Camel Thorn as an Eco-Friendly Biosorbent for Removal of Reactive Dye from Textile Waste Water

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Abstract

The use of cheap, high efficiency and eco-friendly bio sorbent has been studied as an alternative source of activated carbon for the removal of dyes from wastewater. The bio sorption of Methyl Orange (MO) dye from aqueous solution on Camel thorn plant as a local low-cost, available and renewable biological adsorbent was studied. Activated carbon were prepared from camel thorn by chemical activation with 28% H3PO4 followed by pyrolysis at 150°C. Spectrophotometric technique was used for the measurement of concentration of dye before and after adsorption. The effect of various experimental parameters such as contact time, temperature, initial dye concentration and dose of adsorbent were studied. The results showed that the bio sorption of MO as the amount of adsorbent increased, the percentage of dye removal increased accordingly but it decreased with the increase in initial dye concentration and solution temperature. Effect of temperature onto percentage of dye removal shown that the exothermic spontaneity of the bio sorption process .Maximum dye removal was observed at initial dye concentration 20 mgL^{-1} ,dose of adsorbent 1.5 g and contact time 120 min at temperature room. Adsorption kinetic data were tested using pseudo-first-order and pseudo-second-order models. Kinetic studies showed that the bio sorption followed pseudo-second-order kinetic model with high degree of correlation coefficients ($R^2 > 0.99$). Langmuir and Freundlich isotherms were used to analyze the equilibrium data at different temperatures ranging (20-40°C) with the intervals of 5°C. The experimental data were more suitable to the Langmuir model than to the Freundlich model. The adsorption capacity maxi mom was calculated as 20.83 mg g^{-1} at 20°C .The experimental studies were indicated that camel thorn plant had the potential to act as an alternative bio sorbent to remove the MO dye from aqueous solution.

Key words: Bio sorption, isotherm, kinetic, Methyl Orange (MO) dye, Camel thorn plant.

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1. Introduction

In textile industries large amounts of water and chemicals are used for dyeing process. The wastewaters of this process usually consist of a number of contaminants including acids, bases, dissolved solids, toxic compounds and organic dyes. The dye compounds not only esthetically are displeasing, but also impede light penetration in the pans, thus upsetting the biological treatment process within the treatment plant. In addition, many dyes are toxic to some microorganisms and may cause direct destruction or inhibition of their catalytic capabilities [1].

Wastewaters commonly contain moderate concentrations (10–200 mg L^{-1}) of dyestuffs, contributing significantly to the pollution of aquatic ecosystems. The reactive dyes, which represent the largest class of dyes used in textile processing industries, are almost azo compounds, i.e. molecules with one or several Azo (N=N) bridges linking substituted aromatic structures. These dyes are designed to be chemically and photolytic ally stable; they exhibit a high resistance to microbial degradation and are highly persistent in natural environment. The release of these compounds into the environment is undesirable, not only for aesthetic reasons, but also because many Azo dyes and their breakdown products are toxic and/or mutagenic for life [2, 3].

Conventionally, chemical coagulation/flocculation, ozonation, adsorption, oxidation, electrochemical treatment, filtration and floatation etc. are all means used for the removal of dyestuffs. Although they can remove dyes partially, their initial investment and operational costs are so high that they can be widely used in dyeing and finishing industries, especially in developing countries [4-6]. Among these processes, adsorption has been found to be superior to other techniques for wastewater treatment in terms of initial cost, simplicity of design, ease of operation and insensitivity of toxic substances. Activated carbon is the most widely used adsorbent with great success because of its high adsorption capacity, but its use is limited due to its high-cost, has led to a search for cheaper substitutes. Natural materials that are available in large quantities may have potential as inexpensive sorbents. Due to their low-cost, after these materials have been expended, they can be discarded without expensive regeneration. The abundance and availability of agricultural by-products make them good sources of raw materials for activated carbons. Material such as rice bran, sugarcane bagasse pith, bagasse fly ash, pomegranate peel, coconut shell, Ulva lactuca and Sargasso, Azadirachta ndica leaf, hazelnut shell, Coir Pith, orange peel, walnut shells,etc.as adsorbents for the removal of dyes from wastewaters [1, 5-17].

