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Preparation of effective green sorbents using *O. Princeps* alga biomass with different composition of amine groups: Comparison to adsorption performances for removal of a model acid dye

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ABSTRACT

In the present study, various green biosorbents based on *Oscillatoria princeps* biomass were developed for removal of dyes from wastewaters. For this, alga biomass was modified with three different amine containing ligands [i.e., tetraethylene tetramine (TETA), *para*-amino benzamidine (PAB) and polydopamine (PDA)]. These modified algal biomasses were used for removal of Reactive Red 120 dye (RR-120). The prepared biosorbents were characterized using Fourier transform infrared spectroscopy, zeta seizer, and contact angles studies. The zeta potential values of the TETA, PAB and PDA modified biosorbents were varied from 42.3 to −18.4 mV, 36.7 to −14.8 mV and 30.7 to −12.6 mV, in the pH range of 2.0–11.0, respectively. Batch experiments were performed to determine the effect of operational parameters on the biosorption of RR-120 dye on the biosorbents (i.e., pH: 2.0–8.0, biosorbent dose: 0.1–1.0 g/L, initial dye concentration: 25–500 mg/L, temperature: 15–35 °C, and contact time: 0–120 min). The biosorption capacities of the native, TETA, PAB, and PDA modified algal biomasses for RR-120 dye were found to be 148.7, 687.1, 451.8, and 260.3 mg/g, respectively, at pH 3.0, at 25 °C in 120 min. These results showed that the biosorption of the RR-120 dye on the algal biomass preparations was achieved by hydrogen bonding, ion-exchange, electrostatic, and π-π interactions. The biosorption process of the RR-120 by algal biomasses was well described by the Langmuir isotherm model and pseudo-second-order kinetic model. The adsorption enthalpies for the biosorption of dye on the biomass preparations had been found to be between 21.5 and 90.3 kJ/mol. Furthermore, the modified algal biomasses displayed good regeneration capabilities, and the modification of the algal biomass with different ligands remarkably increased the RR-120 dye biosorption performances compared to native algal biomass.

1. Introduction

Natural or synthetic dyes have been used widely for coloring textile, leather, newspaper, cosmetics, plastic, and many foods [1–3]. Reactive dyes have been significantly employed in the textile industry that utilizes more than 10,000 diverse dyes and pigments. They are largely used in coloring cotton and other cellulose-based fibers. Reactive Red 120 is a polyaromatic complex dye and generally used for the dying of textiles. It could be easily attached to the textile fibers via nucleophilic substitution reaction between hydroxyl groups of cotton and chlorine groups of dye. The RR-120 dye is well-recognized because of their shining color, easy-application and water-fast characteristics.

The disposed wastewaters from these industries contain many colored compounds and most of them are toxic, mutagenic and even carcinogenic. Hence, these colored compounds should be removed from industrial wastewaters to prevent substantial environmental problems [4–10]. The mostly used removal methods are ion-exchange, chemical oxidation, membrane separation, and enzymatic or microbial biodegradation [11–16]. Since these approaches are frequently very expensive, necessitating large amounts of chemical reagents and energy involvement. Hence, there is a need for developed methods to eliminate dyes from wastewaters with low price, easy process, and simple maintenance. In the recent years, materials from biological origin have been proposed as potential alternative adsorbents for the removal of pollutants from aqueous medium [17–19]. As reported in the earlier studies, the biomasses have been achieved important credibility due to their biological nature, high performance, and low

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cost production for bioremediation of pollutants [19–22]. The algae can be unicellular or multicellular organisms. They are important ecologically and environmentally because they are responsible for the production of approximately 70% of the oxygen and organic matter in aquatic environments. Additionally, the living or nonliving algal biomasses have been reported as satisfactory biosorbents for the removal of pollutants [13–26]. Some important algal biomasses such as *Graesiella emmersonii*, *Spirulina platensis, Chlamydomonas reinhardtii*, and *Scenedesmus quadricauda* have been used as biosorbents for removal of pollutants from aqueous solution [27–29]. The algae cell-wall structures contain polysaccharides, proteins and lipid molecules with a large number of various functional groups. These major functional groups are amino, carboxyl, sulfate, phosphate and hydroxyl, and they are easily interacted with the pollutants and remove them from aqueous medium [19,24]. Also, modification of a biosorbent surface with different functional groups can improve the performance of biosorbent and increase biosorption capacity. A large number of algal, fungal, and microbial biomasses have been modified with various ligands for improvement of their adsorption capacities [13,17,19,24,30–35].

Hence, there is a requirement to develop novel biosorbents from the cheap and abundant biomass sources with enhanced biosorption capacity that display high performance to remove toxic dyes from wastewaters. As reported earlier, the active absorptive sites on the surface of biomasses could be improved by covalent attachment of functional groups. To the best of our knowledge, there has been no reports on the modification of *O. princeps* biomass with different chemical ligands for removal of toxic RR-120 dye from wastewater. The alga (i.e., *O. princeps*, *a Cyanobacteria, Family oscillatoriaceae*) was isolated from Mogan Lake in Ankara and chemically modified with three different ligands namely, tetraethylene tetramine, p-amino benzamidine, and poly (dopamine). *O. princeps* is an unbranched filamentous blue-green alga, living in lakes and freshwater ponds, which is an abundantly available sustainable biomass especially in Turkey, has been selected as the biomass for preparation of biosorbents. The modification of the algal biomass with the different ligands which could provide maximum biosorption capacity could give to increase adsorptive sites based on presenting functional amine groups.

In this work, for the first time we prepared chemically modified novel biosorbents from *O. princeps* biomass and their performance were compared to RR-120 dye removal efficiency analysis from an aqueous solution. Such type's biosorbents have the potential to adsorb dyes with high efficiency from the textile wastewater. The operating parameters were optimized including pH, adsorbent dose, contact time, temperature, and initial dye concentration. Influence of salt concentrations on biosorption performance of biosorbents was also considered. The equilibrium isotherms and kinetics and thermodynamic parameters were evaluated to understand the adsorption mechanism of RR-120 on the native, and TETA, PAB, and PDA modified algal biomasses. Furthermore, the presented work can propose a new strategy that will be applied to the other biomasses.

2. Materials and methods

2.1. Materials

p-Amino benzamidine (PAB), tetra ethylene tetramine (TETA), L-dopamine (L-DOPA), glutaraldehyde, Tris-HCl Glycerol, diiodamethane and Reactive Red 120 were obtained from Sigma-Aldrich Chemical Co. All the chemicals were of analytical grade and obtained from Merck AG (Darmstadt, Germany).

2.2. Cultivation and modification of Oscillatoria princeps biomass

The BG-11 medium consisted of the following ingredient in 1.0 L of distilled water: $NaNO_3$ (1.5 g), K_2HPO_4 (0.04 g), $MgSO_4{\cdot}7H_2O$ (0.075 g), $CaCl_2{\cdot}2H_2O$ (0.036 g), Citric acid (0.006 g), Ferric ammonium citrate (0.006), EDTA (0.001 g, sodium salt), Na_2CO_3 (0.02 g). Trace metals solution was prepared from the following ingredients in distilled water g/L: H_3BO_3 (2.86 g), $MnCl_2{\cdot}4H_2O$ (1.81 g), $ZnSO_4{\cdot}7H_2O$ (0.222 g), $NaMoO_4{\cdot}2H_2O$ (0.39 g), $CuSO_4{\cdot}5H_2O$ (0.079) and $Co(NO_3)_2{\cdot}6H_2O$ (0.005 g). A 1.0 mL of this solution was added to the BG11 medium (1.0 L) and sterilized at 121 °C for 15 min. The pH was adjusted to 6.8 ± 0.2 after sterilization. It was used for cultivation of *O. princeps* cells, and as previously reported [25]. *O. princeps Vaucher ex Gomont* is an unbranched filamentous blue-green algae and belong to the Cyanobacteria division. *O. princeps* biomass sample was collected from the Mogan Lake (Ankara Province, Turkey), and sequentially washed with tap water and with deionized water for the removal of impurities. The pure culture of *O. princeps* alga was isolated from the above cleaned samples by micromanipulation method [25]. The isolated algal cells were inoculated in 500 mL BG-11 medium at pH 6.8 ± 0.2 under sterile conditions and incubated at 23 ± 2 °C, 16 h of light and 8 h of dark period [25]. Sterile fresh air was introduced to the culture medium using an air pump. After 14 days, algal biomass was harvested by filtration and dried overnight under reduced pressure at 40 °C. Thereafter, it was referred as the native algal biomass. For activation of *O. princeps* biomass, a 3.0 g of algal biomass was transferred in Tris–HCl buffer solution (100 mL, 50 mM, pH 8.0) and continuously stirred at 100 rpm at 25 °C for 30 min. Then, glutaraldehyde (GA) solution (75 mL, 1.0%) was added in the medium as a bi-functional agent for attachment of the selected ligand molecules. The activation and cross-linking reaction were carried out at 50 °C for 4.0 h in a water bath. After this period, the algal biomass was filtered and washed with deionized water. Approximately 1.0 g of GA activated *O. princeps* biomass was transferred into 100 mL of ethanol:water mixture (40:60, v/v ratio) containing 50 mg/mL of PAB or TETA ligand. The reaction was carried out at 45 °C for 6.0 h, after this period, the PAB or TETA modified biomasses were washed several times with deionized water, and dried under reduced pressure at 40 °C for 18 h. Some of the algal biomass was also modified by coating with poly (dopamine) as described earlier [36,37]. The modification reaction protocols of the *O. princeps* biomass with PAB, TETA and PDA are presented in Fig. 1. The weight gain (WG) was designed by using percent increase in weight of the algal biomass preparations:

$$WG(\%) = (W_f - W_i)/W_i \times 100 \quad (1)$$

where W_i and W_f are the weights of the algal biomass preparation before and after modification with different ligands, respectively.

