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Adsorption of Congo Red dye by native amine and carboxyl modified biomass of *Funalia trogii*: Isotherms, kinetics and thermodynamics mechanisms

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Abstract−Native, iminodiacetic acid and triethylenetetraamine modified biomasses of *Funalia trogii* were used for removal of Congo Red dye (CRD) from aqueous medium. The native and modified fungal biomasses were characterized using ATR-FTIR, Zeta potential, contact angle studies and analytical methods. FTIR studies of the native and chemically modified adsorbent preparations show that amine, carboxyl and hydroxyl groups are involved in the adsorption of the model dye (i.e., Congo Red). The maximum adsorption of the CRD on the native, carboxyl and amine groups modified fungal biomasses was obtained at pH 5.0. The amount of adsorbed dye on the adsorbent samples increased as the initial concentration of CRD in the solution increased to 200 mg/L. The adsorption capacities of native, carboxyl groups and amine modified fungal preparations were 90.4, 153.6 and 193.7 mg/g dry adsorbents, respectively. The data was fitted well with the Langmuir isotherm model, and followed the pseudo-second-order equations. Thermodynamic parameters (ΔG^o, ΔH^o and ΔS^o) were also calculated. The results showed that triethylenetetraamine (TETA) modified biomass of *F. trogii* presented an excellent dye removal performance and can be used in various environmental applications such as various micro-pollutants removal from aqueous medium.

Keywords: Fungal Biomass, Modification, Adsorption, Congo Red Dye, Surface Complexation, Wastewater Treatment

INTRODUCTION

Synthetic dyes are mostly utilized in cosmetics, paper and textile industries [1-5]. Among them, the azo dyes are categorized by the existence of azo bond, aryl groups, sulfate and amino groups. Azo dyes are generally recalcitrant due to their xenobiotic character and exhibit significant resistance to microbial degradation [6-8]. Various processes are based on physical or chemical methods for removal of dyes such as chemical oxidation, membrane separation and adsorption [9-12]. Adsorption is one of the available important methods for the adsorptive removal of organic and inorganic micro-pollutants from aqueous medium [13-17]. Recent advances towards effective treatment methods for the adsorption of micro-pollutants in aqueous media involve the use of microbial biomasses. Recently, to increase adsorption capacity, microbial biomasses have been modified with various ligands [7,18]. Various fungal biomasses have been also used as adsorbent for the adsorption of micro-pollutants from wastewaters, including *Funalia trogii*, *Trametes versicolor*, *Lentinus concinnus*, *Aspergillus niger* and *Rhizopus* spp. [19-23]. These fungal biomasses have been proven to be economic materials, as they can be easily cultivated using cheap and abundant carbon sources such as cellulose and waste carbon source [23]. In addition, they have high pollutant adsorption capacities due to the presence of several useful groups on their cell surfaces such as amino, hydroxyl, carboxyl and sulfate [5,23]. The adsorption capacity of a microbial biomass depends on its surface property as governed by the presence of functional groups on its biomass surfaces. Additional functional groups on the microbial biomass can improve the adsorbent performance and adsorption capacity. Recently, several modification methods have been reported to increase of the adsorption capacity of the microbial biomass using different ligands [24-27].

This aim of this work was to examine the equilibrium adsorption of a model micro-pollutant (i.e., Congo Red dye) on the natural, IDA and TETA modified fungal biomasses. Modifications of microbial biomasses have recently been proposed and have been used for removal of micro-pollutants from wastewaters. The experimental data obtained from the modified adsorbent after adsorption of target pollutant is to be used to determine the improvement of ligand on the adsorption capacity of the native fungal biomass. To achieve this goal, the biomass of *F. trogii* was modified with two different ligands: iminodiacetic acid, IDA and triethylenetetraamine, TETA. The removal of CRD was studied under different experimental conditions using native and modified fungal biomasses in a batch system. The effects of contact time, dye concentration, adsorbent dosage and pH were evaluated. The Langmuir and Freundlich models were used for testing of the experimental data. The pseudo-first-order and -second-order kinetic models were studied to determine the adsorption mechanism. Thermodynamic parameters were also determined: ΔG^o, ΔH^o and ΔS^o. The positive and negative values of ΔS^o and ΔG^o of these systems, respectively, showed that the adsorption process are spontaneous.

MATERIALS AND METHODS

1. Materials

Congo Red dye (CRD) was supplied from Sigma-Aldrich Chem-

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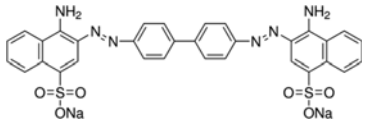
Table 1. The general characteristics of Congo Red dye

IUPAC name of dye	Disodium 4-amino-3-[[4-[4-[(1-amino-4-sulfonato naphthalen-2-yl) diazenyl]phenyl] phenyl]diazenyl] naphthalene-1-sulfonate
Synonym	Direct Red 28, Congo Red 4B
Color index number	22120
Chemical formula	$C_{32}H_{22}N_6Na_2O_6S_2$ 
Molecular weight (g/mol)	696.66
Chemical/Dye class	Diazo
λmax (nm)	662 nm

ical Co., St. Louis, MO, USA; the properties of the dye are presented in Table 1. Iminodiacetic acid (IDA), triethylenetetraamine (TETA), glutaraldehyde (GA), glycerol and diiodamethane were also purchased from Sigma Chem. Co.

