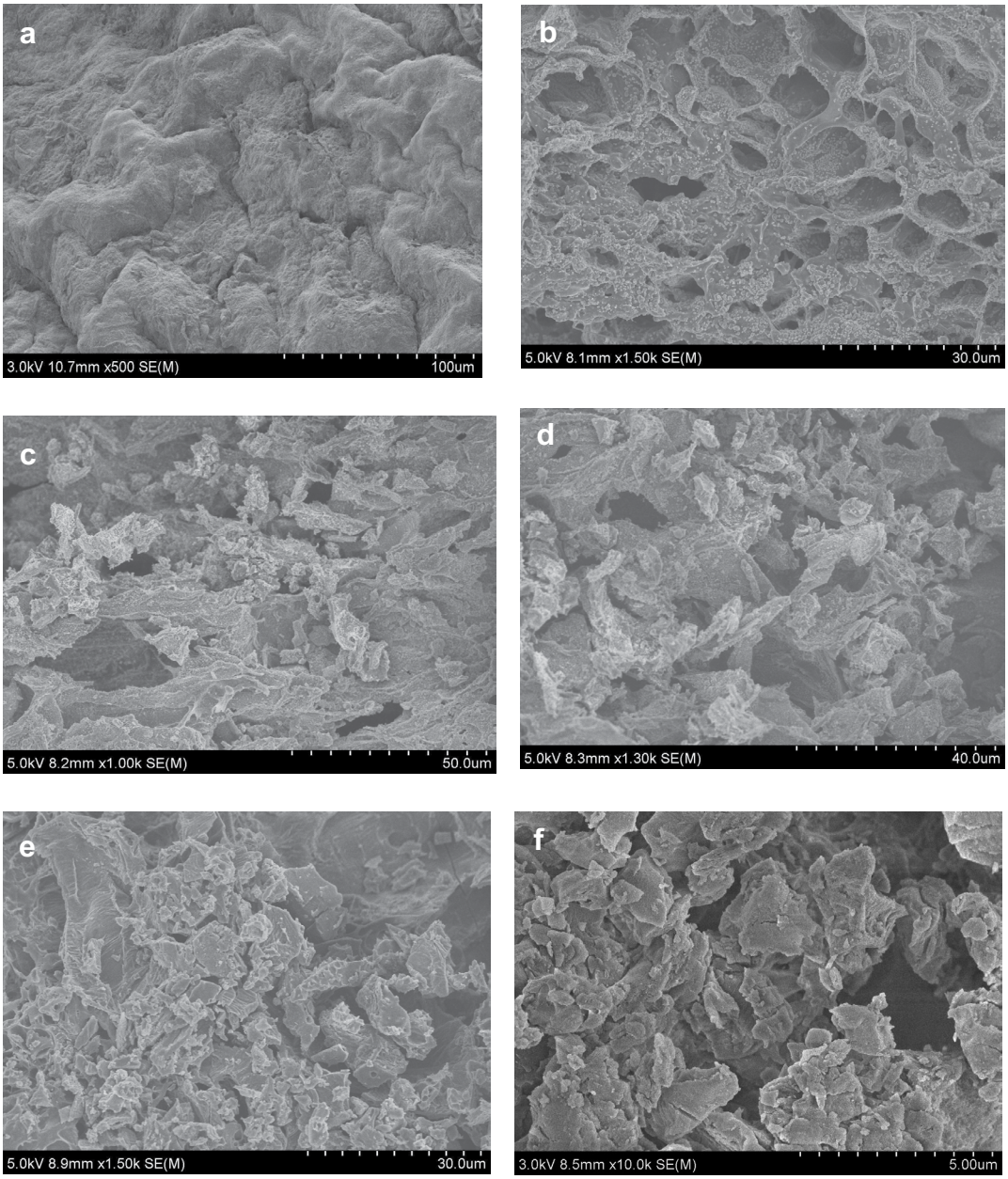

Fig. 9. Scanning electron micrographs of *C. scalpelliformis* (a), *C. scalpelliformis* derived biochar (b), RBB loaded biochar (c), RBV5R loaded biochar (d), RBO3R loaded biochar(e) and RBBR loaded biochar (f) [43].

the increase in temperature decreased the biochar yield. The maximum carbon content of 34.2% is attained at a temperature of 300°C for *U. lactuca* derived biochar, whereas carbon content of 27.6% is attained at a temperature of 500°C. The same significance is observed for *Ulva reticulata* and *Caulerpa scalpelliformis*. So, from the results obtained from elemental analyzer, it is evident that increase in temperature from 300°C to 500°C has decreased the carbon yield and it is in accordance with the results obtained from pyrolysis experiments. From Table 3 it is also evident that the increase in temperature decreased H (%), O (%), N (%) and S (%) content. So, the pyrolysis temperature of 300°C is considered as an optimum temperature for the maximum biochar yield.