In the present study activated carbon was prepared from low-cost adsorbent (Camel thorn plant) as a new bio sorbent for the removal of MO dye from aqueous solutions. The effect of different parameters such as temperature, contact time, adsorbent dose and initial dye concentration were investigated. The kinetic data and equilibrium data on batch adsorption studies were carried out to understand the adsorption process.

2. Materials and methods
1,2. Materials

Reactive Methyl Orange ($C_{14}H_{14}N_3NaO_3S$) is an anionic dye (Scheme 1). It was used as received without further purification. A stock solution of MO (1000 mg L^{-1}) was prepared and suitably diluted to the required initial concentration. The concentration of the dye was determined at 470 nm, using UV/Vis spectrophotometer (Perkin Elmer Lambda 25).
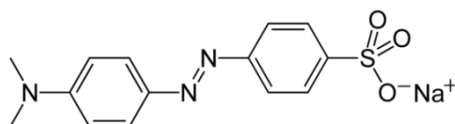

Figure1. The structure of Methyl Orange (MO)

2,2. Biosorbent Preparation

The Camel thorn plant collected from agriculture solid waste were washed several times with distilled water and dried in air and soaked for 24 hour in a solution of phosphoric acid (28%).After decantation, the sample was washed with distilled water and then was dried in an oven at 150°C, overnight. The dried material thus obtained was then stored in desiccators for subsequent studies.

3,2. Biosorption studies

Batch adsorption experiments were carried out at room temperature (20°C) . Exactly 200 ml of reactive dye solution of known initial concentration (10–80 mg L^{-1}) was shaken at the constant agitation speed (700 rpm) with a required dose of adsorbents (0.1-1.5 g L^{-1}) for a specific period of contact time (10-240 min) in a mechanical shaker. After

equilibrium, the final concentration (C_e) was measured. The percentage removals of dye were calculated using the equation (1):

%Removal of dye= (C_0 –C_e) 100/ C_0 (1)

Where C_0 and C_e are the initial and final (equilibrium) concentrations of dye (mg L^{-1}), respectively. Kinetics of adsorption was determined by analyzing adsorptive uptake of the dye from aqueous solution at different time intervals. For adsorption isotherms, dye solutions of different concentrations (20-80 mg L^{-1}), at different temperatures (20-40 °C) were agitated with known amounts of adsorbents until the equilibrium was achieved. Equilibrium adsorption capacity was calculated from the equation (2):

q_e= (C_0-C_e).V/W (2)

Where q_e (mg g^{-1}) is the equilibrium adsorption capacity, C_e is the dye concentration at equilibrium, V (L) is the volume of solution and W (g) is the weight of biosorbent.

3. Results and discussion

1,3. Investigation of Sorption Parameters

1,1,3. Effect of Initial Concentration of Dye and Temperature on Adsorption of MO Dye

The effect of initial concentration of dye on the removal of MO (in terms of percentage removal) on bio sorbent was studied as shown in Fig. 1. The percentage removal of the dye was found to decrease with the increase in initial dye concentration. This indicates that there exist reductions in immediate solute adsorption, owing to the lack of available active sites required for the high initial concentration of MO. Similar results have been reported in literature [5].

