

Biosorption of synthetic dyes (Direct Red 89 and Reactive Green 12) as an ecological refining step in textile effluent treatment

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Abstract With the use of cost-effective natural materials, biosorption is considered as an ecological tool that is applied worldwide for the remediation of pollution. In this study, we proposed *Lemna gibba* biomass (LGB), a ligno-cellulosic sorbent material, for the removal of two textile dyes, Direct Red 89 (DR-89) and Reactive Green 12 (RG-12). These azo dyes commonly used in dyeing operations of natural and synthetic fibres are the most important pollutants produced in textile industry effluents. For this purpose, batch biosorption experiments were carried out to assess the efficacy of LGB on dye treatment by evaluating the effect of contact time, biomass dosage, and initial dye concentration. The results indicated that the bioremoval efficiency of 5 mgL⁻¹ DR-89 and RG-12 reached approximately 100 % after 20 min of the exposure time; however, the maximum biosorption of 50 mgL⁻¹ DR-89 and 15 mgL⁻¹ RG-12 was determined to be about 60 and 47 %, respectively. Fourier transform infrared spectroscopy used to explain the sorption mechanism showed that the functional groups of carboxylic acid and hydroxyl played a major role in the retention of these pollutants on the biomass surface. The modelling results using Freundlich, Langmuir, Temkin, Elovich, and Dubini Radushkevich (D-R) isotherms demonstrated that the DR-89 biosorption process was better described with the Langmuir theory ($R^2=0.992$) while the RG-12 biosorption process fitted well by the D-R isotherm equation ($R^2=0.988$). The maximum biosorption capacity was found to be 20.0 and 115.5 mgg⁻¹ for DR-89 and RG-12, respectively, showing a higher ability of duckweed biomass for the bioremoval of the green dye. The thermodynamic study showed that the dye biosorption was a

spontaneous and endothermic process. The efficacy of using duckweed biomass for the bioremoval of the two dyes was limited to concentrations ≤ 50 mgL⁻¹, indicating that *L. gibba* biomass may be suitable in the refining step of textile effluent treatment.

Keywords Biosorption · Duckweed biomass · Textile dye · Wastewater treatment

Introduction

The development of several industries promotes the rapid increase of environmental pollution. The dye and pigment pollution originating from the textile, paper, printing, leather and other industries is considered as a significant source of aquatic ecosystem disequilibria (Rafatullah et al. 2010). In particular, the textile industry, which consumes large volumes of water in different wet processes, produces considerable amounts of textile wastewaters which are charged with dyes and other undesirable chemicals (Vajnhandl and Le Marechal 2005; Gupta et al. 2007a; Sayilgan and Cakmakci 2012). Textile dyes are one of organic substances whose effects on human, animals and the different ecosystems have been well demonstrated (Gupta et al. 2007c, e; Ju et al. 2008; Rafatullah et al. 2010; Mona et al. 2011). In addition, these pollutants can be transferred to the food chain and thus are threatening human health. Therefore, the treatment of industrial effluents charged with these undesirable products is necessary before their discharge in aquatic ecosystems.

In spite of several technological processes used for the treatment of textile effluents (electrocoagulation, membrane filtration, biodegradation, extraction, photocatalytic degradation, etc.) sorption techniques both in batch and column mode have been largely employed (Gupta et al. 2006a; Gupta et al. 2010b; Gupta et al. 2011). A wide variety of

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natural or synthetic materials, both organic and inorganic, have been employed in dye sorption processes: siliceous materials (Walker et al. 2003; Dogan et al. 2007), activated carbon (Malik 2003), natural polymers (Crini 2008; Sekhar et al. 2009; Sreelatha et al. 2011), agriculture and industrial by-products (Jain et al. 2004; Gupta et al., 2006c; Gupta et al. 2007d; Nurchi and Villaescusa 2008; Dulman and Cucu-Man 2009; Ahmaruzzaman and Gupta 2011), waste animal material (Gupta et al. 2006b; Mittal et al. 2012), bacteria (Sayilgan and Cakmakci 2012) and dead biomass. Removal of synthetic dyes by dead biomass called biosorption was of concern in many recent researches (Hai et al. 2008; Vasanth Kumar et al. 2006; Gupta et al. 2010a; Tan et al., 2010). Biosorption is a term that describes the removal of contaminants by the passive binding to non-living biomass from an aqueous solution without any metabolic control (Kim et al. 2007). The removal can be achieved by a number of independent processes (physical and chemical adsorption, ion exchange, complexation, chelation, and micro-precipitation) taking place essentially in the cell wall. Biosorption is very interesting since it is simple, effective, inexpensive and sustainable with the use of natural and renewable source as sorption materials. Additionally, this technique becomes more interesting if the biomass originated from sedentary abundant plants which can live under many extreme environments (e.g. duckweed). On the other hand, this technique is applied frequently on large scale and can produce a high quality of water without producing notorious sludge, residual contaminants, etc. (Gupta et al. 2007b).

