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COMPARISON OF BOMAPLEX BLUE CR-L REMOVAL BY ADSORPTION USING RAW AND ACTIVATED PUMPKIN SEED SHELLS

Abstract: In this study, removal of colour from wastewaters prepared synthetically using Bomaplex Blue CR-L was investigated using raw and activated pumpkin seed shells by adsorption in a batch system. The effects of stirring speed, adsorbent concentration, dye concentration, temperature and pH on colour removal were investigated, and adsorption capacities of raw and activated pumpkin seed shells were determined. In addition, adsorption kinetics, isotherm coefficients, activation energies and thermodynamic parameters were calculated. The optimal adsorption conditions were determined as pH = 2, stirring speed of 200 rpm, adsorbent concentration of 10 g L⁻¹ and 30 °C. Under the optimal conditions, the maximum removal efficiency of Bomaplex Blue CR-L using raw pumpkin seed shells was 73.01 %. This value rose to 79.71 % after activation processing was applied. Experimental adsorption data show that the adsorption is more suited to the Langmuir adsorption model and works in accordance with the pseudo-first-order kinetics model. As a result of thermodynamic research, ΔH° and ΔS° were 31.515 kJ mol⁻¹ and 109.952 kJ mol⁻¹ K⁻¹ for the raw adsorbent, respectively. For the activated adsorbent, ΔH° and ΔS° were 43.118 kJ mol⁻¹ and 152.237 kJ mol⁻¹ K⁻¹, respectively. The activation energy of adsorption was calculated as 10.918 kJ mol⁻¹ for the raw adsorbent and 9.882 kJ mol⁻¹ for the activated adsorbent.

Keywords: adsorption, pumpkin seed shell, removal of colour, textile dyes

Introduction

Dyestuffs are widely used in many industries, from the textile industry to the automobile industry. These industries consume large amounts of water. Wastewaters from these industries contain high concentrations of dyes and colours [1-3]. Among these industries, the textile industry releases the highest amount of dye waste to the environment [4]. Due to high water consumption, the amount of wastewaters in the textile industry is high. The pollution sources in these wastewaters are various chemicals and dyestuffs used in production. Colourful textile wastewaters discharged into receiving waters disrupt the esthetic appearance and reduce light transmission in water. The colour parameter is one of the first parameters to be examined in the determination of wastewater pollution. The colour contents of wastewaters vary greatly depending on the dyestuff used and the process applied [5]. The dyestuff concentrations in industrial wastewaters can vary between

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10 ppm - 500 ppm. Dye removal in the aquatic environment is extremely important in terms of human health. Most of these dyes consist of toxic and carcinogenic materials and these materials cause skin allergies [6, 7]. In addition, the discharge of dye-containing wastewaters into the receiving environment adversely affects the living life in the environment and harms the proper use of the waters [8, 9]. Even if industries producing coloured wastewater treat their wastewater up to discharge standards, they often cannot meet the colour discharge standards without additional treatment [10, 11].

Most of the processes with high efficiency in colour removal are expensive systems. In addition, sufficient efficiency cannot be obtained in many processes or the by-products formed threaten life. Various researches are still continuing today for colour removal in wastewater.

Adsorption is one of the most effective and cheapest methods used for colour removal [12, 13]. Powder and granular activated carbon are the most commonly used adsorbent types. But, activated carbon is a high-cost adsorbent because it is commercially produced today and is difficult to regenerate. For this reason, the search for adsorbent with lower cost and higher colour removal continues today [14]. In recent years, colour removal has been achieved at different rates by using more economical materials such as fly ash, coal, sawdust, fruit waste, slag, apricot kernel, walnut shell, bentonite clay, corn cob, peanut shell, rice husk, cotton waste and other agricultural wastes [15-18]. These adsorbents can be used directly as adsorbents, or they can be modified by various methods, increasing their surface area and changing their charge [19-22].

In this study, the potential to be a suitable adsorbent in the removal of dyestuffs from industrial wastewaters of waste shells with low economic value from pumpkin seeds, which are quite abundant in our country and used as an industrial raw material, was investigated. In this study, the potential for use in dye removal of raw and modified pumpkin seed shells was investigated.

In the literature, there are studies on the use of pumpkin seed shell by adding it to some products such as animal feed. However, studies on its use as an adsorbent are limited and mostly focused on inorganic material removal [23-26]. In this study, pumpkin seed shells which leave a very high amount of waste when consumed, was used both as a raw adsorbent and as an activated adsorbent, and dye removal from wastewaters was investigated. In the study, optimum values of parameters that affect the adsorption process and their effects on reaction kinetics were determined for raw and activated pumpkin seed shells.

Materials and methods

Materials

The pumpkin seeds were obtained as a result of collecting the shells of commercial pumpkin seeds consumed at home. Pumpkin seed shells used as adsorbents were washed several times with boiling water and then treated with distilled water. The materials were dried at 105 °C for 4 hours. These shells were ground and sieved to a particle size of 0.5 mm to 1 mm and placed in a glass bottle. The surface area of raw pumpkin seed shells was measured as approximately 0.4419 m² g⁻¹. This material was used without chemical treatment in the experiments.

Bomplex Blue CR-L which is one of the synthetic textile dyes was used as adsorbate in adsorption experiments. Bomplex Blue CR-L dye used in this study was supplied from

a textile mill in Turkey (dye textile industry company project, Gaziantep). The molecular structure of the textile dye is shown in Figure 1.

