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Biosorption Performance of Powdered Waste Sludge for Removal of Congo Red: Equilibrium and Kinetic Modeling

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Abstract:

Dyes are important water pollutants generally present in the effluents of textile industries. A high level of worldwide production and extensive use of dyes generate substantial volumes of colour ed wastewaters. Industrial effluents treatment is becoming an obligation in Tunisia both environmentally and for water re-use. Another important waste produced by contemporary society in abundant quantity is industrial and municipal sewage sludge, which calls out for efficient and environmentally friendly approaches to its valorisation. The aim of the present work was to develop an effective and inexpensive technology for removing dyes from aqueous solution using powdered waste sludge (PWS). Congo Red (CR) was chosen as a dye model. The effects of operation variables, such as pH of the solution, adsorbent amount, initial CR concentration and agitation speed were investigated using batch adsorption technique. Sorption kinetics, isotherms and thermodynamic parameters were conducted. The results showed that the retention capacity of the mud increases with the increase of the sorbent quantity, the temperature, the CR concentration, as well as the agitation speed. The best sorption amounts were obtained at pH 6. The parameters of both kinetic and equilibrium modelling showed that the kinetic data were accurately described by the pseudo-second-order model. The equilibrium data were analyzed using five isotherms models, Langmuir, Freundlich, Redlich-Peterson, Temkin, and Elovich models. Results showed a good fit with Redlich-Peterson and Langmuir models suggesting monolayer coverage of dye molecules onto the biosorbent surface and adsorption active sites of quite similar affinities toward the experimental textile pollutant. The thermodynamic parameters such as Gibbs free energy change ΔG_0, standard enthalpy ΔH_0, and standard entropy ΔS_0 indicated that Congo Red adsorption onto powdered sludge was endothermic, spontaneous, involving a chemical bonding. This study indicates then that the sewage sludge has the potential to be used as a biomaterial for dye removal process from contaminated waters.

Keywords: Biosorption, Congo Red, sewage sludge, kinetics, isotherm modeling.

1. Introduction

Growing concerns in developing countries about the environment have resulted in the development of new environmental technologies, new materials, and new ways to reduce and to minimize wastes [1]. One of the wastes produced by contemporary society in abundant quantity is industrial and municipal sewage sludge. Sewage sludge is a biomass waste generated from the regular biological activities of municipal wastewater treatment plants. The volume being produced is likely increased with increasing municipal wastewater to be treated, which calls out for efficient and environmentally friendly approaches to its valorisation [2]. Various methods have been used to dispose of or to utilize municipal sewage sludge, including incineration, land filling, road surfacing, conversion to fertilizer, compression into building blocks, etc [3, 4]. Rather than simply disposing of the sludge, considered use of this waste material seems to be a promising way of turning it into a resource. One application that has received increasing attention is the utilization of sewage sludge as a low cost alternative adsorbent for the removal of pollutants from wastewater [5, 6]. While the mechanism involves a phase transfer of chemicals from the aqueous to the solid phase like an adsorption process, the term "biosorption" is used instead to indicate the processes involving the uptake and accumulation of chemicals from aqueous solution to biomass surfaces [7, 8]. Biomass from wastewater treatment plant could be used as a biosorbent since it mainly consists of bacteria with cell walls that essentially contain various organic compounds such as acidic polysaccharides, lipids, amino acids, chitins, and other cellular components. These materials interact with chemicals resulting in a passive uptake of chemicals from wastewater to the microbial cell [9, 10]. The main biosorption mechanisms appear to be extracellular interactions, complexation and subsequent accumulation, passive sorption at binding sites on the envelopes of cells, and intracellular accumulation of pollutants [11].

This study takes into consideration industrial coloured wastewaters in general. Dyes are common contaminants in industrial wastewaters and many of them are known to be toxic and carcinogenic. Dyes are widely used in industries, such as textiles, paper, plastics and leather for the colouration of products. The effluents discharged from these industries often contain high concentrations of dye wastes [12]. At least two percent of the dyes produced are discharged directly in aqueous effluent, with a further 10% subsequently lost during the textile colouration process [13]. It has been reported that over 100,000 dyes are commercially available, with a production volume of over 7×105 tonnes per year [14]. The discharge of these dye stuffs from industries into rivers and lakes leads to a reduction in dissolved oxygen concentration causing anoxic conditions, which subsequently affect aerobic organisms [15, 11]. Apart from the toxicological properties of dyes, their colour is one of the first signs of contamination recognized in a wastewater [16]. Since a very small quantity of dyes in water is highly visible, it often affects the aesthetic merit and water transparency [17].

In this present work, Congo Red (CR) was chosen as an anionic dye surrogate indicator due to its chemical composition and environmental concern. Effluent containing CR is produced from textiles, printing, dyeing, paper, and plastic industries [18, 19]. The substance is considered as toxic [20]. Indeed, this anionic dye can cause allergic reactions and can also be metabolised to benzidine, a known human carcinogen [21]. Yet, the treatment of CR contaminated wastewater can be complicated due to its complex aromatic structure, which leads to a bio-physico-chemical and thermal stability of the dye, and thus to its resistance to biodegradation and to photo-degradation. [22].