2.3. Characterization of the biomass preparations

The surface functional groups of the native and modified algal biomasses were determined using Nicolet TM ISTM 50 FTIR spectrometer (Thermo Fisher Scientific, USA). The spectra were conducted between 4000 cm^{-1} and 500 cm^{-1} with 16 scan rate and with a resolution of 4.

The zeta potential of the native and modified algal biomass preparations were analyzed with a Zeta-sizer (Nano ZS, Malvern Instruments Ltd.) in different pH values. For the ξ-potential measurement, each algal biomass preparation (about 0.1 g) was added in purified water (100 mL) and mixed magnetically for 1.0 h, then, the medium pH was adjusted with 0.1 mol/L NaOH or HCl solutions. Zeta potential measurements were achieved in each condi-

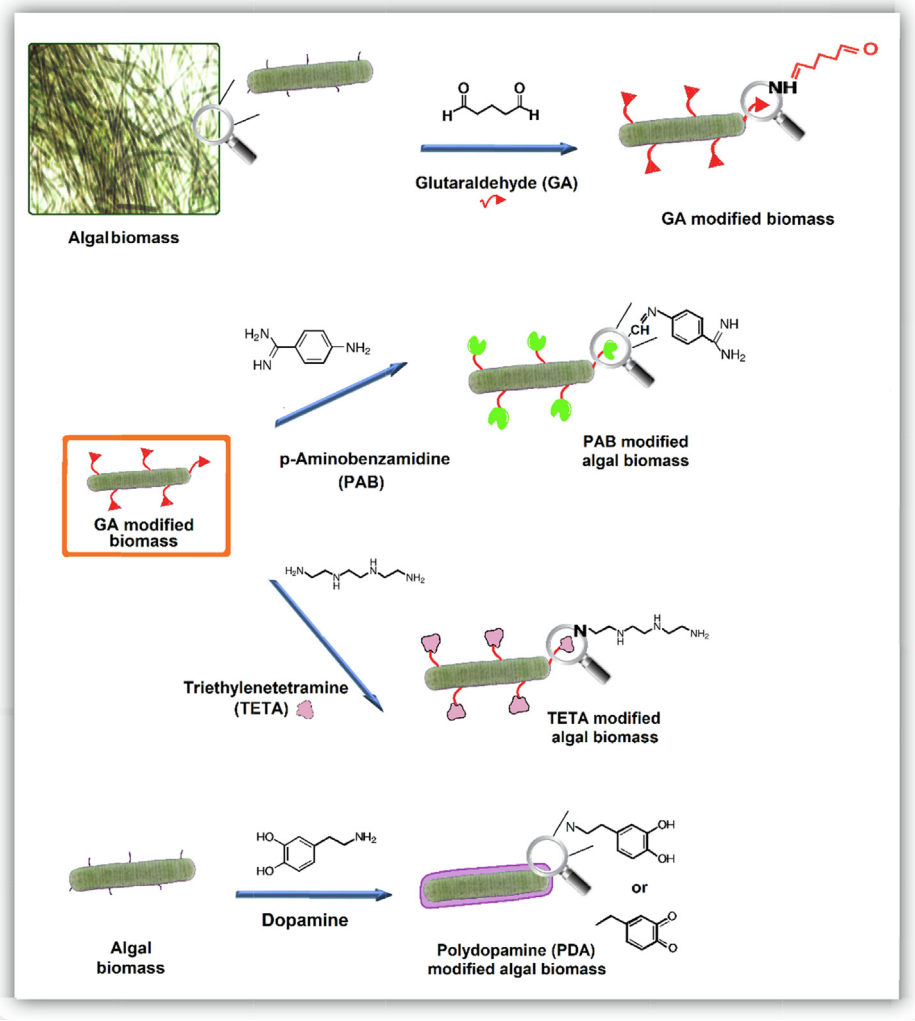

Fig. 1. The schematic representation of the modification protocols of the native algal biomass with different ligands.

tion as three measurement replicates to achieve a reliable data basis for values.

The surface area, average pore size and distribution were determined by the Brunauer-Emmet-Teller (BET) device (Micromeritics, Tristar II, USA). Analyzes were performed by taking approximately 0.2 g from each algal sample and each test was repeated at least three times. The moisture in the samples was removed by degassing device at 70 °C for 6.0 h under reduced pressure. The measurements were carried out in the sample cells placed in liquid nitrogen. The measuring principle is based on the adsorption of nitrogen gas passed over the algal biomasses. The calculation of the adsorbed amount of nitrogen gas was calculated from the changing nitrogen gas pressure. The specific surface areas of the native and modified algal biomasses were measured to determine change in their surface characteristics after modification reaction.

The contact angle values of the native and modified algal biomass preparations were determined using three different test liquids (i.e., water, glycerol and diiodomethane). Digital optical contact angle meter was used for studies of contact angle values of the algal biomasses (Phoenix 150, Surface Electro Optics, Korea). The sessile drop was formed by depositing the liquid from the above using a manual micro-syringe on the sample surface. Both the left- and right-contact angles and drop dimension parameters were automatically calculated from the digitalized image. The contact angles for both sides of each drop were measured between the liquid and samples. The measurements were the averages of 10 contact angles at least operated on three samples. The surface free energy parameters of the native and modified algal biomass preparations and their dye-laden equivalent preparations were calculated using the contact angle data of the probe liquids. The results were analyzed according to van Oss method using following equations [38,39]:

$$\gamma^{TOT} = \gamma^{LW} + \gamma^{AB} \tag{2}$$

The total surface free energy, γ^{TOT}, and where γ^{LW} is the dispersive component of the surface free energy related with Lifshitz–van der Walls interaction, and γ^{AB} designated such acid–base interactions as hydrogen bonding, and γ + and γ − refer to proton and electron donating character. The surface energy parameters s is:

$$(1 + cos\ \theta)\gamma_l = 2\left[\left(\gamma_s^{LW}\gamma_l^{LW}\right)^{1/2} + \left(\gamma_s^{+}\gamma_l^{-}\right)^{1/2} + \left(\gamma_s^{-}\gamma_l^{+}\right)^{1/2}\right] \tag{3}$$

The known parameter values of three liquids and their contact angles on algal biomass preparations were used and the given method equation was solved using Phoenix 150, Surface Electro Optics, software package operated under Windows 7.

2.4. Adsorption studies

Stock solution of the dye was prepared by dissolving of RR-120 dye (1.0 g) in distilled water (1.0 L). The biosorption of RR-120 dye

from aqueous medium onto the native, TETA, PAB, and PDA modified algal biomasses was studied in a batch system. In each set experiment, RR-120 dye solution (50 mL) with known concentration was transferred into a flaks containing 20 mg algal sample, placed on a rotary shaker and operated at 100 rpm at 25 °C for 2.0 h. The effect of pH on the sorption efficiency was studied between pH 2.0 and 8.0. The pH of the medium was adjusted with hydrochloride acid or sodium hydroxide (each 100 mmol/L). The effect of initial dye concentration on the biosorption efficiency of the biosorbents was determined in the range of 25–500 mg dye/L. Effect of biosorbent amount on the biosorption performance of the native and modified algal biomass preparations was studied by varying of the amount of sorbent in the solution between 0.1 and 1.0 g/L. The impact of ionic strength on the biosorption efficacy of the algal biomass preparations was studied by changing salt concentrations between 0.0 and 1.0 mol/L in the medium. The effect of temperature on the RR-120 dye biosorption on the algal biomass preparations was studied at three different temperatures (i.e., 15, 25 and 35 °C). The concentrations of RR-120 in the biosorption media were determined at 535 nm by using UV/Vis spectrophotometer (PG Instruments Ltd., Model T80 +; PRC).

Calculation of the adsorption capacity of the tested sorbent at any time (q_t, mg/g) and equilibrium (q_e, mg/g) was realized using the following equations:

$$q_t = (C_0 - C_t/m) \times V \quad (4)$$

$$q_e = C_0 - C_e/m \times V \quad (5)$$

where C_t and C_e are the concentration of RR-120 dye (mg/L) at any and equilibrium time, respectively. The "m" and "V" are the mass of adsorbent (g) and volume of the biosorption medium (L), respectively.

2.5. Desorption and reusability studies

As presented above, desorption and reusability studies were realized in 100 mL of dye solution containing 40 mg dry algal biomasses. For desorption studies, the adsorbed dye was eluted from algal biomass sample using 20 mmol/L NaOH solution containing 0.5 mol/L NaCl. In each reusability run, the algal biomasses were transferred into a fresh RR-120 dye solution, and separated from the medium after 120 min by filtration. These cycles were repeated seven times with the same algal biomass preparation. After each run of sorption and desorption, the algal biomasses were washed with milli-Q water.

