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Biosorption of Reactive Red-120 dye from aqueous solution by native and modified fungus biomass preparations of *Lentinus sajor-caju*

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Abstract

The capacities and mechanisms of native and treated white-rot fungus "*Lentinus sajur-caju*" biomass preparations in removing of textile dye (i.e. Reactive Red-120) from aqueous solution was investigated with different parameters, such as adsorbent dosage, pH, temperature and ionic strength. In the batch system, the maximum dye uptake on all the tested fungal biomass preparations was observed at pH 3.0, and the dye uptake capacities of the biosorbents (at 800 mg/l dye concentration) were found to be 117.8, 182.9, 138.6 and 57.2 mg/g for native and heat-, acid- and base-treated dry fungal preparations, respectively. The uptake capacities order of the fungal preparations for the dye were found as heat-treated > acid-treated > native > base-treated. The Langmuir, Freundlih and Temkin adsorption models were used for the mathematical description of the biosorption equilibrium. The Freundlich and Temkin models were able to describe the biosorption equilibrium of Reactive Red-120 on the fungal biomass preparations. The dye biosorption on the fungal biomass preparations followed second-order kinetic model and equation.

Keywords: Fungus; *Lentinus sajor-caju*; Adsorption; Biomass; Textile dye; Reactive Red-120; Kinetic; Adsorption isotherm

1. Introduction

The presence of dyes in industrial effluents is a major problem due their adverse effect to many forms of life. The reactive triazine dyes or their metabolites (e.g. aromatic amines) may be highly toxic and potentially carcinogenic, mutagenic and allergenic on exposed organisms [1]. The dyes are adsorbed and reflected of sunlight entering the water [2–4]. The dye components are hardly degradable by physicochemical or biological methods and degradation becomes highly difficult as the textile dyes are constantly being replaced with modern dyes, which resistant to chemical, photochemical, and biological degradation [5,6]. The most commonly used techniques for color removal include chemical precipitation, adsorption, reverse osmosis, and solvent extractions, etc. Among them, the adsorption techniques have been shown to be a reasonable way to treat textile dyeing effluents [5–8]. Activated carbon is used as an adsorbent for removal of the textile dyes from wastewater. However, this technique is found to be ineffectual due to its cost and regeneration. The adsorption of dyes on different adsorbents has been studied in detail such as peat, chitin/chitosan [9–11], polymeric adsorbent [12], rice husk [13] and various microbial biomasses [14]. The later including bacteria, fungi, and algae are capable of removing the different textile dyes by biosorption, biodegradation, or mineralization [15–17]. Different types of low cost fungal materials have been used as biosorbent for the removal of dye and metal ions from aqueous water. These included *Trametes versicolor* [18], *Corynebacterium glutamicum* [9], *Lentinus sajor-caju* [19], *Rhizopus arrhizus* [2], *Aspergillus niger* [4], *Funalia trogii* [20], etc.

The phoenix mushroom, *L. sajor-caju*, is an important edible mushroom widely cultivated with a great commercial value. The fungus is also a white-rot fungus, and it has several wood-destroying enzymes. The fungus is found in Australia and through Asia to Africa. In the previous studies, the fungus has been used in the bioremediation studies [19,21].

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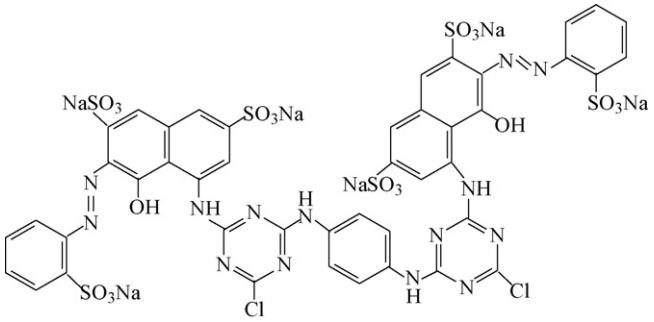
Fungal biomasses such as *A. niger*, *R. arrhizus*, *F. trogii* have been applied to textile dye removal from aqueous medium using either batch or continuous modes [2,4,20]. However, no study has been carried out on the utilization of the fungus for dye removal. In addition, the performance of a fungal biomass could depend on its surface properties as governed by the chemical structure, hydrophobic and hydrophilic characters of the cell wall. Thus, the aim of the pre-treatment is to improve the surface characteristics of the fungal biomass in relation to their dye adsorbing mechanism. This may be in terms of increasing the charge on the cell surface or opening the available sites for the adsorption and enhancing ion-exchange. In this study, the native and physically (heat-treated) and chemically (acid- or base-treated) modified fungal biomasses of *L. sajor-caju* were used for the biosorption of Reactive Red-120 in a batch system. Therefore, the present study aimed to investigate the effects of cell wall pretreatment on the adsorption capacity of the modified fungal biomasses under different experimental conditions. For example, the dye biosorption was studied by changing of solid/liquid ratio, ionic strength, initial dye concentration, temperature, and pH of the adsorption medium. The biosorption phenomena were expressed by the Langmuir, Freundlich and Temkin adsorption model. The experimental data was also analyzed using the first- and second-order kinetic models and kinetic constants were calculated.