2. Cultivation of *Funalia trogii*

Trametes trogii (MAFF 420251) was donoated by the National Institute of Agrobiological Sciences, Genebank, Kannondai, Tsukuba, Ibaraki, Japan, and continued by sub-culturing on malt dextrose agar slants. It was cultivated as described previously [23]. The fungal biomass was collected by filtration. It was washed with sterile saline solution and stored at 4 °C until use.

3. Preparation of Carboxyl and Amine Groups Functionalized *F. trogii*

The biomass of *F. trogii* (about 5.0 g) was incubated at room temperature in Tris-HCl buffer (25 mL, 50 mM, pH 8.0) for 2.0 h. Then, the fungal biomass was reacted with GA in the same buffer (25 mL, 1.0%) at 45 °C while being continuously shaken on a water-bath for 4.0 h. Then, GA reacted fungal biomass (about 5.0 g) was transferred to ethanol : water solution (70 : 30, v : v ratio, 150 mL) containing IDA or TETA (10 mg/mL), and the reaction was realized at 25 °C for 6.0 h. The activated fungal biomass was then separated by simple filtration and cleaned with distilled water and

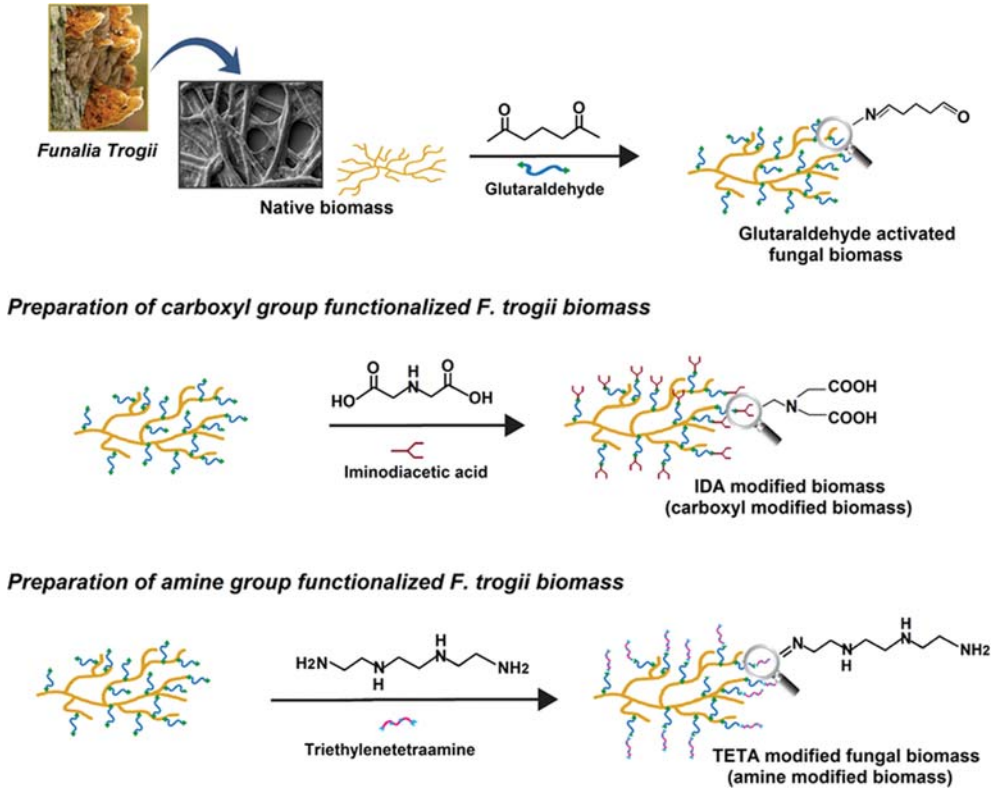


Fig. 1. Preparation of carboxyl and amine groups functionalized *F. trogii* biomasses.

Tris-HCl buffer (100 mM, pH 8.0). The final products were dried at 40 °C for 18 h, and kept in dry form at 4 °C until use. The chemical modifications of native *F. trogii* biomass with IDA and TETA ligands to create carboxyl and amino groups on the fungal biomass surface, respectively, are presented in Fig. 1.

4. Adsorption Studies of Congo Red Dye

Effects of various parameters on the CRD removal performance of the native, IDA and TETA modified biomasses were studied from aqueous solution. Adsorption experiments were realized by knowing amount of adsorbent in 10 mL of dye solution (200 mg dye/L) at 25 °C for 2.0 h. The influence of pH on the dye adsorption performance was studied by ranging medium pH from 1.0 to 9.0. The medium pH was adjusted with 0.1 mol/L HCl or 0.1 mol/L NaOH. The effect of adsorbent amount was studied by varying sorbent dosage between (0.2 and 2.0 g/L) in the medium. The effect of contact time was studied over a range of time (5 to 120 min). The effect of temperature and ionic strength was studied at four different temperatures (between 288 and 318 K) and at different NaCl concentration between 0.1 and 1.0 mol/L at pH 5.0, respectively. The effect of varying concentration of CRD on the adsorption performance was studied by changing the concentration of CRD between 10 and 300 mg/L. Each set of experiments was studied in duplicates with 1.0 g/L adsorbent sample. The dye concentration in the solution was analyzed using a double beam UV/vis spectrophotometer (PG Instrument Ltd., Model T80+; PRC) at 662 nm. A calibration curve for CRD was obtained by plotting absorbance (A_{662}) versus micro-pollutant concentrations, respectively.