3. Results and discussion

3.1. Characterization of the sorbents

In this work, the biomass of *O. princeps* was modified with three different ligands and used as a novel adsorbent for removal of a model pollutant. These modified algal based biosorbents have some important properties such as their non-toxicity, high surface area and biodegradability compared to many commercial adsorbents. The algal biomass was modified with three different ligands namely, p-amino benzamidine, tetra ethylene tetramine, poly (dopamine) having various functional amine groups (Fig. 1). Some algal biomass surfaces were activated with bifunctional glutaraldehyde, the activation reaction was realized to achieve covalent attachment of the TETA and PAB ligands molecules on the biomass surfaces. One-the proximal aldehyde group in each glutaraldehyde molecule was linked to an amine group on the surface of the algal biomass via Schiff base reaction under alkaline condition. The other free aldehyde group of each glutaraldehyde molecule was used for covalent coupling of the amine groups of the TETA or PAB ligand molecules. Moreover, the algal biomass surface was also functionalized with poly (dopamine) coating. In this method, the deposited dopamine monomer on the algal biomass surface undergoes oxidation and self-polymerization in alkaline medium at around pH 8.0 with air as an oxygen source. This self-polymerization reaction of dopamine is extremely facile and does not require any complicated steps. The poly (dopamine) coting on the algal biomass surface could produce many primary amine groups, π-cation interactions, catechol functionalities and aromatic rings.

These ligands could not only increase the number functional groups on the surface of the algal biomass and also provide more available sites for better sorption of pollutants. Furthermore, the algal biomasses due to their biological origin increase the bioactivity of the environment and reduces the toxicity [25]. Therefore, it is very important to use safe materials, especially of biological origin to design novel adsorbents, otherwise, they enter the water environment and cause secondary pollution. Moreover, the surface of the algal biomasses, have many functional groups such as carboxyl, amino, phosphate, and hydroxyl groups. These functional groups can form ion-exchange, electrostatic, H-bonding, and π-π interactions with the target pollutants. The surfaces of the native and modified algal biomasses were well characterized to explain binding properties to the selected model dye.

3.1.1. The surface characteristics of the native and modified O. Princeps

For the determination of the existence functional groups on the native algal biomass and follow the changes after modification, ATR-FTIR spectra of the native and modified algal biomasses were obtained. The native and modified algal biomasses spectra had generally identical principal peaks, whereas their intensities are different. For native algal biomass (Figure S1), the strong peak at around 3400 cm^{-1} was designated as –OH and/or $–NH_2$ groups [40,41]. The peak at 2921 cm^{-1} could be produced by –CH stretching vibration of the alkyl chains. The band at showed at 1653 cm^{-1} could be due to the $–NH_2$ primary amide groups. Whereas the peak at 1531 cm^{-1} was resulted from –NH deformation and implies the presence of a secondary amine group. The peaks at 1390 cm^{-1} and 1079 cm^{-1} could be assigned for C–O bond in carboxyl groups and C–OH stretch of hydroxyl groups, respectively. The peak observed at 1017 cm^{-1} could be due the carbohydrate units (C-O-C) of polysaccharides. Finally, the observed band at 513 cm^{-1} could be due to the C–N–C scissoring and it is merely originated from the protein structure. Figure S1 shows that the difference of functional groups after modification of algal biomass with tetra ethylene tetramine ligand. The broad band at around 3600 and 3300 cm^{-1} was corresponded to the stretching vibrations of O–H and N–H groups. It was highly expanded after modification with TETA ligand compared to the native algal biomass. The symmetrical and asymmetrical stretching vibration peak of –CH, $–CH_2$, and $–CH_3$ groups were superimposed and observed at 2964 cm^{-1}. The stretching vibration and asymmetric stretching vibration peak of $–NH_2$ were observed at 1545 and 1624 cm^{-1}, respectively. Moreover, the bands at between 1000 and 1350 cm^{-1} could be consist of the stretching vibrations of C–O and C–N heterocycles. The additional new bands were observed on the PAB ligand modified algal biomass such as the aromatic rings stretching vibration band (C···C) at 1446 cm^{-1} [42,43] Furthermore, the characteristic band of the PAB ligand related with –NH stretching vibration between 3350 and 3400 cm^{-1} was more broadened after modification with p-amino-benzamidine ligand, and the band related with $–NH_2$ primary amide groups was seen at 1653 cm^{-1}. The FTIR spectrum for the PDA grafted algal biomass is presented in Figure S1. An expanded band for –NH and –OH was observed at between 3500 and 3300 cm^{-1}. The peak at 1629 cm^{-1} could be assigned for the

stretching vibration of the aromatic ring and overlapped bending vibration of –NH group. The NH_2 stretching vibration peak was observed at 1540 cm^{-1}. The peak at 1031 cm^{-1} could be also assigned for –NH vibration of the amide groups. Furthermore, the bands in the area of 1000–1350 cm^{-1} could be comprised of the stretching vibrations of C–O and C–N heterocycles. These results showed that various functional groups such as amine, hydroxyl, carboxyl and carbonyl groups played significant roles in the sorption process of RR-120.

The zeta (ζ) potential plots at different pH values can offer evidence about the surface charge properties of the sorbents. The positive and/or negative values of ζ potential relied on the functional moieties on the adsorbent surface, and the pH value of the solution. For algal biomass preparations, the surface functional groups primarily on the surface are amine, amide, imidazole, hydroxyl, carboxyl, sulfate, and phosphate. These functional groups on the surface of the algal cells could be protonated or deprotonated, consequential to solution pH, and the whole surface charge is zero at the point of zero charges. The zeta potential versus pH plots for the native and modified algal biomasses (i.e., TETA, PAB and PDA modified) were determined using a zeta sizer. The zeta potentials data of the native and TETA, PAB and PDA modified algal biomasses as a function of medium pH (i.e., in the range of 2.0–11.0) are presented in Fig. 2. The zeta potential plot for the native algal biomass displayed weak acidic surface characteristic as observed for the other biomasses. The zeta potential values of all the tested sorbents declined with increasing the medium pH. As can be seen from Fig. 2 the zeta potential value of the native algal biomass was negatively charged within the pH range from 3.0 to 11.0 and the zero potential value was found to be 3.0. Hence, in the pH range 2.0–3.0, the ionization degree of the surface functional groups of algae cells in terms of zeta potential was lesser than the other pH values. Consequently, the sorption capacity of the native algal biomass was lower compared to other tested pH values. The native algal biomass exhibited a positive surface charge where the pH of the medium was less than 3.0. Additionally, when the pH value was less than 3.0, a reduction in the sorption capacity was observed and an initial solution pH of 3.0 was evaluated as the optimum value, and it was used in all the rest experiments. Generally, amine group modified algal biomasses present a net positive charge on their surfaces. Therefore, zeta potential analyzes of amine groups modified algal biomass showed positive surface charge over a wider pH range (up to pH 8.0) compared to native algal biomass. The zero-point zeta potential values of the TETA, PAB and PDA modified algal biomasses were found to be approximately 8.0, 7.0 and 6.5, respectively. The charge densities of the TETA, PAB and PDA in the studied pH range were varied from 42.3 to −18.4 mV, 36.7 to −14.8 mV and 30.7 to −12.6 mV, respectively. Zeta- potential values of the TETA, PAB and PDA modified algal biomasses were found to be higher than those of the native algal biomass. These observations are in agreement with those achieved by FTIR investigations. Sorption of solute on the solid surface is driven generally by van der Waals and electrostatic interactions.

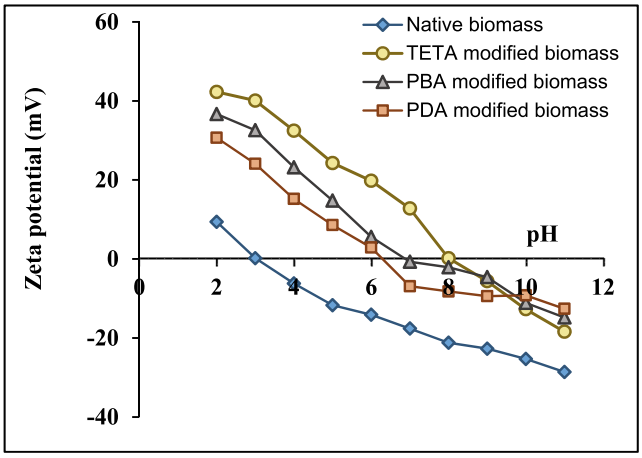

Fig. 2. The zeta potentials data of the native and TETA, PAB and PDA modified algal biomasses as a function of medium pH. Experimental conditions: amount of biosorbent 1.0 g/L; mixing time, 1.0 h. Zeta potential measurements were achieved in each condition as three measurement replicates to achieve a reliable data basis for values.