The purpose of this work was to investigate the potentialities of a low cost and available biomass waste; industrial sewage sludge for adsorptive removal of a textile dye: Congo Red. The effects of several operating parameters on the biosorption process were investigated. In addition, the kinetic parameters of the adsorption process were described and the equilibrium data were analyzed using five isotherms models, Langmuir, Freundlich, Redlich-Peterson, Temkin, and Elovich models.

2. Materials and methods

2.1 Biosorbent and dye solution preparation

The raw sludge used in this study was obtained from the Industrial Society of Textiles (SITEX) (Ksar Hellal, Tunisia). The sludge was washed with distilled water. Then, it was dried in an oven at 105 °C during 48 h to a constant weight. Finally, the dry support was finely ground and stored in a desiccator for further use. The prepared powdered waste sludge (PWS) has not been chemically or physically activated or modified in order to estimate its adsorption capacity in its raw state. Congo Red [1-naphthalenesulfonic acid, 3,3-(4,4-biphenylenebis(azo)) bis(4-amino-) disodium salt] is a benzidine-based anionic diazo dye prepared by coupling tetrazotised benzidine with two molecules of napthionic acid. The molecular structure of CR is illustrated in Figure 1.

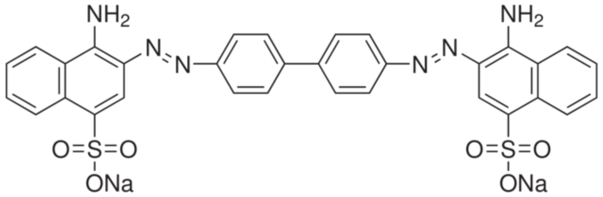

Figure 1: Molecular structure of Congo Red

Stock solution of CR (100 mg/L) used in this study was prepared in deionized water and all desired concentrations of the dye were obtained by diluting with water. Initial pH was adjusted by adding either few drops of diluted hydrochloric acid or sodium hydroxide (0.1 mol/L).

2.2 Experimental adsorption procedure

The biosorption experiments were carried out in batch reactor by suspending a certain quantity of powdered sludge (0.1 - 0.5 g) in 500 mL of dye solution for the desired concentration (10–50 mg/L) and pH (6–10). Studies are conducted in a thermo-regulated water bath at a defined temperature and operating at 120 rpm for the time required to reach the equilibrium state (24 h).

The samples were taken from the shaker at predetermined time intervals for the sorption dynamic assay and at equilibrium time for isotherms.

Every sample was centrifuged twice at 6000 rpm for 5 min prior to analysis in order to minimize interference of the PWS particles with the CR analysis. The concentration of Congo Red was measured at maximum absorbance λ_{max} (496 nm), by means of UV–Vis spectrophotometer (Shimadzu corporation, UV-1800 model).

After measurement of the concentration, the sample was reintroduced in the batch solution.

Similar procedure was followed for another set of batch system containing the same dye concentration without PWS to be used as a blank.

To calculate the dye removal, biosorption capacity at equilibrium time (Qe) and biosorption removal efficiency were determined respectively according to the following equations:

$$Q_e = [(C_0 - C_e) * (V/M)] \quad (mg/g)$$

$$\textit{Sorption removal percent} = [(C_0 - C_e)*100] / C_0 \ (\%)$$

With C_0 and C_e (mg/L) are, respectively, the initial dye concentration in the solution and concentration at equilibrium. V is the volume of the solution, and M is the mass of dry adsorbent used (g).

3. Results and discussion

3.1 Influence of contact time and initial dye concentration

The relationship between contact time and initial dye concentration on CR biosorption onto PWS is shown in Figure 2. It was tested by varying the dye concentration from 10 to 50 mg/L (10, 20, 30, 40, 50 mg/L) at pH 6, solid/liquid ration (S/L) = 1 g/L and at 25°C. Figure 2 reveals that the curves are single, smooth, and continuous, leading to saturation, suggesting the possible monolayer coverage of the dye on the sorbent surface. The biosorption dynamic profile of the studied dye onto powdered sludge can be divided into three main regimes: (a) a linear fast increase in adsorption with time, showing a large availability of sorption sites, (b) a transition regime in which the rate of adsorption decreases, showing a progressive saturation of the sorption sites, and (c) a plateau regime, as a consequence of the total saturation of the sorption sites. The apparent equilibrium was reached after 50–260 min of contact, depending on the dye concentrations. The amount of dye uptake increased with contact time at all initial dye concentrations. Indeed, an increase in initial dye concentration from 10 to 50 mg/L increased the biosorption capacity from 9.75 to 42.11 mg/g. Similar behavior was observed on the same dye sorbed on kaolin [23].