In this study, we proposed the removal of two synthetic dyes, Direct Red 89 (DR-89) and Reactive Green 12 (RG-12), commonly used as dye products in dyeing processes of the textile industry of Algeria, by dead biomass of the duckweed *Lemna gibba* L. native to northeast Algeria. This study concerned the evaluation of the effect of three operating parameters: contact time, biomass dosage and initial dye concentration. The process modelling was studied by the determination of sorption isotherms according to Freundlich, Langmuir, Temkin, Elovich and Dubinin Radushkevich (D-R). The thermodynamic parameters (ΔG , ΔH and ΔS) revealing the nature of dye sorption were also determined.

Materials and methods

Preparation of biosorbent

Fronds of *L. gibba* L. collected from a natural pond located in the city of Annaba (northeast Algeria) were separated, cleaned several times with tap and distilled water and oven-dried at 70 °C during 48 h. After drying, the obtained biomass, called *L. gibba* biomass (LGB), was stocked in desiccators, without any pre-treatment, for further utilization.

Physicochemical data of dyes

The two dyes used in this experimental work were Direct Red 89 (DR-89) and Reactive Green 12 (RG-12) obtained from the manufacture of the textile industry located in the city of Constantine (Eastern Algeria). The two dyes were used without further purification. The molecular formulae, molecular weight and other physicochemical data of the two dyes are reported in Table 1. An aqueous stock solution of 1,000 mgL⁻¹ dye was prepared using distilled water. From this stock solution (conserved at 4 °C), diluted solutions were prepared to conduct the different experiments.

Biosorption experiments

Biosorption assays were elaborated in a banc of four thermostated glass reactors (15 cm height and 10 cm in diameter) containing 1 l of dye solution under static conditions (Fig. 1). Treatments and controls, performed without adjusting solution initial pH (pH~7.1, measured with a pH meter model HANNA 211, is the value resulting from solving the dye in water), were continuously stirred at 200 rpm for 2 h which are sufficient to reach equilibrium. Two different controls were carried out in parallel; biosorption in distilled water (control 1) was carried out to assess the absorbance of green pigments released in water by the plant biomass. In addition, dye solution without biosorbent (control 2) was necessary to ensure that sorption was by plant biomass and not the reactor. All the experimental sets were replicated two times. At defined time intervals, a 2-mL aliquot of each sample was taken from the reactors and diluted with distilled water; the sample was centrifuged at 3,000 rpm during 10 min before analysing the supernatant. The dye concentration was evaluated by measuring the absorbance using a UV-vis spectrophotometer (WPA light wave II) at the maximal wavelength of each dye (Table 1). Calibration curves were established prior to the analysis. The effects of contact time (5–120 min), biomass dosage (0.5–4.0 g/L) and initial dye concentration (5–50 mg/L) were investigated.

The biosorption capacity, Q_e (in milligrams per gram), and the biosorption (or bioremoval) efficiency, BE (in percent), of LGB were calculated as follows:

$$Q_e = (C_0 - C_e) \times \frac{V}{M} \tag{1}$$

$$BE = \frac{C_0 - C_e}{C_0} \times 100 \tag{2}$$

C_0 and C_e are the initial and equilibrium dye concentrations in the solution (in milligrams per litre), respectively; V

Table 1 Physicochemical characterization of the selected dyes

Dye	Direct red 89 (Solophenyl scarlet BNL)	Reactive green 12 (Cibacron green)
Empirical formulae	C ₄₄ H ₃₂ N ₁₀ Na ₄ O ₁₆ S ₄	C ₆₀ H ₂₉ Cl ₃ N ₁₆ NiO ₂₁ S ₆ Na
Abbreviation	DR-89	RG-12
Dye nature	Direct dye	Reactive dye
Molecular weight	1,372	1,837
λ_{\max} (nm)	494	615

is the solution volume (in litres), and M is the mass of LGB (in grams).

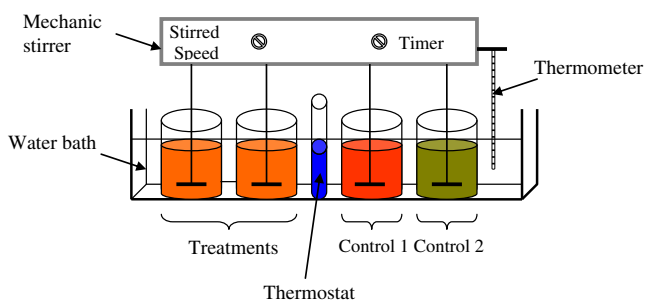
Dye concentration at time t was evaluated from the calibration curve; the corresponding absorbance was calculated from the subtraction of the average of absorbance of the pigments released by the plant biomass (for a given biomass plant) from the measured absorbance.