The surface area and pore size of the native, and TETA, PAB and PDA modified algal biomass preparations were measured and calculated using BET method. The BET analyses data of the native and modified algal biomasses are presented in Table 1. The surface area of the native and TETA, PAB and PDA modified algal biomass was found to be 2.12, 1.73, 1.86, and 1.48 m^2/g, respectively. According to these observations, the native algal biomass displayed higher surface area and pore volume than those of the TETA, PAB and PDA modified algal biomass. Whereas the surface area and pore volume of the PDA modified algal biomass had smaller compared to the TETA and PAB modified algal biomasses. As can be seen from Table 1, the pore size of the algal biomass preparations was varied between 53.2 and 121.4 Å indicating that all the algal preparations were mesoporous. After PDA modification, the surface area and pore volume of the algal biomass were considerably decreased. The reduction in the surface area and pore volume of the PDA modified algal biomass could be due to the filling of the vicinity of the pores by PDA polymer. Similarly, the decreased surface and average pore size of the TETA and PAB modified algal biomasses compared to native algal biomass, could be due to the increase of the ligand density on the pores.

3.1.2. Contact angles and surface free energies of the algal biomass preparations

The contact angle values of water, glycerol and diiodomethane on the native and TETA, PAB and PDA modified algal biomass preparations and their RR-120 dye laden equivalent are shown in Table 2. All these algal biomass preparations were presented completely different surface properties depending on the existence of the surface functional groups. The contact angles values of the TETA, PAB and PDA modified algal biomasses were varied compared to the native algal biomass he hydrophilicity of their surface was decreased. As observed from Table 2, the contact angle values of RR-120 dye-laden algal biomasses modified with TETA, PAB, and PDA were significantly changed compared to their dye free counterparts. Noted that the contact angle value of a substrate surface is highly sensitive upto the outer 10 Å of the surface [38]. Therefore, it could be envisaged that the contact angle value could be substantially altered in this region by the arrangement of the surface functional groups on the tested substrate. As can be seen from Table 2, the adsorption of RR-120 dye on the algal biomass preparations resulted in a reduction of the surface hydrophilicity of the biomass preparations. This could be due to the hydrophobic entities of the RR-120 dye could be presented on the external surfaces (increased the contact angle values) or vice versa for hydrophilic

Table 1
The surface area and pore size of the native, and TETA, PAB and PDA modified algal biomass preparations.

Algal biomass	Surface Area(m^2/g)	Pore Size(Å)
Native	2.12	121.4
TETA-modified	1.73	98.3
PAB-modified	1.86	81.6
PDA-modified	1.48	53.2

Table 2
Contact angles of water, glycerol and diiodomethane on the native and TETA, PAB and PDA modified algal biomass preparations and their RR-120 dye laden equivalent (The measurements were the averages of 10 contact angles at least operated on three samples).

	Test liquids and their surface tension (γ_l)		
Algal biomass preparations	Water (γ_{erg}: 71.3) ($\theta°$)	Glycerol (γ_{erg}: 64.0) ($\theta°$)	Diiodomethane (γ_{erg}: 50.8) ($\theta°$)
Native	57.9 ± 2.6	50.3 ± 1.9	48.9 ± 1.8
Native-RR-120	69.7 ± 1.8	62.4 ± 2.6	34.9 ± 0.9
TETA-modified	74.2 ± 3.1	61.6 ± 2.1	31.8 ± 1.9
TETA-modified-RR-120	70.3 ± 2.7	64.9 ± 1.4	38.7 ± 1.4
PAB-modified	81.4 ± 2.9	79.3 ± 2.6	31.2 ± 0.8
PAB-modified-RR-120	92.8 ± 1.3	77.9 ± 2.2	29.1 ± 1.1
PDA-modified	59.8 ± 3.2	44.8 ± 1.3	39.9 ± 1.9
PDA-modified-RR-120	79.4 ± 1.5	75.8 ± 1.1	28.6 ± 1.2

surfaces (reduced the contact angle values) [38,39]. After RR-120 dye laden on the algal biomass preparations, the contact angle values further increased approximately at between 6° and 11°. As presented in Table S1, RR-120 dye molecule has six acidic sulphonyl groups, two hydroxyls, two chlorine groups, and nine aromatic rings on its structures. Therefore, the RR-120 dye laden algal biomass preparations have larger aromatic hydrophobic entities on their surfaces compared to dye free counterpart. As observed from Table S1, the PAB modified algal biomass was presented a hydrophobic (θ greater than 90°) surface, whereas all the other preparations had hydrophilic surface properties. The wettability of material surfaces could be defined by comparing the contact angle values of water and diiodomethane because these probe liquids are frequently used as reference test liquids in analyses of interactions of polar and apolar solid surfaces.

Micro-scale interactions between adsorbent surface and adsorbate molecule can be divided into Lifshitz–van der Waals (LW) and Lewis acid–base (AB) contributions, and used to speculate the free energy of interaction and structural association of the system [38]. In agreement with the Young calculation, the smaller the surface tension of a test liquid, the smaller becomes the contact angle measured on the sample surface. The entire total surface free energy (γ^{TOT}) could be calculated using the van Oss' method, involving the summation of the Lifshitz–van der Waals (γ^{LW}) and the acid–base constituents (γ^{AB}). The calculated values for all the algal biomass preparations showed different values according to the used test liquids. As given above, di-iodomethane was selected as an apolar liquid, and the other two polar liquids were water and glycerol. As can be seen from Table 3, the studied algal biomass preparations showed different acid-base (γ^{AB}) values of their total surface energies (γ^{TOT}) due to the different functional groups on their surface. The Lifshitz–van der Waals components (γ^{LW}) of all the algal preparations were significantly greater compared to the acid–base components (γ^{AB}). The acid–base components (γ^{AB}) of the surface free energy of all modified algal biomass preparations were significantly decreased after modification with TETA, PAB and PDA ligands whereas a contrary effect were detected for γ^+ components (Table 3). On the other hand, the base component (γ^-) of the algal biomass preparations changed in varying degree after modification with TETA, PAB and PDA ligands and after adsorption of RR-120 dye. As expected, the highest γAB value was detected for the native algal biomass could be due to the presence of different hydrophilic cell wall components on the surface (i.e. glycoproteins and polysaccharides such as cellulose, carrageenan, etc.) [25]. Therefore, the polarity of the native algal biomass was considerably higher (25.6%) than those of the modified algal biomass preparations (between 3.5 and 8.1%; Table 3). Thus, modification of the native algal biomass with TETA, PAB and PDA ligands resulted in a reduction in the surface polarities of these preparations.

As given above, modification of the algal biomass with different ligands changed the surface properties, as observed from the change of the surface energy components and contact angle values. From these explanations, RR-120 dye molecule could differently interact with the modified algal biomass preparations. As observed from Table 3, the nitrogen atoms of the ligand molecules resulted in increases Lewis acid (γ^+) components of the surface energies of modified algal biomasses, and these are active in Lewis acid sites [38–44]. The Lewis acid (γ^+) components of all the ligands attached biomasses were reduced after sorption of RR-120 dye. These results showed that the hydrophilicity/hydrophobicity of the modified algal biomass surfaces were changed according to the surface functional groups of the ligands. As expected, the algal biomass surfaces exhibited different acid/base components (γ^{AB}) of their surface free energies.

3.2. Adsorption studies

3.2.1. Effect of the sorbent dosage

The effect of biosorbent dosage on RR-120 removal efficacy of the native, TETA, PAB, and PDA modified preparations was studied at 100 mg/L initial concentration of RR-120 dye. The biosorbent dosage was selected in the range from 0.1 to 1.0 g/L. The anionic RR-120 dye could be absorbed primarily through electrostatic interaction between its negatively charged sulphonyl groups of the dye and the protonated amino groups of the biosorbents. As can be seen from Figure S2, the amount of RR-120 dye adsorbed exhibited a stable increasing trend with an increment in the tested biosorbent dosage. At a low biosorbent dosage, the adsorptive sites of all the tested biosorbents could be fully employed by the RR-120 dye, and led to surface overload and yielding higher adsorption capacity [11,45]. Also, the removal percentage of the tested sorbents for RR-120 dye followed the order:

Table 3
Surface free energy parameters (mN/m^2) of the native and modified algal biomass preparations according to the van Oss et al.

Algal biomass form	γ^{TOT} [mN/m^2]	γ^{LW} [mN/m^2]	γ^{AB} [mN/m^2]	γ^+ [mN/m^2]	γ^- [mN/m^2]	Polarity (%)[a]
Native	44.7	38.2	6.5	1.4	2.5	14.5
Native-RR-120	44.1	39.4	4.7	0.5	4.8	10.6
TETA-modified	46.7	36.8	9.9	1.7	3.3	21.1
TETA-modified-RR-120	44.6	43.4	1.2	0.2	3.7	2.7
PAB-modified	48.1	44.8	3.3	3.4	0.9	6.8
PAB-modified-RR-120	48.9	47.2	1.7	1.5	0.4	3.5
PDA-modified	46.5	40.1	6.6	0.6	4.9	14.9
PDA-modified-RR-120	50.1	44.8	5.3	0.7	10.2	10.5

Polarity (%) = $(\gamma^{AB}/\gamma^{Total}) \times 100$

TETA > PAB > PDA > native algal biomass preparations. It was observed that the adsorption capacity of the TETA modified algal biomass for RR-120 dye was more than those of the PAB, PDA and native algal biomass preparations. This could be due to the presence of numerous primary and secondary amine groups on the aliphatic chains of the TETA ligand. Thus, these amine groups could interact with sulphonyl groups of the RR-120 dye with a potent electrostatic attraction. As observed from Figure S2, the native algal biomass exhibited a low adsorption performance for RR-120 dye. Because of the native algal biomass had not additional adsorptive sites, and, thus, the removal percentage of the dye was found to be only 33.1% at 0.4 g/L biosorbents. On the other hand, the percent removal efficiencies of the TETA, PAB and PDA modified algal biomasses towards to RR-120 were found to be 99.7%, 81.4% and 59.8% with the same amount of adsorbent dosage, respectively. Further increase in the amount of biosorbent dosage was not significantly affected the removal efficiency. These results could be related to the enhancement of the adsorptive sites (such as ion-exchange, hydrogen bounding and π-π interactions) by incorporation of the TETA, PAB and PDA ligands on the modified biosorbents compared to the native algal biomass. Moreover, the TETA modified algal biomass displayed higher biosorption capacity for RR-120 with respect to the PAB and PDA modified ones. Further increases in the biosorbent dosage had not more impact on the removal efficiencies of the tested biosorbents. Thus, according to these experimental results and economic point of view, the biosorbent dosage was selected as 0.4 g/L for the remaining experiments.