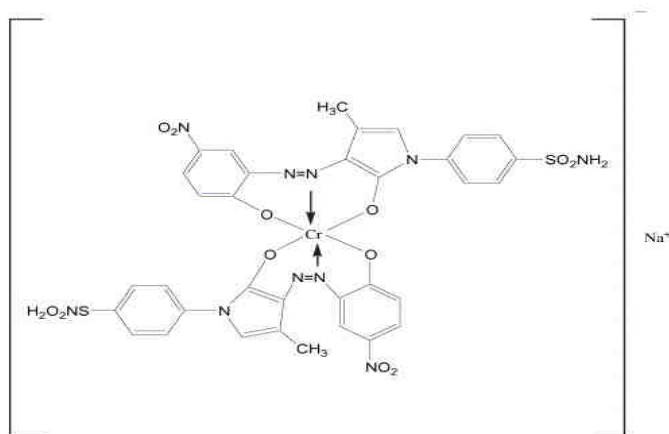


Fig. 1. Molecular structure of the textile dye used

By dissolving Bomaplex Blue CR-L in 50 mL of concentrated HNO_3 and completing to 1 L with distilled water, 1000 mg L^{-1} of stock dye solution was prepared. Different concentrations of solutions (25 mg L^{-1} to 200 mg L^{-1}) were prepared by diluting this stock solution with distilled water in the experiments. The experiments were done with 3 repetitions and their arithmetic mean was calculated.

HNO_3 and NaOH chemicals used for pH adjustment in the experiments are Merck brand and are of analytical purity.

Methods

The pumpkin seed shells after the washing and drying procedure were treated for the activation process. Dried shells were saturated with phosphoric acid (85 % by weight) and the ratio of shell/acid was 1:1. These shells were kept at 500°C for 1 hour in the incubator and washed with hot distilled water until $\text{pH} = 6$. The shells were dried again at 105°C for 4 hours. Then the materials sieved in the range of 0.045 mm to 0.15 mm and were stored in the glass bottles. The surface area of activated pumpkin seed shells was measured at approximately $6.048 \text{ m}^2 \text{ g}^{-1}$.

The experiments were carried out by adding 100 mL of synthetically prepared wastewater solution to 250 mL Erlenmeyer flasks. To investigate the effect of adsorbent concentration on Bomaplex Blue CR-L adsorption, the concentration of adsorbent ranged from 5 g L^{-1} to 20 g L^{-1} . The effect of wastewater dye concentration was determined using dye solutions ranging from 25 mg L^{-1} to 200 mg L^{-1} . The batch experiments were carried out on a mechanical platform shaker (Thermolyne ROSI 1000) at the required temperature, at a fixed stirring speed and pH value for 60 min. Samples were taken at definite time intervals and filtered to remove adsorbent with filter paper. The dye concentration in the samples was analysed using a Shimadzu UV-160A spectrophotometer. The measurement

wavelength for Bomaplex Blue CR-L dye was 625 nm and the maximum wavelengths of dye solutions did not change at different pH values.

The amount of dye, q_e adsorbed per unit weight of adsorbent in equilibrium and the amount of dye, q_t adsorbed per unit weight of adsorbent at any time were calculated as given by equations [27]:

$$q_e = \frac{(C_o - C_e) \cdot V}{m} \text{ [mg g}^{-1}\text{]} \quad (1)$$

$$q_t = \frac{C_o - C}{m} \text{ [mg g}^{-1}\text{]} \quad (2)$$

where C_o and C_e are the initial and equilibrium dye concentrations [mg L^{-1}], V is the volume of the dye solution [L] and m is the adsorbent mass [g].

Classical adsorption models were used to describe the equilibrium between q_e and C_e at constant temperature. Freundlich, Langmuir, BET and Temkin isotherm equations used in the experiments are given respectively [28-31]:

$$\log q_e = \log K_F + \frac{1}{n} \cdot \log C_e \quad (3)$$

$$\frac{1}{q_e} = \frac{1}{a \cdot K_L} \cdot \frac{1}{C_e} + \frac{1}{a} \quad (4)$$

$$\frac{C_e}{(C_s - C_e) \cdot q_e} = \frac{1}{K_B \cdot q_s} + \frac{K_b - 1}{K_B \cdot q_s} \cdot \frac{C_e}{C_s} \quad (5)$$

$$q_e = \frac{R \cdot T}{b_T} \cdot \ln K_T + \frac{R \cdot T}{b_T} \cdot \ln C_e ; B = \frac{R \cdot T}{b_T} \quad (6)$$

where K_F [mg g^{-1}] and n [L mg^{-1}] are Freundlich isotherm constants, a [mg g^{-1}] and K_L [L mg^{-1}] are Langmuir isotherm constants, K_B [L mg^{-1}] and q_s [mg g^{-1}] are the BET isotherm constants, and b_T [J mol^{-1}] and K_T [L g^{-1}] are the Temkin isotherm constants.

Pseudo-first-order and pseudo-second-order reaction kinetics equations were used in the studies to determine the reaction degree and rate constants [32]. Pseudo-first-order and pseudo-second-order reaction kinetics equations are given, respectively:

$$\ln(q_e - q_t) = \ln q_e - k_1 \cdot t \quad (7)$$

$$\frac{t}{q_t} = \frac{1}{q_e^2 \cdot k_2} + \frac{t}{q_e} \quad (8)$$

where k_1 is the first-order rate constant [min^{-1}], and k_2 is the second-order rate constant [$\text{g mg}^{-1} \text{min}^{-1}$].

The equation used to find Gibbs free energy in the adsorption process conducted at a certain temperature is given in Eq. (9) and the equation to find enthalpy and entropy of the adsorption process is Eq. (10) [33]:

$$\Delta G^0 = -R \cdot T \cdot \ln K_c ; K_c = \frac{C_a}{C_e} \quad (9)$$

$$\ln K_c = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{R \cdot T} \quad (10)$$

where K_c is the equilibrium constant, and C_a is the amount of substance that can be retained in the adsorbent [mg L^{-1}].

