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Research Article

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Removal of Reactive Red 120 dye from Colored Textile Wastewater by Lemna Minor Adsorbent: Equilibrium and Thermodynamic Studies

Davoud Balarak[1], Ferdos Kord Mostafapour[1], Ali joghataei[2*]

[1]Department of Environmental Health, Health Promotion Research Center, Zahedan University of Medical Sciences, Zahedan, Iran
[2]Department of Environmental Health, Qom University of Medical Sciences, Qom, Iran
*Corresponding Author: alijoghatayi69@gmail.com

Abstract In current study Lemna Minor (LM) has been utilized as the adsorbent for the removal of a reactive red 120 (RD-120), from aqueous solution using the batch adsorption technique under different conditions such as temperature, contact time and initial dye concentration at pH fixed 7. The optimum sorption conditions were found as following: contact time 90 min, initial dye concentration 25 mg/L and temperature 50 $^{\circ}$C. Different thermodynamic parameters i.e., changes in standard free energy, enthalpy, and entropy have also been evaluated. The ΔH^0 and ΔS^0 values are thus found to be 5.17 KJ/mol and ΔS^0 0.0342 J/K mol, respectively, while the ΔG^0 values were -4.17, 4.89 and -5.38 J in 293-323 K and it has been found that the reaction was spontaneous and endothermic in nature. On the other hand, equilibrium parameters have been investigated with Langmuir and Freundlich. The result of experimental data indicates that Langmuir equation fit better than the other.

Keyword: Lemna Minor, Adsorption, Isotherm, Thermodynamic

Introduction

A direct consequence of the fast development of industrial activities is that the amount and variety of chemical wastes thrown into water resources has rapidly increased [1, 2]. Very often small amounts of synthetic organic compounds (including phenol and its derivatives, pesticides, aliphatic and aromatic hydrocarbons, dyes and surfactants among most representatives) are detected in water streams [3, 4]. These compounds are known to possess high toxicity and low biodegradability, for which their occurrence in wastewater has become an important environmental issue [5].

Population growth increases the demand for industrial products [6]. Dyes are used to colour the final products of different industries, such as textiles, paper and pulp mills, cosmetics, food, leather, rubber, etc [7]. The generation of these products leads to the formation of wastewater contaminated with dyes [8]. The textile industry is responsible for the use of 30% of synthetic dyes. Of all dye textile fibres, cotton occupies the number one position, and more than 50% of its production is dyed with reactive dyes [9]. It is estimated that about 10–60% of reactive dyes are lost during textile dyeing, producing large amounts of coloured wastewater [10]. Reactive dyes which are extensively used in dyeing processes contain negatively charged sulfonate azo groups [11, 12].

The presence of dyes in industrial effluents is a major problem due their adverse effect to many forms of life [13]. The dyes may be highly toxic and potentially carcinogenic, mutagenic and allergenic on exposed organisms [14]. The dyes are adsorbed and reelected of sunlight entering the water [15]. Because these dyes are highly soluble in water, their removal from wastewater is difficult by conventional coagulation and activated sludge processes [16, 17].

Several conventional physiochemical techniques are available in the literature to treat wastewater. These include chlorination, ozonation, adsorption, membrane process, solvent extraction, flocculation, coagulation, etc [18, 19]. Most of them suffer from serious drawbacks such as high cost, tendency of the formation of secondary hazardous byproducts, incompleteness of purification [20]. Many Physico-chemical methods have been tested, but only that of adsorption is considered to be superior to other techniques [21]. This is attributed to its low cost, easy availability, simplicity of design, high efficiency, and ease of operation, biodegradability, and ability to treat dyes in more concentrated forms [22-24]. Activated carbons are widely used because of their high adsorption abilities for a large number of organic compounds. However, the price of activated carbons is relatively high, which limits their usage [25]. This has led many researchers to search for cheaper substitutes such as coal, fly ash, Lemna minor, canola, agricultural wastes, azolla filiculoides, wood wastes, and clay materials [26-28]. They have been applied with varying success in dye removal. Lemna minor (LM) is a floating freshwater aquatic plant, with one; two or three leaves each having a single root hanging in the water. As more leaves grow, the plants divide and become separate individuals [29, 30]. In the present study, LM, an agro-based waste material, was used as adsorbent for the removal of RR-120 from an aqueous solution.