5. Desorption and Regeneration of Adsorbents

Adsorption-desorption rounds were repeated six times by using the same sorbent samples. Desorption of CRD was realized by 10 mmol/L nitric acid solution. The dye laden samples were transferred in desorption solution and agitated at 150 rpm for 2.0 h at 25 °C. After each adsorption-desorption cycle, the adsorbent sample was washed with 0.1 mol/L NaCl solution and added into fresh Congo Red dye solution for the next sorption cycle.

6. Characterization Studies of Adsorbent Preparations

ATR-FTIR spectra of the native, IDA and TETA modified fungal samples were obtained by using an attenuated total reflectance-Fourier-transform infrared (ATR-FTIR) spectrometer (Nicolet IS 5, Thermo Electron Scientific Instruments, WI, USA). The surface areas of the fungal biomasses were measured by the Brunauer, Emmett and Teller (BET) method. Contact angles to water, glycerol and diiodomethane of the native, IDA and TETA modified fungal biomass before and after contacted with CRD were studied at 25 °C with a digital optical contact angle meter Phoenix 150 (Surface Electro Optics, Korea). The amount of amino group of the native and TETA ligand attached biomass samples was determined by titrimetric method as described previously (2). The amounts of total available carboxyl group of the native and IDA modified fungal biomass samples were determined by a titrimetric method as described previously (18).

The ζ potential measurement was studied as described previously (18). The sample was added in a solution with known pH value to conduct potential measurement with a Zetasizer instrument (NanoZS, Malvern Instruments Ltd., Malvern, UK). The FTIR, BET and zeta potential measurements were studied in triplicate. The significance of differences among data was calculated with analysis of variance ($p<0.05$).

RESULTS AND DISCUSSION

1. Properties of the Adsorbent Preparations

In this research, native, IDA and TETA modified *F. trogii* biomasses were used as the adsorbents for adsorption of a model diazo dye from solutions. *F. trogii* is a white rot fungus and grows easily on abundant carbon source like cellulose. The attachment of IDA and/or TETA ligands on the biomass can also provide additional binding sites for the target dye molecules (Fig. 1). The surface areas of the native, IDA and TETA fungal biomass samples were determined by BET method, and found as 0.489, 0.339 and 0.363 m^2/g adsorbent, respectively. The modification of the fungal biomass with IDA and TETA ligand caused a reduction in the surface area of the modified adsorbents compared with native counterpart.

To predict the responsive functional groups for CRD adsorption, ATR-FTIR spectroscopy was used. The ATR-FTIR spectra of the native *F. trogii*, IDA and TETA modified fungal biomass are presented in Fig. 2. The FT-IR spectrum of the native *F. trogii* has intense peaks at around 3,261 cm^{-1} assigned to the stretching vibration of hydroxyl groups and also stretching vibration of -NH groups (Fig. 2(a)). The peaks at 2,935 cm^{-1} can be attributed C-H stretching vibrations. The peaks at 1,629 and 1,556 cm^{-1} represent N-H

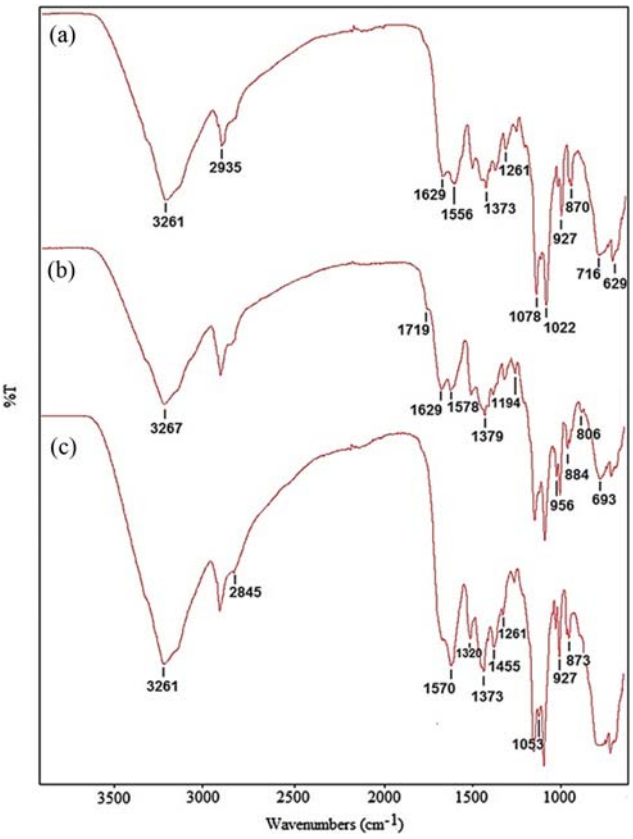


Fig. 2. ATR-FTIR spectra: (a) Native fungal biomass; (b) IDA fungal modified biomass; (c) TETA fungal modified biomass.