It seems that a higher initial dye concentration provides an important driving force to overcome all mass transfer resistances of the dye between the aqueous and solid phases, increasing the number of collisions between dye anions and the biosorbent, which enhances the sorption process. On the other hand, in case of 10 and 20 mg/L, an almost complete dye removal is reached after about half an hour, whereas the sorption percentages at equilibria of higher dye contents are much lower. Such a trend is due to the fact that, at lower concentration, the ratio of the initial number of dye molecules to the available surface area is low; subsequently the fractional adsorption becomes independent of initial concentration. However, at high concentration the available sites of adsorption becomes fewer and hence the percentage removal of dye is dependent upon initial concentration. These observations show that the adsorption is highly dependent on initial concentration of the dye.

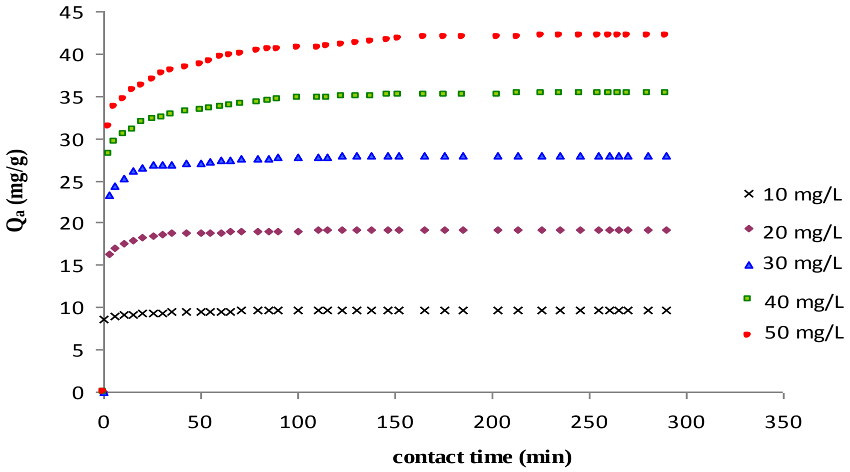

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Figure 2: Influence of contact time and initial dye concentration on the biosorption capacity of Congo Red onto powdered sludge (Solid/Liquid ratio = 1 g/L, pH = 6, Temperature = 25 °C).

3.2 Influence of pH

The initial pH of the aqueous solution influences the molecular form of Congo red in the aqueous solution. In order to examine the effect of initial pH value on CR biosorption in batch, adsorption experiments were done at pH between 4 and 10 and adsorbate/adsorbent contact time was set to 24 h at 25°C (a pH lower than 4.0 could not be used because of change of colour by the dye and hence its structural characteristics).

The results indicated that the sorption capacity of anionic CR increased between pH 4.0 and 6.0, after which the adsorption decreases when pH increases in the tested range. Indeed, for an initial dye concentration of 10 mg/L, the maximum equilibrium adsorbed amount reaches the highest value (9.62 mg/g) at pH 6, and decreases when pH is increased further.

Therefore, a pH of 6 seems to be the optimal pH for biosorption of Congo red. It seems that at higher pH, a negatively charged surface site on the PWS does not favor the adsorption of dye anions due to the electrostatic repulsion. Also, there was competition between OH^- and CR anions for positively charged adsorption sites [22]. However, significant adsorption of the anionic dye on the adsorbent still occurred at alkaline pH values. This suggests that the chemisorption mechanism might be operative.

3.3 Influence of temperature

The effect of temperature on the removal of CR from water solution was investigated from 22 to 60 °C. Studies were conducted by shaking 0.5 g of PWS with 500 mL of the dye solution (i.e. 1 g/L) at pH 6, using a thermo-regulated agitator operating at 120 rpm.

The results shown in Figure 3 indicate that the sorption capacity of CR increases, as the temperature of the system is increased.

Indeed, when the temperature of dye solution was raised from 22 °C to 60 °C, the adsorption capacity Q_a slightly increased from 9.75 mg/g to 9.88 mg/g. From Figure 3, it is also clear that the temperature has an effect on the biosorption kinetics. Indeed the equilibrium is attainted after 71 min at 60 °C but at 22 °C the equilibrium takes more time to be established (123 min).

These results indicate that biosorption of CR onto PWS happens through an endothermic process. The same behavior has also been reported in other previous studies as for the adsorption of CR on and calcium-rich fly ash [24] and the biosorption of textile dyes using *Posidonia oceanica* (L) [25, 26].

3.4 Influence of sorbent amount

In order to investigate the effect of biosorbent amount on the adsorption of CR onto PWS, five different Solid/Liquid ratios were tested for an initial dye concentration of 10 mg/L and at a temperature of 25 °C. The CR adsorption rate with different amounts of powdered sludge is presented in Figure 4.