3.10. Chemometric analysis

3.10.1. Principle component analysis

The scree plot of principle component analysis is shown in Fig. 11. From the figure, it can be perceived that the first principle component has eigenvalue 25.85 and accounts for 95.7% of the total variance. On the other hand, the second and third principle components have eigenvalues 0.613 and 0.256, respectively. They account for 2.3% and 0.9% of data variability. Overall, it is concluded that the first two and the first three principal components represent 98% and 98.9%, respectively, of the total data variability. Thus, it is possible to capture most of the data structure in two or three underlying

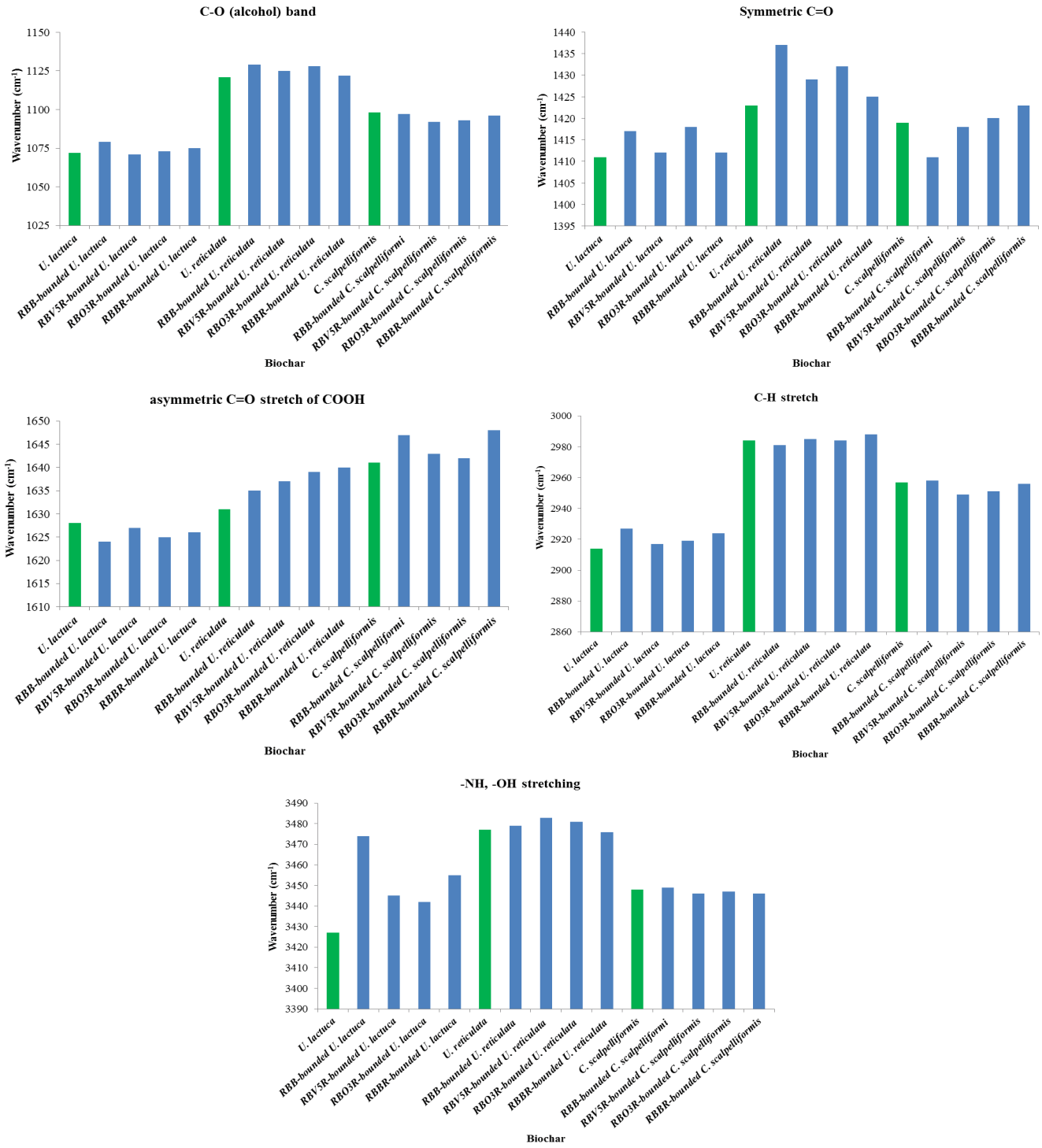

Fig. 10. FT-IR spectra showing strong bands existence for three green marine seaweeds.

dimensions. The remaining principal components represent a very small proportion of the variability (about 0.9%) and are unlikely to be significant.

