

Utilizing of bio-adsorbent in zero waste concept: adsorption study of crystal violet onto the *centaurea solstitialis* and *verbascum thapsus* plants

Sıfır atık konseptinde biyo-adsorban kullanımı: kristal violet'in *centaurea solstitialis* ve *verbascum thapsus* bitkileri üzerine adsorpsiyon çalışması

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Abstract

Adsorption is one of the most widely used methods for dye removal from water. At the end of the adsorption process, the dyed adsorbents emerging as a second-order waste which is the main disadvantage of this process. In this study, the removal of a synthetic dye Crystal Violet (CV) from the synthetic wastewater by using *Centaurea solstitialis* (CS) and *Verbascum Thapsus* (VT) plants was studied by adsorption. At the end of the adsorption process, the reusing potential of the dyed plant was explored by measuring the dyed plant calorific values. Experimental design and modeling were performed using the surface response method (RSM). The regression coefficients for developed models were 0.86 for the CS plant and 0.95 for the VT plant. Adsorption process for CS and VT plants were fitted by Dubinin-Radushkevich isotherm, and Temkin isotherm, respectively. The two plants were pseudo-second-order, endothermic, and found to be chemically. CS plant had a capacity of 84.03 mg.g⁻¹ with a contact time of 85 min. The capacity of the VT plant reached 109.89 mg.g⁻¹ at a contact time of 55 min. The calorific values results show increases in the calorific values for the two plants after the adsorption process. The CS plant increased from 4003.774 to 4458.059 Kcal.Kg⁻¹. Whereas the VT plant increased from 3206.028 to 4120.330 Kcal.Kg⁻¹. These values indicate the using possibility of the two plants as solid fuel by burning the dyed plants in emission controlled industrial facilities by applying the zero-waste concept.

Keywords: Zero waste, Crystal violet, *Centaurea solstitialis*, *Verbascum thapsus*.

Öz

Adsorpsiyon, sudan boya gideriminde kullanılan en yaygın yöntemlerden biridir. Adsorpsiyon yönteminin en önemli dezavantajı, işlem sonunda ikinci bir atık olarak boyalı adsorban maddelerin oluşmasıdır. Bu çalışmada, adsorban olarak *Senturea solstitialis* (CS) ve *Verbascum thapsus* (VT) bitkileri kullanılarak sulu çözeltiden Crystal Violet'in (CV) uzaklaştırılması incelenmiştir. İşlem sonunda elde edilen boyalı adsorbanların kalorifik değerleri belirlenerek farklı amaçlar için kullanılabilirliği araştırılmıştır. Deneysel tasarım ve modelleme, yüzey tepki yöntemi (RSM) kullanılarak gerçekleştirilmiştir. Geliştirilen modeller için regresyon katsayıları CS bitkisi için 0.86 ve VT bitkisi için 0.95 olarak bulunmuştur. Adsorpsiyon işleminde CS ve VT bitkilerinin sırasıyla Dubinin-Radushkevich ve Temkin izotermine uyduğu tespit edilmiştir. Her iki bitki için de adsorpsiyon, sahte ikinci derece kinetik, endotermik ve kimyasal reaksiyon olarak gerçekleşmiştir. CS bitkisi için maksimum adsorpsiyon kapasitesi 84.03 mg.g⁻¹ ve temas süresi 85 dk'dır. VT bitkisi için ise maksimum adsorpsiyon kapasitesi olan 109.89 mg.g⁻¹'e, 55 dk'da ulaşılmıştır. Her iki bitkinin de adsorpsiyon öncesinde ve sonrasında kalorifik değerleri ölçülmüş ve adsorpsiyon işlemi sonrasında elde edilen boyalı adsorbanların kalorifik değerlerinin arttığı tespit edilmiştir. CS bitkisinde kalorifik değer 4003.774'ten 4458.059 Kcal.Kg⁻¹'e yükselirken VT bitkisinde 3206.028'den 4120.330 Kcal.Kg⁻¹'e yükselmiştir. Bu değerler, adsorpsiyon işlemi sonrasında ikinci bir atık olarak ortaya çıkan boyalı bitkilerin emisyon kontrollü endüstriyel tesislerde yakıt olarak kullanılabilmesini göstermiştir. İşlem bir bütün olarak ele alındığında sıfır atık hedefine ulaşmaktadır.

Anahtar kelimeler: Sıfır atık, Kristal viyole, *Centaurea Solstitialis*, *Verbascum thapsus*.

1 Introduction

With the increase in industrial activities in recent years, the amount of dyes used to color products has also increased [1]. Significant amounts of dyes are used, especially in the textile, paper, leather, paint, printing, food and plastic industries. In industries where dyes are used, the discharged wastewater resulting from the process without color removal sufficiently causes significant environmental problems. The discharged dyes affect the chemical structure of the water. Also, it disrupts the aesthetic appearance of the water and prevents the passage of light into the water body. All these have negative effects on the aquatic ecosystem [1],[2].

Following the Regulation on Water Pollution Control (RWPC) in Turkey published in the Official Gazette dated 31.2.2004, and

numbered 25687 within the scope of the Environmental Legislation, the color parameter was added to the discharge criteria for treated wastewater with the amendment dated 24/4/2011 and numbered 27914. According to this regulation, the color parameter for the composite samples after 2 h should be 280 Pt-co and 260 Pt-co after 24h [3].

Crystal Violet (CV), also methyl violet or basic violet, is a cationic triphenylmethane dye [4]. Triphenylmethane dyes are well soluble in water since they contain sulfonic acid [5]. CV dye can be used as a pH indicator, it is used to classify gram bacteria, textiles, food additives, cosmetics, plastics, and paper prints [6],[7]. Despite its wide range of applications, CV dye is known to have toxic effects [8],[9]. For these reasons, to protect water

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resources and human health, the CV dye should be treated before being delivered to the receiving environment [9].