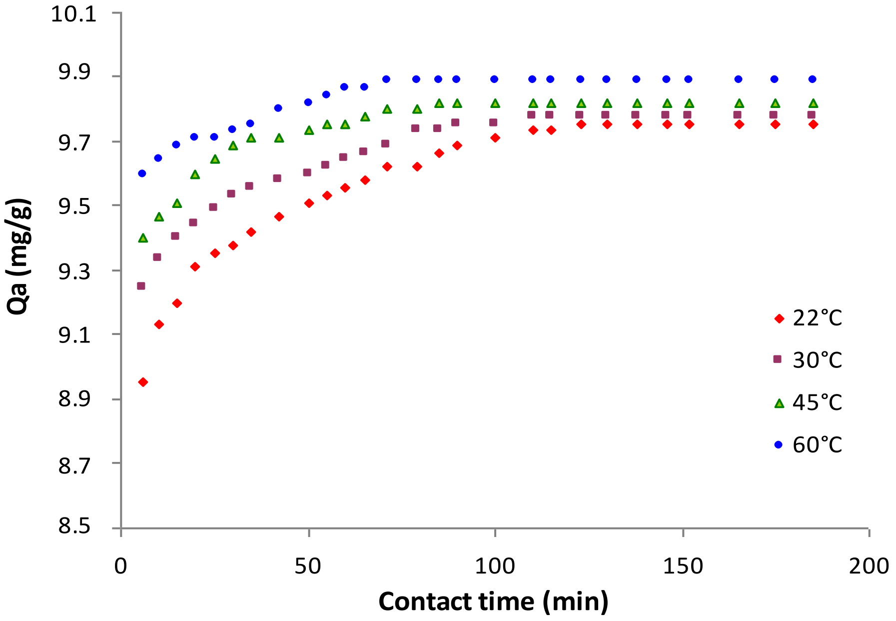


Figure 3: Effect of temperature on the biosorption of CR onto powdered sludge (concentration: 10 mg/L, Solid / Liquid = 1g/L, pH = 6, 120 rpm)

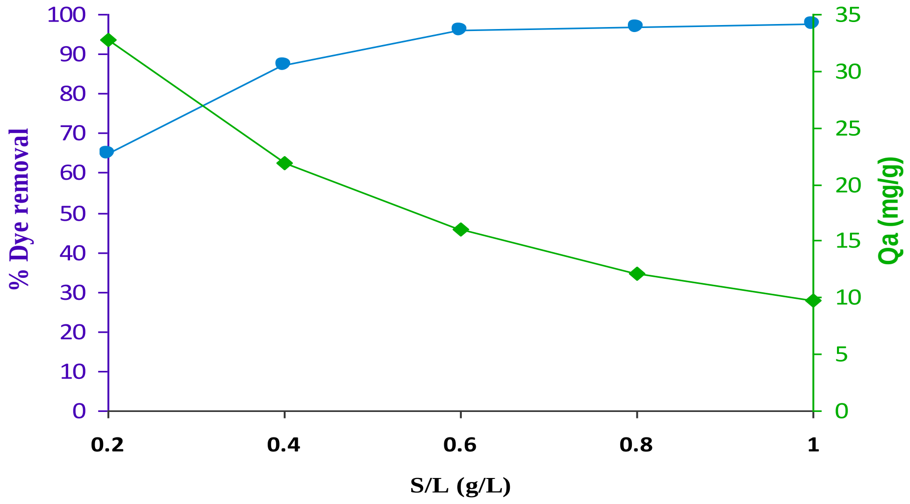


Figure 4: Influence of biomass dosage S/L on the biosorption capacity Qa of Congo Red onto powdered sludge (C_0=10 mg/L; Temperature = 25 °C; 120 rpm; pH = 6)

It is clear that an increase in the biosorbent dosage from 0.2 to 0.6 g/L increased the biosorption capacity from 65.1% to 96.2% even if Qa values were reduced from 32.7 to 12.1 mg/g. This adsorptive enhancement can be attributed to an increase of the global surface area of the sorbent which results in the increase of the number of available sorption sites. Ncibi et al (2006 and 2009a) [25, 26] and Ben Hamissa et al (2008) [27] reported the same findings.

3.5 Modeling of the adsorption process

3.5.1 Modeling of the kinetics

In order to predict the mechanism involved during of the present biosorption process, two kinetic models were used to fit the experimental data, namely, first-order (Lagergren) and Pseudo-second-order models [28]. The best-fit model was selected based on both the linear regression correlation coefficient (R^2) and the calculated *Qe* values. The mathematical equations of these models are given in Table 1.