In addition to the scree plot, the score plot of principle component analysis is shown in Fig. 11. It can be seen from Fig. 12 that *C. scalpelliformis* RBBR, *C. scalpelliformis* RBO3R and *C. scalpelliformis* RBV5R formed a cluster in the first quadrant. Thus, it can be concluded that *C. scalpelliformis* derived biochar shows almost similar sorption capability in treating RBBR, RBO3R and RBV5R dyes. This trend exhibits that uniform porosity and the presence of various functional groups such as –OH and =C–H on the surface of *C. scalpelliformis* derived biochar presented active sorption sites to treat different dyes. A similar observation was reported

Table 3
Ultimate analysis of biochar derived at different pyrolysis temperatures

Biochar	Temperature (°C)	C (%)	H (%)	O (%)	N (%)	S (%)
Ulva lactuca-derived biochar	300	34.2 ± 1.2	4.2 ± 0.2	25.9 ± 0.8	5.9 ± 0.2	6.9 ± 0.8
	350	32.1 ± 1.3	3.9 ± 0.3	25.5 ± 0.9	5.3 ± 0.2	7.2 ± 0.2
	400	30.6 ± 1.1	3.2 ± 0.2	24.6 ± 1.2	4.9 ± 0.1	7.6 ± 0.2
	450	28.4 ± 0.9	2.8 ± 0.1	24.1 ± 1.3	4.5 ± 0.1	7.8 ± 0.1
	500	27.6 ± 0.4	2.2 ± 0.1	18.5 ± 0.6	4.7 ± 0.1	7.2 ± 0.2
Ulva reticulata-derived biochar	300	31.2 ± 1.2	3.6 ± 0.2	23.9 ± 0.8	4.9 ± 0.2	5.9 ± 0.8
	350	29.1 ± 1.3	3.2 ± 0.3	23.5 ± 0.9	4.3 ± 0.2	6.2 ± 0.2
	400	27.6 ± 1.1	2.9 ± 0.2	22.6 ± 1.2	3.9 ± 0.1	6.6 ± 0.2
	450	25.4 ± 0.9	2.3 ± 0.1	22.1 ± 1.3	3.5 ± 0.1	6.8 ± 0.1
	500	24.6 ± 0.4	1.5 ± 0.1	16.5 ± 0.6	2.7 ± 0.1	6.2 ± 0.2
Caulerpa scalpelliformis-derived biochar	300	29.2 ± 1.2	3.2 ± 0.2	22.9 ± 0.8	4.7 ± 0.2	5.7 ± 0.8
	350	27.1 ± 1.3	3.0 ± 0.3	22.5 ± 0.9	4.1 ± 0.2	6.0 ± 0.2
	400	25.6 ± 1.1	2.7 ± 0.2	21.6 ± 1.2	3.7 ± 0.1	6.4 ± 0.2
	450	23.4 ± 0.9	2.1 ± 0.1	21.1 ± 1.3	3.2 ± 0.1	6.6 ± 0.1
	500	22.6 ± 0.4	1.2 ± 0.1	15.5 ± 0.6	2.5 ± 0.1	6.0 ± 0.2

Mean ± SD.

Table 4
Similarity and distance level of clusters

Step	Number of clusters	Similarity level	Distance level	Clusters joined		New cluster	No of observations in new clusters
1	11	99.9217	0.0015661	11	12	11	2
2	10	99.8946	0.0021078	2	4	2	2
3	9	99.8696	0.0026085	7	8	7	2
4	8	99.8204	0.0035928	5	6	5	2
5	7	99.7938	0.0041235	5	11	5	4
6	6	99.7378	0.0052446	5	7	5	6
7	5	99.7110	0.0057800	5	9	5	7
8	4	99.7090	0.0058191	2	3	2	3
9	3	99.6629	0.0067424	5	10	5	8
10	2	99.6379	0.0072426	2	5	2	11

in the work conducted by Yarui et al. [44]. From the score plot, it can also be seen that *U. reticulata* RBO3R and *U. lactuca* RBO3R formed a close clustering. This trend discloses that almost similar sorption performance could be exhibited by *U. reticulata* and *U. lactuca* derived biochar in treating RBO3R. In addition to RBO3R, these two seaweed-derived biochar exhibit analogous performance in treating Remazol dyes such as RBBR and RBV5R under different operating conditions. Moreover, it can be seen from the plot that all three seaweed derived biochar demonstrate comparable performance in treating RBB. One possible reason for this trend could be the presence of a strong symmetric C=O band in all seaweed derived biochars.