2. Materials and methods

2.1. Materials

Reactive Red-120 (Procion Red H-E3B) was obtained from Sigma-Aldrich Chemical Co., St. Louis, MO, USA. The chemical structure and some properties of the Reactive Red-120 dye are presented in Fig. 1 and Table 1. All other chemicals were of analytical grade and were purchased from Merck AG (Darmstadt, Germany). The water used in the following experiments was purified using a Barnstead (Dubuque, IA, USA) ROpure LP reverse osmosis unit with a high flow cellulose acetate membrane (Barnstead D2731) followed by a Barnstead D3804 NANOpure organic/colloid removal and ion-exchange packed-bed system.



Reactive Red 120

Fig. 1. The chemical structure of the Reactive Red-120.

Table 1
The general characteristics of Reactive Red-120

Name of dyes	Procion Red HE-3B
Chemical formula	$C_{44}H_{24}Cl_2N_{14}O_{20}S_6Na_6$
Molar mass	1470
Color Index name	Reactive Red-120
λ_{max} (nm)	511

2.2. Cultivation of fungus

The fungus "*L. sajor-caju*" strain MAFF 430306 was obtained from the National Institute of Agrobiological Sciences, Tsukuba, Ibaraki, Japan. The cultivation condition of the fungus was described in our previous studies. [19,21]. Briefly, the white-rot fungus *L. sajor-caju* was cultivated in liquid medium using the shake flask method. The growth medium consisted of (g/l of distilled water); D-glucose (10.0); KH_2PO_4 (20.0); $MgSO_4{\cdot}7H_2O$ (0.5); NH_4Cl (0.1); $CaCl_2{\cdot}H_2O$ (0.1); thiamine (0.001). The pH of the medium was adjusted to 4.5 before autoclaving. Once inoculated, flasks were incubated on an orbital shaker at 150 rpm for 7 days at 30 °C. After incubation, the biomass was harvested from the medium and washed with distilled water.

2.3. Modification of L. sajor-caju biomass

Heat-treated form of was prepared in physiological saline solution by heating at 100 °C at 10 min and after treatment referred as heat-treated fungal biomass. The native fungal biomass was transferred into 0.1 M HCl and/or NaOH solutions and the mixture was stirred at 250 rpm for 1.0 h at ambient temperature and, hereafter they called acid-treated and/or base-treated fungal biomass. Each treated fungal biomass was centrifuged at 5000 rpm for 10 min, washed with sterile physiological saline buffer solution and dried in a vacuum oven at 50 °C.

2.4. Biosorption studies

The biosorption of Reactive Red-120 on the native and heat-, acid- and base-treated fungal biomass preparations were investigated in a batch system. A stock solution (1000 mg/l) of dye was obtained by dissolving the dye in purified water. The ranges of concentrations of dye were prepared from stock solutions. To determine the effect of initial concentrations of the dye on the biosorption rate and capacity on the fungal preparations, the initial concentration of each dye was varied between 25 and 800 mg/l in the biosorption medium.

Different quantities of fungal biomass preparations, varying from 20 to 100 mg dry fungal biomass preparations in each 50 ml of dye solution (200 mg/l) were stirred at 150 rpm for 6 h at 25 °C. Once the optimum biomass dosage was determined, the effect of pH, temperature and ionic strength were conducted. The effects of the medium pH on the biosorption capacities of the fungal biomass preparations were investigated in the pH range 3.0–10.0 (which was adjusted with H_2SO_4 or NaOH at the begin-

ning of the experiment and not controlled afterwards) at 25 °C. The effect of temperature and ionic strength were studied at four different temperatures (i.e. 5, 15, 25 and 35 °C) at pH 3.0 and at three different KCl concentrations (i.e. 0.1, 0.25 and 0.5 M), respectively. All experiments were conducted in duplicates with 50 mg fungal biomass preparations and initial concentration of each dye was 200 mg/l in each set experiments. Before analysis of the remaining dye concentration, the sample was centrifuged at 3000 rpm for 10 min. The amount of biosorbed dye per unit fungal biomass (mg dye per g dry biomass) was obtained by using the following expression:

$$q = \frac{(C_0 - C)\,V}{M} \tag{1}$$

where q is the amount of dye biosorbed onto the unit amount of the biomass (mg/g); C_0 and C the concentrations of the each dye in the initial solution (mg/l) and after biosorption, respectively; V the volume of the aqueous phase (l) and M is the amount of the biomass (g). The dissolved dye concentrations of the samples were analyzed using a double beam UV/vis spectrophotometer (Shimadzu, Tokyo, Japan; Model 1601) at 511 nm for Reactive Red-120. Results given in averages were obtained from the experiments repeated three times.