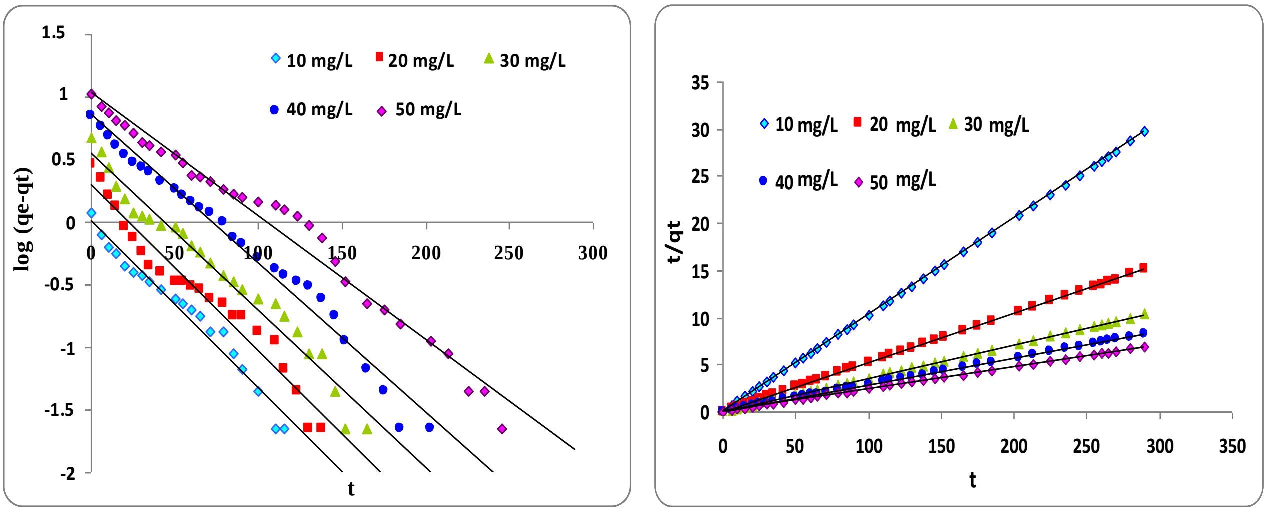
Table 1: Equations of the two used kinetic models

Kinetic model	Equation		Integrated form	
First-order	$\frac{dq}{dt} = K_I (Qe - Q)$	(3)	$\log(Qe - Q) = \log Qe - \frac{K_I}{2.303} t$	(4)
Pseudo-second-order	$\frac{dq}{dt} = K_{II} (Qe - Q)^2$	(5)	$\frac{t}{Q} = \frac{1}{K_{II} . Qe^2} + \frac{t}{Qe}$	(6)

In most studied adsorption systems, the irreversible first-order equation of Lagergren does not fit well over the entire adsorption period and is generally applicable over the first 20-30 min of the sorption process. The pseudo-second-order model is based on the biosorption capacity of the solid phase and it generally predicts the “chemisorption” behaviour over the whole time adsorption [29].

Table 2: Adsorption kinetic rate constants calculated from Lagergren first-order and pseudo-second order models

	C_0 (mg/L)	**10**	**20**	**30**	**40**	**50**
	$Q_{e,exp}$ (mg/g)	9.76	19.22	28.02	35.24	42.11
First-order model	q_{1e} (mg/g)	1.02	1.99	3.56	7.20	10.81
	K_1 (1/min.10)	30.86	30.63	28.79	27.41	22.57
	R_1^2	0.9655	0.9698	0.9799	0.9505	0.9763
Pseudo-second-order model	q_{2e} (mg/g)	9.79	19.31	28.17	35.59	42.74
	K_2 (g/mg.min .10^3)	101.31	53.66	26.99	11.73	6.03
	h (mg/g.min)	9.72	20.00	21.41	14.86	11.01
	R_2^2	**1.000**	**1.000**	**1.000**	**1.000**	**0.9999**



(a) **(b)**

Figure 5: Linearized first-order kinetic plots (a) and pseudo-second order kinetic plots (b) at different initial concentration of CR. *(Solid/Liquid ratio = 1 g/L, pH = 6, Temperature = 25 °C).*

The plots *log (Qe-Q)* versus *t* and *t/Q* versus *t* (Figure 5) should give the kinetic parameters related to first-order and pseudo-second-order models, respectively. The results, given in Table 2, show that the first-order model data do not fall on straight lines indicating that this model was less appropriate. Besides, the calculated *Qe* determined from the model differ substantially from those determined experimentally, suggesting that the studied adsorption phenomenon is not a first-order reaction. On the other hand, the correlation coefficients for the second-order kinetic model are equal to 1 for all investigated initial dye concentrations and the predicted values of *Qe* are acceptable compared to the experimental ones. This suggests that, the biosorption of CR onto mud particles is a chemisorption process involving exchange or sharing of electrons mainly between the dye ions and the sorbent functional groups.

3.5.2 Adsorption isotherm modeling

Five models; Freundlich, Langmuir, Redlich–Peterson, Temkin, and Elovich models were studied to describe the equilibrium data in order to understand the biosorption process of powdered sludge for CR dye at a constant temperature.

The most widely used two-parameter Langmuir equation, valid for monolayer chemisorption onto a homogeneous surface with a finite number of similar active sites is given by Equation (3) and the derived linear forms in Equation (4) [30, 31].

$$Q_e = \frac{Q_0 k_L C_e}{1 + k_L C_e} \qquad \textbf{(3)}$$

$$\frac{C_e}{Q_e} = \frac{1}{k_L . Q_o} + \frac{C_e}{Q_o} \qquad (4)$$

The empirical Freundlich equation based on a monolayer adsorption by the adsorbent with a heterogeneous energy distribution of active sites is given below by Eq. (5) and the derived linear forms in Equation (6) [32].