3.10.2. Cluster analysis

The tree diagram of cluster analysis is shown in Fig. 13. It can be seen from the tree diagram (Fig. 13) that different groups are formed by amalgamation at each step and their similarity level. Also, the similarity level and distance level of each cluster joined are depicted in Table 4. This plot was created using a final partition of three clusters. The first cluster (far left) is composed only *C. scalpelliformis* RBB. The second cluster, directly to the right is composed of *C. scalpelliformis* RBV5R, *C. scalpelliformis* RBO3R and *C. scalpelliformis* RBBR. The third and last cluster on far right cluster is composed *U. lactuca* RBB, *U. lactuca* RBV5R, *U. lactuca* RBO3R, *U. lactuca* RBBR, *U. reticulata* RBB *U. reticulata* RBV5R, *U. reticulata* RBO3R and *U. reticulata* RBBR. Overall, two observations were made from the cluster analysis. The first observation is that *C. scalpelliformis* derived biochar illustrates comparable adsorptive capability in treating three out of four remazol dyes chosen. The second observation is that *U. reticulata* and *U. lactuca* exhibit almost similar adsorptive capability in treating all four chosen dyes.

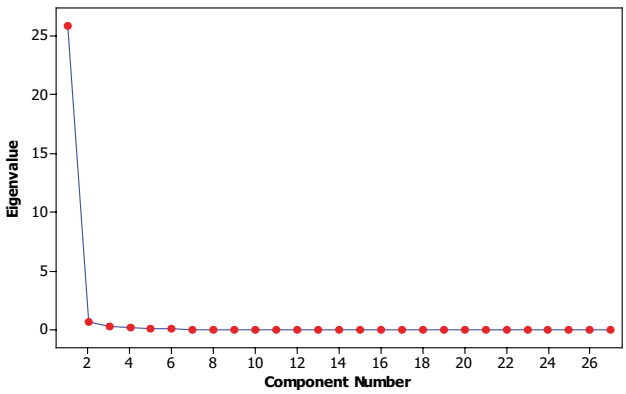

Fig. 11. Scree plot of principal component analysis.

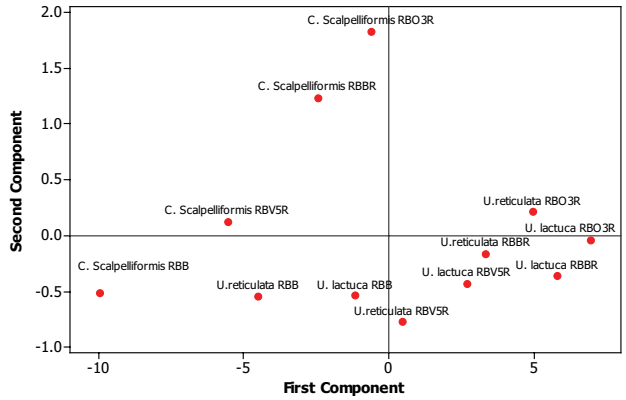

Fig. 12. Score plot of principle component analysis based on the different biochar dosage, pH, temperature and concentration for the removal of different dyes.

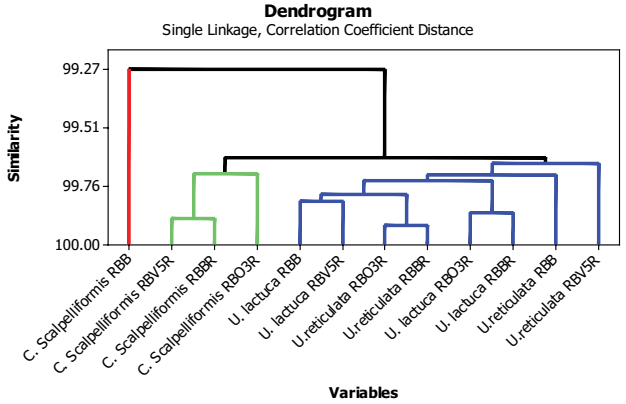

Fig. 13. Dendrogram obtained from cluster analysis based on the different biochar dosage, pH, temperature and concentration for the removal of different dyes.

4. Conclusions

In the present research, biochar derived from three different marine seaweeds through pyrolysis was found to be effective at the temperature of 300°C. Of the different experimental parameters studied, pH is found to be the main parameter that affects the removal efficiency of dyes. A maximum dye removal % is achieved at a pH of 1.75. Similarly, it is concluded that the optimum biochar dosage, temperature and initial concentration are 2 g/L, 30°C, 0.05 mmol/L. The experimental results indicated that *Ulva lactuca* derived biochar showed that maximum dye removal % for all four types of remazol dyes. Similarly, Remazol Brilliant Orange 3 R showed the maximum removal % with all three types of biochar. Through chemometric analysis, it is concluded that *U. reticulata* and *U. lactuca* show signs of similar adsorptive capability in treating all four chosen dyes when compared with *C. scalpelliformis*.

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