Spectroscopic characterization of LGB

In order to explain the phenomenon of dye sorption by LGB, Fourier transform infrared (FT-IR) spectroscopy was performed on plant samples before and after dye treatment. The samples were prepared by mixing LGB with spectroscopy-grade potassium bromide at a weight ratio of 1:100 (KBr/LGB) and compressing into discs. The discs were analysed by a PerkinElmer FT-IR spectrophotometer (IRAffinity-1 model: Shimadzu) with a 4-cm⁻¹ resolution from 4,000 to 450 cm⁻¹. The samples related to dye treatment concerned the biosorption of 15 mgL⁻¹ dye (DR-89 or RG-12) exposed to 2 mgL⁻¹ LGB during 1 h. After treatments, dye solutions were filtered, and duckweed biomasses were washed well with distilled water. The samples were dried at 70 °C during 48 h, crushed into powder in an analytical mill and stocked in desiccators until analysis.

Isotherm studies

Biosorption isotherm studies were carried out on five selected isotherm models: Langmuir, Freundlich, Temkin, Elovich and Dubini Radushkevich (D-R). These isotherms were studied at 20 °C using initial DR-89

**Fig. 1** Experimental setup for the biosorption assays

concentrations of 5–50 mgL⁻¹ and RG-12 concentrations of 5–15 mgL⁻¹ (the efficacy of using duckweed biomass for the bioremoval of RG-12 was limited to concentrations ≤ 15 mgL⁻¹). The coefficient of determination, R^2 , was used to test the best-fitting isotherm to the experimental data. Linearized forms of these isotherms and related constants are given in Table 2.

Thermodynamic study

In order to examine the effect of temperature on dye biosorption and to assess the nature of the process, Gibb's free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS) might be determined at selected temperatures. For this purpose, a set of biosorption assays at temperatures of 20, 30, 40 and 50 °C were carried out for the operating conditions of 200 rpm, pH of 7.1 and 2 gL⁻¹ LGB. ΔG was evaluated as follows:

$$\Delta G = -RT \ln K_L \quad (3)$$

where K_L is the equilibrium constant (in litres per gram) estimated as:

$$K_L = \frac{Q_e}{C_e} \quad (4)$$

The parameters of enthalpy and entropy change were calculated from the Van't Hoff equation:

$$\ln K_L = -\frac{\Delta G}{RT} = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad (5)$$

R is the gas constant (in joules per mole per Kelvin), and T the absolute temperature (in kelvins).

The plot of $\ln K_L$ against $1/T$ allows evaluating ΔH (from the slope) and ΔS (from the intercept) (Yurdakoç et al. 2005).

Results

Effect of operating parameters

Controls

Two different controls were necessary to explain the dye biosorption by LGB. Control 1 was conducted to assess the

Table 2 Sorption isotherm models: linearized forms and related constants

Isotherm model	Linearized form	Related constants
Langmuir	$\frac{1}{Q_e} = \frac{1}{Q_{max}} + \frac{1}{K_L Q_{max}} \left(\frac{1}{C_e}\right)$	Q_{max} (mg g ⁻¹) and K_L (L mg ⁻¹)
Freundlich	$\text{Ln } Q_e = \text{Ln } k_F + \frac{1}{n} (\text{Ln } C_e)$	K_F (mg ^{1-(1/n)} L ^{1/n} g ⁻¹) and n (-)
Temkin	$Q_e = \frac{RT}{b_T} \text{Ln } k_T + \frac{RT}{b_T} (\text{Ln } C_e)$	K_T (L mg ⁻¹) and b_T (J mol ⁻¹)
Elovich	$\text{Ln } \frac{Q_e}{C_e} = \text{Ln } \frac{K_E}{Q_{max}} + \frac{1}{Q_{max}} (Q_e)$	K_E (L mg ⁻¹)
D-R	$\text{Ln } Q_e = \text{Ln } Q_{max} - \beta (\varepsilon^2)$ where $\varepsilon = RT \text{Ln} \left(1 - \frac{1}{C_e}\right)$	β (mol ² J ⁻²) and ε (J mol ⁻¹)

R universal gas constant (in joules per mole per kelvin), *T* absolute temperature (in kelvins)

absorbance of pigments released in water by plant biomass. It was observed that dried biomass of duckweed released during agitation green pigments which absorbed at 494 and 615 nm. The pigment absorbance increased slightly with the increase of plant biomass. The average values of the pigment absorbance for different plant biomass given in Table 3 were subtracted from the different measured absorbances.

Control 2 was carried out to ensure that sorption was by the plant biomass and not the reactor. The measured absorbance of the different controls revealed that there was no significant change in DR-89 and RG-12 concentration during the experiments for all the initial concentrations selected in this work (data not shown). Thus, we concluded that LGB was responsible for the disappearance of the organic pollutants from aqueous solution.