$$Q_e = K_F \cdot (C_e)^{1/n} \qquad (5)$$

$$\ln Q_e = \ln K_F + \frac{1}{n} \ln C_e \qquad (6)$$

The three-parameter Redlich-Peterson model incorporates the features of the Freundlich and Langmuir isotherms into a single equation and is given by Eq. (7) and Eq. (8), where K_R, a_R and β are the Redlich-Peterson parameters. β lies between 0 and 1 [33]. For β = 1 Equation (7) converts to the Langmuir form (Eq. 3).

$$\mathbf{Qe = (A_R Ce)/(1 + K_R C^{\beta}_e)} \qquad \textbf{(7)}$$

$$\mathbf{\ln[(A_R Ce/Qe) - 1] = \beta \ln(Ce) + \ln(K_R)} \qquad \textbf{(8)}$$

The Temkin model [34] main assumption is the uniformity in the distribution of binding energies up to some maximum binding energy. It is tributary of the reaction temperature and the involved sorbent/sorbate interactions. The equation of the Temkin model and its linear form are presented by Equations (9) and (10).

$$\mathbf{Qe = (RT/A_T) \, Ln \, (B_T . \, Ce)} \qquad (9)$$

$$\mathbf{Qe = B_T \, Ln \, (Ce/Qe) + A_T} \qquad (10)$$

The Elovich model supposes a multilayer sorption during which the active sites increase exponentially [35]. Its equation and the related linear form are expressed by Eq. (11) and (12).

$$Q_e/Q_E = K_E . \, C_e . \, \mathrm{Exp} \, (-Q_e/Q_E) \qquad (11)$$

$$\mathrm{Ln} \, (Q_e/C_e) = \mathrm{Ln} \, (K_E . \, Q_E) - (Q_e/Q_E) \qquad (12)$$

The accuracy of each model was quantitatively determined based on:

(a) The squared regression correlation coefficient: (R^2)

(b) The average relative error deviation (ARED) [Eq. (13)]:

$$\mathrm{ARED} = 1/N \; \Sigma \left| (Qe_{,cal} - Qe_{,exp}) / Qe_{,exp} \right| * 100 \qquad (13)$$

(c) The normalized standard error deviation (NSED) [Eq. (14)]

$$\mathrm{NSED} = [\; (\; \Sigma \; ((Q_{exp} - Q_{cal})/Q_{exp})^2 / \; (N\text{-}1)) \;]^{1/2} \qquad (14)$$

(d) The Marquardt's percent standard error deviation (MPSED) [Eq. (15)]

$$\text{MPSED} = \left[\left(\Sigma \left((Q_{exp} - Q_{cal})/Q_{exp} \right)^2 / (N\text{-}P) \right) \right]^{1/2} \qquad (15)$$

(e) The sum of the squares of the errors (SSE)

$$\text{SSE} = \Sigma \, (Qe_{,cal} - Qe_{,exp})^2 \qquad (16)$$

(f) The hybrid fractional error function (HYBRID):

$$\text{HYBRID} = 1/(N - P) \, \Sigma \left| Qe_{,exp} - Qe_{,cal} / Qe_{,exp} \right| * 100 \qquad (17)$$

The model is considered most suitable to satisfactorily describe the biosorption process if it provides the highest R^2 and the lowest error calculation values. The results of the Freundlich, Langmuir, Redlich–Peterson Temkin, and Elovich adsorption constants, in addition to the error calculation, are mentioned in Table 3. The graphic correlation between the experimental data and the theoretical models for the adsorption systems are given in Figure 6.

Table 3: Calculated parameters of the five studied modelling isotherms related to the biosorption of CR onto powdered sewage sludge

Freundlich model		***Temkin model***	
n (g/L^3)	2.440	**A_T** (L/g)	67.470
K_F (mg/g)	19.230	**B_T** [$(L/mg)^{\beta}$]	15.350
R^2	0.973	**R^2**	0.990
ARED	7.902	**ARED**	5.224
NSED	9.319	**NSED**	7.008
MPSED	10.76	**MPSED**	8.093
SSE	20.175	**SSE**	6.100
HYBRID	13.171	**HYBRID**	8.708
Langmuir model		***Elovich model***	
Q_0 (mg/g)	46.948	**Q_E** (mg/g)	15.504
K_L (L/mg)	0.852	**K_E** (L/mg)	5.143
R^2	0.992	**R^2**	0.990
ARED	2.798	**ARED**	6.556
NSED	3.883	**NSED**	8.103
MPSED	4.484	**MPSED**	9.356
SSE	1.636	**SSE**	21.366
HYBRID	4.663	**HYBRID**	10.927
Redlich-Peterson model			
A_R (J/mol)	15.503		
K_R (L/g)	5.143		
β	0.990		
R^2	0.999		
ARED	1.425		
NSED	2.216		
MPSED	3.134		
SSE	2.973		
HYBRID	3.564		