Adsorbent characterisation

SEM, FTIR, XRD analyses and zeta measurements were carried out in order to characterise the pumpkin seed shells before and after the adsorption process, and these tests were performed separately for raw and activated adsorbents. FT-IR spectra were obtained using PerkinElmer, Spectrum Two model FT-IR Spectrometer equipped with diamond ATR. FTIR analyses of adsorbents were used to characterise the bonds between molecules or compounds in the structure and functional groups. Morphological features of the adsorbents were obtained with a Zeiss Sigma 300 Scanning Electron Microscope. All samples were glued to the sample stub and covered with 10 nm gold-palladium layer for SEM images. X-ray diffraction data were obtained using Bruker D8 Discover XRD device to determine the structural features of adsorbents. Zeta potentials were measured with a zeta-meter (Zeta-Meter 3.0+542) for the characterisation of colloidal suspensions.

Results and discussion

Effect of contact time and pH on Bomaplex Blue CR-L adsorption

The pH experiments were performed by separately adding 1 g of raw and activated adsorbent to 100 mL wastewater containing 100 mg L^{-1} of Bomaplex Blue CR-L. The pH of wastewater was adjusted using 5 N HNO_3 and 5 N NaOH . According to the results obtained from the experiments, the change in Bomaplex Blue-R removal efficiencies for the raw and activated pumpkin seed shells after 60 minutes of contact time versus pH is shown in Figure 2a. The change in dye removal efficiency over time for $\text{pH} = 2$ is given in Figure 2b.

The error bars in Figures 2a and 2b show that the reproducibility of the adsorption reaction is high. This provides great advantages in plant operation.

Studies with both raw and activated adsorbents show that the adsorption efficiency decreased significantly above $\text{pH} = 3$. As the pH increased, the removal efficiencies gradually decreased, and reached 10 % for $\text{pH} = 9$. At $\text{pH} = 1$ and 2, removal efficiencies for raw adsorbent were 78.07 % and 73.01 %, respectively, at 60 minutes contact time. With the activated adsorbent at the same pH values, these removal efficiencies increased to 84.33 % and 79.18 %, respectively. Even if the time to reach equilibrium is shorter for the raw adsorbent, the removal efficiencies are approximately 10 % higher in the activated adsorbent, as the activation process creates a significant increase in the adsorbent surface area. It was observed that the pH of the solution greatly affected the removal efficiencies in the study. Electrostatic attraction between the negatively-charged dye anions and the positively-charged adsorbent surfaces can cause higher adsorption at lower pHs. Also, the functional groups of dyes are positively charged at these acidic pH values. As the pH of the wastewater increases, the number of negatively-charged sites increases. The reason for the decrease in dye adsorption in highly basic conditions may be the electrostatic repulsion between the negatively-charged dye molecules and the negatively-charged pumpkin seed shells. Similar results were reported by researchers working on different adsorbents for dye removal [34-37]. Even if coloured wastewaters are not treated by different processes after the adsorption process, it is thought that the pH will reach neutral pH if they are discharged into the sewer system or the receiving environment. In addition, the dyeing process is

carried out in process waters with low or high pH, depending on the characteristics of the dye used. It is also possible to reuse these waters as process water after being treated.

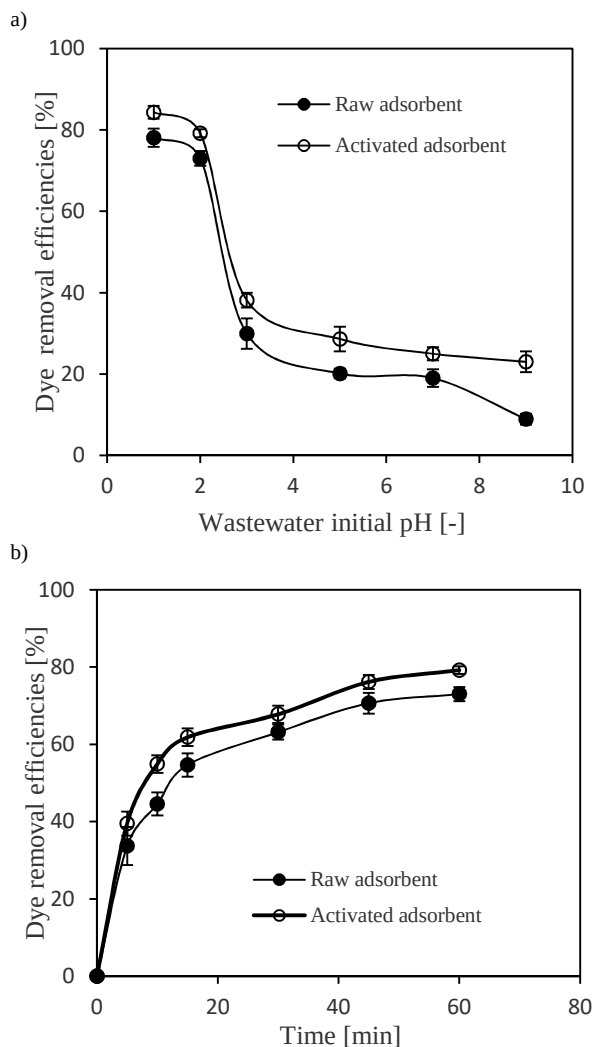


Fig. 2. a) The effect of pH on the adsorption of Bomaplex Blue CR-L by using raw and activated pumpkin seed shells, b) Dye removal efficiencies versus time at pH = 2

The results and standard deviation values obtained for the 3-repetition pH studies performed to examine the reproducibility of the experiments are given in Table 1.

