Removal of FD&C Red No.40 Food Dye from an Aqueous Solution by Vine-Trimming Waste

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***Abstract*—The purpose of this study is to examine the removal of the food dye FD&C Red No.40 from an aqueous solution by means of vine-trimming waste. The adsorption experiments focused on the parameters such as contact time, pH of the aqueous solution, the amount of adsorbent, initial dye concentration and the temperature of the aqueous solution. Moreover, a study was carried out to make sure that the adsorption was in compliance with the Langmuir and Freundlich isotherm models and thermodynamic parameters were determined.**

***Index Terms*—Vine-trimming waste, food dye, adsorption.**

I. Introduction

Issues such as consumer awareness and expectations of variety, increasing market share and requirements for national and international standards make it necessary to use additives in the food industry. Of these additives, food dyes are referred to as substances that impart or restore colour to foods and contain natural food components and natural resources that are not generally consumed as they are directly and that are not used as the characteristic components of foods as well as peparations that are produced through the selective extraction of pigments in such a way that they do not contain other nutrient and aromatic constituents that are physically and/or chemically extracted from food substances and other renewable natural resources [1].

7×10^5 tons of over 100 types of food dyes are produced worldwide that are aimed at the textile, food, paper, plastic and other sectors [2]. However, large losses and waste from the production and use of these dyes prove detrimental to the human health and environment.

In general, four different methods, namely chemical, physical, biological and radiation-electrical-acoustic methods, are employed for treating wastes that contain food dyes [3]. These include a large variety of methods such as flocculation, precipitation, filtration, flotation, membrane filtration, ozonization, oxidation, ion exchange, coagulation and adsorption that are used in various industries [3]-[7]. Of these methods, adsorption stands out as a more advantageous method compared to the others for treating industrial waste water as it is economical and takes into account environmental concerns. There are not many studies that deal with the adsorption of food dyes using various adsorbents. The existing ones deal with the adsorption of acid blue 9 and food yellow 3 using chitosan [8], [9], the adsorption of sunset yellow dyes on CaAl-LDH-NO_3 [10], the adsorption of FD&D Red No.40 by means of chitosan [11]-[14], the adsorption of Brilliant Blue food dye with hen feathers [15], the adsorption of Tartrazine, Allura Red, Sunset Yellow and Indigo Carmine food dyes on Lewatit MonoPlus M-600 [16] and tartrazine allura red adsorption over *Spirulina platensis* [17].

FD&C Red No.40 is a food dye that belongs to the azo dyes group and bears the names of Allura red, E129, Food Red 17 and C.I. 16035. It is dark red in colour, water-soluble and derived from coal [18]. This food dye is used in fruit juices and powdered beverages, bakery products, dairy products, chewing gums and sweets, meat and fish products, canned food, fruits and vegetables, deserts, soups, sauces, pharmaceutics and cosmetic products.

This study deals with the adsorption of FD&C Red No.40 food dye from an aqueous solution using wine-trimming wastes.

II. Experimental

A. Materials

The food dye FD&C Red No.40, which was bought from a local firm, has a purity of 85%.

The vine-trimming waste samples selected as adsorbent were dried at a temperature of 105 °C for 24 h and reduced to the testing sizes in the range of 0,250-0,840 mm. The chemical analysis of the samples was performed in accordance with ASTM standards and the results are given in Table I.

TABLE I: Chemical Analysis Results of the Vine-Trimming Waste

Ash[a]	VM[a]	FC[a]	C[b]	H[b]	N[b]
2,51	79,42	18,07	46,23	5,98	1,11

a, on dry basis , %
b, on dry and ash free basis, %

B. Method

Stock solutions were prepared which had a dye concentration of 1 g/L. The adsorption experiments were conducted in a water bath at a stirring rate of 150 rpm. The pH of the aqueous solution was adjusted using the solutions O,1N HCl and 0,1N NaOH. Following the adsorption experiments, the dye solution was filtered and the maximum dye absorbances in the filtrate were measured at the maximum wave length (500nm) in a PG Instrument model Uv-Vis spectrophotometer. In addition, the Langmuir and Freundlich

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adsorption isotherms were applied and the thermodynamic parameters calculated.

The variables that were used during the experiments are contact time (5, 10, 20, 40, 60, 90, 120 and 180 min.), pH of the aqueous solution (2, 3, 4, 5, 6, 7, and 8), the amount of adsorbent (100, 250, 500, 750, 1000, 1500 and 2000 mg/L), initial dye concentration (50, 75, 100, 200, 300, 400 and 750 mg/L) and the temperature of the aqueous solution (25, 45 and 65 ℃).