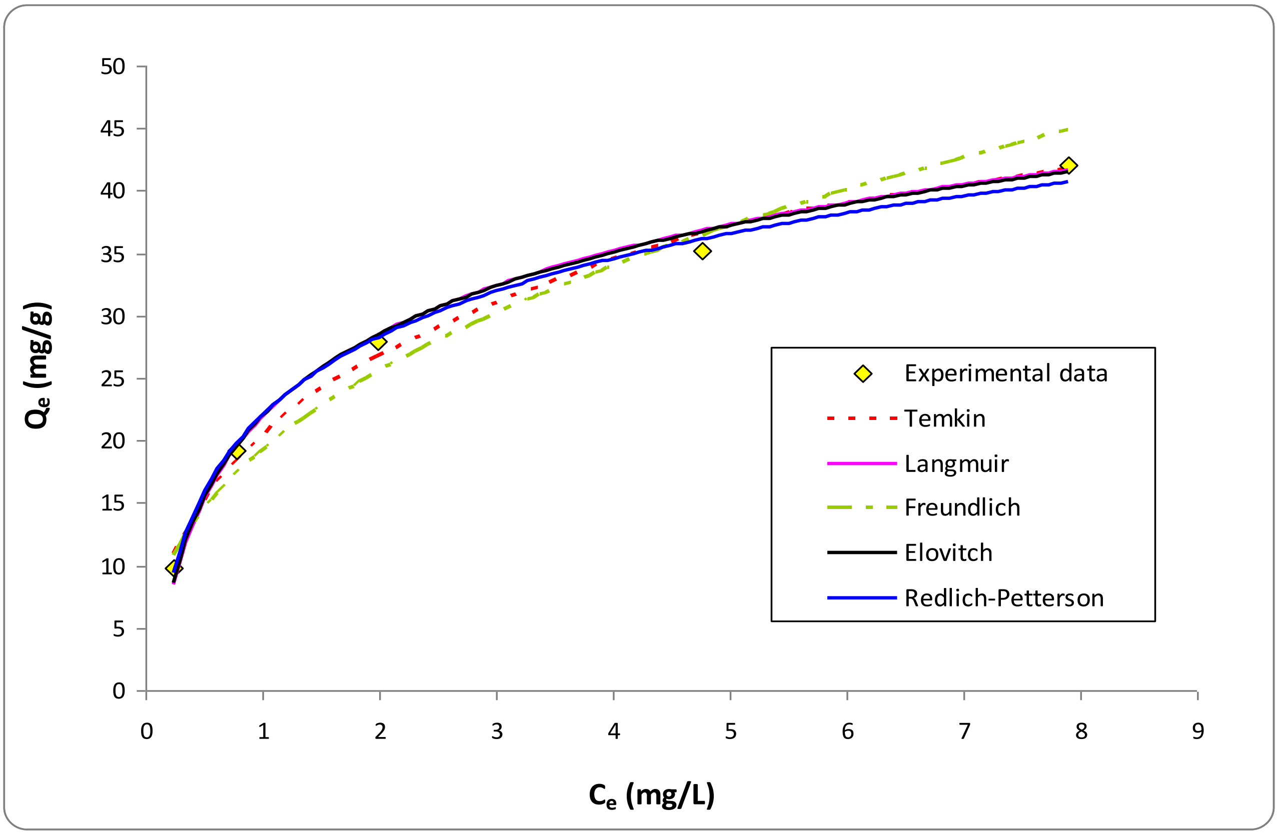


Figure 6: Adsorption isotherm modelling of CR onto powdered sludge (Solid/Liquid ratio =1 g/L, pH = 6, 120 rpm, temperature = 25 °C).

It is seen from the data in Table 3 that the experimental data were best described by the Redlich–Peterson model followed by Langmuir with high squared correlation coefficients of 99.9% and 99.2%, respectively, and the lowest error calculation values. A β value (0.99) closer to unity than to 0, show the closeness of the model to the Langmuir isotherm. It should be noted that normally β lying between 0 and 1, indicated a favorable adsorption of dye for the sorbent. Indeed, the suitability of Langmuir model indicates that the sorption process of CR onto powdered mud is monolayer onto a completely homogeneous surface with a finite number of identical sites and with negligible interaction between adsorbed molecules and has a constant adsorption energy.

Moreover and in order to confirm the favorability of the adsorption process, an extension of the Langmuir equation was made by introducing a dimensionless equilibrium parameter, R_L [36] that is defined by the following equation:

$$R_L = 1/\left(1 + K_L\, C_0\right)$$

The parameter R_L indicates the shape of the isotherm. If the R_L values are higher than 1, it indicates unfavourable adsorption. If the R_L values are 1, it indicates linear adsorption. R_L values between 0 and 1 indicate favourable adsorption. If the R_L values are zero, it indicates irreversible adsorption. Here, R_L values obtained are listed in Table 4.

Table 4: Separation factor, R_L, calculated for the biosorption of Congo red onto powdered waste sludge

Initial dye concentration (mg/L)	10	20	30	40	50
R_L	0.105	0.055	0.037	0.028	0.022

All R_L values for the adsorption of Congo red onto powdered sludge are in the ranges of 0.022–0.105 mg/L (Table 4). It shows that the biosorption process of CR onto powdered sewage sludge is favorable under the studied experimental conditions. On the other hand, the Freundlich constant n value, in the range of 1-10 (see Table 3), indicates that CR is favorably adsorbed. The constant n is an empirical parameter that varies with the degree of heterogeneity indicating the degree of nonlinearity between dye uptake capacity and non sorbed dye concentration and is related to the distribution of bonded ions on the sorbent surface [37].