Table 2. Contact angle values of water, glycerol and diiodamethane for the native, IDA, and TETA modified fungal biomass preparations

Fungal biomass	Water, θ(°) (γ^{erg}=71.3)	Glycerol, θ(°) (γ^{erg}=64.0)	DIM, θ(°) (γ^{erg}=50.8)
Native	107.4±2.1	95.8±1.6	52.3±2.4
Native-Congo Red	92.4±1.8	88.9±1.8	45.5±1.3
IDA modified	61.3±0.9	54.7±1.9	28.9±1.3
IDA modified-Congo Red	87.6±2.4	79.2±1.3	41.5±1.6
TETA modified	53.4±0.4	49.7±2.1	25.4±1.2
TETA modified-Congo Red	82.3±0.7	74.1±0.8	39.6±1.4

γ_{erg}: surface tension of test liquid

bending (scissoring) and they can be due to the chitin moiety of the fungal sample. The peaks at 1,373 and 1,022 cm^{-1} denote -CH_3 and C-OH stretching vibrations, respectively. The phosphate group shows a peak at around 1,078 cm^{-1} related to P=O stretching (Fig. 2(a)). As can be seen in these spectra, the functional groups for interaction of CRD could be involving carboxyl, hydroxyl, phosphoryl and polyamine groups. After modification with IDA, the stretching vibration peak at 1,629 cm^{-1} was increased, which corresponds to N-H stretching (Fig. 2(b)). Additionally, increase in the peak area at around 3,261 and 1,570 cm^{-1} is observed due to the -NH stretching peaks. After TETA attachment, a characteristic peak of -NH_2 is observed at 1,373 cm^{-1}. An addition, the stretching vibration band of N-H at 3261 is broadened (Fig. 2(c)).

The contact angle values for different test liquids (water, glycerol and diiodomethane) on the native, IDA and TETA modified biomass of *F. trogii* are presented in Table 2. The native, IDA and TETA modified biomass of *F. trogii* surfaces have different composition of functional groups such as -OH, -NH_2, -NH, -COO-, -CH_3 and aryl groups for interactions with the target dye molecules. These functional groups are most important for designing a new adsorbent in the area of adsorption technology. Therefore, contact angle studies were performed in the description of the adsorbent surfaces to define possible interaction mechanisms. The wettability of an adsorbent can be determined by comparing the contact angle values of both water and diiodomethane. Since, both solvents are often used as reference liquids in analyses of interaction of hydrophilic or hydrophobic liquids with solid. As can be seen from Table 2, all the studied samples represented very different contact angle values depending on their surface properties. The native fungal biomass had hydrophobic character (i.e., θ>90°) as shown by contact angle measurement (Table 2). The contact angle values of the IDA and TETA modified fungal biomasses decrease can be due the attachment of hydrophilic functional carboxyl and amine groups. Therefore, the adsorption capacity of both IDA and TETA modified fungal biomass increased compared to the native counterpart due to the increment of the adsorptive site (amine and/or carboxyl groups) on the fungal biomass surface (Table 2). After Congo Red dye adsorption, the contact angle values of all the tested adsorbents (i.e., the native *F. trogii*, IDA and TETA modified fungal biomass) were also changed due to interaction of CRD with the modified biomasses. It may be due to the domination of hydrophobic entities of the Congo Red dye molecule on the adsorbent surface.

The zeta potential value was realized in the pH range 2.0-11.0 with the native, IDA and TETA modified fungal biomass preparations (Fig. 3). The zeta potential of the native fungal biomass decreased steadily from 11.3 to −34.8 mV as pH increased from 2.0 to 11.0. The surface charge of the both IDA and TETA modified biomasses substantially altered when compared with the native fungal biomass. The IDA ligand with two carboxylic acid group was incorporated to enhance dye adsorption capacity of the fungal biomass. The zeta-potential value of IDA modified biomass was decreased from 7.4 to −44.3 in the pH range 2.0-11.0. This can be due to the dissociation of carboxyl groups of the IDA ligand. The zeta potential value of the TETA incorporated fungal biomass was decreased gradually from 29.6 to −27.9 mV as pH increased from 2.0 to 11.0, respectively. Note that the zeta potential is also a very important parameter to determine the degree of ionized groups of the dye at a given pH value.

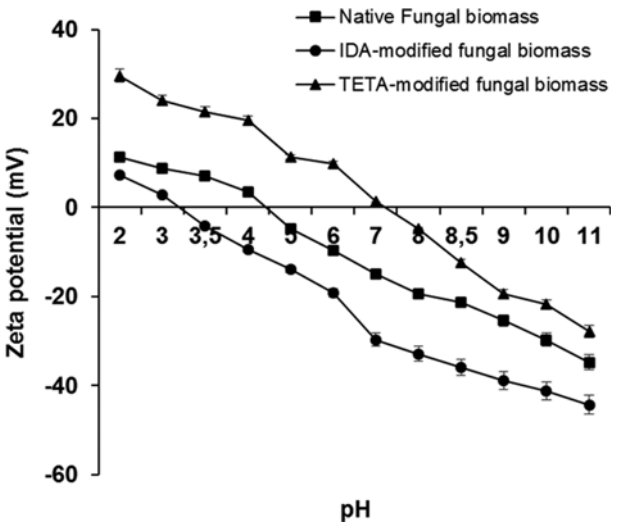


Fig. 3. pH versus zeta potential plots for the native fungal biomass, IDA and TETA modified fungal biomass preparations.