There are different methods used in dye removal from water. Some of them; coagulation-flocculation [10], photocatalytic oxidation [11], reverse osmosis [12], ozonation [13], chemical oxidation [14], membrane filtration [15] and adsorption. Adsorption is a preferred method for dye removal among other advanced treatment techniques, due to its economic and environmental friendliness [7]. The limitation of this technique is the generation of the second-order contaminant.

Adsorption is the process by which molecules in one substance adhere or attach to the surface of another substance [16]. In the adsorption process, the properties of the adsorbents and the adsorbed substances are affected by factors such as pH, temperature, presence of ions in the environment, adsorption kinetics and time [17].

Adsorbent materials are divided into two as natural and synthetic adsorbent materials. Natural adsorbents are classified as inorganic (zeolite, clay, perlite, etc.) and organic according to their structure. The most common synthetic and inorganic adsorbent is activated carbon. It has the highest adsorption capacity. Because of its costs, the researchers are investigating alternative adsorbent materials. The use of natural, organic, and inanimate adsorbents such as agricultural by-products and plant wastes as adsorbents is cheaper and environmentally friendly [18],[19].

These adsorbents are preferred because they do not dissolve in water, have a large surface area, and contain functional groups such as lignin, hydroxyl (OH) and carboxyl (COOH), which are connect to the dyes in wastewater and remove it from the water [20]. It is also possible to increase the adsorption capacity by replacing these functional groups with simple activation processes [21]. The only disadvantage of natural herbal adsorbent materials is that they are not suitable for every dye [22].

As mentioned above, the limitation of the adsorption process is the generation of the second-order contaminant. The dyed adsorbents remaining after the adsorption process are evaluated as hazardous wastes. These wastes cannot be disposed of in landfills, but they can be disposed of in hazardous waste disposal facilities. Hazardous waste incineration license plant is one of the possible solutions as they can be used within the scope of Waste Derived Fuel (ATY). According to Turkish Communique (2014), the wastes with the energy larger than 2500 kcal/kg will be used together as additional fuel to obtain energy in incineration plants. The communique stated that adsorbents and filter materials contaminated with dangerous substances can be accepted to the facilities as ATY [23].

Response Surface Method (RSM) is a method using statistical and mathematical techniques for experimental design, model development and investigation of the effect of independent variables [24],[25]. It is important to use RSM in experimental design and modeling to reduce the use of chemicals and shorten the test times.

Centaurea solstitialis (CS) is a thorny plant observed in many parts of the world. It also found in agricultural areas in Turkey in the vacant land and arid slopes [26]. It obstacle the development and production yield of the plant grown on agricultural land. The CS plant, which is removed from agricultural lands by various means, emerges as waste with no economic value [27].

Verbascum Thapsus (VT) is a leaf hairy plant that grows in many parts of Turkey. The flower part of this plant contains essential oil and glycoside. Also, because the seeds are poisonous to fish is used in fishing. The flower part and the leaf part are generally considered to be good for some diseases such as colds and are considered to be medicinal plants by local people [28].

This study aims to investigate the CV removal possibility by CS and VT plants as low-cost bio-adsorbents from the aqueous solution. It also aims to study the potential reusing of the dyed plants in emission controlled industrial facilities to eliminate the second-order contaminants by applying the zero-waste concept.

2 Material and method

2.1 Adsorbent preparation

The CS plant was obtained from Çevttepesi of Erdemli District of Mersin Province. The VT plant was collected from the Harfilli Neighborhood of Erdemli District of Mersin Province. CS and VT plants were washed with pure water to remove dust, soil, etc. It was then dried in a HAREUS oven at 105 °C for 24 hours. The dried adsorbents were milled with the ISOLAB blender. Based on the preliminary experiment results, the adsorbents were passed through a 35 mesh sieve (Figures 1 and 2).



Figure 1. (a): CS plant. (b): CS adsorbent (35 mesh).

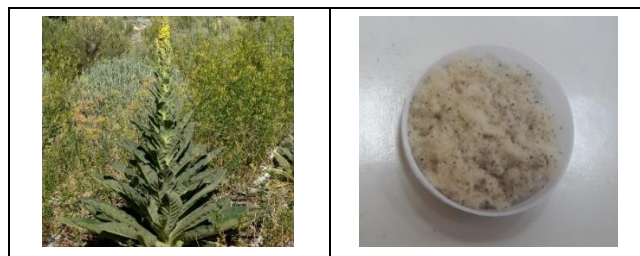


Figure 2. (a): VT plant. (b): VT adsorbent (35 mesh).

2.2 Crystal violet preparation

The chemical formula of the cationic CV dye is $C_{25}H_{30}N_3Cl$ (Figure 3), with a molecular weight of 407.98 $g \cdot mol^{-1}$. 1000 ppm CV stock solution prepared from MERCK brand dye was used in the experiments. In the experiments, 0.1 M NaOH and 0.1 M HCl were used to adjust the pH.

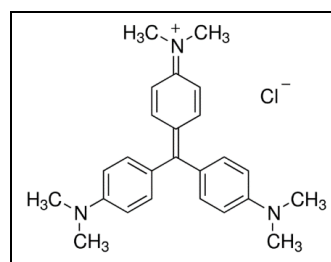


Figure 3. The chemical structure of the CV.