Moreover, according to Figure 6 and the Table 3, it can be observed that the Temkin and Elovich models describe also relatively well the CR adsorption process onto powdered sludge with an ARED of 5.24 and 6.56, respectively.

3.6 Thermodynamic characterization of CR biosorption

In order to better understand the effect of temperature on the adsorption of RC onto PWS, the free energy change (ΔG°), enthalpy change (ΔH°), and entropy change (ΔS°) were determined using equilibrium constants varying with temperature. Such parameters reflect the feasibility and spontaneous nature of the process [38]. Experiments were performed using 10 mg/L dye solutions with 1 g/L powdered sludge for 24 h at various temperatures.

The apparent equilibrium constant K_c of the adsorption is defined as:

$$K_c = Ca_{eq}/ Ce$$

The Gibbs free energy of adsorption ΔG° by using equilibrium constant (Kc) indicates the capability of powdered mud to retain a solute and also the extent of its movement in a solution phase is calculated from the following equation:

$$\Delta G^\circ = -RT \ln K_C$$

The relationship between the Kc and temperature is given by the Van't Hoff equation [39]:

$$\ln K_C = \Delta G^\circ/R - \Delta H^\circ/RT$$

The enthalpy and entropy can be obtained from the slope and intercept of van't Hoff plot of ln K_C versus 1/T. Thermodynamic parameters obtained are given in Table 5.

Table 5: Calculated thermodynamic parameters for adsorption of Congo Red onto powdered sewage sludge

Temperature (K)	K_C	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/K/mol)
293	9.511	-5.487	0.015	0.299
303	9.555	-5.686		
318	9.644	-5.992		
333	9.778	-6.313		

The negative value of ΔG° decreased with an increase in temperature, indicating that the feasibility and the spontaneous nature of adsorption of CR are proportional to temperature.

The positive value of ΔH° for biosorption process (0.015 kJ/mol) suggests the endothermic nature of adsorption process favorable and possible strong bonding between dye and the sorbent, while slightly positive ΔS° of Congo Red adsorption process indicates an irregular increase of the randomness at the PWS -solution interface during adsorption.

Other previous studies, such as [40] and [41], showed positive ΔH° and ΔS°, and negative ΔG° values for adsorption of Congo red and from aqueous solutions onto chitosan composite microparticles, in agreement with the present work.

Conclusion

The aim of the present work was to contribute in developing an effective and inexpensive technology for removing dyes from aqueous solution by valorizing sewage sludge as a biosorbent. Congo Red (CR) was chosen as a dye model.

The effects of operation variables, such as pH of the solution, adsorbent amount, initial CR concentration and agitation speed were investigated using batch adsorption technique. Sorption kinetics, isotherms and thermodynamic parameters were conducted.

It was shown that the highest dye removal capacity was found at pH 6.1 g/L biomass dosage was sufficient for showing very high adsorption amounts of CR (up to 98%). The parameters of both kinetic and equilibrium modelling showed that the kinetic data were accurately described by the pseudo-second-order model, assuming therefore a chemisorption process. Adsorption modelling parameters for Freundlich, Langmuir, Temkin, Redlich–Peterson, and Elovich isotherms were determined and, based on R^2 and various error distribution functions, the equilibrium data fit well with both Redlich–Peterson and Langmuir models, suggesting homogeneous monolayer surface binding sites in the raw PWS toward CR dye molecules. The thermodynamic parameters such as Gibbs free energy change ΔG_0, standard enthalpy ΔH_0, and standard entropy ΔS_0 indicated that Congo Red adsorption onto powdered sludge was endothermic, spontaneous, confirming an adsorption process through a chemical bonding.

This study identified sewage sludge – at its raw state and without any physical or chemical activation – as a suitable low cost adsorbent to be used for removal of CR dye from aqueous solution. The very rapid adsorption and high uptake capacity for CR (63 to 86% of CR removal rate in less than 3minutes) make the PWS a quite interesting alternative to more costly materials such as activated carbons. More technical and experimental optimisations and treatments should be realised to improve the adsorption capacity of sewage sludge. For example, use of more effective pre-treatment methods and reduction in particle size (larger specific adsorption area, m^2/g) may further improve the rate and the extent of adsorption of dyestuffs onto PWS.

Besides, the CR-loaded biomass itself has to be treated to avoid a pollution transfer. Indeed, one of the more common questions aroused by biosorption processes involves the fate of the biosorbent after the process. Care must be taken that solving one problem should not create another. The sorbed CR could be recovered by extraction from the biomass in order to be concentrated and then stored, reused, or eliminated. Also, the decontamination of the CR-loaded biomass by biodegradation is a very interesting approach. Studies on theses topics are in progress.

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