2. Effect of Adsorbent Dosage

The removal capacity of Congo Red dye was performed by changing the sorbent dosage between 0.2 and 2.0 g/L at a fixed dye concentration of 200 mg/L and at pH 5.0. The effect of adsorbent dosage for the native, IDA and TETA modified fungal biomass samples is presented in Fig. 4. From this figure, the percentage removal of the CRD was enhanced with increasing the sorbent dose from 0.2 g to 1.0 g/L, and further increase of the adsorbent dose did not show enhancement in the percentage of the dye re-

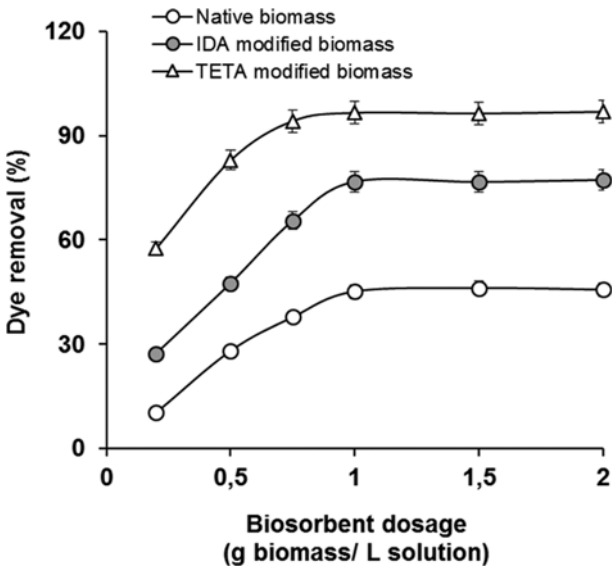


Fig. 4. Effect of adsorbent amount on the adsorption of Congo Red dye on the native fungal biomass, IDA and TETA modified fungal biomass.

moval. At sorbent dosage >1.0 g/L, the increase in the percent removal of the dye with increasing in the amount adsorbent was less, and the removal percentage of the native, IDA and TETA modified fungal biomass preparations at 1.0 g/L biomass dose was determined as 45.2, 76.8 and 96.6%, respectively. The removal percentage of the Congo Red dye increased as the amount of adsorbent dose increases in the medium. This can be due to the large availability of the adsorptive sites or surface area at high concentration of the adsorbent. This result shows that there is an optimal dose of adsorbents, which in this case is 1.0 g/L. Therefore, remaining studies were performed using 1.0 g/L adsorbent dosage.

3. Effect of pH on Congo Red Dye Adsorption

The fungal cell surfaces contain chitin/chitosan, proteins, lipids and teichoic acid, and these macromolecules contain several adsorptive sites such as, amino, carboxyl, thiol and phosphate groups. The ionization state of these surface functional groups and the dye molecules in solution depends on the medium pH [27-29]. Therefore, the adsorption behavior of the aforementioned dye was studied at different pH values with the native, IDA and TETA modified fungal biomasses (Fig. 5). Note that CRD is a diazo dye and has two sulfates, two primary and secondary amino groups, several hydrophobic entities (Table 1). Generally speaking, at low pH values both carboxylic groups of the dye and IDA ligand are protonated, and also the hydronium ions compete with dye molecules to be interacted with amine groups of the dye and TETA ligand, leading to a reduced adsorption capacity. As observed from Fig. 5, the adsorption capacity decreased in pH values above and below 5.0 for all the tested adsorbent preparations. Maximum adsorption capacities of the native, IDA and TETA modified fungal biomasses at pH 5.0 were determined to be 90.4, 153.6 and 193.7 mg/g, respectively. The pK_a value of the sulfate and the -NH_2 groups of the dye molecule is 1.87 and 8.5, respectively. The removal of CRD enhanced with increasing pH from 1.0 to 3.0 and decreased at pH>5.0, indicating that the removal of the dye was strongly affected by the medium pH. The adsorption of CRD is interpreted from the relative distribution of charged groups of the dye in solutions and the used adsorbent surface properties. Thus, adsorption of CRD on the native and both modified fungal biomasses is mainly due to the electrostatic interactions between the protonated N atoms of TETA or deprotonated carboxyl groups of the IDA on the adsorbent surface and the zwitterion form of the dye. Furthermore, it is expected that removal of CRD would be lower at low pH ranges due to competition for binding sites between CRD and the H^+ ions [23]. Thus, the lower sorption of CRD on fungal biomass preparations with increasing pH could be attributed to an increased electrostatic repulsion between the positively charged dye molecule and positively charged adsorbent surfaces [30,31]. Maintaining the solution pH at 5.0 could help obtain high capacity removal efficiency; therefore, the remaining experiments were realized at pH 5.0 for all the used adsorbents.

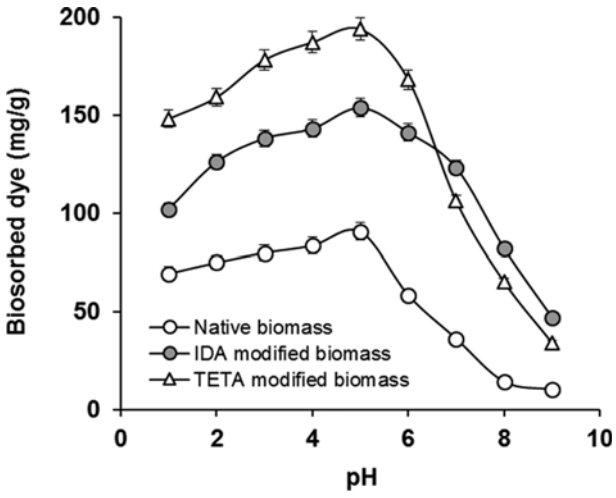


Fig. 5. Effect of pH on the adsorption of Congo Red dye on the native fungal biomass, IDA and TETA modified fungal biomass.