Maximum adsorptions were obtained at pH = 1 for both of the adsorbents. But the results observed at pH = 2 were very close to those observed at pH = 1. Therefore, further experiments were carried out with pH = 2 because it is both economic and easy to set.

Table 1

Results and standard deviation values *SD* obtained for the 3-repetition pH studies

pH	Raw adsorbent					Activated adsorbent				
	Repetition			Average	SD	Repetition			Average	SD
	1	2	3			1	2	3		
1	77.50	79.20	77.54	78.08	0.97	82.50	85.10	85.42	84.34	1.60
2	72.60	75.01	71.42	73.01	1.83	80.20	79.10	78.24	79.18	0.98
3	31.20	28.90	29.69	29.93	1.17	40.20	37.60	36.65	38.15	1.84
5	19.80	21.10	19.52	20.14	0.84	29.90	29.90	26.03	28.61	2.23
7	18.60	19.50	18.87	18.99	0.46	23.30	25.10	26.54	24.98	1.62
9	9.50	10.10	8.36	9.32	0.88	22.50	23.80	22.73	23.01	0.69

Effect of adsorbent concentration on Bomaplex Blue CR-L adsorption

The effect of adsorbent concentration on the removal of Bomaplex Blue CR-L was studied at the initial dye concentration of 100 mg L^{-1} . The experiments with different adsorbent concentrations were conducted at 200 rpm stirring speed, 25°C and $\text{pH} = 2$. The change in dye removal efficiencies according to the adsorbent concentration is given in Figure 3.

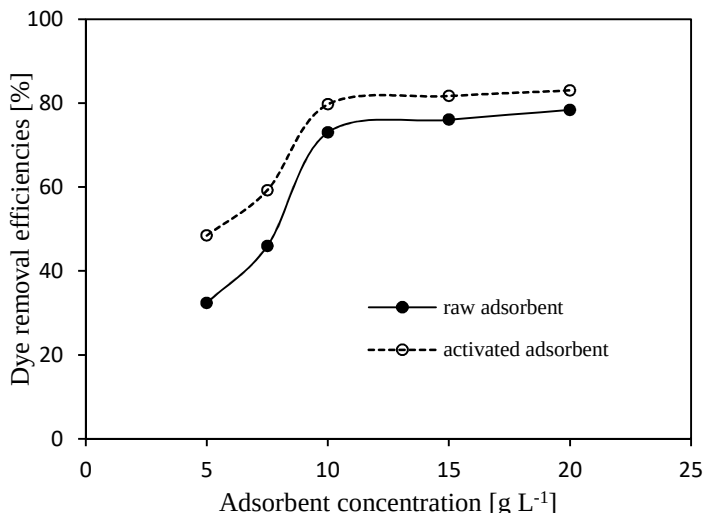


Fig. 3. Change in dye removal efficiencies according to adsorbent concentration by using raw and activated pumpkin seed shells

As seen from Figure 3, the adsorption of dye increased by increasing adsorbent concentration for raw and activated adsorbents. As the removal efficiency for raw adsorbent increased from 32.37 % to 73.01 % for the doses of adsorbents varying from 5 g L^{-1} to 10 g L^{-1} , these values increased from 48.45 % to 79.18 % for activated adsorbent. This can be explained by increases in the effective surface area of the adsorbent at high adsorbent concentrations. The interactions between the functional groups on the surface and dye increased owing to increasing numbers of sites being available for adsorption. The results for both adsorbents indicated that the difference in dye removal efficiencies between 10 g L^{-1} and 20 g L^{-1} adsorbent concentrations was about 5 %. Other researchers also reported a similar trend [38, 39].

Effect of wastewater dye concentration on Bomaplex Blue CR-L adsorption

The effect of initial concentration of Bomaplex Blue CR-L on adsorption by raw and activated adsorbents is shown in Figure 4. The experiments about the effect of adsorbate concentration were carried out with adsorbent concentration of 10 g L^{-1} and $\text{pH} = 2$. The removal efficiencies for Bomaplex Blue CR-L by raw and activated pumpkin seed shells decreased with the increase in initial Bomaplex Blue CR-L concentration from 25 mg L^{-1} to 200 mg L^{-1} . When the initial Bomaplex Blue CR-L concentration increased from 25 mg L^{-1} to 100 mg L^{-1} , the adsorption capacities of the raw and activated adsorbent increased from 2.2 mg g^{-1} to 7.3 mg g^{-1} and from 2.34 mg g^{-1} to 7.97 mg g^{-1} , respectively. At dye concentration of 200 mg L^{-1} , the adsorption capacities of raw and activated adsorbents reached 9.14 mg g^{-1} and 11 mg g^{-1} , respectively. This can be explained as the increase in dye concentration in the solution causing active sites on the adsorbents to be occupied by more Bomaplex Blue CR-L ions. Thus, the adsorption process proceeds more effectively [40, 37].