Effect of contact time and biomass dosage

The first objective of these tests using 50 mg L⁻¹ of DR-89 (or RG-12) was the assessment of the equilibrium time. Figure 2 (restricted to a treatment time of 60 min) shows that there was a decrease in dye concentration until values corresponding to the equilibrium reached a plateau; a time of 20 and 30 min, depending on biomass dose, was necessary to achieve the biosorption of DR-89 and RG-12, respectively. In addition, these experiments elaborated with various biosorbent dosages showed that with the increase of duckweed biomass (from 0.5 to 4.0 g), the equilibrium concentration of DR-89 decreased from approximately 40 to 20 mg L⁻¹ achieving a removal percentage of 20–60 %. However, the equilibrium concentration

of RG-12 could not decrease down to 43 mg L⁻¹ which corresponded to 13 % removal percentage. These results (confirmed by those of Fig. 3b) demonstrated that LGB was not very effective in the biosorption of high concentrations of RG-12 (≥20 mg L⁻¹). Additionally, removal efficiency of the two dyes was independent of the material dose in solution for a value ≥2 g L⁻¹; a further increase in the biomass dose did not affect the bioremoval efficiency due to unavailability of the adsorbate (Gupta et al. 2010a). Therefore, the following experiments were elaborated with a biomass dosage of 2 g L⁻¹.

Effect of initial dye concentration

To assess the effect of initial dye concentration on the treatment, various concentrations of DR-89 and RG-12 (5–50 mg L⁻¹) were selected. Figure 3b shows as a first result that the treatment of 20–50 mg/L RG-12 was not significant since the dye abatement from the contaminated solution was only observed in the case of low concentrations. Figure 3

Table 3 Average absorbance values of the green pigments released in water by *L. gibba* biomass

LGB (g DM)	λ_{max} (nm)	
	494	615
0.5	0.0030	~0.000
1.0	0.0070	0.0015
2.0	0.0093	0.0025
3.0	0.0152	0.0060
4.0	0.0230	0.0120

The values corresponded to defined operational conditions of temperature (20 °C), pH (7.1) and stirring speed (200 rpm)

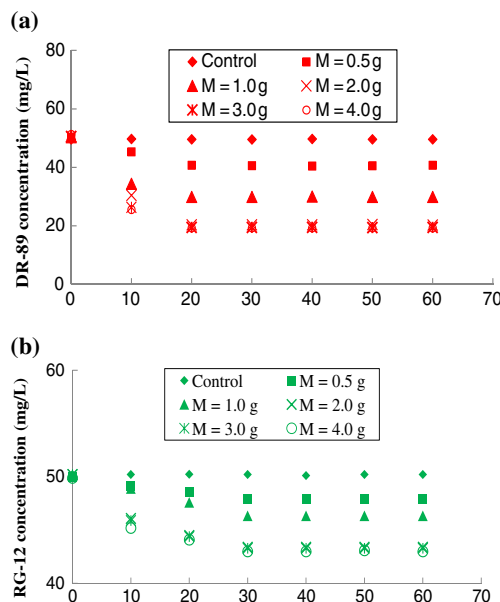


Fig. 2 Effect of time and different biosorbent dosages on the removal of a DR-89 and b RG-12 (solution volume, 1 L; T, 20 °C; stirring speed, 200 rpm; pH7.1)

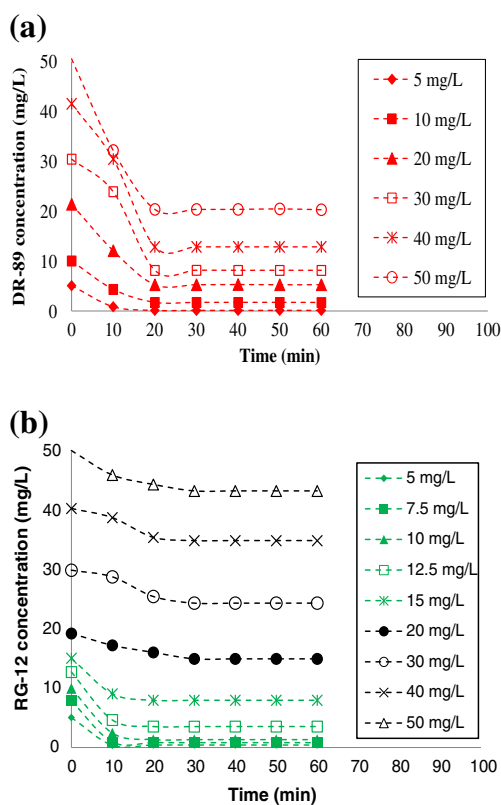


Fig. 3 Effect of initial dye concentration on the disappearance of **a** DR-89 and **b** RG-12 from solution (solution volume, 1 L; T, 20 °C; stirring speed, 200 rpm; pH7.1; biosorbent dosage, 2 gL⁻¹)

also shows that the kinetic removal of the two dyes consisted of two stages: an initial and rapid phase and a second and slower phase in which the bioremoval reached equilibrium. After the equilibrium time, significant amounts of DR-89 and RG-12 (for concentrations that ranged between 5 and 15 mg/L) were effectively removed from aqueous solution, and the biosorption efficiency of dead plants varied from 40 to 100 % and 75 to 94 %, respectively. The different curves on Fig. 3 served as data to determine the different adsorption isotherms.