4. Effect of Ionic Strength on Congo Red Dye Adsorption

The effect of ionic strength on Congo Red dye adsorption was evaluated at pH 5.0 with the native, IDA and TETA modified fungal biomass samples. When the electrostatic forces between adsorptive sites on the sorbent and target pollutant are opposite, then an increase in salt concentration will result in a reduction in the adsorption capacity of sorbent [24,25,33,34]. Therefore, the ionic strength of solution was changed between 0.00 and 1.0 M by varying salt concentration. As can be seen in Fig. 6, for all the studied fungal samples, the amount of adsorbed CRD decreased with increasing ionic strength. This can be due to the decreasing electrostatic attraction between the dye molecules and the binding groups on the adsorbent surface with increasing ionic strength. The addition of Na+ and Cl– ions in the adsorption medium can shade the interactive sites of the adsorbent, and the electric binary layers of the adsorbent surface are compressed, leading to a reduction in the electrostatic interactions [35,36]. This observation shows that ion-exchange could be responsible for CRD adsorption process for all the used fungal preparations.

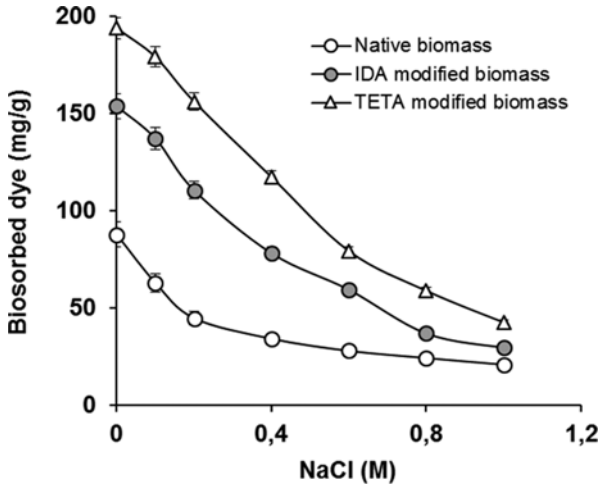


Fig. 6. Effect of ionic strength on the adsorption of Congo Red dye on the native fungal biomass, IDA and TETA modified fungal biomass.

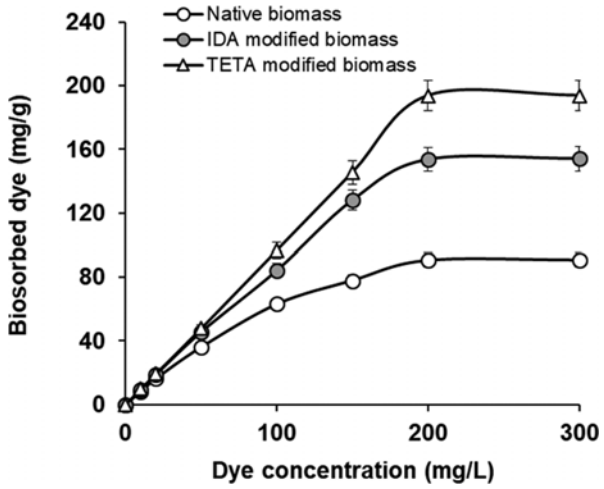


Fig. 7. Effect of initial Congo Red dye concentration on the adsorption capacity of the native fungal biomass, IDA and TETA modified fungal biomass.

5. Effect of Initial Dye Concentration

The adsorption capacities of the native, IDA and TETA modified fungal biomass samples are presented in Fig. 7 by varying initial concentrations of Congo Red dye within the solutions. At the first stage, the dye was rapidly adsorbed on the external surface of native fungal biomass, whereas later stage, followed by a slower internal diffusion process which may be the rate determining step, and similar observations were also reported earlier [23]. On the other hand, the adsorption of dye on both modified adsorbent preparation was very steep until reaching saturation values. We noted that the adsorption capacity of the fungal biomass preparations enhanced with increasing the initial concentration of Congo Red dye and reached saturation values of 200 mg/L. The amount of Congo Red dye adsorbed on the native fungal biomass was 90.4 mg/g dry adsorbent. Upon modification with IDA and TETA ligands the adsorption capacity significantly increased for Congo Red dye up to 153.6 and 193.7 mg/g adsorbents. The order of dye adsorption capacities of the adsorbents was found as: TETA modified>IDA modified>native fungal biomass. The modification of fungal biomass with IDA and TETA ligands led to increase in the adsorption capacities about 1.69 and 2.14 folds compared with the native fungal biomass. A long chain ligand molecule (i.e., TETA) coated surface of the fungal biomass eventually caused more Congo Red dye adsorption compared with IDA modified counterpart. This can be due to the presence of large quantity positive changes (i.e., one primary amine and three secondary amine groups) on each ligand molecule with six carbon atom extender. In addition, the six extender carbon atoms with multi-positive charges on the TETA ligand can facilitate its versatility for interactions in aqueous medium with carboxyl groups of the Congo Red dye molecules. On the other hand, IDA ligand has only two negative charges and may be buried on the surface of the fungal biomass and may be donating fewer available interaction sites compared with TETA ligand. Thus, TETA ligand modified fungal biomass yielded a high adsorption capacity compared to IDA ligand modified counterpart.