2.3 Adsorbent Characterization

In this study, the weights were measured by ISOLAB precision balance. MICRO TEST-ELECTROFOREST shaking incubator was used to mix the solutions at definite temperatures and 150 rpm. ISOLAB pH meter was used for acid-base determination. UV spectrophotometer (HACK DR-3900) was used to determine the color change in the experiments at 585 nm wavelength. Fourier Transform Infrared Spectroscopy (FTIR) was used to measure the infrared spectra of adsorbents (CS and VT). The surface area determinations were carried by Brunauer, Emmett, and Teller (BET). Scanning Electron Microscopy (SEM) (Gemini Zeiss Supra 55) devices were used to determine surface morphology.

2.4 Adsorption experiments

In the adsorption experiments; pH, adsorbent mass, initial concentration of crystal violet, temperature and the contact time were optimized. 100mL solution volume was used. The solutions were placed in 250 mL flasks in case of overflow during agitation. After the experiment, efficiency (%) and adsorbent capacity (qe) (mg.g⁻¹) were calculated using Equation 1 and Equation 2, respectively [29].

$$\text{Efficiency \%} = \frac{(C_i - C_f)}{C_i} \times 100 \quad (1)$$

$$q_e = \frac{(C_i - C_f) \times V}{m} \quad (2)$$

Where, Ci is the initial concentration (mg.L⁻¹) of the CV dye; Cf is the CV final concentration (mg.L⁻¹); V solution volume (L); m indicates the adsorbent mass (g).

Desorption process was carried out as shown in the previous studies [27],[29] with some modification. The dyed adsorbent obtained at the end of the adsorption process was shaken with 0.1 M HCl and 0.1 M NaOH solutions at 150 rpm for 24 hours to calculate the percentage of recovery (desorption). The recovery percentage was calculated using Equation 3:

$$\text{Recovery \%} = \frac{\text{Desorption Concentration}}{\text{Adsorbed Dye Concentration}} \times 100 \quad (3)$$

2.5 Adsorption isotherms

To explain the relationship between adsorbent and adsorbed substance; Langmuir [30], Freundlich [31], Temkin [32] and Dubinin-Radushkevich (D-R) isotherms were used [27],[32]. Langmuir isotherm is based on the assumption of single-layer adsorption on the homogeneous surface of the adsorbent (Equation 4) [30]. Freundlich isotherm refers to an empirical equation in the adsorption process (Equation 5) [31]. Temkin isotherm explains the adsorption mechanism by energy distribution (Equation 6) [32]. Dubinin-Radushkevich (D-R) isotherm explains the distribution of Gaussian energy on a heterogeneous surface [27]. Furthermore, D-R isotherm is related to the porous structure of the adsorbent and provides information about the physical or chemical adsorption process (Equation 7). If the term $[RTL \ln \left(1 + \frac{1}{C_A}\right)]^2$ has a value higher than 8 kJ.mol⁻¹, the adsorption occurs chemically [33].

$$\frac{C_A}{q_A} = \frac{1}{b_A q_m} + \frac{C_A}{q_m} \quad (4)$$

$$\text{Log}(q_A) = \text{log}(K_A) + \left(\frac{1}{n}\right) \text{log}(C_A) \quad (5)$$

$$q_A = \frac{RT}{b_T} \text{Ln}A_T + \frac{RT}{b_T} \text{Ln}C_A \quad (6)$$

$$\text{Ln}q_A = \text{Ln}q_s - K_{ad} [RTL \ln \left(1 + \frac{1}{C_A}\right)]^2 \quad (7)$$

Where C_A is the concentration of adsorbate A at the equilibrium (mg.L⁻¹). b_A is Langmuir constant for the adsorbate A (L.mg⁻¹). Q_M maximum adsorbent capacity at saturation (mg.g⁻¹). K_A is Freundlich adsorption capacity parameter (mg.g⁻¹) (L.mg⁻¹). 1/n is the intensity parameter. R is the universal gas constant (8.314J.K⁻¹.M⁻¹). T is the absolute temperature. b_T is Temkin isotherm constant. A_T is the binding constant (L.g⁻¹). q_s is the theoretical saturation capacity (mg.g⁻¹). K_{ad} is the isotherm constant (mol².kJ⁻²).

2.6 Adsorption kinetics

Adsorption kinetic models have been used to express the behavior of the adsorption reaction. Also, the models describe the mechanism by which the adsorbent substance interacts with the adsorbed substance [17],[32]. The linear forms of the pseudo-first-order kinetic model [34] and pseudo-second-order kinetic model [35] are shown in Equation 8 and Equation 9 respectively.

$$\text{Log}(q_e - q_t) = \text{Log}q_e - \frac{K_1}{2.303} t \quad (8)$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \quad (9)$$

In the equations; q_e is the amount of adsorbed material in equilibrium; q_t is the amount of adsorbed material at the end of time t; K₁ represents the first-order rate constant (min⁻¹) of adsorption and K₂ shows the false second-order rate constant (g.mg⁻¹.h⁻¹).

2.7 Adsorption thermodynamics

To examine the Adsorption thermodynamics, enthalpy (ΔH), entropy (ΔS), and Gibbs free energy (ΔG) were determined according to Equation (10-12) [36].

$$\Delta H = -R \left(\frac{T_2 T_1}{T_2 - T_1} \right) \text{Ln} \frac{b_2}{b_1} \quad (10)$$

$$\Delta S = \frac{\Delta H - \Delta G}{T} \quad (11)$$

$$\Delta G = -RTL \text{Ln} b \quad (12)$$

In the equations; ΔH is the enthalpy change (kJ. mol⁻¹); ΔS is the entropy change (kJ.mol⁻¹.°K⁻¹); ΔG is the Gibbs free energy change (kJ.mol⁻¹); R is the gas constant (8.314 J.°K⁻¹.mol⁻¹); T indicates temperature (°K) and b indicates Langmuir constant (mg⁻¹).