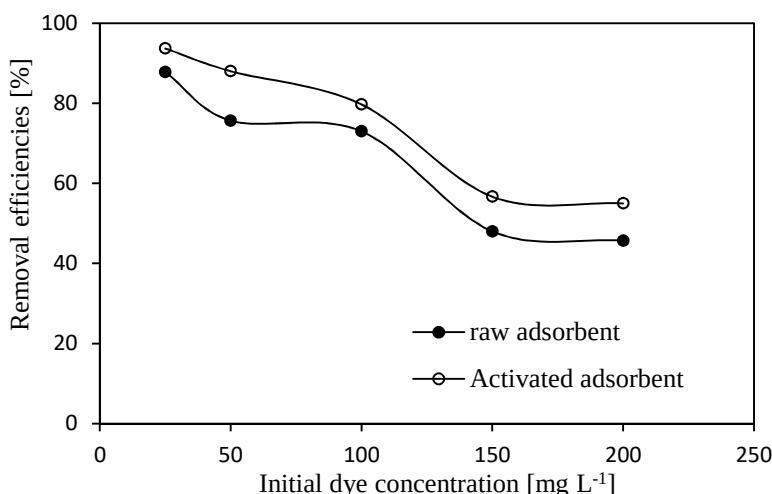


Fig. 4. Effect of dye concentration of wastewater on adsorption of Bomaplex Blue CR-L using raw and activated pumpkin seed shells

In the studies conducted with activated adsorbents, both adsorption capacities and removal efficiencies were higher than the studies with raw adsorbents. This case can be clarified by the increase in surface area of the adsorbent from $0.4419 \text{ m}^2 \text{ g}^{-1}$ to $6.048 \text{ m}^2 \text{ g}^{-1}$ because of the activation process.

Effect of stirring speed on Bomaplex Blue CR-L adsorption

Stirring speed is an important parameter affecting system efficiency. In batch adsorption experiments, provision of the most effective contact between the adsorbent and dye is desired. At low stirring speeds, the desired efficiency cannot be achieved due to the adsorbent settling to the bottom and not being sufficiently in contact with the pollutants. Desorption may occur, which is an undesirable process for physical adsorption, due to

instability at very high stirring speeds. Therefore, optimum stirring speed must be determined. In practice, stirring speed is also important in terms of energy costs. In the study, 200 rpm was found to be the most suitable stirring speed for raw and activated adsorbents (Fig. 5).

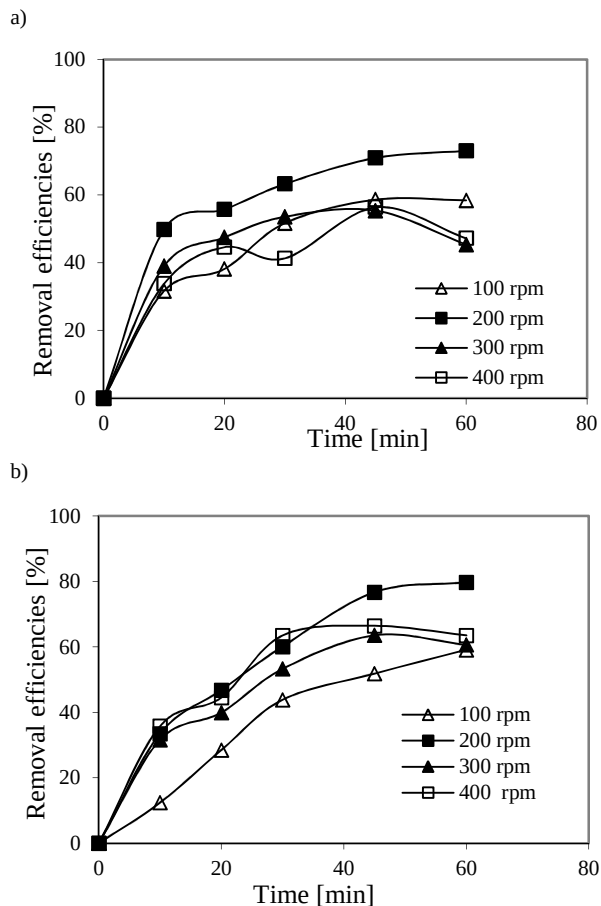


Fig. 5. Effect of stirring speed on adsorption of Bomaplex Blue CR-L using raw (a) and activated (b) pumpkin seed shells

In this study, the stirring speed was varied in the range of 100 rpm-400 rpm. The efficiency remained low as the adsorbent and adsorbate could not be in sufficient contact at 100 rpm stirring speed. Also, the time to reach equilibrium was prolonged. At high stirring speeds, desorption occurred due to the breaking of physical bonds formed during adsorption. This shows that the adsorption is actually physical adsorption. The physical bonds between the adsorbent and adsorbate are broken due to turbulence at high stirring speeds and desorption occurs [41]. When Figures 5a and 5b are examined, the raw pumpkin seed shell was affected more by the stirring speed compared to the activated pumpkin seed shell, and it appears that further desorption occurs with the raw adsorbent.

Effects of temperature on the removal of Bomaplex Blue CR-L

The effects of temperature were investigated at 20 °C, 30 °C, 40 °C and 50 °C for 60 minutes of contact time at 100 mg L⁻¹ dye concentration and stirring rate of 200 rpm. The results obtained from experiments show that increasing the temperature increased the efficiency of adsorption. As can be seen from Figure 6, while the removal efficiency is quite low at 20 °C, the removal efficiencies are close to each other at 30 °C, 40 °C and 50 °C. The experiments at different temperatures show that the adsorption reactions are endothermic. In addition, activation energies were calculated using these data and it was determined that adsorption was physical adsorption.