2.5. Adsorption isotherm models

The Langmuir [22] and Freundlich [23] adsorption isotherm models which are widely used to analyze data for water and wastewater treatment applications have been shown to describe the biosorption equilibrium. These equations can be written in the form given below to predict the adsorption capacities of the biosorbent.

$$q_{eq} = \frac{q_m b C_{eq}}{1 + b C_{eq}} \tag{2}$$

$$q_{eq} = K_F (C_{eq})^{1/n} \tag{3}$$

For the Langmuir model (Eq. (2)), the constant b is related to the energy of adsorption, C_{eq} the equilibrium concentration of the dye in solution q_{eq} the amount of adsorbed dye on the biosorbent surface at equilibrium and the constant q_m represents the maximum binding at the complete saturation of biosorbent binding sites. K_F and n are the Freundlich adsorption isotherm constants characteristic of the system. K_F and n are indicative of the extent of the adsorption and the degree of non-linearity between solution concentration and adsorption, respectively. On the other hand, the Temkin isotherm model assumes that adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy (ΔG_{max}), which results in the following isotherm equation [24–26],

$$q_{eq} = q_T \ln(1 + K_T C) \tag{4}$$

where K_T (M^{-1}) is the equilibrium binding constant corresponding to the maximum binding energy ($K_T = \exp(-\Delta G_{max}/RT)$), and q_T is the differential surface capacity for dye biosorption per unit binding energy.

2.6. Determination of kinetic parameters

The kinetics of dye biosorption on the fungal biomass preparations was determined with two different kinetic models, i.e. the first- and second-order. The first-order rate equation of Lagergren is one of the most widely used equations for the sorption of solute from a liquid solution [27,28]. It may be represented as follows:

$$\frac{dq_t}{dt} = k_1 (q_{eq} - q_t) \tag{5}$$

where k_1 is the rate constant of pseudo-first-order biosorption (min^{-1}) and q_{eq} and q_t denote the amounts of biosorption at equilibrium and at time t (mg/g), respectively. After integration by applying boundary conditions, $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, gives:

$$\log\left(\frac{q_{eq}}{q_{eq} - q_t}\right) = \frac{k_1 t}{2.30} \tag{6}$$

A plot of $\log(q_{eq} - q_t)$ against t should give a straight line to confirm the applicability of the kinetic model. In a true first-order process $\log q_{eq}$ should be equal to the intercept of a plot of $\log(q_{eq} - q_t)$ against t.

In addition, a pseudo-second-order equation based on the adsorption equilibrium capacity may be expressed as follows [29–32]:

$$\frac{dq_t}{dt} = k_2 (q_{eq} - q_t)^2 \tag{7}$$

where k_2 (g/mg/min) is the rate constant of the pseudo-second-order biosorption. Integrating Eq. (7) and applying boundary conditions lead to

$$\left(\frac{1}{q_{eq} - q_t}\right) = \left(\frac{1}{q_{eq}}\right) + k_2 t \tag{8}$$

$$\left(\frac{t}{q_t}\right) = \left(\frac{1}{k_2 q_{eq}^2}\right) + \left(\frac{1}{q_{eq}}\right) t \tag{9}$$

A plot of t/q_t versus t should give a linear relationship for the applicability of the second-order kinetic. The rate constant (k_2) and adsorption at equilibrium (q_{eq}) can be obtained from the intercept and slope, respectively, and there is no need to know any parameter beforehand [30–32].

2.7. Characterization of the fungal biomass

Scanning electron micrograph of the nature biomass *L. sajor-caju* was obtained using a JEOL, JMS 5600 scanning electron microscope, after coating with thin layer gold under reduced pressure. The IR spectra of native, acid-, base- and heat-treated *L. sajor-caju* were obtained by using a FT-IR spectrophotometer (Mattson 1000 FT-IR, England). For FT-IR spectra, approximately 0.01 g biosorbent sample were encapsulated in 0.1 g KBr and pressed into a tablet form by pressing the ground mixed material with the aid of a bench press. The FT-IR spectrum was then recorded. The water content of the fungal biomass was

determined using a gravimetric method. The biomass preparations of *L. sajor-caju* was allowed to soak in saline solution for 24 h, swollen biomass was weighed after removing of the excess water and then was dried in vacuum oven at 60 °C for 24 h until constant weight. Contact angles to different test liquids (i.e. water, glycerol and DIM) of all the investigated *L. sajor-caju* biomass film preparations were measured by sessile drop method at 25 °C by using a digital optical contact angle meter CAM 200 (KSV Instruments Ltd, Helsinki, Finland). Both the left- and right-contact angles and drop dimension parameters of the fungal samples were automatically calculated from the digitalized image using CAM 200 software operated under Windows 98. The measurements were the average of five contact angles at least operated on three fungal biomass film samples.

3. Results and discussion

3.1. Properties of L. sajor-caju biomass

The dried native and treated fungal biomasses were sieved, and 75–150 μm size of fraction was used in the dye biosorption studies. The surface morphology of the native *L. sajor-caju* mycelia is exemplified by the scanning electron micrograph in Fig. 2. As shown in the SEM micrograph, the fungal mycelia have rough and porous surface. The porous surface structure of the fungal biomass should be considered as a factor providing an increase surface area. In addition, these pores reduce the mass transfer resistance and facilitate the diffusion of dye molecules because of high internal surface area with low diffusional resistance in the biomass preparations (imply high adsorption capacity and rate). In order to confirm the existence of functional biosorption groups (i.e. amino, carboxyl and phosphate) on the fungal biomass, the FT-IR spectra of fungal biomass preparations were obtained. The spectra for fungal biomass preparations are presented in Fig. 3. In general, the FT-IR spectra of all the fungal preparations (i.e. native, heat-, acid- and base-treated) have intense peaks at a frequency level of 3500–3200, and 1540 cm^{-1} representing amino groups stretching vibrations.