3.2.2. Effect of pH on the biosorption efficiency

The pH of biosorption medium is evaluated as a crucial factor for effective removal of dye due to it strongly affects the surface charges of both pollutant and sorbent [6,46,47]. Additionally, it also affects the percentage of dissociation of the dye solution, and ionic strength of sorbent and pollutant [47–49]. The influence of pH on biosorption efficiencies of the RR-120 by the native, and TETA, PAB, and PDA modified preparations were studied between 2.0 and 8.0 by keeping constant the other adsorption parameters. As can be seen from (Fig. 3A), the equilibrium biosorption of the dye was reached maximum at around pH 3.0. At this optimal pH value, the maximum dye biosorption capacities of the native and TETA, PAB, and PDA modified algal biomass preparations were found to be 72.3, 249.2, 201.8, and 149.8 mg/g, respectively. At this pH value, the presence of large numbers of H + ions in the medium leads to the protonation of the amine groups of the native and modified algal biomass preparations. These groups are responsible for the electrostatic interactions with the negatively charged sulphonyl groups of the RR-120 dye molecules and the positively charged protonated binding sites of the tested biosorbents. As observed from (Fig. 3A), the RR-120 equilibrium sorption showed increase for all the algal biomass preparations with the pH values increased from 2.0 to 3.0, and then with increasing the pH above 3.0, the removal performance of the sorbents gradually decreased. The pH dependency of RR-120 sorption can be described regarding both the surface charge distributions of algal biomass preparations, and the degree of ionization of the RR-120 molecule. As observed from (Fig. 3A), the amount of the biosorbed dye on the tested biomass preparations was increased with increasing the medium pH from 2 to 3. When the pH value was increased above 3.0, an opposite trend was observed, while the removal performance of the sorbents gradually decreased. This observation could be related with the surface charge distributions of the tested biosorbents and the dye molecules. The RR-120 dye structure comprised of six negatively charged sulphonyl groups, two secondary amine groups, twelve H-bond donors, thirty-four H-bond acceptor and hydrophobic entities. These functional groups are responsible for ion-exchange, electrostatic, hydrogen bounding, and π– π interactions with the tested biomass preparations (Table S1). On the other hand, the native algal biomass surface has a large number of surface functional groups [25] such as carboxyl, sulfate, hydroxyl, amine etc. After modification of the algal biomass with TETA and PAB ligands four amine groups on an aliphatic chain and a primary and secondary amine groups on an aromatic ring were introduced, respectively. While, the PDA modification provided many –OH, –NH_2 and π– π interactions sites. All these groups could be readily interacting with the RR-120 dye molecules in the aqueous medium. At acidic pH conditions, the existence of a large number of H^+ ions in the medium protonate the amine groups of the algal biomass preparations, and accordingly, the overall surface charges of the algal biomass preparations could be positively charged [25,31]. As the pH increased above 3.0, the concentration of hydrogen ions could gradually decrease and less RR-120 dye molecules could occupy the binding sites on the algal biomass preparations through electrostatic attraction. At pH values greater than 7.0, the biosorption capacities of all the biosorbents were declined for the dye due to the deprotonation of amine groups. At pH 7.0, the reduction in the amount of the adsorbed RR-120 dye on the biosorbents was the following order: TETA modified > PAB modified > PDA coated > native algal biomass. Furthermore, the variation of the zeta potential values of the algal biomass preparations (i.e., TETA, PAB, PDA, and the native) were determined at different pH values by using a zeta sizer (Fig. 2). The zeta potential value of the algal biomass preparations is very significant parameter to define the degree of ionized groups of the sorbents at a given pH value. As observed from Fig. 2, the raising of pH values from 2.0 to 11.0, the zeta potential values of the modified algal biomass preparations decreased from 42.3 mV at pH 2.0 to −18.4 mV at pH 11.0. Whereas the zeta potential value of the native algal biomass showed more negative value within the same pH range (9.4 mV at pH 2.0 and −28.6 mV at pH 11.0). The zeta potential data agreed with the adsorption performance at different pH values of the algal biomass preparations.

3.2.3. Effect of ionic strength on RR-120 sorption

The influence of ionic strength on the RR-120 dye removal was studied at pH 3.0 using the native and TETA, PAB, and PDA modified algal biomass preparations. As reported earlier, when the electrostatic potency between functional groups on the adsorbent and the binding sites of the pollutant are opposite, then an increment in salt concentration can effect in a decrease in the sorption capacity of sorbents [24]. Accordingly, the concentration of NaCl was changed in the medium between 0.00 and 1.0 mol/L. As shown in (Fig. 3B), for all the tested algal biomass preparations, the adsorbed amount of RR-120 dye reduced with increasing the ionic strength of the medium. At 1.0 mol/L NaCl concentration, the decrease in the amount of the adsorbed RR-120 dye was found to be 89.9%, 76.8%, 84.2% and 90.4 % for the native, TETA, PAB, and PDA modified algal biomasses, respectively. These observations could be resulted from the reduction of the electrostatic force between RR-120 dye and the adsorptive sites of the algal biomass preparations by increment the salt concentration. The presence of Na + and Cl- ions in the solution could shade the interaction between RR-120 dye and the adsorptive sites of the algal biomass preparations. Thus, the electrical double layers of the native and modified algal biomasses surfaces could constrict, and lead to a depletion in the electrostatic interlinkages [7]. These results showed that ion-exchange and electrostatic interactions could be operative main forces for the biosorption of RR-120 dye on the algal biomass preparations. Similar results have been reported in the earlier studies [24,25].

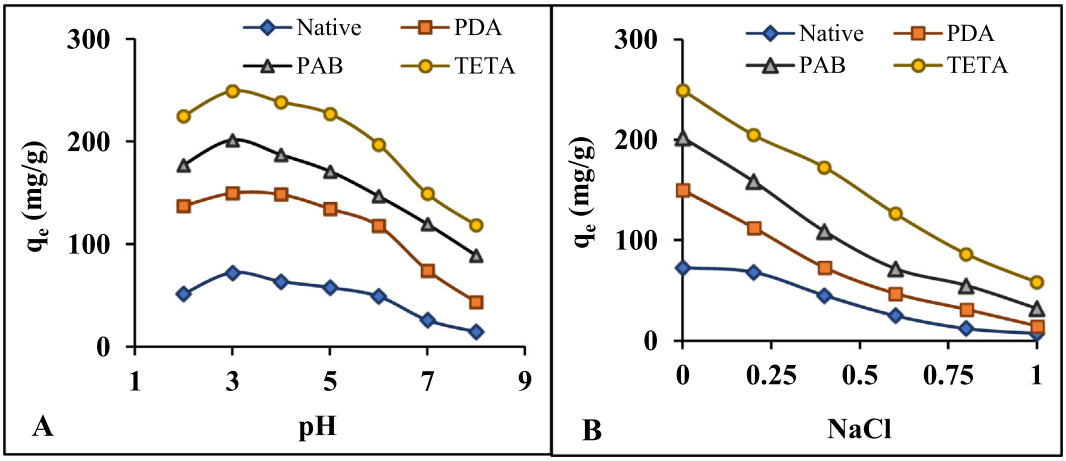

Fig. 3. (A) The effect of pH on the sorption efficiencies of the RR-120 dye on the native and TETA, PAB, and PDA modified algal biomass preparations. Experimental conditions: initial dye concentration: 100 mg/L; adsorbent dose: 20 mg/50 mL; agitation speed: 100 rpm; temperature: 25 °C; contact time: 120 min. **(B).** The effect of ionic strength on the sorption efficiencies of the RR-120 dye on the native and TETA, PAB, and PDA modified algal biomass preparations. Experimental conditions: initial dye concentration: 100 mg/L; pH: 3.0; adsorbent dose: 20 mg/50 mL; agitation speed: 100 rpm; temperature: 25 °C; contact time: 120 min.