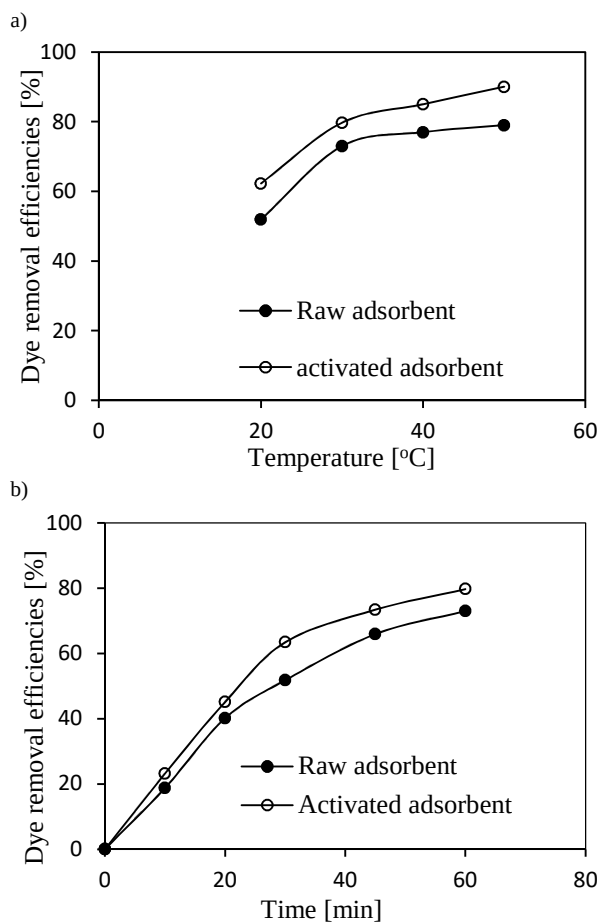


Fig. 6. a) Effect of temperature on adsorption of Bomaplex Blue CR-L, b) Change in Bomaplex Blue-R removal efficiencies versus time at 30 °C by using raw and activated pumpkin seed shells

Adsorption isotherms

Results obtained in isotherm studies using raw and activated pumpkin seed shells were applied to the Langmuir, Freundlich, BET and Temkin isotherm equations. The isotherm constants obtained from these equations are given in Table 2.

When Table 2 is examined, R^2 values for the other 3 isotherms, except the BET isotherm, are close to each other. But the adsorption has better fit to the Langmuir isotherm than the others. This situation shows that adsorption proceeds in a monolayer and the adsorption rate is directly proportional to the adsorbate concentration and active sites on the surface [29].

Table 2
Langmuir, Freundlich, BET and Temkin isotherm constants for Bomaplex Blue CR-L adsorption by using raw and activated pumpkin seed shells at 30 °C

Adsorbent	Langmuir isotherm constants			Freundlich isotherm constants		
	K_L [L mg ⁻¹]	a [mg g ⁻¹]	R^2 [-]	K_F [mg g ⁻¹]	n [L mg ⁻¹]	R^2 [-]
Raw pumpkin seed shell	0.052	5.889	0.9922	0.759	2.214	0.9701
Activated pumpkin seed shell	0.018	16.744	0.9901	0.446	1.332	0.9832
Adsorbent	BET isotherm constants			Temkin isotherm constants		
	K_B [L mg ⁻¹]	q_s [mg g ⁻¹]	R^2 [-]	K_T [L g ⁻¹]	b_T [J mol ⁻¹]	R^2 [-]
Raw pumpkin seed shell	-3.568	0.081	0.9356	0.429	17.852	0.9829
Activated pumpkin seed shell	-5.020	0.075	0.9512	0.223	8.470	0.9830

The fact that the K_L value obtained for the raw adsorbent is higher than the K_L value for the activated adsorbent indicates that Bomaplex Blue CR-L has higher affinity for the raw adsorbent. However, the value obtained for the activated adsorbent is greater than that obtained for the crude adsorbent. This shows that the surface area of the activated adsorbent is larger. In the surface area measurements, the surface area was 0.4419 m² g⁻¹ for the raw adsorbent and 6.048 m² g⁻¹ for the activated adsorbent, confirming these data.

Adsorption kinetics and thermodynamic constants of Bomaplex blue CR-L adsorption

Pseudo-1st-order and pseudo-2nd-order kinetic graphs were drawn with the data obtained from studies conducted to examine the effect of the amount of adsorbent. The graphs obtained are given in Figure 7. The reaction rate constants obtained from these results are shown in Table 3.

Table 3
Reaction rate constants at different reaction temperatures

Adsorbent	Pseudo-first-order [min ⁻¹]	R^2	Pseudo-second-order [g mg ⁻¹ min ⁻¹]	R^2
Raw adsorbent	0.0502	0.9768	0.1025	0.9067
Activated adsorbent	0.0578	0.9841	0.1112	0.9286

When these data are examined, the reaction takes place in accordance with the pseudo-first-order rate equation. Therefore, pseudo-first-order rate constants were used for determining activation energy.

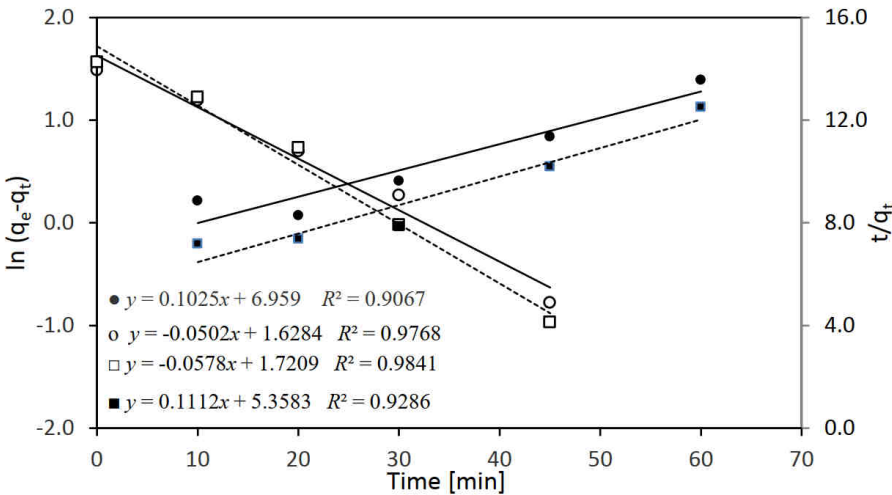


Fig. 7. Pseudo-first-order and pseudo-second-order reaction kinetics for Bomaplex Blue CR-L adsorption by using pumpkin seed shells at 30 °C (o raw adsorbent - pseudo-first-order, ● raw adsorbent - pseudo-second-order, □ activated adsorbent - pseudo-first-order, ■ activated adsorbent - pseudo-second-order)