Fig. 2 illustrates the effect of temperature on adsorption for different initial concentration of dye. It is shown that the adsorption of MO dye on activated carbon decreases as the solution temperature increases. Similar results were obtained by various authors for the bio sorption of dyes on various bio sorbents [7]. This can be explained by the exothermic

spontaneity of the bio sorption process and by the weakening of bonds between dye molecules and active sites of bio sorbent at high temperatures.
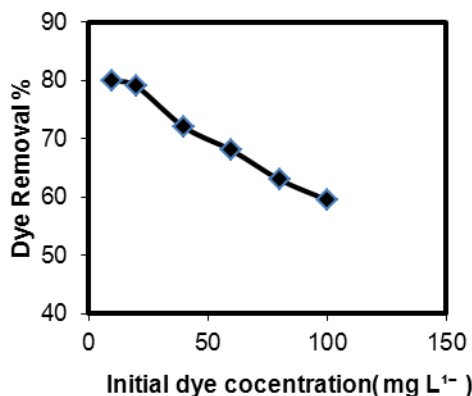

Figure2. Effect of initial concentration on MO dyes removal by activated carbon (dose of bio sorbent=0 sorbent=0.5 g)
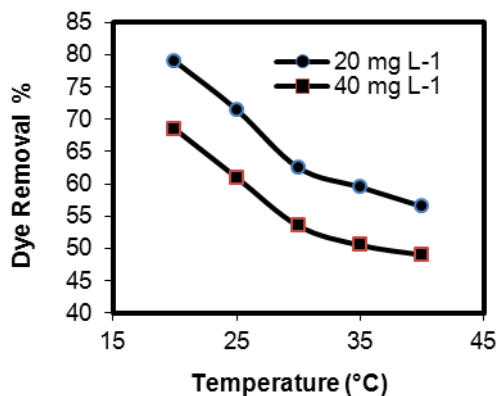
Figure3. Effect of temperature on MO dye removal by activated carbon (dose of bio

2,1,3. Effect of Contact Time

The effect of contact time on the percentage removal of MO dye was investigated at initial dye concentration (10-80 mg L^{-1}) as shown in Fig. 3. The percentage removal of dye by activated carbon was rapid in the beginning but it gradually decreased with time until it reached equilibrium. The plots reveal that maximum percent removal of the dye after about 90 min of shaking. The rate of removal is higher in the beginning due to larger surface area available of adsorbent. After adsorption, the rate of dye uptake is controlled by the rate of dye transported from the exterior to the interior sites of the adsorbent particles[1, 5, 6].
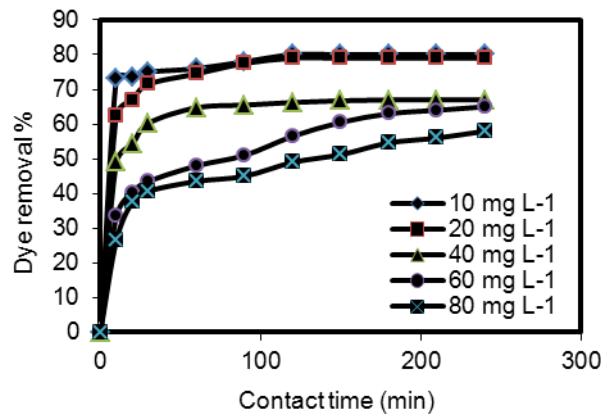
Figure4. Effect of contact time on MO dye removal by bio sorbent at different initial concentration

3,1,3. Effect of Dose of Bio sorbent

The percentage removal of MO increased with the increase in dose of adsorbent (Fig 4). This may be due to the increase in availability of surface active sites resulting from the increased dose and conglomeration of the bio sorbent [5].
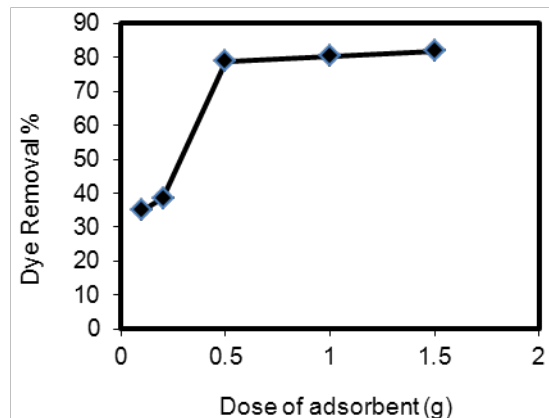

Figure5. Effect of dose bio sorbent C_0=20 mg L^{-1}, contact time=2 hour

2,3. Adsorption Kinetic Study

The bio sorption of a solute by a solid in aqueous solution is a phenomenon with often complex kinetics.