3.3. Effect of initial concentration of RR-120 dye removal efficiency and sorption isotherm models studies

The influence of the initial RR-120 dye concentration on the biosorption capacities of the native, TETA, PAB and PDA modified algal biomass preparations was studied at initial concentrations of RR-120 between 25 and 500 mg/L. The adsorbed amount of RR-120 on the algal biomass preparations was rapidly increased with increasing the initial dye concentration in the solution. The difference in the biosorption capacities of the algal biomass preparations at varying initial RR-120 dye concentrations is shown in (Fig. 4A). As observed from this figure, the amounts of the adsorbed dye on the native, and TETA, PAB and PDA modified algal biomass were enhanced by increasing the initial concentration of the dye in the solution. The initial quick stage of the adsorbed amount of dye could be due to biosorption by ion exchange mechanism on the biomass surface and the succeeding lower stage could involve other mechanisms such as complexation, micro-precipitation or π-π interactions. Moreover, the initial biosorption rate of the TETA and PAB modified algal biomasses was considerably higher than those of the PDA coated and native algal biomasses. The observed quick removal rates of RR-120 by the TETA and PAB modified algal biomasses could be probable associated to the accessibility of quite large number of ion exchange groups on the biomasses surfaces at the early stage of the biosorption process [50–54]. The maximum biosorption capacities of the native, and TETA, PAB, and PDA modified algal biomass were found to be 148.7, 687.1, 451.8, and 260.3 mg/g, respectively. It should be noted that, a significant enhancement in the biosorption performance of the TETA ligand modified algal biomass was observed compared to the other tested algal biomass preparations. This could be due to the incorporation of the amine groups on aliphatic chains on the surface of the algal biomass, and this showed that the chosen ligand was more suitable for the improvement of the biosorption capability.

Two different isotherm models (i.e., Langmuir and Freundlich) were used on experimental data to describe the nature of biosorption processes. The adsorption isotherm experiments were conducted using dye solutions (in the range from 25 to 500 mg/L) at three different temperatures (15, 25, and 35 °C). The linear expressions of Langmuir, and Freundlich model equations are as follows, respectively [12,55–57].

$$C_e/q_e = C_e/q_m + 1/K_a q_m \quad (6)$$

$$lnq_e = ln\ K_F + 1/n\ ln\ C_e \quad (7)$$

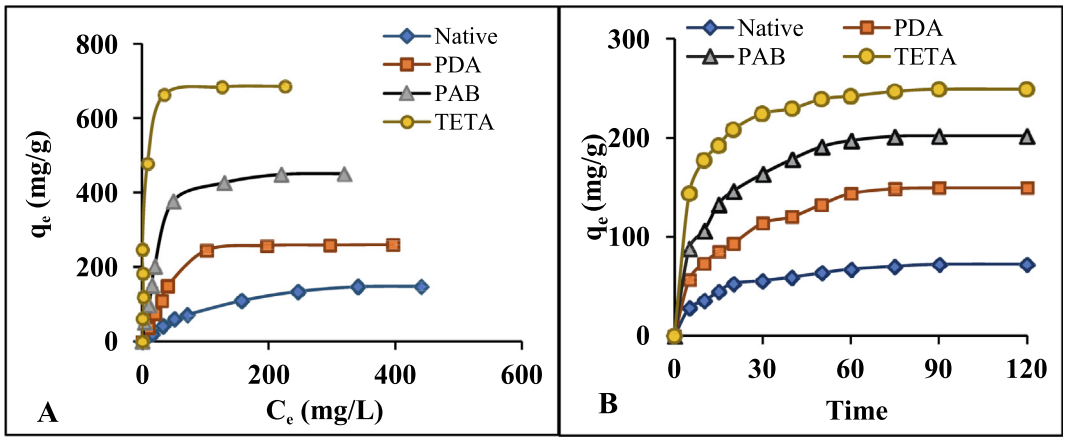

Fig. 4. (A) PDA modified algal biomass preparations. Experimental conditions: pH: 3.0; adsorbent dose: 20 mg/50 mL; agitation speed: 100 rpm; temperature 25 °C; contact time: 120 min. **(B).** The effect of contact time on the sorption efficiencies of the RR-120 dye on the native and TETA, PAB, and PDA modified algal biomass preparations. Experimental conditions: initial dye concentration: 100 mg/L; pH: 3.0; adsorbent dose: 20 mg/50 mL; agitation speed: 100 rpm; temperature: 25 °C.

The essential features of the Langmuir isotherm can be expressed by a dimensionless constant is called separation factor (R_L, also called equilibrium parameter) which is defined by the following equation.

$$R_L = 1/1 + K_a C_o \quad (8)$$

Where C_0 (mg/L) is the initial dye concentration. The value of R_L indicates the shape of the isotherms to be either unfavorable (R_L-greater than 1), linear (R_L = 1), favorable (0 < R_L) According to basic adsorption theory, adsorption can be regarded as a reaction between sorbate molecules and active sites of sorbent [12,55–57].

The data obtained from the adsorption process for the RR-120 dye with the native and, PDA, PAB and TETA modified algal biomasses over the concentration range of 25–500 mg/L at three different temperatures has been correlated with the Langmuir isotherm. A graph of C_e/q_e versus C_e at 25 °C was plotted and a linear plot was obtained to determine the equilibrium biosorption and affinity binding constant and nature of sorption of the RR-120 dye onto the native and modified algal biomass preparations (Figure S3). Based on relatively high correlation coefficient (R^2), the Langmuir model showed satisfactory fitting for the biosorption of RR-120 at various temperatures. The theoretical maximum equilibrium adsorption capacities (q_m) of the native, and PDA, PAB and TETA modified algal biomass preparations to the RR-120 dye calculated at 298 K is 193.8, 312.5, 504.5 and 699.3 mg/g, respectively (Table 4). The maximum adsorption capacity (q_m) and the affinity constant (M^{-1}) which is related to the energy of adsorption (K_a) values of this plot, respectively. Fundamentally, due to the increase in positively charged surface species, one should expect an increase in affinity to surface regions (indicated by K_a) depending on the type of the used biomass in this adsorption system. Considering Table 4, the K_a values obtained as $0.124x10^5$, $0.295x10^5$, $0.484x10^5$ and $4.129x10^5$ M^{-1} for the native, PDA, PAB and TETA modified algal biomass, respectively, confirmed this assessment. At pH 3.0, the surface sites of the TETA modified algal biomass are more positively charged compared to other biomass (Fig. 2), thus the surface will express a greater affinity for adsorbing negatively charged dye molecules. In addition, the increase in K_a values for the TETA modified biomass from $0.79x10^5$ to $9.15x10^5$ M^{-1} or the native, and PDA and PAB modified ones, with the increase of the medium temperature from 15 to 35 °C, could be explained by the increase in hydrophobic interactions as well as the regions with positive surface charge (Table 5).

One of the main characteristics of the Langmuir isotherm is the feasibility of the adsorption process could be judged by the value of the dimensionless equilibrium parameter or separation factor, R_L that can predict the sorption system is favorable or unfavorable. In these biosorption systems, the R_L values were obtained as 0.192, 0.091, 0.057, and 0.007 according to Equation (7) for biosorption of RR-120 on the native, and PDA, PAB and TETA modified algal biomass preparations, respectively (Table 4). These results indicated that the tested biosorbents are favorable for the RR-120 dye biosorption from aqueous solution.

The equilibrium experimental adsorption isotherm data given in (Fig. 4A) were applied to the linear Freunlich equation ($\ln q_e = \ln K_F + 1/n \ln C_e$). The logarithm of the equilibrium adsorption capacities (q_e) and equilibrium concentrations (C_e) was taken and plotted ($\ln C_e$ - $\ln q_e$ plot) at 25 °C. As can be seen from Figure S4, lines with increasing slope were obtained. Therefore, the value of n calculated from the slope was positive. In the literature, it was reported that the value of n between 2 and 10 is a good adsorption [56]. The calculated n values for the adsorption of the RR-120 dye with the native, PDA, PAB and TETA modified algal biomass were 1.74, 2.02, 2.06 and 3.30. It was showing good efficiency for dye adsorption by the modified biomasses as the adsorbents. In this study, the Langmuir model is a better predicator than the Freundlich model with high R^2.

3.4. Effect of contact time and adsorption kinetics models

Fig. 4B shows the effect of contact time on RR-120 sorption by the native and PDA, PAB and TETA modified algal biomass preparations. The adsorbed amount of the dye was very high within the initial 20 min period, this could be due to the strong ion-interactions between the amine groups of the algal biomass preparations and sulfonyl groups of the RR-120 dye. The equilibrium time was reached around 90 min, and the initial fast biosorption could be due the easy accessibility of the unoccupied surface binding sites with the dye molecules on the native and PDA, PAB and TETA modified algal biomass preparations. After this period, the occupation of these sites with the dye molecules resulted an increase in the equilibrium adsorption time. The equilibrium amounts of RR-120 adsorbed on the native and PDA, PAB and TETA modified algal biomass preparations were found to be 72.3, 249.2, 201.8, and 149.8 mg/g at 100 mg/L initial dye concentration, respectively (Fig. 4B). To understand the steps controlling the biosorption process and to investigate the biosorption mechanism, different kinetic models were applied including pseudo-first-order and pseudo-second-order. The time-dependent biosorption of dye using all the native and TETA, PAB, and PDA modified algal biomass preparations was performed at various temperatures (15, 25 and 35 °C) and examined with kinetic models. Other parameters such as dye concentration, sorbent dosage solution volume and pH were kept constant. In relation to the pseudo-first-order kinetic, a single molecule of sorbate gets adsorbed on a single binding site of sorbent and the linearized form of this equation is as follows:

$$log(q_e - q_t) = log\ q_e - (k_1/\ 2.303)t \quad (11)$$

Where, q_e and q_t (mg/g) are sorption efficiencies of sorbents at equilibrium and any contact time (min), k_1 (min^{-1}) indicates the rate constant of first-order sorption. According to this equation, if log

Table 4
Isotherm models constants and correlation coefficients for adsorption of Reactive Red 120 dye on the native and TETA, PAB, and PDA modified algal biomass. (Experimental conditions: pH 3.0; adsorbent dose: 20 mg/50 mL; agitation speed: 100 rpm; temperature: 25 °C; contact time: 120 min.)