Characterization of LGB and sorption mechanisms

The FT-IR spectra of LGB (Fig. 4) show several vibrational and stretching bands. In general, the three spectra exhibited the same pattern and displayed a number of peaks, indicating the complex nature of the biomaterial (Additional absorption bands are present in the spectra due to combinations of the fundamental vibrations). However, some modifications between the untreated and the dye-contaminated biomass were observed. In the case of DR-89 biosorption (Fig. 4b), some shifts in wave number from 2,933 to 2,916 cm⁻¹ and from 2,366 to 2,333 cm⁻¹ suggest that the functional groups of C–H (alkane) and O–H (carboxylic acid and derivatives) could participate in dye

biosorption on the surface of LGB. Similarly, the displacement of the peaks from 2,933, 2,366, 1,158 and 666 cm⁻¹ to respectively 2,900, 2,333, 1,150 and 658 (Fig. 4c) revealed a possible participation of C–H (alkane), O–H (carboxylic acid and derivatives), O–C (carboxylic acid) and O–H (alcohols) in RG-12 biosorption (Tan et al. 2010).

Isotherm studies

As mentioned above, five isotherm models (Table 2), commonly used in sorption processes, were chosen to describe the experimental data. These models are often used as empirical relations between the concentration of a sorbate on the surface of an adsorbent and the concentration of the sorbate in the solution at equilibrium (Tan et al. 2010). By plotting the function (the first term of each equation) against the variable (between brackets), it was possible to obtain the different constants from the intercepts and the slopes. The various constants related to these isotherms were thus determined. Table 4 shows that the Langmuir model described well the bioremoval of DR-89 by the duckweed biomass ($R^2=0.992$). In the case of RG-12, it seems that the best fit was obtained by the D-R equation as compared with the other equations because it had the highest coefficient of

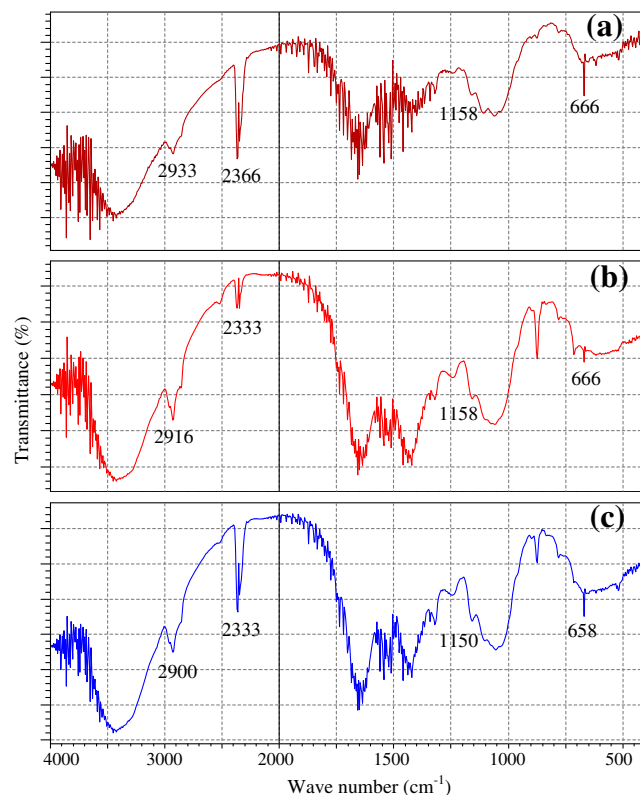


Fig. 4 FT-IR spectra of LGB **(a)** before dye treatment, **(b)** after DR-89 treatment and **(c)** after RG-12 treatment

Table 4 Isotherm model parameters for the biosorption of DR-89 and RG-12 by LGB

Model	DR-89	RG-12
Langmuir		
Q_{max} (mg g ⁻¹)	20.0	6.13
K_L (L mg ⁻¹)	0.15	1.45
R^2	0.992	0.959
Freundlich		
K_F (mg ^{1-(1/n)} L ^{1/n} g ⁻¹)	1.66	3.42
n (-)	1.81	3.17
R^2	0.972	0.803
Temkin		
b_T (J mol ⁻¹)	225.04	2269.32
K_T (L mg ⁻¹)	1.12	27.23
R^2	0.970	0.851
Elovich		
Q_{max} (mg g ⁻¹)	11.11	2.04
K_E (L mg ⁻¹)	38.23	39.01
R^2	0.902	0.664
Dubini Radushkevich		
Q_{max} (mg g ⁻¹)	2.99	115.5
β (mol ² J ⁻¹)	0.015	0.012
R^2	0.824	0.988

The isotherm models were established for initial dye concentrations that ranged in the intervals of 5–50 and 5–15 mg/L for DR-89 and RG-12, respectively

determination ($R^2=0.988$). The maximum sorption capacity (Q_{max}) was found to be 20 and 115.5 mg g⁻¹ for DR-89 and RG-12, respectively.