2.8 Response surface method (RSM)

RSM is a modeling technique derived from a group of mathematical and statistical data based on experimental data [37]. In these experiments, the ranges of pH, CS and VT masses, CV concentration, contact time, and temperature were determined. A model was created by Design Expert v11 program. The ranges of the parameters are shown in Table 1.

Table 1. Parameters limit values.

Parameter	Unit	Low	High
A	pH	-	5
B	Mass	G	0.5
C	Time	min	35
D	CV concentration	mg.L ⁻¹	250
E	Temperature	°C	36

2.9 The changes in the calorific values of the adsorbents

The utilizing of the bio-adsorbents in the zero waste concept was assessed by study the reusing potentiality of the bio adsorbents as solid fuel for the emission controlled industrial facilities. The calorific value for the two plants were measured by CKIC 5E-C5500 calorimeter. To study the adsorption effects on the calorific values for the two plants, the calorific values were measured before and after the adsorption process. The change in the calorific values were notices and recorded.

3 Result and discussion

3.1 Adsorbent characterization

In this study, the surface areas for CS and VT plants were determined by BET analysis. The surface area decreased for both plants after the adsorption process. BET and Langmuir surface areas of both plants decreased after adsorption (Table 2).

Table 2. BET and Langmuir surface areas of CS and VT plants in raw and dyed form.

	CS Plan		VT Plant	
	Raw	Dyed	Raw	Dyed
BET Surface Area (m ² .g ⁻¹)	4.97	0.68	4.84	2.29
Langmuir Surface Area (m ² .g ⁻¹)	6.91	0.81	6.33	2.94

Surface morphologies for two plants were obtained by SEM analysis. Figure 4 shows the adsorbent morphology before and after the adsorption process.

The FTIR analysis shows a shifting in the peaks. It also shows change in the intensity of those peaks. This can support the occurrences of the adsorption process. By comparison between

the graphs before and after the adoption process, many peaks disappeared at the end of the adsorption process (Figures 5 and 6).

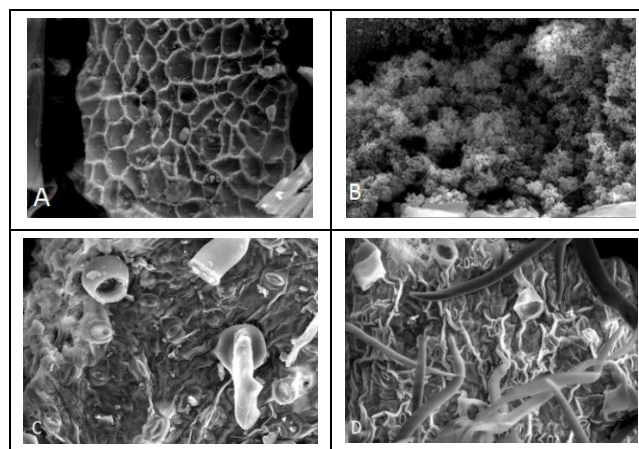


Figure 4. (a): CS before adsorption. (b): CS after adsorption. (c): VT before adsorption. (d): VT after adsorption.

In CS plant, peaks at bands of 490.79, 536.11, 1317.14, and 1603.52 cm⁻¹ were not recorded after the adsorption process. In contrast, many new peaks were noticed. The peak at the band of 2328 cm⁻¹ shows C≡N starch bond. C-H bend bond was recorded at the peak of 1455cm⁻¹. N-O asymmetric stretch bond at 1506 cm⁻¹ was detected. In addition to that, a new peak at 1584 cm⁻¹ shows a possible N-H bend bond formation. C-CL bond was also noticed at the band of 828.28 cm⁻¹. The formation of new peaks gives a hint about the type of adsorption.

In the VT plant, new peaks were not be recorded. By contrast, many peaks have been shown in the raw VT and have not been recorded after the adsorption process. The following peaks bands are examples on this phenomena 471.51, 504.29, 532.26, 593.00, 895.77, 1316.18, 1453.10, 1505.17, 2319.95 and 2850.27 cm⁻¹. This change in the chemical bonds also gives a hint about the type of the adsorption type. It also can be considered a chemical adsorption.

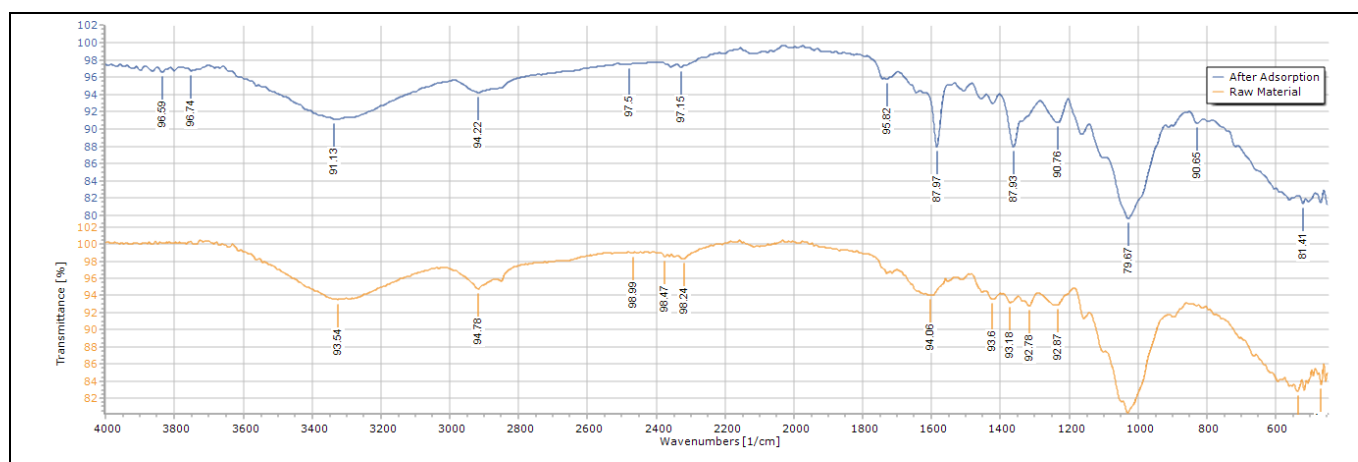


Figure 5. FTIR analysis for CS before adsorption and after adsorption.