Expression formula		Langmuir $[C_e/q_e = C_e/q_m + 1/K_a q_m]$				Freundlich $[lnq_e = ln\ K_F + 1/n\ ln\ C_e]$		
Biomass	q_{exp} (mg/g)	q_m (mg/g)	$K_a x10^{-5}$ (M^{-1})	R^2	R_L*	K_F	n	R^2
Native	148.7	193.8	0.124	0.995	0.192	5.44	1.74	0.973
PDA	260.3	312.5	0.295	0.997	0.091	17.9	2.02	0.936
PAB	451.8	504.5	0.484	0.999	0.057	37.3	2.06	0.947
TETA	687.3	699.3	4.129	0.998	0.007	168.9	3.30	0.869

*Initial concentrations (C_o) of dye, 500 mg/L

Table 5
Kinetic parameters for biosorption of Reactive Red 120 on the native and TETA, PAB and PDA modified algal biomass from aqueous solutions. (Experimental conditions: pH: 3.0; adsorbent dose: 20 mg/50 mL; agitation speed: 100 rpm; temperature: 25 °C; contact time: 120 min.)

Expression formula		First-order $[log(q_e - q_t) = logq_e - -k_1 t/2.303]$			Second-order $[t/q_t = 1/(k_2 q_e^2) + (t/q_e)]$			
Biomass	q_{exp} (mg/g)	q_e (mg/g)	$k_1 x10^2$ (1/min)	R^2	q_e (mg/g)	$k_2 x10^4$ (g/mg min)	h $x10^{-2}$ (mg/g min)	R^2
Native	148.7	238.8	7.13	0.912	164.4	5.23	0.14	0.999
PDA	260.3	527.3	8.09	0.934	294.8	2.51	0.22	0.998
PAB	451.8	870.9	9.17	0.947	495.1	2.17	0.53	0.999
TETA	687.3	977.2	8.29	0.889	724.6	2.12	1.11	0.998

(q_e-q_t) is plotted against time, k_1 rate constant and sorption capacity are found from slope and intercept values, respectively.

Second-order kinetic assumes that the sorption capacity is proportional to the number of active sites occupied on the sorbent and the linearized form of this equation is as follows [57].

$$t/q_t = 1/k_2 q_e^2 + (1/q_e)t \quad (12)$$

where k_2 is the rate constant for pseudo second-order (g/mg/min).

The initial rate of sorption (h, mg/g/min) was then calculated through the simplification of Eq.12.

$$h = dq_{t=0}/dt = k_2 q_e^2 \quad (13)$$

By plotting a graph among t/q_t and time, linear lines for the second-order sorption kinetics were attained, by which q_e, h and k_2 can be determined from the slope and intercept of the plots of t/q against t.

The first-order and second-order models are frequently used to determine the adsorption controlling mechanism on sorbents [57]. The kinetic model parameters are presented in Table 5. According to values of R^2 (correlation coefficient) were quite low and the experimental sorption capacity (qexp) data did not fit well with the theoretical qe data for the pseudo-first-order model in Table 5. As observed from the table, the pseudo-first-order model was not well described the adsorption process. The pseudo-second-order was also used to examine the sorption kinetics (Table 5). According to values of R^2 and the experimental equilibrium "q_{exp}" fit well with the corresponding theoretical q_e value. The correlation coefficients for the linear plots from the pseudo-second order rate law are greater than 0.998 for all the native and modified algal biomass for contact times of 120 min [7]. The rate constant (k_2) and the initial rate of reaction (h) decreased with increasing biosorption capacities of the biosorbents.

The pseudo-second-order rate constants decreased from $7.8x10^{-4}$ to $4.3x10^{-4}$ g/mg/min for the native biomass, from $3.6x10^{-4}$ to $2.2x10^{-4}$ g/mg/min for the PDA coated biomass, from $2.6x10^{-4}$ to $1.9x10^{-4}$ g/mg/min for the TETA modified, and from $2.8x10^{-4}$ to $1.7x10^{-4}$ g/mg/min for the PAB modified algal biomasses. On the other hand, the initial rate of reaction increased from $0.09x10^2$ to 0.17 $x10^2$, from $0.16x10^2$ to 0.25 $x10^2$, from $0.44x10^2$ to 0.62 $x10^2$ and from $0.87x10^2$ to 1.45 $x10^2$ mg/g min as the temperature increased from 15 °C to 35 °C for native, PDA coated and TETA and PAB ligands modified algal biomasses, respectively.

The chi-square (χ^2) error function was employed in this study to find out the best fit the isotherm and kinetic models to the experimental equilibrium data. The mathematical statement of Chi-square (χ^2) test was evaluated using Equation (14):

$$\chi^2 = \Sigma(q_{exp} - q_m)^2/q_m \quad (14)$$

Where q_m is the equilibrium capacity obtained by calculating from the model (mg/g), and q_{exp} is the experimental data of the equilibrium capacity (mg/g). If data from the model are similar to the experimental data, χ^2 will be a small number; if they are different, χ^2 will be a large number. Therefore, the data sets were analyzed using the Chi-square test to confirm the best- fit isotherm and kinetic for the adsorption system. The Langmuir isotherm and second-order kinetic models showed a high degree of correlation with the Chi-square test, χ^2 values (Table S2 and S3). Thus, the non-linear sum of the Chi-square test, χ^2 analysis proved that the best-fit isotherm and kinetic models were the Langmuir isotherm and second-order kinetic models and these methods could avoid the errors.

3.5. Effect of temperature and thermodynamic studies

The influence of temperature on the biosorption of the RR-120 dye on all the algal biomass preparations was studied at three different temperatures (i.e., 288, 298 and 308 K). The data are presented in Table 6. The temperature of the solution could be an important factor for the energy dependent processes in pollutants removal by the adsorbents. The biosorption capacities of the native, and modified algal biomass preparations for the RR-120 dye increased with the rising temperature from 288 to 308 K. The enhancement in the biosorption performance with increment temperature showed endothermic nature of the biosorption process. In the earlier studies, similar endothermic property of the adsorption process has been described for many adsorbent systems [7,12]. Thermodynamic data were obtained by calculating the different thermodynamic variables including change in Gibbs free energy (ΔG^0), change in enthalpy (ΔH^0) and change in entropy (ΔS^0) from the dye removal data attained by all adsorbents by using the following equations,

$$\Delta G^0 = -RTlnK_a \quad (9)$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (10)$$

Thermodynamic parameters were also calculated by using the adsorption data in the temperature range of 288–308 K with a dye concentration of 500 mg/L. Isotherm models were not only used to identify the adsorbate-adsorbent relations but also to determine the thermodynamic parameters. Therefore, the effect of temperature on the biosorption capacity of the biosorbent was investigated at different initial dye concentration (from 25 to 500 mg/L) and at different temperatures (i.e., 15, 25, and 35 °C). Various thermodynamic parameters, including enthalpy change (ΔH^0, kJ/mol) entropy change (ΔS^0, J/molK), and Gibbs free energy change (ΔG^0, kJ/mol), are calculated and tabulated in Table 6. The -ΔG^0 value increased with increasing the temperature from 15 °C to 35 °C for RR-120 (Table 6). The negative values of ΔG^0 indicated that the biosorption process on the native and modified algal biomasses was spontaneous at all the tested temperatures. The biosorption enthalpy values, for the RR-120 dye were found to be 21.5, 30.1, 72.3 and 90.3 kJ/mol for the native and PDA, PAB and TETA modified algal biomass, respectively. Furthermore, the posi-

Table 6
Thermodynamic parameters for Reactive Red 120 biosorption on the native, and PDA, PAB and TETA modified algal biomass from aqueous solutions. (Experimental conditions: pH: 3.0; adsorbent dose: 20 mg/50 mL; agitation speed: 100 rpm; temperature: 25 °C; contact time: 120 min.)