Thermodynamic parameters

The calculated thermodynamic parameters for different temperatures are summarized in Table 5. The free energy change (ΔG) increased with the increase of temperature. The values were found to vary in the range of -84.54 and -88.94 kJ mol⁻¹ for DR-89 and in the range of -11.12 and -11.88 kJ mol⁻¹ for RG-12; the negative values of ΔG revealed that the biosorption of the two dyes using dried LGB occurs spontaneously and confirmed that an affinity of LGB for the two textile dyes may exist. On the other hand, the positive value of ΔH implies that the biosorption of the two dyes is endothermic, and the negative value of ΔS revealed the increased randomness at the solid solution interface during the fixation of the dye on the active sites of the adsorbent (Gupta et al. 2011).

Discussion

Based on their availability and low cost, natural materials may be used as substitutes for activated carbon which is considered as the most effective agent for the removal of different types of dyes (Gupta et al. 2000; Gupta and

Sharma 2003; Gupta and Suhas 2009; Wang 2010; Mittal et al. 2005). In this experimental work, we tested dried biomass of the duckweed *L. gibba* L. which is an invasive aquatic plant in northeast Algeria overlapping many aquatic ecosystems including lakes, streams and effluent lagoons (Khellaf and Zerdaoui 2009). The use of this kind of biomass for wastewater is interesting because of its availability in large quantities at low cost. Based on our literature research, no sufficient experimental work on the biosorption of dyes using duckweed biomass has been investigated. The different biosorption experiments conducted in batch mode in this work demonstrated that the initial DR-89 concentration decreased rapidly after the dye exposure to plant biomass. The bioremoval of RG-12 was more rapid than the red dye and required 10–20 min to reach the equilibrium for an initial concentration range of 5–15 mg L⁻¹. The biosorption efficiency of biomass plants, depending on dye concentration initially present in water, varied from 40 to 100 % and 75 to 94 % for DR-89 and RG-12, respectively. LGB was thus more efficient in dye removal at low concentrations; similar results were reported by several studies using waste materials as biosorbents of hazardous pollutants (Gupta and Sharma 2003; Mittal et al. 2005).

In separation processes, an isothermal model is often needed to describe the experimental equilibrium data. Many models have been developed to study the sorption phenomena. In order to model the biosorption of the azo dyes DR-89 and RG-12 using LGB, we tested the Langmuir Freundlich, Temkin, Elovich and D-R equations. In the Langmuir theory, the basic assumption is that the sorption takes place at specific homogeneous sites within the sorbent. The results of our modelling showed that the DR-89 biosorption process was better described with the Langmuir theory. However, RG-12 biosorption data fitted well with the D-R isotherm equation ($R^2=0.992$) compared with the other models which were not able to describe the equilibrium data. The D-R model which is more general than that of Langmuir assumes a homogeneous surface and describes adsorption on a single type of uniform pores. The thermodynamic study revealed

Table 5 Thermodynamic parameters of biosorption of DR-89 and RG-12 using LGB

Dye	T (K)	ΔG (kJ mol ⁻¹)	ΔH (kJ mol ⁻¹)	ΔS (J mol ⁻¹ K ⁻¹)
DR-89	20	-84.54	4.99	-17.65
	30	-86.01		
	40	-87.48		
	50	-88.95		
RG-12	20	-11.12	9.39	-30.65
	30	-11.38		
	40	-11.63		
	50	-11.89		

Table 6 Biosorption capacities of various biomasses for DR-89

Biosorbent	Biosorption capacity (mg g ⁻¹)	Concentration range (mg L ⁻¹)	Temperature (°C)	Reference
PAC Chemviron GW	8.4	30–250	20	Martin et al. (2003)
Sludge-based AC	49.2	30–250	20	Martin et al. (2003)
<i>L. gibba</i> biomass	20.0	5–50	20	The present study

AC activated carbon

that biosorption of the two dyes was a spontaneous and endothermic process with a physisorption mechanism ($\Delta H < 30$ kJ mol⁻¹) of target compounds on the LGB surface. Additionally, the decrease in the negative value of the free energy with an increase in temperature indicated that the process became more favourable at higher temperatures. The maximal capacity of biosorption, Q_{\max} , which measures the monolayer adsorption of the biosorbent, was found to be 20 and 115.5 mg g⁻¹ for DR-89 and RG-12, respectively, indicating a higher capacity of duckweed biomass for the bioremoval of green dye than the red one. It seems that the reactive dye displayed the best physical and/or chemical interaction with the biosorbent surface.