The activation energies and the thermodynamic constants for dye adsorption were calculated using the results obtained in the experiments conducted to determine the effect of temperature on the removal of Bomaplex blue CR-L. The graphs drawn for this purpose are given in Figure 8 and the data found are given in Table 4.

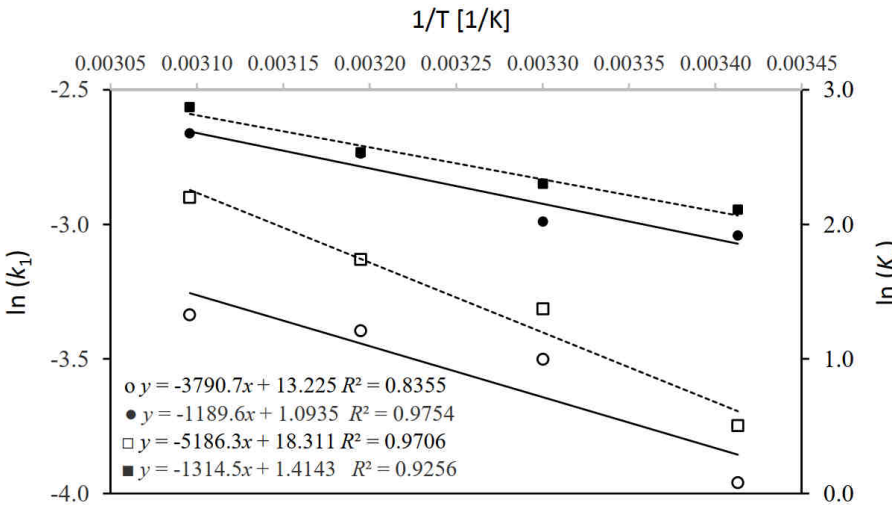


Fig. 8. Graphs plotted to find activation energies and thermodynamic constants for Bomaplex Blue-R adsorption using raw and activated pumpkin seeds (o raw adsorbent thermodynamic constants, ● activated adsorbent activation energy, □ activated adsorbent thermodynamic constants, ■ raw adsorbent activation energy)

With the help of the data obtained from Figure 8, $E_a = 10.918 \text{ kJ mol}^{-1}$ for the raw adsorbent and $9.882 \text{ kJ mol}^{-1}$ for the activated adsorbent. If the activation energy is between 5 kJ mol^{-1} and 40 kJ mol^{-1} , adsorption is defined as physical adsorption [42]. When the activation energy is examined, adsorption is physical adsorption and occurs rapidly. The positive ΔH° value indicates that the reaction is endothermic, and the negative ΔG° value indicates that the adsorption process is spontaneous. The positive ΔS° value indicates that the adsorption process is random [43]. Gibbs free energy is defined as physical adsorption if it is between -20 kJ mol^{-1} and 0 kJ mol^{-1} , and chemical adsorption if it is between -80 kJ mol^{-1} and -400 kJ mol^{-1} [44]. The values obtained indicate physical adsorption.

Table 4

Thermodynamic constants for raw and activated pumpkin seed shells

	$T \text{ [K]}$	$\Delta G^\circ \text{ [kJ mol}^{-1}\text{]}$	$\Delta S^\circ \text{ [kJ mol}^{-1} \text{ K}^{-1}\text{]}$	$\Delta H^\circ \text{ [kJ mol}^{-1}\text{]}$	$E_a \text{ [kJ mol}^{-1}\text{]}$
Raw	293	-0.189	109.952	31.515	10.918
	303	-2.424			
	313	-2.939			
	323	-3.229			
Activated	293	-1.220	152.237	43.118	9.882
	303	-3.333			
	313	-4.229			
	323	-5.352			

The higher the entropy value in the activated adsorbent, the higher the randomness for this adsorbent. A high enthalpy value means that more energy is needed for the reaction in the activated adsorbent. Activation energies for both adsorbents were found to be close to each other. This indicates that the adsorption mechanism works the same in both adsorbents. The slightly lower activation energy for the activated adsorbent indicates that adsorption requires less energy initially. As the Gibbs free energy value is higher for the activated adsorbent, the equilibrium constant is greater. In this case, it means that the equilibrium concentration decreases and the removal efficiency increases. Gibbs free energy indicates the degree of spontaneity of an adsorption process and a higher negative value means better adsorption with higher energy [45]. In this case, it appears that the activated pumpkin seed shells are the more suitable adsorbent.

Adsorbent characterisation

The adsorbents were examined before and after the experiments in the XRD device and the diagrams were given in Supplementary Material in Figure S1.

When XRD imaging is examined, the peaks at 15° and 35° on the raw pumpkin seed shell disappear after activation. In addition, from the shape of the peaks, it appears both adsorbents do not have a crystalline structure but have an amorphous structure.

In Figure S2, FTIR spectra are given for raw and activated pumpkin seed shells before and after adsorption.