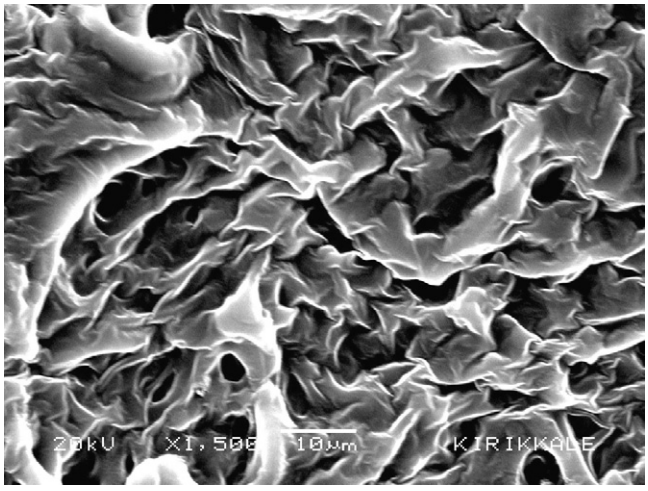


Fig. 2. Representative SEM micrograph of the fungus.

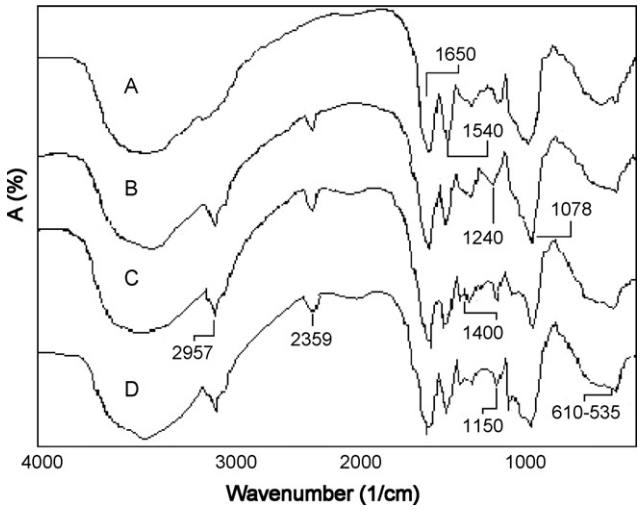


Fig. 3. FT-IR spectra of the fungal biomass preparations: (A) native, (B) heat-treated, (C) acid-treated and (D) base-treated.

The amino groups stretching vibrations bands of fungal preparations are superimposed on the side of the hydroxyl group band at 3500–3300 cm^{-1}. The strong peaks at around 1650, 1400 and 1240 cm^{-1} are caused by the C=O stretching band of carbonyl groups. The phosphate groups show some characteristic adsorption peaks around 1150 and 1078 cm^{-1} representing P=O and P–OH stretching, respectively. The band between 610 and 535 cm^{-1} for the fungal preparation represents C–N–C scissoring and it is only found in protein structure. It should be noted that the FT-IR spectrum of the fungal biomass preparations supports the presence of amine groups, which is mainly responsible for the binding of Reactive Red-120 molecules.

Contact angle data with three different test liquids (i.e. water, glycerol and diiodomethane) for the native, heat-, acid- and base-treated fungal biomass and their dye-adsorbed counterpart biomass are tabulated in Table 2. All the tested fungal preparations gave different contact angle values depending on the surface properties. Physical and chemical treatments of the fungal biomass resulted in increase in the hydrophilicity of the fungal biomass compared to native form. The same trend was observed for the different dye biosorbed fungal preparations compared to the dye-free counterparts. The native form of the fungus was hydrophobic $\theta > 90$. As seen from the table, after heat, acid or base treatment most of the hydrophobic entities

Table 2
Contact angles of various test liquids for the tested fungal preparations

Fungal biomass	Water θ (°) ($\gamma_{erg} = 71.3$)	Glycerol θ (°) ($\gamma_{erg} = 64.0$)	Diiodomethane θ (°) ($\gamma_{erg} = 50.8$)
Native	100.6 ± 0.7	95.8 ± 0.5	57.6 ± 0.8
Native-RR	63.5 ± 0.8	86.7 ± 1.1	42.8 ± 0.8
Heat-treated	82.2 ± 0.8	85.3 ± 1.2	33.1 ± 1.1
Heat-treated-RR	58.7 ± 0.4	83.4 ± 0.7	38.4 ± 0.9
Acid-treated	77.9 ± 1.6	86.3 ± 1.4	30.1 ± 1.1
Acid-treated-RR	54.1 ± 2.1	79.7 ± 1.1	47.8 ± 0.3
Base-treated	81.8 ± 1.4	79.3 ± 0.5	31.1 ± 2.4
Base-treated-RR	59.8 ± 1.5	75.4 ± 1.1	41.8 ± 1.6

γ_{erg}: surface tension of test liquid; Reactive Red-120: RR.