C. *Adsorption Isotherm Models*

Adsorption isotherms were applied to the data obtained from the experiments which involved the adsorption of aqueous solutions having an initial dye concentrations of 50, 75, 100, 200, 300, 400 and 750 mg/L at the solution temperatures of 25, 45 and 65 ℃.

The Langmuir isotherm is expressed by the following equation:

$$C_e/q_e = 1/Q_{\max} \times b + C_e/Q_{\max} \quad (1)$$

where C_e denotes equilibrium dye concentration (mg/L), q_e the amount of dye adsorbed per unit mass of the equilibrium adsorbent (mg/g), $Q_{\max}$ adsorption capacity (mg/g) and b the Langmuir constant (L/mg). The slope of the line obtained by plotting a graph of C_e/q_e against C_e yields the value $1/Q_{\max}$ and the point of intersection gives the value of $1/Q_{\max} \times b$ [19].

Moreover, since the Langmuir isotherm assumes that adsorption takes place in a single layer, the separation factor R_L indicates the type of the isotherm.

$$R_L = 1 / 1+b \times C_0 \quad (2)$$

where b indicates the Langmuir constant (L/mg) and C_0 initial concentration (mg/L) [20], [21].

The value of R_L>1 indicates that the isotherm is unsuitable. If the value is 1, it is indicative of a linear isotherm. In the case of a value in the range of 0-1, the isotherm is considered to be suitable**.** If the value is 0, it denotes that the isotherm is irreversible.

According to the Freundlich isotherm is expressed as:

$$\log q_e = \log K_F + (1/n)\log C_e \quad (3)$$

where q_e represents the amount of dye adsorbed per unit mass of the equilibrium adsorbent (mg/g), C_e equilibrium dye concentration (mg/L), K_F adsorption capacity (mg/g) and n adsorption intensity. The slope of the line obtained by drawing a graph of the $\log q_e$ value versus the $\log C_e$ value yields 1/n and the point of intersection gives the $\log K_F$ value [22].

The thermodynamic parameters such as Gibbs free energy, enthalpy and entropy that are released during the adsorption process were calculated using the following equations:

$$\Delta G^{o} = - RT \ln K_c \quad (4)$$

$$\ln K_c = - \Delta H^{o} / RT + \Delta S^{o} / R \quad (5)$$

$$K_c = C_{ad} / C_e \quad (6)$$

where ΔG^{o} denotes standard Gibbs free energy, ΔH^{o} standard enthalpy, ΔS^{o} standard entropy, K_c adsorption equilibrium constant, C_{ad} dye concentration during the adsorption process (mg/L), C_e the concentration of dye that remained unadsorbed in the solution (mg/L), R gas constant (8,314 j/molK) and T solution temperature (K). The slope and point of intersection in the graph of ln Kc versus 1/T help calculate ΔH^{o} and ΔS^{o} [23], [24].

III. Results and Discussion

A. *The Effect of Experimental Parameters on Adsorption*

The effect of contact time on adsorption is illustrated in Fig. 1. The increase in the adsorption percentage with increasing time indicates that the adsorption time affects adsorption capacity. When adsorption time was increased from 5 min to 180 min, the adsorption yield rose from %27 to %97,15. The optimum adsorption time was determined to be 60 minutes.

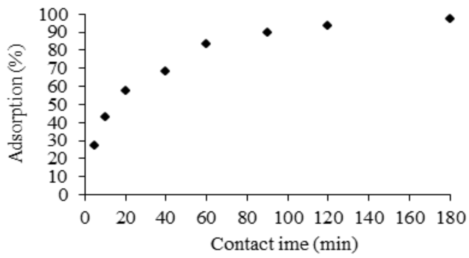

Fig. 1. The effect of contact time on adsorption. (Vine-trimming waste:1 g/L, pH:6, FD&C Red No.40:100 mg/L, temperature:25 ℃).

Fig. 2 illustrates the effect of pH on adsorption. When the pH value was increased up to 6, the adsorption yield rose to as high as 83.6 % and above this value, it was found to decrease. It was established that the pH of the solution where adsorption occurred had an effect on the adsorption percentage. The optimal pH value was determined to be 6.

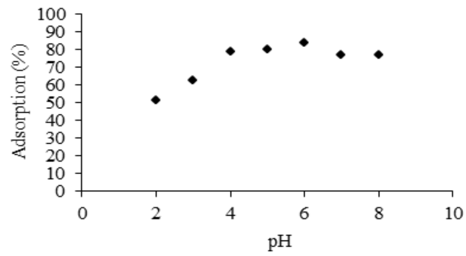

Fig. 2. The effect of pH on adsorption (Vine-trimming waste:1 g/L, FD&C Red No.40:100 mg/L, temperature:25 ℃, time:60 min).

Fig. 3 shows the effect of varying amounts of adsorbent on adsorption. As the amount of vine-trimming waste was increased, there was an increase in the adsorption percentage as well. The optimal amount of adsorbent was determined to be 1 g/L.