In recent years, a large number of research works have been investigated in the removal of textile dyes using several materials. A completed review on the use of different materials for the removal of several dyes has been presented by Gupta and Suhas (2009). Additionally, Waranusantigul et al. (2003), investigating the sorption of basic blue 9 (methylene blue) onto the biomass of another species of duckweed, *Spirodela polyrrhiza*, found that the duckweed biomass exhibited a high sorption capacity for the blue dye ($Q_{\max} = 119$ – 145 mg g⁻¹). However, only few studies have been focused on the biosorption of the textile dye DR-89. Martin et al. (2003) investigated the removal of DR-89 by biosorption on Chemviron GW, a commercial activated carbon (AC) and a sludge-based AC at 20 °C. The authors found that, for concentrations ranging from 30 to 250 mg L⁻¹, the sludge-based AC possessed greater capacity (42.2 mg g⁻¹) than the commercial sorbent. It can also be seen that the sorption capacity of the sludge-based AC for DR-89 is higher than the dried biomass of *L. gibba* used in this work (Table 6). This can be attributed to the fact that duckweed biomass developed a low surface area; biomass pre-treatment (acid, alkali or heat treatment) is probably needed in this case to ameliorate the sorption potential of plant biomass in the removal process (Gupta et al. 2010a). Till now, to our knowledge (based on our literature research in the different scientific databases), no study on the biosorption of RG-12 has been published.

Conclusions

In this work, the biosorption of two synthetic dyes, Direct Red 89 and Reactive Green 12, using dried biomass of *L.*

gibba has been investigated in batch experiments. A series of bioassays revealed that dye removal depended on biosorbent dosage and initial dye concentration. The biosorption capacity for RG-12 was 115.5 mg g⁻¹; however, the sorption capacity for DR-89 was relatively low at 20 °C. The duckweed biomass can be considered as a good biosorbent for the two textile dyes when present in water at low concentrations. The process may be applied as a final refining treatment of textile effluents before their final discharge. On the other hand, further experiments are needed to ameliorate the sorption capacity of LGB for the bioremoval of the textile dye DR-89.

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References

- Ahmaruzzaman M, Gupta VK (2011) Rice husk and its ash as low-cost adsorbents in water and wastewater treatment. *Ind Eng Chem Res* 50(24):13589–13613
- Crini G (2008) Kinetic and equilibrium studies on the removal of cationic dyes from aqueous solution by adsorption onto a cyclodextrin polymer. *Dye Pigment* 77:415–426
- Dogan K, Akgul E, Sema T, Ferruh E, Mehmet AK, Mustafa T (2007) Basic and reactive dye removal using natural and modified zeolites. *J Chem Eng Data* 52:2436–2441
- Dulman V, Cucu-Man SM (2009) Sorption of some textile dyes by beech wood sawdust. *J Hazard Mater* 162:1457–1464
- Gupta VK, Sharma S (2003) Removal of zinc from aqueous solutions using bagasse fly ash—a low cost adsorbent. *Ind Eng Chem Res* 42(25):6619–6624
- Gupta VK, Suhas (2009) Application of low-cost adsorbents for dye removal. *J Environ Manag* 90:2313–2342
- Gupta VK, Srivastava SK, Tyagi R (2000) Design parameters for the treatment of phenolic wastes by carbon columns (obtained from fertilizer waste material). *Water Res* 34(5):1543–1550
- Gupta VK, Mittal A, Gajbe V, Mittal J (2006a) Removal and recovery of the hazardous Azo dye acid orange 7 through adsorption over waste materials: bottom ash and de-oiled soya. *Ind Eng Chem Res* 45(4):1446–1453
- Gupta VK, Mittal A, Kurup L, Mittal J (2006b) Adsorption of a hazardous dye, erythrosine, over hen feathers. *J Colloid Interface Sci* 304(1):52–57