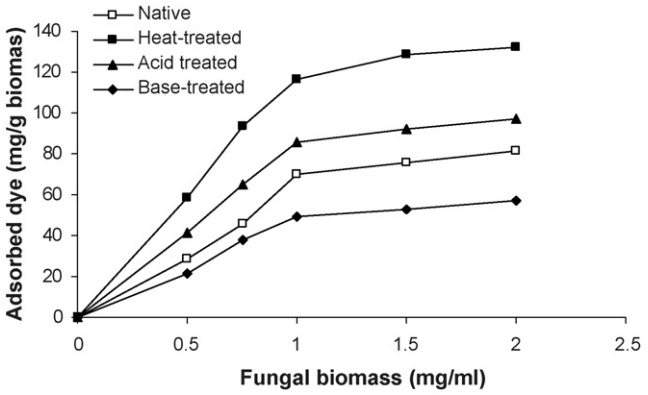


Fig. 4. Effect of solid/liquid ratio on the biosorption capacities of the native, heat-, acid- and base-treated fungal biomass preparations. Initial Reactive Red-120 concentration: 200 mg/l; temperature: 25 °C; biomass concentration: 0.5–2.0 mg/ml; pH: 3.0.

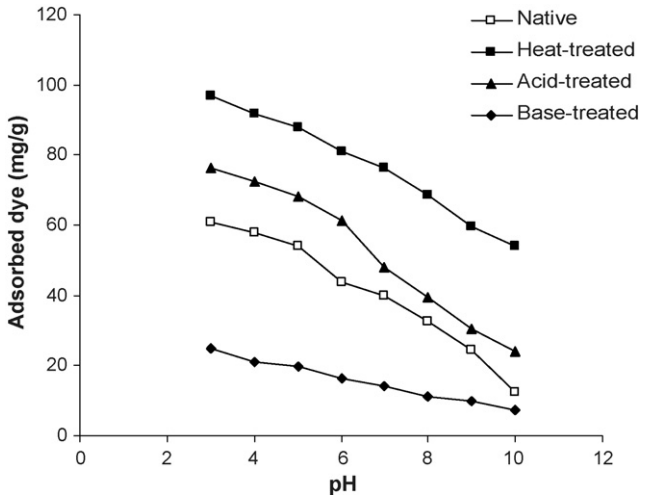


Fig. 5. Effect of pH on the biosorption capacities of the native, heat-, acid- and base-treated fungal biomass preparations. Initial Reactive Red-120 concentration: 200 mg/l, temperature: 25 °C; biomass concentration: 1.0 mg/ml.

of the fungal cell surfaces were removed as shown by contact angle measurement. It should be noted that physical and chemical treatments change the surface properties with respect to native form. Such changes cause contact angles and later adsorption capacity changes too. The heat-treated fungal preparation had higher adsorption capacity for both dyes than those of the native, acid-treated and base-treated forms Fig. 4.

3.2. Effect of solid/liquid ratio

The effect of the solid/liquid ratio on the biosorption capacities of the fungal biomass preparations was studied for an initial concentration of dye (200 mg/l) and the content of solid 0.5–2.0 mg/ml in biosorption medium and is presented in Fig. 4. The resulted increase in the amount of dye removed from medium with the increase of the solid/liquid ratio can be explained by the augment of the number of active sites of the fungal biomass preparations. An increase solid/liquid ratio from 0.5 to 1.0 mg/ml in the biosorption medium leads to increase up to 2-folds in the dye removal efficiency. In the remaining study, 50 mg fungal biomass preparation was used in 50 ml biosorption medium.

3.3. Effect of pH on biosorption

The fungal cell wall is composed of polysaccharides (i.e. chitin and chitosan), proteins, lipids and melanin with several functional groups (such as, amino, carboxyl, thiol and phosphate groups) capable of binding the dye molecules [33–35]. The ionic forms of the dye in solution and the surface electrical charge of the biomass depend on the solution pH. Therefore, solution pH influences both the fungal biomass surface dye binding sites and the dye chemistry in the medium [36–43]. At lower pH values the fungal biomass will have a net positive charge. It is expected that amino groups of the fungal cell wall compounds will also be protonated at acidic pH values. In the presented work, the maximum dye biosorption was observed at pH 3.0 for native (60.8 mg/g), heat-treated (96.9 mg/g), acid-treated (76.2 mg/g) and base-treated (24.8 mg/g) fungal biomasses and the dye removal profiles of the fungal preparations at different pH values are presented in Fig. 5. As seen from the figure, as the pH was decreased, the biosorption of Reactive Red-120 dye on the fungal biomass preparations increased. Reactive Red-120 is an acidic dye and it has six sulfonate, two hydroxyl and six secondary amino groups (Fig. 1). The pK_a value of the sulfonate groups of the dye molecule is 2.1. This functional group can be easily dissociated and thus, the dye molecule has net negative charges in the working experimental conditions. Therefore, the positive sites of the fungal biomass preparations such as protonated form of amino groups (i.e. $-NH_3^+$; pK_a values between 7.0 and 10.0) can play an important role in the biosorption of Reactive Red-120 molecules. With increasing pH, the binding sites increases, and thereby the biosorption of Reactive Red-120 increases. The reduction in the biosorption capacities of the fungal biomass preparations with increasing medium pH can be resulted from the change of the surface positive charge distribution. Thus, as the medium pH increases, the number of negative charge distribution on fungal biomass surface increases. Other researcher has reported similar results. Hu reported that the maximum adsorption of different reactive dyes on the *Aeromonas* sp. biomass was observed at pH 3.0 [39]. Aksu and Tezer, studied biosorption of different Reactive dyes on *Chlorella vulgaris* biomass and the maximum dye biosorption were observed at pH 2.0 [41].