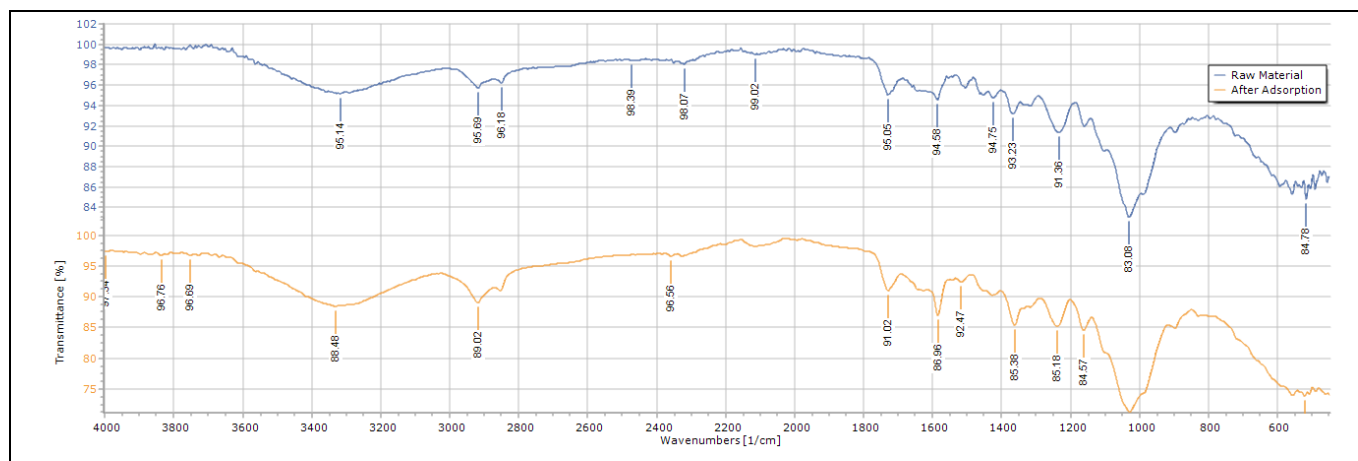


Figure 6. FTIR analysis for VT before adsorption and after adsorption.

3.2 RSM results

The developed models for the CV adsorption onto the adsorbents (CS and VT) were established by RSM. The two models were tested statistically and founded to be significant. No transformation needed for the CS plant, while a square root transformation was used for the VT plant. According to the sequential model sum of squares tests, the 2FI model and quadratic model were the most appropriate for CS plant and VT plant respectively. Appendix A1 and A2 show the sequential model sum of squares tests results for both plants. Based on these tests the correlation coefficients for the developed modes were 0.86 for CS plant and 0.95 for the VT plant.

The developed models were analyzed by analysis of variance ANOVA tests. The two models were founded to be significant. The F-values for developed models based on the removal of CV by CS plant and VT plant were 20.79 and 46.69. There is only 0.01% for these values to occur due to noise. The ANOVA tests for the models are presented in Appendix B1 and B2. The adsorbent capacity of CV onto CS and VT can be predicted by equations 13 and 14, respectively.

$$\begin{aligned}
 \text{Capacity} = & 34.331 - 6.345pH + 40.852\text{Mass} \\
 & + 0.224\text{Time} + 0.034\text{Concentration} \\
 & - 0.601\text{Temperature} + 1.586pH \\
 & * \text{Mass} + 0.008pH * \text{Time} - 0.003pH \\
 & * \text{Concentration} + 0.128pH \\
 & * \text{Temperature} - 0.141\text{Mass} * \text{Time} \\
 & - 0.099\text{Mass} * \text{Concentration} \\
 & - 1.052\text{Mass} * \text{Temperature} \\
 & - 0.0002\text{Time} * \text{Concentration} \\
 & - 0.004\text{Time} * \text{Temperature} \\
 & + 0.003 \text{Concentration} \\
 & * \text{Temperature}
 \end{aligned} \quad (13)$$

$$\begin{aligned}
 \text{sqrt}(\text{capacity} + 55) = & 9.085 + 0.149pH - 3.545\text{Mass} \\
 & + 0.031\text{Time} + 0.007\text{Concentration} \\
 & - 0.041\text{Temperature} + 0.008pH \\
 & * \text{Temperature} - 0.005\text{Mass} \\
 & * \text{Concentration} - 0.030pH^2 \\
 & + 3.208\text{Mass}^2 - 0.0002\text{Time}^2
 \end{aligned} \quad (14)$$

3.3 Effects of parameters

Upon adsorption of CV dye onto CS plant; the effects of pH and mass parameters were determined. The pH has the minimum effect for the adsorption capacity. The mass has an inverse relationship with capacity. The maximum capacity was reached at 0.5 g of plant and pH 8, Figure 7(a).

For the VT plant; the capacity has a proportional relationship with pH, although it has an inverse relationship with mass. The maximum capacity has been reached at pH 8, and 0.5 g of plant mass is shown in Figure 7(b).