- Gupta VK, Mittal A, Krishnan L, Mittal J (2006c) Adsorption treatment and recovery of the hazardous dye, Brilliant Blue FCF, over bottom ash and de-oiled soya. *J Colloid Interface Sci* 293(1):16–26
- Gupta VK, Ali I, Saini VK (2007a) Adsorption studies on the removal of Vertigo Blue 49 and Orange DNA13 from aqueous solutions using carbon slurry developed from a waste material. *J Colloid Interface Sci* 315:87–93
- Gupta VK, Ali I, Saini VK (2007b) Defluoridation of wastewaters using waste carbon slurry. *Water Res* 41(15):3307–3316
- Gupta VK, Jain R, Mittal A, Mathur M, Shalini Sikarwar S (2007c) Photochemical degradation of the hazardous dye Safranin-T using TiO₂ catalyst. *J Colloid Interface Sci* 309:464–469
- Gupta VK, Jain R, Varshney S (2007d) Removal of Reactofix golden yellow 3 RFN from aqueous solution using wheat husk—an agricultural waste. *J Hazard Mater* 142(1–2):443–448
- Gupta VK, Jain R, Varshney S (2007e) Electrochemical removal of the hazardous dye Reactofix Red 3 BFN from industrial effluents. *J Colloid Interface Sci* 312:292–296
- Gupta VK, Jain R, Malathi S, Nayak A (2010a) Adsorption–desorption studies of indigocarmine from industrial effluents by using deoiled mustard and its comparison with charcoal. *J Colloid Interface Sci* 348(2):628–633
- Gupta VK, Rastogi A, Nayak A (2010b) Adsorption studies on the removal of hexavalent chromium from aqueous solution using a low cost fertilizer industry waste material. *J Colloid Interface Sci* 342(1):135–141
- Gupta VK, Gupta B, Rastogi A, Agarwal S, Nayak A (2011) A comparative investigation on adsorption performances of mesoporous activated carbon prepared from waste rubber tire and activated carbon for a hazardous azo dye-Acid Blue 113. *J Hazard Mater* 186:891–901
- Hai FI, Yamamoto K, Nakajima F, Fukushi K (2008) Removal of structurally different dyes in submerged membrane fungi reactor biosorption/PAC-adsorption, membrane retention and biodegradation. *J Membr Sci* 325:395–403
- Jain AK, Gupta VK, Jain S (2004) Removal of chlorophenols using industrial wastes. *Environ Sci Technol* 38(4):1195–1200
- Ju DJ, Byun IG, Park IJ, Lee CH, Ahn GH, Park TJ (2008) Biosorption of a reactive dye (Rhodamine-B) from an aqueous solution using dried biomass of activated sludge. *Bioresour Technol* 99:7971–7975
- Khellaf N, Zerdaoui M (2009) Phytoaccumulation of zinc by the aquatic plant, *Lemna gibba* L. *Bioresour Technol* 100(23):1637–1640
- Kim SU, Cheong YH, Seo DC, Hur JS, Heo JS, Cho JS (2007) Characterisation of heavy metal tolerance and biosorption capacity of bacterium strain CPB4 (*Bacillus* spp.). *Water Sci Technol* 55(1–2):105–111
- Malik PK (2003) Use of activated carbons prepared from sawdust and rice-husk for adsorption of acid dyes: a case study of acid yellow 36. *Dye Pigment* 56:239–249
- Martin MJ, Artola A, Balaguer MD, Rigol M (2003) Activated carbons developed from surplus sewage sludge for the removal of dyes from dilute aqueous solutions. *Chem Eng J* 94:231–239
- Mittal A, Kurup L, Gupta VK (2005) Use of waste materials—bottom ash and de-oiled soya, as potential adsorbents for the removal of Amaranth from aqueous solutions. *J Hazard Mater* 117(2–3):171–178
- Mittal A, Thakur V, Gajbe V (2012) Adsorptive removal of toxic azo dye Amido Black 10B by hen feather. *Environ Sci Pollut Res*. doi:10.1007/s11356-012-0843-y
- Mona S, Kaushik A, Kaushik CP (2011) Biosorption of reactive dye by waste biomass of *Nostoc linckia*. *Ecol Eng* 37:1589–1594
- Nurchi VM, Villaescusa I (2008) Agricultural biomasses as sorbents of some trace metals. *Coord Chem Reviews* 252:1178–1188
- Rafatullah M, Sulaimana O, Hashima R, Ahmad A (2010) Adsorption of methylene blue on low-cost adsorbents: a review. *J Hazard Mater* 177:70–80
- Sayilgan E, Cakmakci O (2012) Treatment of textile dyeing wastewater by biomass of *Lactobacillus*: *Lactobacillus* 12 and *Lactobacillus rhamnosus*. *Environ Sci Pollut Res*. doi:10.1007/s11356-012-1009-7
- Sekhar CP, Kalidhasan S, Rajesh V, Rajesh N (2009) Bio-polymer adsorbent for the removal of malachite green from aqueous solution. *Chemosphere* 77(6):842–847
- Sreelatha G, Ageetha V, Parmar J, Padmaja P (2011) Equilibrium and kinetic studies on reactive dye adsorption using palm shell powder (an agrowaste) and chitosan. *J Chem Eng Data* 56:35–42
- Tan C, Li G, Lu XQ, Chen Z (2010) Biosorption of basic orange using dried *A. filiculoides*. *Ecol Eng* 36:1333–1340
- Vajnhandl S, Le Marechal AM (2005) Ultrasound in textile dyeing and the decolouration/mineralization of textile dyes. *Dye Pigment* 65:89–101
- Vasanth Kumar K, Ramamurthi V, Sivanesan S (2006) Biosorption of malachite green, a cationic dye onto *Pithophora* sp., a fresh water algae. *Dye Pigment* 69:102–107
- Walker GM, Hansen L, Hanna JA, Allen SJ (2003) Kinetics of a reactive dye adsorption onto dolomitic sorbents. *Water Res* 37:2081–2089
- Wang XS (2010) Invasive freshwater macrophyte alligator weed: novel adsorbent for removal of malachite green from aqueous solution. *Water Air Soil Pollut* 206:215–223
- Waranusantigul P, Pokethitiyook P, Kruatrachue M, Upatham ES (2003) Kinetics of basic dye (Methylene Blue) biosorption by giant duckweed (*Spirodela polyrrhiza*). *Environ Pollut* 125:385–392
- Yurdakoç M, Seki Y, Karahan S, Yurdakoç K (2005) Kinetic and thermodynamic studies of boron removal by Siral 5, Siral 40, and Siral 80. *J Colloid Interface Sci* 286:440–446