Materials and Methods

Reactive Red 120 dye [CAS Number 61951-82-4; EC Number 263-351-0; Chemical Formula = $C_{44}H_{24}Cl_2N_{14}O_{20}S_6Na_6$; Molecular Weight = 1469.98 g; and λ max = 660 nm] supplied by Sigma Aldrich Co, was used as adsorbate without purification. A stock solution of 1000 mg/L RR-120 dye was prepared by dissolving the appropriate amount of RR-120 in double distilled water. Experimental solutions of desired concentrations were obtained by dilution of stock solution using double distilled water.

The Lemna minor was collected from the Anzali wetland, Iran and was taxonomically classified as Lemna minor. It was then sun dried and using a disk mill to obtain material with an average particle size of 1 mm. The crushed particles were then treated with 0.1M HCl for 5 h followed by washing with distilled water and then kept for shaded dry. The resultant biomass was subsequently used in sorption experiments.

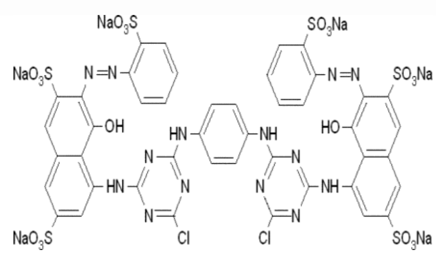

Figure 1: Chemical structure of Reactive Red 120

Adsorption experiments were carried out by batch techniques using a mechanical shaker at 150 rpm using 200 ml capped conical flasks. The pH was fixed at 7 by adding 0.1M NaOH or 0.1M HCl for adjustment and measured using a pH meter, temperature (20, 35 and 50 ℃), initial RR-120 concentration (25-200 mg/L) and contact time (10-120 min) on the performance of LA biomass were evaluated. After the adsorption process, the contents were filtered using a Whatman filter paper and the supernatant solution was analyzed using a UV-visible spectrophotometer (DR 5000) by recording the absorbance changes at wavelength of 511 nm. The amount of RR-120 dye adsorbed per unit weight of LM biomass adsorbent at time t, q_t (mg/L) and percentage RR-120 dye adsorption capacity was calculated using following equations [31-33]:

$$q_t = (C_0 - C_e)\frac{V}{M}$$

$$R\% = \frac{C_0 - C_e}{C_0} \times 100$$

Results and Discussion

To gain insights into the RR-120 adsorption mechanism onto LM biomass, two frequently used isotherm models (Langmuir and Freundlich) were employed to fit the adsorption equilibrium data**.** Langmuir model can be applied to elucidate homogeneous adsorption systems where adsorption is a monolayer reaction took place on a homogeneous adsorption sites. Whereas the Freundlich equation is proposed as an empirical equation implying that the adsorption is a multilayer heterogeneous adsorption.

The linearized form of the Langmuir isotherm is represented by following equation [34**,** 35]:

Langmuir equation: $\frac{1}{q_e} = \frac{1}{q_{max}} + \frac{1}{q_{max}\ K_L} \times \frac{1}{C_e}$

Where, C_e is the equilibrium concentration of the adsorbate (mg/L), q_e is the amount of adsorbate adsorbed per unit mass of the adsorbent (mg/g), q_m and K_L is the Langmuir constants related to adsorption capacity and energy of adsorption. The values of q_m and K_L were determined from slope and intercepts of the plot of (C_e/q_e) versus C_e (Fig 2).