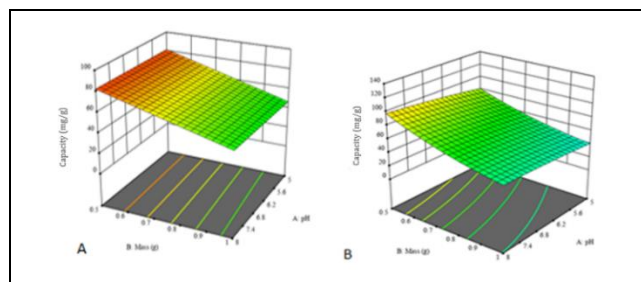


Figure 7. pH and mass effects on the capacity for. (a): CS plant. (b): VT plant.

The capacity of each adsorbent increases as the dye concentration increases. The contact time (85 minutes) required to achieve equilibrium capacity in the CS plant is greater than the contact time (50 min.) of the VT plant. The relationship between concentration and time is shown in Figure 8.

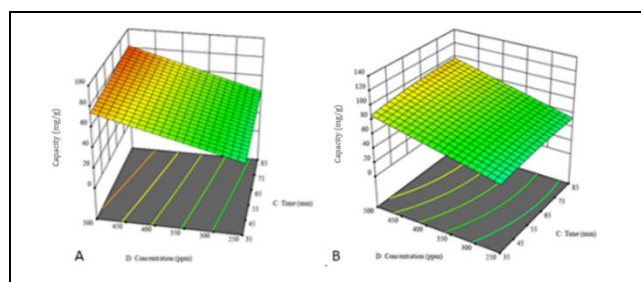


Figure 8. Dye concentration and the contact time effects on the capacity for. (a): CS plant. (b): VT plant.

The effect of temperature on the adsorption process was examined. In CS plant the capacity has increased sharply with temperature. VT plant capacity had also increased with temperature but with more flat trend. The temperature effects are shown in Figure 9.

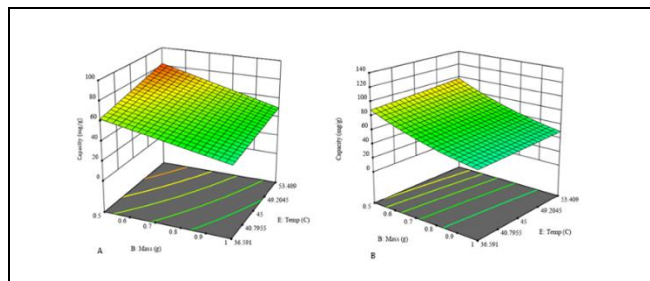


Figure 9. Adsorbent mass and the temperature effects on the capacity for. (a): CS plant. (b): VT plant.

3.4 Adsorption isotherm

In this study, Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich (D-R) isotherms were examined. Isotherm coefficients and regression coefficient results are given in Table 3. For the CS plant, the D-R isotherm had a higher regression value ($R=0.9906$) than the other isotherms. The adsorption expected to occur chemically, because the value of $[RT \ln (1 + (1/C_A))]^2$ ($23.57 \text{ kJ.mol}^{-1}$) is higher than 8 kJ.mol^{-1} . For the VT plant, Temkin isotherm had the best fit with a regression value of 0.9221 .

Table 3. Isotherm coefficients and regression coefficients.

Isotherm		CS Plant	VT Plant
Langmuir	q_m (mg.g ⁻¹)	113.63	96.153
	b_A (L.mg ⁻¹)	0.0035	-0.006
	R^2	0.8672	0.5072
Freundlich	$1/n$	0.691	1.5755
	K_A (mg.g ⁻¹) (L.mg ⁻¹) ^{1/n}	1.226	0.0913
	R^2	0.9604	0.8965
Temkin	A_T (L.g ⁻¹)	-3.418	0.0327
	b_T	105.93	30.335
(D-R)	R^2	0.9764	0.9221
	K_{ad} (mol ² .kJ ⁻²)	0.0009	0.0004
	q_s (mg.g ⁻¹)	51.48	124.536
	R^2	0.9906	0.9185

3.5 Adsorption kinetics

In this study, pseudo-first-order and pseudo-second-order kinetics were examined. The kinetics coefficient results are given in Table 4.

Table 4. Kinetics coefficients and regression coefficients.

Kinetic	Parameter	CS Plant	VT Plant
Pseudo-first-order	R^2	0.9942	0.9943
	K_1 (min ⁻¹)	0.0262	0.052
	q_e (mg.g ⁻¹)	20.469	72.227
Pseudo-second-order	R^2	0.9998	0.9999
	K_2 (g.mg ⁻¹ .min ⁻¹)	0.0025	0.0009
	q_e (mg.g ⁻¹)	84.033	109.89

The regression coefficients of CS and VT plants were 0.9942 and 0.9943; pseudo-second-order kinetics are 0.9998 and 0.9999, respectively. According to these results, the adsorption kinetics of both plants were found to be suitable for pseudo-second-order kinetics (Table 4). The Kinetic results explain the absence of chemical and physical equilibrium. It also states that there are two reactions. The first is faster and reaches the equilibrium state faster, the second one is slow reaction and reaches the equilibrium state in a long time.

3.6 Adsorption thermodynamics

In this study, enthalpy (ΔH), entropy (ΔS), and Gibbs free energy (ΔG) were studied for the CS and VT plants. The results are given in Table 5.

Table 5. Adsorption thermodynamics.