1,2,3. Pseudo-First-Order Model

The pseudo-first-order model was described by equation (3) [2, 7]:

$$\log (q_e - q_t) = \log (q_e) - k_1\, t/2.303 \tag{3}$$

Where q_e and q_t refer to the amount of dye adsorbed (mg g^{-1}) at equilibrium and at any time, t (min), respectively and k_1 is the equilibrium rate constant of pseudo-first-order adsorption (min^{-1}).

2,2,3. Pseudo-Second-Order Model

The pseudo-second-order model [2, 7] is represented by equation (4):

$$t/q_t = 1/k_2\, q_e^2 + t/q_e \tag{4}$$

Where k_2 is the equilibrium rate constant of pseudo-second-order adsorption (g mg^{-1} min^{-1}).

Experimental kinetic data were adjusted according to the indicated models (Fig .5). The results of Table 1 showed that the second order equation model provided the best correlation with experimental results. This fact indicates that the sorption of MO dye on adsorbent follows the pseudo-second order kinetic model [2, 7].

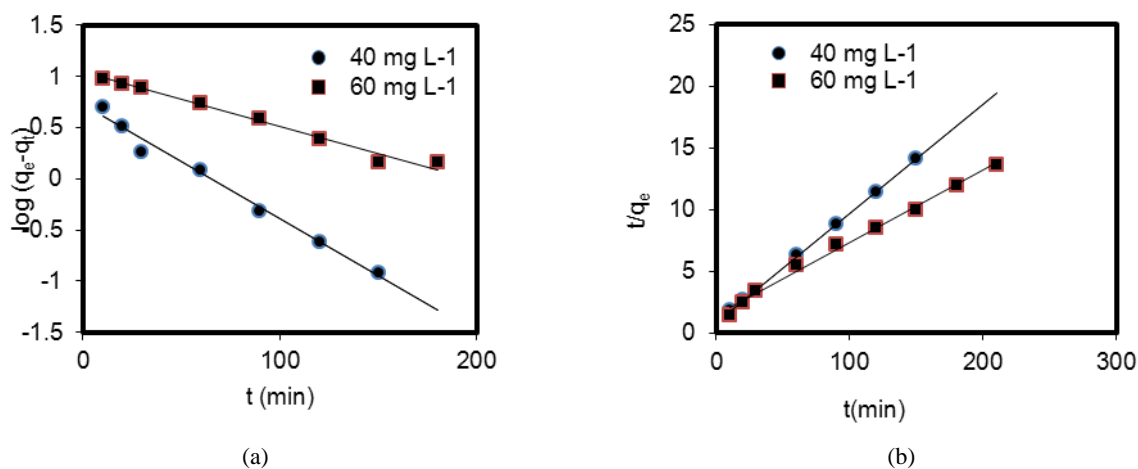(a)   (b)

Figure6. (a) Pseudo-first - order and (b) pseudo- second - order kinetic models for MO dye onto biosorbent

Table 1. Rate Constants for Different Kinetic Models

Dye Concentration (mg L^{-1})	Pseudo-First- Order Kinetic Model		Pseudo -Second- Order Kinetic Model	
	k_1 (min^{-1})	R^2	k_2 (g mg^{-1} min^{-1})	R^2
40	0.025	0.986	0.0087	**0.999**
60	0.011	0.981	0.0021	**0.993**

3,3. Adsorption Equilibrium Study

Equilibrium data, commonly known as adsorption isotherms, are basic requirements for the design of adsorption systems. In order to discover the adsorption capacity of activated carbon prepared from camel thorn, the experimental data points were fitted to the Langmuir and Freundlich isotherm equations(5,6) and the constant parameters of these equations were calculated (Fig .6). Langmuir model [1, 7]:

$$C_e / q_e = 1/Q_0 K_L + C_e / Q_0 \tag{5}$$

Where K_L is the Langmuir adsorption constant (L mg^{-1}) and Q_0 is the theoretical maximum adsorption capacity (mg g^{-1}) and in Freundlich model [4]:

$$\log q_e = \log K_F + 1/n \log C_e \tag{6}$$

Where K_F (L mg^{-1}) and *n* are isotherm constant the capacity and intensity of the bio sorption, respectively.