3.4. Effect of ionic strength

The enthalpy of biosorption would be affected not only by the pH value on the electron donating capability, but also by the salt concentration on the hydrophobic and electrostatic interaction between dye and surface functional adsorptive sites of the fungal biomass preparations. The adsorption capacities of fungal biomass preparations to Reactive Red-120 were not significantly affected with increasing NaCl concentration from 0 to 0.5 M and exemplified for heat-treated fungal biomass preparations (Fig. 6). This indicates that Cl^{1-} ions do not compete with

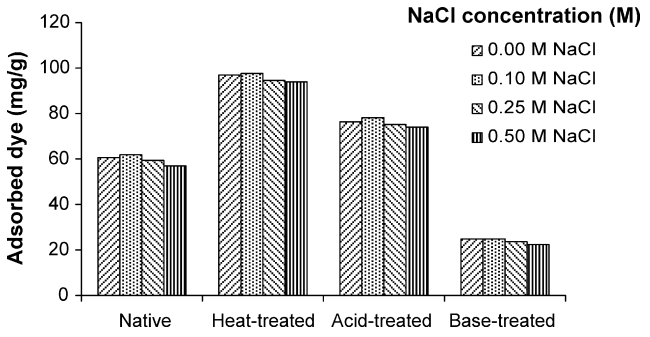


Fig. 6. Effect of ionic strength on the biosorption capacities of the native, heat-, acid- and base-treated fungal biomass preparations. Initial Reactive Red-120 concentration: 200 mg/l, temperature: 25 °C; biomass concentration: 1.0 mg/ml; pH: 3.0.

sulfonate groups of the dye molecules for amine sites of the fungal biomass. Dyeing processes consume large amounts of salt. Therefore, the concentration of salt in dye wastewaters can be normally high. From this point of view, this result indicates that the biomass of *L. sajur-caju* can be used for removal of acidic reactive dyes from salt containing water.

3.5. Effect of temperature on dye biosorption

Various textile dye effluents are produced at relatively high temperature, therefore temperature can be an important factor for the real application of the fungal biomass. The effect of temperature on the equilibrium biosorption capacity of the native, heat-, acid- and base-treated fungal biomass preparations was studied in the temperature range of 5–35 °C at an initial dye concentration of 200 mg/l. As shown in Fig. 7, the biosorption of dye increased with increasing temperature from 5 to 35 °C due to increased surface activity and increased kinetic energy of the dye molecules. Similar observations were reported in the literature [38–41]. For example, the adsorption capacity of the green alga *C. vulgaris* for Ramazol Black B dye increased with increase temperature [41].

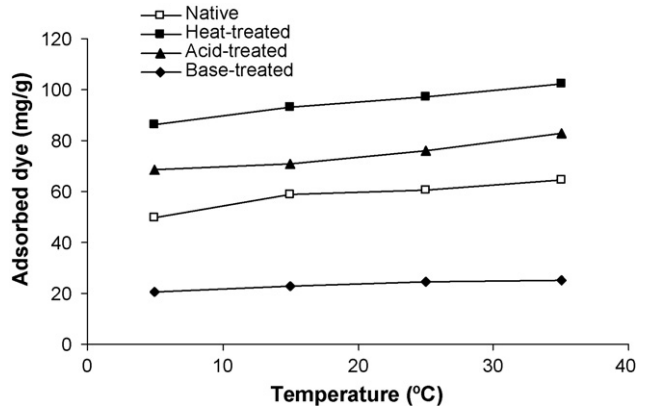


Fig. 7. Effect of temperature on the biosorption capacities of the native, heat-, acid- and base-treated fungal biomass preparations. Initial Reactive Red-120 concentration: 200 mg/l, biomass concentration: 1.0 mg/ml; pH: 3.0.

3.6. Effect of treatment on dye biosorption

The use of physically or chemically treated microbial biomass in biosorption is more advantageous for wastewater treatment in that dead microorganisms are not affected by toxic wastes, they do not require a continuous supply of nutrients and they can be regenerated and reused for many cycles [17,40]. The biosorption capacities of the native fungal biomass for Reactive Red-120 dye were 117.8 mg/g dry biomass. The biosorption capacities of the acid and heat-treated fungal biomass were increased about 1.55- and 1.18-fold compared to native form, respectively, whereas a decrease in the biosorption capacity of the base treated biomass was observed about 2.05-fold. The highest biosorption capacity was observed with the heat-treated biomass, could be explained by the increase in the additional binding sites via denaturation of proteins on the cell wall surfaces. The acid-treatment was also effective in increasing the biosorption capacity of the fungal biomass. The acid-treatment causes degradation of acid labile cell wall components into oligomers (i.e. polysaccharides and protein). On the other hand, the base-treated biomass had a low biosorption capacity compared to other treatment. The base treatment causes hydrolysis of the phospholipids portion of the cell membrane, thus a decrease in availability of adsorptive sites for binding with the dye molecule due to the disintegration of the fungal cell membranes. The biosorption capacity order of the fungal biomass preparations was observed as follows: heat-treated > acid-treated > native > alkali-treated.