Temperature (°K)	CS Plant			VT Plant		
	ΔG (KJ.mol ⁻¹)	ΔH	ΔS	ΔG (KJ.mol ⁻¹)	ΔH	ΔS
310	-15.54	4.6	0.07	-14.65		
319	-16.11	2		-15.54	15.	0.10
325	-15.54			-16.11	50	

In both plants;

- The adsorption event occurs spontaneously since the Gibbs free energy (ΔG) was found to be negative for all temperatures,
- The positive values of the Enthalpy (ΔH) indicate that the adsorption is the endothermic reaction,
- Entropy values (ΔS) were positive. This indicates that there may be structural changes between CS and VT plants and CV dye.

3.7 Desorption

Desorption experiments were carried out as a result of adsorption experiments. The plants with dye were shaken in 0.1 M HCl and 0.1 M NaOH solutions at 150 rpm in the shaker for 24 hours. The maximum desorption yield was obtained by the interaction of both plants with acid for 120 minutes. Desorption percentages for the CS plant and VT plant were 0.76% and 1.88%, respectively. According to the results, the adsorption process was considered to be chemical because there was no dye recovery.

3.8 Zero waste concept utilization

The zero waste concept was successfully applied in this study. The second order contaminants from the adsorption process were planned to be reused as solid fuel in emission controlled industrial facilities. To achieve that, the calorific values were measured and recorded as shown in Table 6.

The results show increases in the calorific values for the two plants after the adsorption process. The CS plant increased from $4003.774 \text{ Kcal.Kg}^{-1}$ to $4458.059 \text{ Kcal.Kg}^{-1}$, whereas, the VT plant increased from $3206.028 \text{ Kcal.Kg}^{-1}$ to $4120.330 \text{ Kcal.Kg}^{-1}$. even though the calorific values for the CS plant is higher than the VT plant, the changes in the calorific values for the VT plant was notable. These values indicates the possibility to use the two plants in the solid fuel sector.

Table 6. Calorific values for raw and dyed plants.

Plant	Weight (g)	Temperature Rise (°K)	C-Coefficient (°K)	Heat Capacity (J.°K ⁻¹)	Calorific Values (Kcal.Kg ⁻¹)
CS- Raw	1.0945	1.8469	0.0212	9848	4003.774
CS- Dyed	1.1692	2.1970	0.0241	9848	4458.059
VT- Raw	1.1227	1.5200	0.0153	9848	3206.028
VT- Dyed	1.1703	2.0337	0.0214	9848	4120.330

3.9 Comparison with other studies

The interaction of CV dye with other adsorbent substances has been studied by many researchers. Khan et al (2016) used tea dust as a bio adsorbent to remove CV from aqueous solution with maximum adsorption capacity of 175.4mg.g⁻¹ [38]. Mittal et al (2010) deploy the waste generated from the soya bean industry as low cost to remove CV. The maximum recovery of the dye was 95% [39]. Azolla and Fig Leaves Modified with Magnetite Iron Oxide Nanoparticles were used as adsorbent for CV removal with a maximum capacity of 30.21 mg.g⁻¹ for Azolla and 53.47 mg.g⁻¹ for Fig Leaves [40]. The adsorption of CV onto a natural clay mineral from aqueous solution between 293.15 and 323.15 K was implemented [41]. Kulkarni et al (2017) founded the adsorption capacity of CV onto water hyacinth to be 322.58 mg.g⁻¹ [42]. Table 7 shows some of these studies.

Even though the adsorption capacity stated in this study is relatively smaller than the literature studies, both plants show a high removal efficiency of CV from aqueous solution. In addition to that the capacity is larger than the powdered activated carbon (PAC) and Afsin-Elbistan fly ash obtained by Eren and Nacar (2006) [43].

4 Conclusion

In this study, the differences between adsorption processes of *Centaurea solstitialis* (CS) and *Verbascum Thapsus* (VT) plants separately were compared for removal of Crystal Violet (CV) from aqueous solution. The experimental design was made by Surface Response Method (RSM) method; the model regression coefficients for CS and VT plants were 0.86 and 0.95, respectively. Adsorption process for CS plant was fitted by D-R isotherm with the regression value of R²=0.9906 and is suitable for pseudo-second-order kinetics (R²=0.9998). For the VT plant, Temkin isotherm was found to have the highest regression value (R²=0.9221) and was suitable for a pseudo-second-order (R²=0.9999) kinetics. Adsorption processes of both plants with CV were endothermic. The maximum desorption rate for the CS and VT plants were 0.76% and 1.88%, respectively. Based on these results, it was found that there was no dye recovery from both plants.

By comparison between the two plants, the VT plant might be preferred than the CS plant for the following reasons:

1. The maximum capacity of the VT plant was higher than the CS plant (109.89 mg/g > 84.03mg/g),

2. The contact time to reach the equilibrium capacity for the VT plant is shorter than the CS plant,
3. Change in calorific values for the VT plant was higher than the changes in the CS plant.

In this study, it has been proven that CS and VT plants are effective, inexpensive and easily available adsorbents in KV dye adsorption from aqueous solution. The calorific values of the dyed adsorbent materials obtained at the end of the adsorption were 4458.059 kcal.kg⁻¹ for CS and 4120.330 kcal.kg⁻¹ for VT. In other studies, the lower heat value of fuel produced from waste was found to be 2800 kcal.kg⁻¹ [47],[48]. According to these values, the dyed adsorbents can be used within the scope of waste derived fuel (ATY).

Cheremisinoff (2003) has reported that the waste can be converted to energy by incineration method, which is the second most frequent method [49]. Concerning that, the adsorption by-products could be used to generate energy by using it as a possible partial replacement of coal in the emission controlled industrial factories. Thus, many benefits will be achieved; CV will be removed from aqueous solution by low-cost materials, the adsorption by-products will be used as fuel, the uses of coal expected to be lower. In addition to that, the air pollution resulting from the raw plant burning process as a disposal method by the farmers will be decreased.