The linearized form of the Freundlich isotherm is represented by following equation [36**,** 37]:

Freundlich equation: $\text{Log } q_e = \frac{1}{n} \log Ce + \log K_F$

Where q_e is the amount of adsorbed at equilibrium (mg/g), Ce is the equilibrium concentration of dye in solution (mg/L). K_F and n are Freundlich constants representing adsorption capacity and adsorption intensity or surface heterogeneity, respectively and determined from slope and intercepts of the plot of log q_e versus log C_e.

The corresponding parameters calculated from the two adsorption models at three different temperatures are summarized in Table 1. As can be seen, by comparing the value of correlation coefficients (R^2)**,** it was clear that the Langmuir model could describe the adsorption data better than the Freundlich model. This phenomenon confirmed that a monolayer homogeneous coverage of RR-120 on the interface of the material was formed**.**

To investigate more about adsorption characteristics of RR-120 on LM biomass, the thermodynamic analysis was performed. Thermodynamic parameters such as a change in free energy (ΔGº), enthalpy (ΔHº), and entropy (ΔSº) was determined using the following equations [38-40]:

$$K_c = \frac{q_e}{C_e}$$

$$\Delta G^{\circ} = -RT\ Ln\ K_c$$

$$\ln K_c = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}$$

Where T (K) is the solution temperature and K_a is the adsorption equilibrium constant. Enthalpy (ΔH°) and entropy (ΔS°) were calculated from the slope and intercept from the plot of Ln q_e/C_e versus 1/T.

The thermodynamic parameters (ΔG°, ΔH°, and ΔS°) are presented in Table 2. From Table 2, the ΔG° values were negative at all of the test temperatures, confirming that the adsorption of RR-120 onto LM biomass was spontaneous and thermodynamically favorable. The positive values of ΔH° reflected the typical endothermic nature of adsorption process of RR-120 on LM biomass, which was suggested by the study for effect of temperature. Compared with the movement of RR-120 in aqueous solution, the movement of RR-120 absorbed on LM biomass was easier, which was supported by the positive values of ΔS°.

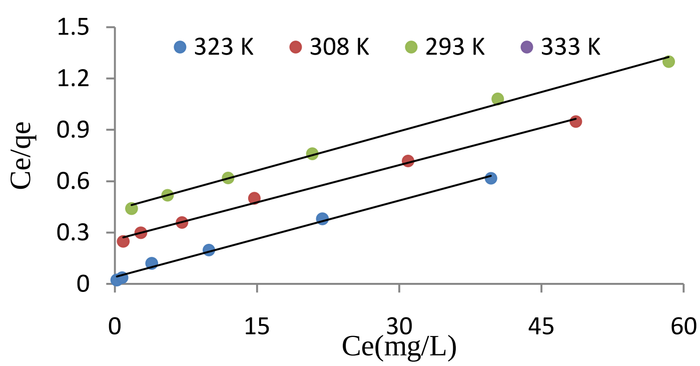

Figure 2: Langmuir models for the adsorption of RR-120 by LM at different temperature

Table 1: isotherm parameters for adsorption of RR-120 on LM

Models	Parameters	Temperature (K)		
		293	**308**	**323**
Langmuir	q_m	53.11	56.39	58.08
	K_L	8.25	11.45	13.42
	R_L	0.271	0.347	0. 259
	R^2	0.994	0.995	0.997
Freundlich	K_F	2.94	3.81	4.65
	1/n	0.37	0.21	0.63
	R^2	0.912	0.904	0.885

Conclusion

Biosorption of RR-120 dye from aqueous solution using LM biomass was investigated in a batch mode. The adsorbent LM biomass was productively used for the biosorption of dye from its aqueous solution. The effects of initial dye concentration, contact time and temperature on dye removal were studied. The equilibrium sorption isotherms have been analyzed by the Freundlich and Langmuir models. Sorption Thermodynamic parameters such as the free energy change (ΔG^o), enthalpy change (ΔH^o) and entropy change (ΔS^o) were determined from Van't Hoff plot. The data reported shows the adsorption process is endothermic in nature.

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