6. Isotherm Models Studies

Two different isotherm models, Langmuir and Freundlich, were tested for evaluation of experimental data. The used isotherm models equations are:

The Langmuir isotherm model:

$$C_e/q_e=(1/q_{max})\,(C_e)+(1/q_{max}\,K_a) \quad (1)$$

where q_{max} is the maximum adsorption capacity (mg/g), C_e is the equilibrium Congo Red concentration (mg/L) and K_a is the equi-

Table 3. Adsorption isotherm models constants for adsorption of Congo Red dye on the native, IDA and TETA modified fungal biomass preparations from aqueous solution (*Initial concentrations (C_o) of Congo Red dye, 200 mg/L)

		Model parameters				
	Fungal biomass	q_{max} (mg/g)	q_{max} (mg/g)	$K_a\times10^{-5}$ (L/mol)	R^2	*R_L
Langmuir	Native	90.4	100.2	0.338	0.998	0.094
	IDA modified	153.6	169.5	0.598	0.996	0.055
	TETA modified	193.7	203.6	1.366	0.999	0.026
			K_F	n	R^2	
Freundlich	Native		7.59	1.92	0.994	
	IDA modified		15.0	1.68	0.992	
	TETA modified		31.3	1.79	0.992	

librium adsorption constant (the association coefficient) (L/mol).

The linear Freundlich isotherm model equation:

$$\ln q_e = (1/n) \ln C_e + \ln K_F \quad (2)$$

K_F and n are the Freundlich adsorption isotherm constants.

The calculated isotherm models parameters are presented in Table 3. In addition, the important characteristic of the Langmuir model is presented in terms of an equilibrium parameter, R_L, which is specified in Eq. (3)

$$R_L = 1/(1+b\,C_o) \quad (3)$$

The R_L values between 0 and 1 show satisfactory absorption. Also, R_L values equal to 0 designate irreversible absorption, R_L=1 is linear and R_L>1 is unfavorable. The obtained R_L values for Congo Red dye adsorption on the native, IDA and TETA modified fungal biomasses ranged from 0.026 to 0.094 (Table 3); therefore, the removal of Congo Red by the fungal sample seemed to be feasible. In addition, higher correlation of coefficients of Langmuir model was observed compared to the Freundlich model. It shows that the adsorption equilibrium is well defined by the Langmuir model (Table 3). From the linear plots of Freundlich model constants (K_F and n) for the native, IDA and TETA modified fungal biomass samples presented positive cooperativity in binding and heterogeneous nature of adsorption (Values of n>1 for the Congo Red dye at 25 °C) (Table 3).

7. Adsorption Time and Kinetic Models

The equilibrium adsorption time of Congo Red dye on the native, IDA and TETA modified fungal biomasses from aqueous solution was also studied. The results are presented in Fig. 8, and the change in the amount of adsorbed Congo Red with time is also given in this figure. From the figure, adsorption equilibrium was nearly saturated after 30 min, and after this period, the amount of adsorbed Congo Red dye did not considerably change further with contact time.

The experimental data was evaluated with pseudo-first-order and pseudo-second-order equations:

$$\log (q_e - q_t) = \log q_e - (k_1 \cdot t)/2.303 \quad (4)$$

$$(t/q_t) = (1/k_2\, q_e^2) + (1/q_e)\, t \quad (5)$$

where q_e (mg/g) is the experimental amount of Congo Red dye adsorbed at equilibrium, q_t (mg/g) is the amount of Congo Red dye adsorbed at time t, k_1 (min^{-1}) and k_2 (g/mg/min) are the equilibrium rate constants of the pseudo-first- and second-order kinetic models, respectively. The constant k_2 is considered to determine the initial adsorption rate 'h' (mg/g/min), at t→0 by using $h = k_2 q_e$.

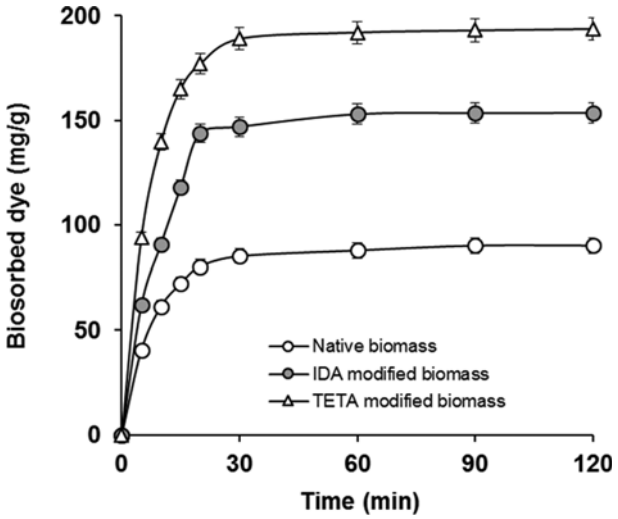


Fig. 8. Effect of contact time on the adsorption of Congo Red dye on the native fungal biomass, IDA and TETA modified fungal biomass.

The calculated constants for the used kinetic equations are given in Table 4. From the table, the correlation coefficients (R^2) calculated from the pseudo-second-order plots were above 0.998 for the native, IDA and TETA modified fungal biomasses. All the adsorbent samples fitted better with respect to the pseudo-first-order equation. In addition, the experimental adsorption capacities (q_e) of samples were well fitted with the calculated adsorption capacities of the pseudo-second-order model (Table 4).