As a result of FTIR examinations, the data given in Tables 5 and 6 were obtained [46-49]. When Table 4 is examined for the raw adsorbent, the peaks at 580 cm^{-1} , 680 cm^{-1} , 870 cm^{-1} , 1220 cm^{-1} , 1372 cm^{-1} , 1460 cm^{-1} , 2854 cm^{-1} , 2924 cm^{-1} and 3336 cm^{-1} , that were not present before adsorption, appeared in the adsorbent after adsorption. Likewise, for the activated adsorbent in Table 5, peaks appeared after adsorption at wavelengths of

1032 cm^{-1} , 1574 cm^{-1} and 1693 cm^{-1} that were not present before adsorption. It is clearly seen that amides, alkyls, aldehydes and alcohols that are not found in the structure of pumpkin seeds enter the structure of the adsorbent. Considering the molecular structure of Bomaplex Blue-CR-L, it can be easily said from these results that adsorption has occurred.

Scanning electron microscopy (SEM) is widely used to study the surface morphology of materials. SEM images magnified 10000 times for raw and activated pumpkin seed shells are given in Figure S3. Pumpkin seed shell has heterogeneous pores required for adsorption both in raw and activated state. It can be seen from the SEM graphs that the activation process expands the pores.

Table 5

Peaks obtained in the FTIR spectrum for raw pumpkin seed shells

Wavelength [cm^{-1}]	Chemical bond before adsorption	Chemical bond after adsorption
580	No peak	alkynes and alkyl halides. C–Cl stretches C–Br stretches
680	No peak	alkynes and alkyl halides. C–Cl stretches C–Br stretches
870	No peak	C–O, C–C and C–H stretching
1030	C–O stretch	C–O stretch
1102	C–O stretch	C–O stretch
1160	C–O stretch	C–O stretch
1220	No peak	C–O stretch
1372	No peak	
1460	No peak	to carbon–carbon stretching vibrations
1513	Amides	amides
1650	amides	amides
1744	No peak	C=O stretching in aldehyde
1920-2390	aldehyde	aldehyde
2854	No peak	O=C–H stretches in aldehydes
2924	No peak	O=C–H stretches in aldehydes
3336	No peak	H–OH group of alcohols and phenols

Table 6

Peaks obtained in the FTIR spectrum for activated pumpkin seed shells

Wavelength [cm^{-1}]	Chemical bond before adsorption	Chemical bond after adsorption
566	C–Br stretches, C–Cl stretches	C–Br stretches, C–Cl stretches
1032	No peak	C–O stretch
1574	No peak	Amides
1693	No peak	Amides
1734	Amides	No peak
1920-2390	Aldehyde	Aldehyde
2880	O=C–H stretches in aldehydes	O=C–H stretches in aldehydes

The phosphoric acid impregnation rate was effective in creating high surface area with well-developed pores on the surface of activated pumpkin seed shells. In the activation process, pore diameter and pore volume increase due to the reaction between raw pumpkin seed shells and H_3PO_4 and new pores are created [46, 50].

Conclusion

At the beginning of this study, some studies were found using Bomaplex Red CR-L in the literature, but no study was found using Bomaplex Blue CR-L. Also, in the literature, studies with pumpkin seed shells generally dealt with heavy metal removal. The shells of pumpkin seeds, which are consumed at a very high rate in many parts of the world, are generally disposed of as solid waste. The use of this waste with high organic content for dye removal, which is an important problem especially for industrial wastewater, is an important development for waste management. In the studies, no article was found showing how the activation process affects removal efficiency and speed and how variation in thermodynamic parameters.

In this study, the treatment of Bomaplex BCR-L textile dye with the adsorption method was investigated using raw pumpkin seeds. While the pumpkin seed shell was used raw, it was also used after the activation process was applied. Optimum pH, adsorbent concentration, dye concentration, temperature and stirring speed values were determined for removal of Bomaplex blue CR-L for both adsorbents. Attempts were made to determine how the activation process affects the adsorption efficiency.

According to the results obtained from the experiments for both adsorbents, low pHs were more effective for removal of Bomaplex Blue CR-L. Although the removal efficiency of the dyes at pH below 3 was above 70 %, this value fell below 30 % above pH = 3. When the synthetically-prepared dye solution was analysed, values lower than the concentration in the solution prepared at pH > 3 values were obtained. This showed that Bomaplex Blue CR-L dyestuff has higher solubility at low pH and is more easily adsorbed on the adsorbent at this pH.

The optimum stirring speed was determined as 200 rpm for both raw and activated adsorbents. Efficiency is reduced at stirring speeds below 200 rpm due to insufficient contact. Although equilibrium is reached more quickly at higher stirring speeds, the removal efficiency is adversely affected due to desorption.

Activation energies were calculated as a result of experiments examining the effects of temperature. The obtained activation energies showed that adsorption is physical adsorption. Although removal efficiencies do not change much at temperatures above 30 °C, they decrease significantly at low temperatures. Also, kinetic constants were calculated for Freundlich, Langmuir, BET and Temkin adsorption isotherms in these studies. It was determined that the adsorption on both adsorbents occurs in accordance with the pseudo-first-order reaction. In the studies calculating thermodynamic constants, the reaction was determined to be endothermic, spontaneous and random.

As a result, it can be said that pumpkin seed shells can be used effectively for dye removal and the activation process increases the removal efficiency considerably. The activation process did not cause any change in the adsorption mechanism, but only increased the amount of adsorbed dye per unit adsorbent mass. This shows that the increase in efficiency is due to this process which increases the specific surface area, rather than the activation process.

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