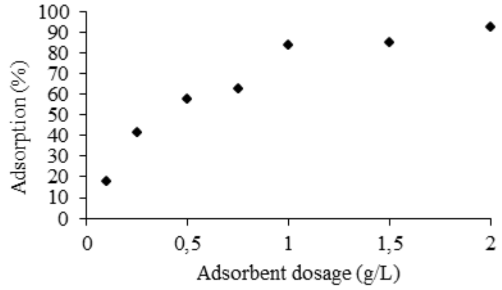

Fig. 3. The effect of the amount of vine-trimming waste on adsorption. (FD&C Red No.40:100 mg/L, temperature:25 ℃, pH:6, time:60 min).

Fig. 4 illustrates the effect of initial dye concentration at different temperatures 25, 45 and 65 ℃ on adsorption. It was determined that as initial dye concentration at all the three temperatures was increased, there was a decrease in the adsorption yield. It was found that with increasing temperature the adsorption percentage decreased. It was also established that temperature has an effect on adsorption capacity. The most suitable temperature was determined to be 25 ℃.

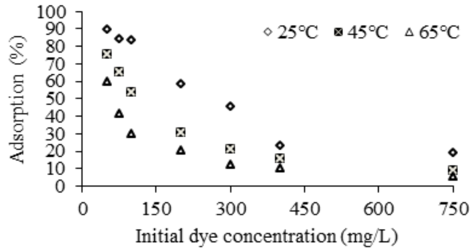

Fig. 4. The effect of initial dye concentration at different temperatures on adsorption (Vine-trimming waste:1 g/L, pH:6, time:60 min).

B. Adsorption Isotherms

The Langmuir and Freundlich isotherms were applied to the values in Fig. 4 and the values calculated are given in Table II and Table III.

TABLE II: LANGMUIR ISOTHERM CONSTANTS

Temperature (℃)	Q_{max} (mg/g)	b (L/mg)	R^2
25	135,14	0,044	0,9411
45	66,23	0,082	0,9992
65	42,55	0,055	0,9974

It was found that, according to the Langmuir isotherm model, as the temperature of the aqueous solution is increased, adsorption capacity decreases.

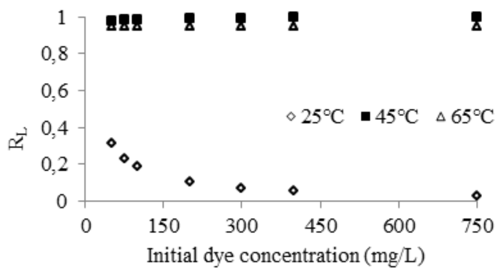

Fig. 5. The effect of initial dye concentration on the R_L value.

Fig. 5 gives the effect of initial dye concentration on the RL value. The fact that the R_L values are in the range of 0-1 indicates that adsorption is suitable and vine-trimming waste is suitable for the adsorption of the food dye FD&C Red No.40.

TABLE III: FREUNDLICH ISOTHERM CONSTANTS

Temperature (℃)	K_F (mg/g)	n	R^2
25	39,1	4,88	0,7580
45	30,7	7,92	0,8636
65	20,61	8,93	0,8241

It was determined that, according to the Freundlich isotherm model as well, with increasing aqueous solution temperature adsorption capacity decreases.

Since the correlation value of the Langmuir isotherm model was established to be higher than that of the Freundlich isotherm model, adsorption by means of vine-trimming waste can be said to be suited to the Langmuir isotherm.

Table IV gives the thermodynamic parameters that were calculated as a function of temperature. The fact that the value for the Gibbs free energy was found to be negative indicates that adsorption takes place on its own. As for the enthalpy value, if it proves to be negative, this indicates that adsorption occurs in an exothermic manner.

TABLE IV: THERMODYNAMIC PARAMETERS

Temperature (℃)	$\Delta G°$ (J/molK)	$\Delta H°$ (KJ/molK)	$\Delta S°$ (J/molK)
25	-4320,81	-40,75	-122,50
45	-1626,46		
65	-557,67		

IV. CONCLUSION

This study makes it clear that vine-trimming waste that cannot be utilized for economic purposes can be used for the removal of the food dye FD&C Red No.40 from an aqueous solution. It was established that adsorption by means of vine-trimming waste is affected by such variables as pH of the aqueous solution, the amount of adsorbent, initial dye concentration and solution temperature. The optimal adsorption parameters were determined to be 1 g/L of vine-trimming waste, the food dye FD&C Red No.40 with a concentration of 100 mg/L, an aqueous solution with a pH of 6, a solution temperature of 25 ℃ and a time period of 60 min. Langmuir adsorption isotherm model was determined to be more appropriate.

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