8. Thermodynamic Parameters

In this study, the removal of Congo Red by the native, IDA and TETA modified fungal biomass was temperature dependent between 15 and 45 °C, and the maximum binding values of the fungal samples were enlarged with increasing temperature (Table 5). The values of the equilibrium adsorption constant were calculated by using Langmuir Eq. (1) in M^{-1} unit. Table 5 shows the variation in K_a values for Congo Red adsorption on the native, IDA and TETA incorporated fungal biomass preparations as changing tempera-

Table 4. Kinetic parameters for adsorption of Congo Red dye on the native, IDA and TETA modified fungal biomass preparations from aqueous solution

		Model parameters				
	Fungal biomass	$q_{e,exp}$ (mg/g)	$q_{e,cal}$ (mg/g)	$k_1 \times 10^2$ (min^{-1})	R^2	
First-order	Native	90.4	69.7	7.83	0.962	
	IDA modified	153.6	98.6	8.07	0.987	
	TETA modified	193.7	95.4	5.62	0.951	
		$q_{e,exp}$ (mg/g)	$q_{e,cal}$ (mg/g)	$k_2 \times 10^3$ (g/mg min)	$h \times 10^{-2}$ (g/mg min)	R^2
Second-order	Native	90.4	94.3	2.25	0.21	0.999
	IDA modified	153.6	162.6	1.12	0.18	0.998
	TETA modified	193.7	200.8	1.39	0.28	0.999

Table 5. The distribution coefficient, adsorption constants and the thermodynamic parameters for adsorption of Congo Red dye on the native, IDA and TETA modified fungal biomass preparations from aqueous solution at different temperatures

Fungal biomass	T (K)	q_{exp} (mg/g)	q_m (mg/g)	$K_a \times 10^{-5}$ (M^{-1})	R^2	ΔG^o (kJ/mol)	ΔH^o (kJ/mol)	ΔS^o (kJ/mol K)
Native	288	83.7	96.1	0.16	0.997	−23.2	38.1	0.21
	298	90.4	100.2	0.33	0.998	−25.8		
	308	98.1	106.3	0.48	0.996	−27.6		
	318	102.6	107.5	0.72	0.999	−29.7		
IDA modified	288	126.4	142.9	0.25	0.991	−24.2	69.0	0.32
	298	153.6	169.5	0.60	0.996	−27.1		
	308	164.3	169.5	1.73	0.998	−30.5		
	318	171.8	174.5	3.56	0.998	−33.8		
TETA modified	288	169.2	192.3	0.47	0.989	−25.8	77.6	0.36
	298	193.7	203.6	1.36	0.999	−29.3		
	308	208.9	208.3	4.01	0.999	−33.0		
	318	219.5	220.6	9.85	0.999	−36.5		

tures. Their values were found to increase by increasing temperature of the adsorption medium. The following equations were used for determination of the thermodynamic parameters such as enthalpy (ΔH^o), Gibbs free energy (ΔG^o) and entropy (ΔS^o).

$$\Delta G^o = -RT \ln K_a \quad (6)$$

$$\ln K_a = -\Delta G^o/RT = -\Delta H^o/RT + \Delta S^o/R \quad (7)$$

where R is the gas constant (8.314 J/mol/K) and T shows the absolute temperature (K). The values of ΔH^o and ΔS^o were determined from the slope and intercept of the van't Hoff plot of ln K_a versus 1/T.

The calculated data of the thermodynamic parameters are presented in Table 5. The obtained data of Gibbs free energy indicated that the adsorption system was a spontaneous process, and the decreasing of ΔG^o with the increasing of temperature showed that the adsorption was more satisfactory at elevated temperatures. The positive values of ΔH^o established the endothermic process for the adsorption of Congo Red, consistent with the increase of adsorption capacity as temperature increased. The positive ΔS^o value of the adsorbent system indicated that the increasing randomness between the solid/solution interface during the adsorption process.

9. Desorption Studies

Desorption of Congo Red dye was realized by 10 mmol/L HNO_3 solution. Each dye-laden adsorbent preparation was added in the desorption solution and agitated at 100 rpm for 2 h at room temperature. After each cycle, the adsorbent sample was washed with 0.1 mol/L NaCl solution and added into CRD solution for operation next cycle. When 10 mmol HNO_3 solution was selected for desorption of CRD from the native, IDA and TETA modified adsorbents and the desorption ratios were found to be 88.9, 92.8 and 95.3%, respectively.

Adsorption capacities of the native, IDA and TETA modified fungal biomass preparations were decreased about 15.2, 11.4 and 6.8% in the first cycle. On the other hand, there was a gradual decrease in Congo Red dye adsorption with an increase in the number of cycles, and these were more pronounced for the native fungal biomass preparation.

CONCLUSION

Native fungal biomass was chemically modified with IDA and TETA ligand under mild experimental conditions and characterized by FTIR, Zeta potential studies and analytical methods. The modified fungal biomass with IDA and/or TETA ligands containing di-carboxyl and four amine groups per ligand molecules, respectively, were tested for the purpose of removing CRD from aqueous solutions. The removal performance of the CRD on the samples depends on the adsorption parameters. High sorption capacity for CRD is achieved through the ion exchange interaction by TETA incorporated samples. The maximum sorption capacities of the native, IDA and TETA incorporated fungal biomasses were determined as 90.4, 153.6 and 193.7 mg/g, respectively. The experimental data was well described by the Langmuir model with high R^2 values. The pseudo-second order model was proper to designate the sorption kinetic of the native, IDA and TETA modified fungal biomasses. The TETA modified fungal biomass is a potential candidate as an adsorbent with high efficiency to remove pollutants from aqueous solutions. For example, the basic nature of the grafted TETA ligand could strengthen the interaction with transition metals according to the acid-base Lewis theory. Thus, the TETA-modified fungal biomass can be also proposed for adsorption of transition metals from aqueous solutions. The adsorption capacity of the TETA modified biomass may be extensively increased compared to native counterpart because of a strong interaction of basic amino groups with transition metal ions [37,38].

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