3.7. Effect of initial dye concentration on dye biosorption

The amount of biosorbed Reactive Red-120 onto the fungal biomass preparations at equilibrium were studied and plotted as a function of the initial concentration of dye in the biosorption medium (Fig. 8). The biosorption capacity of the biomass preparations increased with increasing of the initial concentration of dye in the biosorption medium. The maximum biosorption capacities for the Reactive Red-120 with native and heat-, acid-

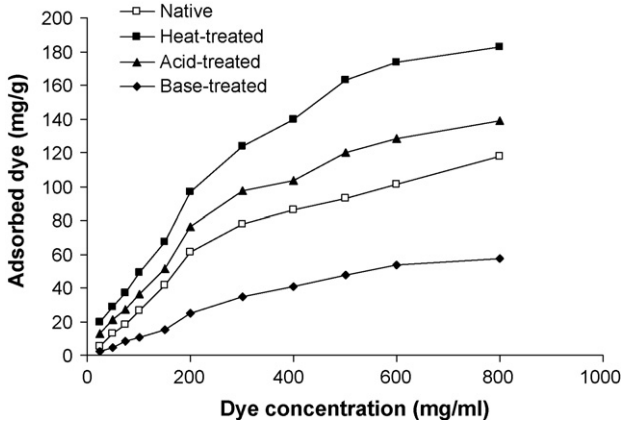


Fig. 8. Effect of initial dye concentration on the biosorption capacities of the native heat-, acid- and base-treated fungal biomass preparations. Initial Reactive Red-120 concentration: 25–800 mg/l, temperature: 25 °C; biomass concentration: 1.0 mg/ml; pH: 3.0.

and base-treated biomass was found 117.8, 182.9, 138.6 and 57.2 mg/g dry fungal biomass, respectively (Fig. 8). Netpratdit et al. studied the adsorption of Reactive Red-120 on the metal hydroxide sludge. The adsorption capacity of the adsorbent at different temperatures was between 42.37 and 51.55 mg/g [44]. The adsorption capacity of the activated carbon prepared from agricultural waste was reached up to 200 mg/g for Reactive Red-120 [45]. In this work, the heat treatment led to increase in the biosorption capacity of the *L. sajur-caju* biomass up to 182.9 mg/g. So, this result was comparable with the other adsorbents reported in the literature.

Three theoretical isotherm models were used to fit the experimental data: Langmuir, Freundlich and Temkin model. The Langmuir model is based on assumption homogeneity such as equally available adsorption sites, monolayer surface coverage, and no interaction between adsorbed species. Since the Langmuir model is formulated for homogenous adsorption. The Temkin and the Freundlich isotherm models are usually adopted for heterogeneous adsorption. The Freundlich isotherm is frequently used to describe the adsorption. It relates the adsorbed concentration as the power function of solute concentration. One limitation of the Freundlich model is that the amount of adsorbed solute increases indefinitely with the concentration of solute in the solution. This empirical equation takes the form:

$$q_{eq} = K_F(C_{eq})^{1/n} \quad (10)$$

where K_F and n are the Freundlich constants characteristic of the system. K_F and n are indicator of the adsorption capacity and adsorption intensity, respectively. The slope and the intercept of the linear Freundlich equation are equal to $1/n$ and $\ln K_F$, respectively. The Temkin isotherm model describes the behavior of many adsorption systems on heterogeneous surface and it is based on the following equation:

$$q = q_T \ln(1 + K_T c) \quad (11)$$

where K_T (ml/mg) is the equilibrium binding constant corresponding to the maximum binding energy ($K_T = \exp(-\Delta G_{max}/RT)$), c (mg/g) the concentration of dye in the solution at equilibrium, q (mg dye/g biosorbent) the amount of dye adsorbed on the tested biosorbents surface, and q_T (mg dye/g biosorbent) is the differential surface capacity for dye adsorption per unit binding energy. In the case of Temkin-type fit the experimental data, the semi logarithmic plot of $\ln C_{eq}$ versus q_{eq} was employed to generate the intercept value of $\ln K_T$ and the slope of q_T.

Table 3
The Langmuir model constants and correlation coefficients for biosorption of Reactive Red-120 "RR" on the fungal biomass preparations

Fungal biomass	Langmuir constants			
	q_{exp} (mg/g)	q_m	K_d (10^5 M)	R^2
Native-RR	117.84	178.9	5.78	0.817
Heat-treated-RR	182.97	244.2	2.35	0.869
Acid-treated-RR	138.61	196.4	1.26	0.856
Base-treated-RR	57.22	84.7	12.3	0.789

The corresponding semi-reciprocal Langmuir plots and Scatchard plots gave a non-linear plot for biosorption of the Reactive Red-120 on the fungal biomass preparations. In other words, a non-linear Scatchard plot indicates the adsorption heterogeneity [26]. The Langmuir isotherm model constants are summarized in Table 3. The maximum Reactive Red-120 biosorption capacity (q_m value) of the fungal biomass preparations was found to be significantly higher compared to experimental result value for each tested fungal biomass preparation. In addition, the correlation coefficient of the Langmuir plot (R^2) was not in the confidence limit for all the tested preparations. Thus, the adsorption of the dye onto the fungal biomass preparations cannot be reasonably described in terms of the Langmuir model. The magnitude of K_F and n values of Freundlich model showed easy uptake of dye from aqueous medium with a high adsorption capacity of the fungal biomass preparations. Values of $n > 1$ for both dyes molecules indicates positive cooperativity in binding and a heterogeneous nature of adsorption (Table 4).