(a)   (b)
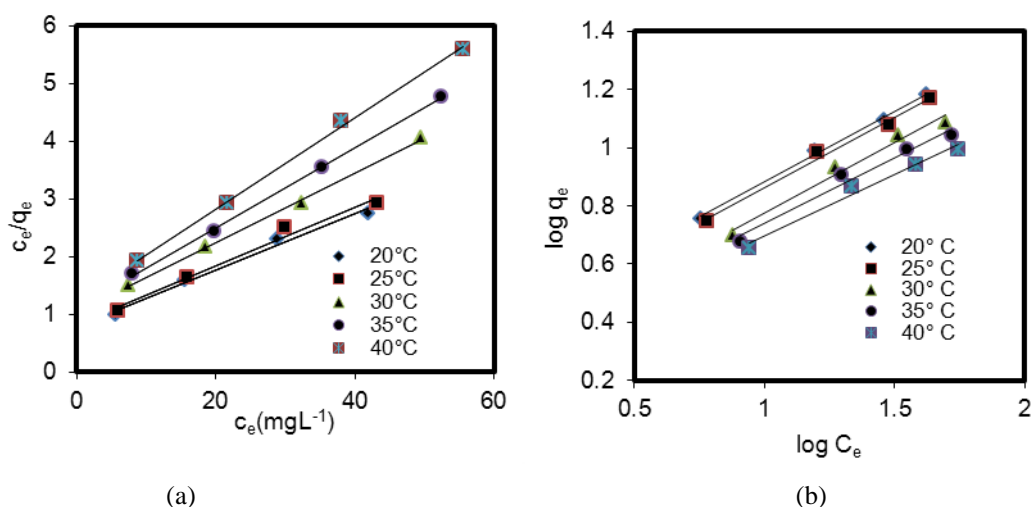
Figure7. (a) Langmuir and (b) Freundlish plots for the adsorption of the MO dye onto adsorbent

The values in Table 2 show that the experimental data were more suitable to the Langmuir model than to the Freundlich model. Corresponding to monolayer coverage of the binding sites availed in the bio sorbent [2].

Table 2. Freundlish and Langmuir Bio sorption Constants at Different Temperatures

T(K)	Freundlich Isotherm			Langmuir Isotherm		
	K_F	1/n	R^2	K_L	Q_0	R^2
293	2.496	0.484	0.997	0.0607	20.83	**0.985**
298	2.421	0.479	0.991	0.0618	19.61	**0.984**
303	1.959	0.484	0.977	0.0619	16.67	**0.998**
308	1.932	0.452	0.971	0.0620	14.49	**0.999**
313	2.042	0.399	0.982	0.0630	12.66	**0.998**

4. Conclusion

In this work, Camel thorn plant has been used successfully as a bio sorbent for the removal of reactive MO dye from aqueous solutions. Bio sorption was influenced by various parameters such as initial dye concentration, dose of adsorbent, contact time and temperature. Removal efficiency increased with decreasing the dye concentration and increasing dose of adsorbent. The effect of temperature on bio sorption for different initial concentration of dye shown that the exothermic spontaneity of the bio sorption process. The Langmuir and Freundlich adsorption isotherm models were used for the description of the adsorption

equilibrium of MO dye onto bio sorbent. The data were in good agreement with Langmuir isotherms. The results were shown that the bio sorption of MO onto camel thorn best fitted by pseudo second order model.

Since camel thorn, an agriculture solid waste, used in this study, locally available, the bio sorption process is expected to be economically viable for wastewater treatment.

5. References

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