Expressionformula		$[\Delta G^o = -RT\ ln\ K_a = \Delta H^o - -\Delta S^o]$				$[ln\ k_2 = lnA - E_a/RT]$		
Biomass	T (K)	q_{exp} (mg/g)	q_m (mg/g)	$K_a x10^{-5}$ (M^{-1})	ΔG (kJ/mol)	ΔH (J/mol)	ΔS (kJ/mol K)	E_a (kJ/mol)
Native	288	99.2	134.7	0.10	−22.1			
	298	148.7	194.1	0.12	−23.3	21.5	0.151	21.9
	308	182.9	208.3	0.18	−25.1			
PDA	288	184.5	227.1	0.19	−23.6			
	298	260.3	312.5	0.29	−25.5	30.1	1.85	18.2
	308	301.6	333.2	0.43	−27.3			
PAB	288	377.1	454.7	0.25	−24.3			
	298	451.8	504.5	0.48	−26.7	72.3	13.5	12.4
	308	526.6	543.4	18.0	−30.9			
TETA	288	526.9	561.5	0.79	−27.0			
	298	687.3	699.3	4.13	−32.0	90.3	36.9	19.0
	308	883.7	892.1	9.15	−35.1			

tive value of enthalpy is related to the physical nature of the biosorption and its endothermic property. Also, the entropy values for RR-120 using the native, and PDA, PAB and TETA modified algal biomass were found to be 0.151, 1.85, 13.5, and 36.9 kJ/mol K, respectively. Thus, these results proposed that the RR-120 dye biosorption on the algal biomass preparations could realize spontaneously under the given experimental conditions.

3.6. Biosorption mechanism of RR-120 dye by the algal biomass preparations

The biosorption efficiencies of the native and TETA, PAB and PDA ligand modified algal biomass were studies in batch system. The FTIR, zeta sizer and contact angles studies revealed that the sorption of the RR-120 dye by algal biomass preparations involve various mechanisms such as ion-exchange, electrostatic and π-π interactions. Amongst them, the ion-exchange interactions could be more pronounced effective force for biosorption of dye on the modified algal biomass preparations. Additionally, further explored the biosorption mechanism by analyzing the adsorption isotherms, thermodynamic parameters, and kinetics models. From these experimental data, the biosorption capacities of the algal biomass preparations for RR-120 dye were in the following order TETA > PAB > PDA > native. As presented in Table 5, the lowest quantity of the RR-120 dye was adsorbed with the native algal biomass. The amount of adsorbed RR-120 dye was found to be 148.7 mg/g on the surface of the native algal biomass which mainly comprised of the amine, carboxyl and hydroxyl groups. Whereas after modifications of the algal biomass surfaces with the TETA, PAB and PDA ligands and the sorption capacities amplified about 1.75, 3.05 and 4.62 folds compared to the native algal biomass. These results show that the ion-exchange interactions between the protonated amine groups of the modified algal biomasses and the sulphonyl groups of the RR-120 dye played a key role for the dye biosorption. After modification with the TETA ligand the biosorption capacity of the biosorbent for RR-120 dye increased to 687.1 mg/g compared to native biomass 148.7 mg/g. The TETA ligand is an amine group rich molecule on an aliphatic chain structure, whereas the PAB ligand has a primary and secondary amine groups on an aromatic structure. Both ligands could be easily cooperating with the sulphonyl groups of the RR-120 dye molecules via ion-exchange interaction. Additionally, the dye molecules could be also successfully interacted with these ligand molecules via hydrogen bounding, π-π and n → π interactions. On the other hand, the PDA modified algal biomass has many nitrogen and oxygen donating groups with hydrophobic entities, and thus, these groups could generate a cluster for interact with the RR-120 dye molecule. It could be considerably affect the biosorption capacity of the PDA modified biomass via ion-exchange, electrostatic and π-π interactions. According to above results, the type and number of binding sites on the algal biomass preparations played an important and effective role for sorption of the RR-120 dye. These results indicated that the TETA ligand modified algal biomass is a good biosorbent for cationic pollutants removal.

3.7. Regeneration and reusability

For treatment of wastewater, the regeneration of the pollutant laden sorbent is an important factor economic point of view. As reported in the earlier studies, when dye sorption is electrostatic attraction or ion exchange, then, it could be desorbed under extremely alkaline or acidic conditions [7]. In this work, the maximum amount of the RR-120 dye sorption was attained for all the tested algal biomass under acidic pH value, therefore, the dye laden biomass could be easily regenerated under the alkaline condition [25]. In Figure S5, the released dye percentages from the dye laden native, PDA, PAB and TETA modified algal biomasses were found to be 84, 93, 90 and 96% with 20 mmol/L NaOH solution containing 0.5 mol/L NaCl at 25 °C. In alkaline medium, the interaction between the amine groups of all the algal biomass preparations and the sulphonyl groups of the dye molecule could be destabilized by the deprotonation of the amine groups. Thus, the RR-120 dye molecules could desorb from the adsorptive sites of the sorbents. Approximately 10–13% reduction in sorption of the RR-120 dye was observed after seven biosorption–desorption runs (Figure S5). The TETA modified algal biomass exhibited high regeneration ability and good reusability appearance even after seven runs.

3.8. Comparison of the related studies

It is important to compare biosorption capacity of a new biosorbent with the avaiable biosorbents for environmental applications (Table 7). As can be seen from the table, it was observed that the adsorption capacities of TETA, PAB and PDA-modified biosorbents (i.e. RR-120) for the model acid dye were comparable to the biosorption capacities of the biosorbents reported in the literature [21,46,48,49,53,58–61]. These observations had been resulted from the ion-exchange interactions between the sulphonyl groups of the dye molecules and the amine groups of the modified algal biomasses. The TETA ligand modified algal biomass was observed to be favorable for removal of the acidic dye from aqueous medium. The high adsorption capacity of the TETA modified algal biomass for the RR-120 dye could be due to the pendant amino groups on the aliphatic chains.

Table 7
Comparison of the adsorption capacities of different biosorbents to different dyes with this work.

Biosorbents	Dye Adsorption capacity (mg/g)	References
Prunus dulcis biomass (surfactant modified)	97.1	[21]
Ulva lactuca biomass (NaOH treated)	625.0	[46]
Algal-polymer-sheets	273.0	[48]
Agaricus bisporus (macro-fungus) biomass	372.0	[49]
Magnetically responsive *Sargassum horneri* biomass	193.8	[53]
Ficus racemosa biomass (fallen leaves treated with H_2SO_4 / NaOH	61.4 /119.1	[58]
Prunus dulcis biomass (NaOH and surfactant activation)	59.5	[59]
Prunus Dulcis biomass (NaOH activated dead leaves)	50.8	[60]
Ficus racemosa biomass (NaOH treated leaves)	83.3	[61]
O. princeps biomass (polydopamine coated)	260.3	[In this work]
O. princeps biomass (p-amino benzamidine modified)	451.8	[In this work]
O. princeps biomass (tetraethylene tetramine modified)	687.1	[In this work]

4. Conclusions

O. princeps biomass was modified with the TETA, PAB and PDA ligands. They were used for removal of the RR-120 dye from aqueous solutions using the native algal biomass as a control system. The native and modified algal biomass preparations were characterized by FTIR, zeta seizer, BET and contact angle measurements. After attachment of the ligands, the surface area and pore size of the modified algal biomass preparations were reduced compared to native one. The zeta potential values showed a variation trend after incorporation of different amine groups, the positive surface potential values of the modified algal biomass preparations were markedly increased compared to the native biomass. The surface free energy parameters were calculated from the contact angles of apolar and polar liquids on algal biomass samples. The van Oss method was used for calculation of surface free energy and provided a simply way to characterize the surface properties of the algal samples in relation to each other and native one. The experimental results displayed a strong effect of the operational parameters such as pH, temperature, contact time and sorbent dosage on biosorption performance of the tested biosorbents. The modification of the algal biomass surface with TETA ligand was resulted with the most suitable change to improve the capability of *O. princeps* biomass to remove RR-120 dye. The adsorption capacities of the TETA, PAB and PDA modified algal biomasses were increased about 4.64, 3.05 and 1.76-folds for RR-120 dye with respect to native algal biomass. The study showed that the modification of algal biomass surfaces with different ligands changed the binding characteristic of the algal preparations to the model dye RR-120. The order of the sorption capacities of the algal biomass preparations was found to be TETA > PAB > PDA > native. The Langmuir isotherm model proposed that biosorption mechanism involved on surface of the tested biosorbents. In the biosorption process electrostatic interaction, hydrogen bonding and π-π interactions played key roles. According to the calculated thermodynamic data, the biosorption process was observed to be spontaneous, endothermic and entropy increasing process. With respect to studied kinetic models, the biosorption predominantly occurred as a physical mechanism involving ion-exchange, hydrogen bounding and van der Waals interactions, and followed by the generation of chemisorption. The TETA, PAB and PDA ligand modified algal biomasses displayed good regeneration capability and preserved their adsorption efficacies even after seven sorption–desorption cycles. Finally, the obtained data had a remarkable proposal on the removal of the model RR-120 dye using native and modified algal biomass preparations. These biosorbents have also a potential candidate to become green biosorbent in naive, environmental eco-friendly environmental technologies. The presented strategy could be also used to support of the environmental sustainability.

CRediT authorship contribution statement

Gulay Bayramoglu: Validation, Formal analysis, Writing – original draft, Writing – review & editing. **Selin Burcu Angi:** Investigation. **Ilkay Acikgoz-Erkaya:** Investigation, Data curation. **Mehmet Yakup Arica:** Conceptualization, Writing – original draft, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.molliq.2021.118375.

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