In the case of the Temkin model, the corresponding semi-logarithmic plots gave rise to linear plot for the biosorption of dye to fungal biomass preparations and the correlation coefficient of the semi-logarithmic plots (R^2) was above 0.985 for the biomass preparations, indicating the Temkin model best fitted the experimental data. The fitted curves and the fitted parameter values for Temkin model are presented in Table 4. For the biosorption process of a dye, the possible binding sites can be non-specific (such as ionic, hydrophobic, etc.) or specific (affinity). All these interactions between dye molecules and fungal biomass adsorptive sites should result in uniform binding energies, up to some maximum binding energy (ΔG_{max}). In these cases, ΔG_{max} values were decreased from −8.98 to −9.67 kcal/mol for the dye on the fungal biomass preparations as the adsorbed dye increase on the biomass surface. These results indicate that there is a relationship between the surface interactions groups of the dye molecule with the fungal biomass

Table 4
The Freundlich and Temkin models constants and correlation coefficients for biosorption of Reactive Red-120 "RR" on the fungal biomass preparations

Fungal biomass	Freundlich constants			Temkin constants			
	n	K_F	R^2	q_T (mg/g)	K_T (M^{-1})	R^2	ΔG (kJ/mol)
Native-RR	1.12	0.39	0.985	34.71	42.80	0.980	−9.31
Heat-treated-RR	1.41	1.93	0.992	53.84	49.61	0.983	−9.67
Acid-treated-RR	1.37	1.26	0.990	40.64	49.26	0.978	−9.66
Base-treated-RR	1.06	0.14	0.992	17.66	37.49	0.976	−8.98

Table 5
The first- and second-order kinetics constants for biosorption of Reactive Red-120 on the fungal preparations

Fungal biomass	Experimental, q_{exp} (mg/g)	First-order kinetic			Second-order kinetic		
		$k_1 \times 10^2$ (min^{-1})	q_{eq} (mg/g)	R^2	$k_2 \times 10^4$ (g/mg/min)	q_{eq} (mg/g)	R^2
Native-RR	117.84	2.74	199.02	0.964	1.90	125.01	0.998
Heat-treated-RR	182.97	2.02	151.74	0.991	2.49	192.31	0.997
Acid-treated-RR	138.61	1.69	99.58	0.972	3.04	142.50	0.998
Base-treated-RR	57.22	1.26	44.01	0.987	4.47	62.48	0.996

preparations. From these observations, the range and distribution of binding energies should depend on the density, and type of functional groups, both on the dye molecules and the modified fungal biomass surface. As indicated in the Temkin model, the binding energy decreased with increasing the amounts of adsorbed dye on the biomass surface (Table 4).

3.8. Kinetic studies

Reactive Red-120 biosorption rate was obtained by following decrease of the concentration of each dye within the adsorption medium with time. The time necessary to reach equilibrium for the removal of the dye molecules by native, heat-, acid- and base-treated fungal biomass preparations from aqueous solution was established about 4 h. After equilibrium, the amount of adsorbed dye did not change significantly with time.

The experimental kinetic data of biosorption studies were applied to the first- and second-order kinetic models. First-order kinetic indicates that the process of biosorption occurs at a rate proportional to dye concentration, which is particularly suitable for low concentrations. Second-order kinetic is thought to drive from biosorption processes in which the rate-controlling step is an exchange reaction [2,41,42]. The rate constants, k, for the biosorption of the dye molecules on native and/or treated biomass preparations were determined from the first- and second-order rate equations and tabulated in Table 5. The data obtained by the first-order kinetic equation was not well-described biosorption of the dye on all the tested biomass preparations. The second-order kinetic model was able to suitable for description of biosorption kinetic for the removal of dye from aqueous solution onto native and heat-, acid- and base-treated biomass of *L. sajor-caju*. The experimental value of maximum biosorption capacity (q_{exp}) for the Reactive Red-120 dye on all the tested biosorbents are very close to calculated theoretical values (q_{eq}) of the second-order kinetic model, and also indicated that this process followed the second-order kinetic model (Table 5).

4. Conclusions

The biosorption of Reactive Red-120 dye from aqueous solution on the native, heat- and acid-treated fungal biomass preparations was studied in a batch system with respect to solid/liquid ratio, medium pH, ionic strength, temperature and initial dye concentration. The results of the study clearly showed that physical and chemical surface modification methods can be used to maximize the dye removal efficiency of the fungal biomass. The medium pH played a significant role in affecting the biosorption capacities of fungal biomass preparations. The biosorption of dye on the fungal biomass preparations increased with increasing temperatures under given experimental conditions. The biosorption capacities of the native, heat-, acid-, and base-treated fungal biomass preparations for Reactive Red-120 were 117.8, 182.9, 138.6 and 57.2 mg/g dry fungal biomass. The biosorption capacities order of the fungal biomass preparations were observed as follows: heat-treated > acid-treated > native > base-treated fungal biomass. The Temkin isotherm models were more applicable to the type of biosorption achieved by native, heat-, acid-, and base-treated fungal biomass of *L. sajor-caju*. The first- and second-order kinetic models were applied to the biosorption of the dye on the fungal biomass preparations and it was observed that the interactions could be better explained on the basis of second-order kinetic equations.

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