As a result from this study, the two plants (CS and VT) had been used successfully in CV removal from aqueous solution. Also the utilization of these plant in zero waste concept was achieved successfully.

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1 Author contribution statements

In the scope of this study, Mutlu YALVAÇ in the formation of the idea, the writing and editing, and the literature review; Hüdaverdi ARSLAN in the supplying the materials used; Mohammed SALEH in the formation of the idea, the writing and editing, the design and the literature review, Melis GÜN in the assessment of obtained results, and examining the results; Muhammed Şahin HEKİM in the experiment step in terms of content were contributed.

Table 7. Comparison with other studies.

Adsorbent	Isotherm	Capacity (mg/g)	Kinetic Model	Thermodynamic	Reference
<i>Centaurea solstitialis</i> (CS)	Dubinin-Radushkevich (D-R)	84.03	Pseudo-second-order	Endothermic	This study
<i>Verbascum thapsus</i> (VT)	Temkin	109.89	Pseudo-second-order	Endothermic	This Study
<i>Tectona grandis</i> (Sawdust)	Langmuir	131.58	Pseudo-second-order	Endothermic	[44]
Palm fiber	Langmuir	0,66*10 ⁻⁶	Pseudo-second-order	Exothermic	[45]
Centaurea stem	Langmuir	476.19	Pseudo-second-order	Endothermic	[46]

2 Ethics committee approval and conflict of interest statement

There is no need to obtain permission from the ethics committee for the article prepared.

There is no conflict of interest with any person / institution in the article prepared.

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Appendix

Appendix A.1. Sum of squares for the sequential model for CS plant.

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Mean vs Total	94294.28	1	94294.28			
Linear vs Mean	12152.92	5	2430.58	43.88	< 0.0001	
2FI vs Linear	1002.95	10	100.30	2.38	0.0293	Suggested
Quadratic vs 2FI	369.11	5	73.82	2.01	0.1069	
Cubic vs Quadratic	1059.77	16	66.24	156.56	< 0.0001	Aliased
Residual	5.50	13	0.4231			
Total	1.089E+05	50	2177.69			

Appendix A.2. Sum of squares for the sequential model for VT plant.

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Mean vs Total	5085.86	1	5085.86			
Linear vs Mean	48.24	5	9.65	59.36	< 0.0001	
2FI vs Linear	1.56	10	0.1560	0.9486	0.5035	
Quadratic vs 2FI	3.93	5	0.7866	13.75	< 0.0001	Suggested
Cubic vs Quadratic	1.62	16	0.1013	34.63	< 0.0001	Aliased
Residual	0.0380	13	0.0029			
Total	5141.26	50	102.83			

Appendix B.2. ANOVA results for CCD during removal of CV by CS.

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	13155.87	15	877.06	20.79	< 0.0001	significant
A-pH	2.25	1	2.25	0.0532	0.8189	
B-Mass	4797.31	1	4797.31	113.71	< 0.0001	significant
C-Time	331.41	1	331.41	7.86	0.0083	significant
D-Concentration	6479.30	1	6479.30	153.58	< 0.0001	significant
E-Temp	542.66	1	542.66	12.86	0.0010	significant
AB	11.32	1	11.32	0.2684	0.6078	
AC	2.79	1	2.79	0.0661	0.7987	
AD	11.73	1	11.73	0.2780	0.6015	
AE	82.89	1	82.89	1.96	0.1701	
BC	25.06	1	25.06	0.5940	0.4462	
BD	311.33	1	311.33	7.38	0.0103	significant
BE	156.47	1	156.47	3.71	0.0625	significant
CD	23.68	1	23.68	0.5614	0.4589	
CE	18.11	1	18.11	0.4292	0.5168	
DE	359.57	1	359.57	8.52	0.0062	significant
Residual	1434.38	34	42.19			
Lack of Fit	1434.38	27	53.13			
Pure Error	0.0000	7	0.0000			
Cor Total	14590.25	49				

Appendix B.2. ANOVA results for CCD during removal of CV by VT.

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	53.73	20	2.69	46.96	< 0.0001	significant
A-pH	0.9100	1	0.9100	15.91	0.0004	significant
B-Mass	25.08	1	25.08	438.39	< 0.0001	significant
C-Time	1.10	1	1.10	19.21	0.0001	significant
D-Concentration	21.19	1	21.19	370.39	< 0.0001	significant
E-Temp	0.0235	1	0.0235	0.4115	0.5262	
AB	0.0967	1	0.0967	1.69	0.2038	
AC	0.0370	1	0.0370	0.6461	0.4280	
AD	0.1919	1	0.1919	3.35	0.0773	significant
AE	0.3055	1	0.3055	5.34	0.0282	significant
BC	0.0295	1	0.0295	0.5159	0.4783	
BD	0.6688	1	0.6688	11.69	0.0019	significant
BE	0.1239	1	0.1239	2.16	0.1520	
CD	0.0985	1	0.0985	1.72	0.1998	
CE	0.0060	1	0.0060	0.1056	0.7476	
DE	0.0024	1	0.0024	0.0422	0.8386	
A ²	0.2559	1	0.2559	4.47	0.0432	significant
B ²	2.24	1	2.24	39.10	< 0.0001	significant
C ²	0.8592	1	0.8592	15.02	0.0006	significant
D ²	0.0673	1	0.0673	1.18	0.2870	
E ²	0.0078	1	0.0078	0.1369	0.7141	
Residual	1.66	29	0.0572			
Lack of Fit	1.66	22	0.0754			
Pure Error	0.0000	7	0.0000			
Cor Total	55.39	49				