Iğdır Üniversitesi Fen Bilimleri Enstitüsü Dergisi, 11(4): 2645-2659, 2021
Journal of the Institute of Science and Technology, 11(4): 2645-2659, 2021

ISSN: 2146-0574, eISSN: 2536-4618

Çevre Mühendisliği / *EnvironmentalEngineering* **DOI: 10.21597/jist.1003271**

Araştırma Makalesi / *Research Article*

Geliş tarihi / Received: 01.10.2021 **Kabul tarihi / Accepted:18.10.2021**

Atıf İçin: Bingul Z, 2021. The Use of Waste Green Tea Leaves for Crystal Viyole Adsorption: Kinetic, Equilibrium and Thermodynamics Studies. Iğdır Üniversitesi Fen Bilimleri Enstitüsü Dergisi, 11(4): 2645-2659.

To Cite: Bingul Z, 2021. The Use of Waste Green Tea Leaves for Crystal Viyole Adsorption: Kinetic, Equilibrium and Thermodynamics Studies. Journal of the Institute of Science and Technology, 11(4): 2645-2659.

The Use of Waste Green Tea Leaves for Crystal Viyole Adsorption: Kinetic, Equilibrium and Thermodynamics Studies

Züleyha BİNGÜL[1*]

ABSTRACT: In this study; the adsorption of crystal violet (CV) dyestuff in cationic form on waste green tea leaves was investigated and the effects of adsorbent particle size, initial dyestuff concentration, stirring speed, initial pH, temperature and adsorbent amount on adsorption capacity and dye removal efficiency were optimized. To determine the characterization of waste green tea leaves, pHpzc analysis was performed and pHpzc of waste green tea leaves was determined as 5.511. In adsorption of CV dye on waste green tea leaves, the highest dye removal efficiency was obtained at the natural pH (5.58) of the solution. As the initial dye concentration increased, the amount of dye adsorbed per unit adsorbent increased, while the dye removal efficiency decreased. It has been observed that increasing temperature decreases the adsorption capacity. While CV adsorption capacity of waste green tea leaves was 227.049 mg g-1 at 0.1 g L-1 adsorbent dosage, CV adsorption capacity decreased to 8.788 mg g-1 at 5 g L-1 adsorbent dosage. Freundlich, Langmuir, Halsey and Dubinin-Radushkevich models were used for mathematical modeling of adsorption equilibrium on CV adsorption. The degree of suitability of isotherms for adsorption of CV dye is Freundlich=Halsey>Langmuir>Dubinin-Radushkevich, respectively. Two different kinetic models (pseudo-first-order and pseudo-second-order) were used for the kinetic data, and the calculated kinetic parameter constants showed that the adsorptions fit the pseudo-second-order kinetic model. In addition, thermodynamic parameters of CV adsorption showed that the adsorption process occurs spontaneously ($\Delta Go<0$) and is exothermic ($\Delta Ho>0$).

Keywords: Adsorption, isotherm, kinetic, thermodynamic, waste green tea

[1]Züleyha BİNGÜL (**Orcid ID:** 0000-0003-2472-9077), Iğdır Üniversitesi, Mühendislik Fakültesi, İnşaat Mühendisliği Bölümü, Iğdır, Türkiye

***Sorumlu Yazar/Corresponding Author:** Züleyha BİNGÜL, e-mail: zuleyha.bingul@igdir.edu.tr

INTRODUCTION

Dye is a fluid material formed by the combination of solvents, pigments, fillers and additives added to a binder, and at the same time forms a very thin layer by clinging to the surface on which it is applied (Arslan et al., 2021). Approximately 15% of dyes, which are used in a variety of sectors to provide color to products such as cosmetics, textiles, carpets, food, plastic, printing and paper are discharged as waste into the aquatic environment (Önal et al., 2017; Jawad et al., 2020). The presence of dyes in aquatic environments not only causes aesthetic problems but also decreases light penetration, photosynthetic activity and oxygen productivity in water (Meghwal et al., 2020; Yu et al., 2020). In addition, dyes cause toxic effects by accumulating on fish and other aquatic organisms living in water sediments. In the short term, dyes cause asthma, allergic reactions, jaundice, skin irritation in humans, as well as long-term carcinogenic and mutagenesis effects (Hasanzadeh et al., 2020; Liu et al., 2020; Hasan et al., 2021).

Crystal violet (CV) is a cationic and water-soluble dye that belongs to the triarylmethane dye family. It's commonly utilized in the textile and dyeing industries, as well as dermatology, medicine, veterinary medicine, ink manufacture and the plastics industry. It is also used in gram staining to classify microorganisms and as a food additive. CV, on the other hand, is a carcinogenic, mutagenic, and poisonous dye. Because it is not biodegradable, it lasts a long period in the environment. Exposure to CV dye causes skin and eye irritation, kidney and respiratory failure (Chakraborty et al., 2011; Shoukat et al., 2017). For these reasons, CV should be removed from wastewater before it is discharged into the receiving environment to protect human health and water resources.

To remove dyes from wastewater, many technologies such as electrolysis (Liu et al., 2020), electrodialysis (Lafi et al., 2019), flocculation (Zhao et al., 2020), oxidation (Güzel et al., 2017), adsorption (Farizoglu et al., 2019), membrane process (Yang et al., 2018) and ion exchange (Joseph et al., 2020) are utilized. Adsorption, which is one of these methods, is the most preferred method in terms of simplicity, ease of use and cost.

Adsorption is a surface phenomenon based on the interaction between adsorbates in the gas or liquid phase and adsorbents in the solid phase. The efficiency, capacity and reusability of the adsorbent material depend on the functional groups on the adsorbent surface. It is very important to use economical and highly efficient adsorbents in adsorption applications (Afroze and Sen, 2018). Adsorbents, which are abundant in nature, require very little processing, and are industrial waste or by-products, are defined as economic adsorbents (Zuorro and Lavecchia, 2010). Many investigations on the use of carbon-containing agricultural by-products and wastes as an alternative adsorbent in wastewater treatment have been done in recent years. In these studies, agricultural waste such as coconut shell (Ayub and Changani, 2014), cherry kernel (Altun, 2019), olive kernel (Jamshidi et al., 2013), almond shell (Duran et al., 2011), peach shell (Markovic et al., 2015), apricot shell (Namal and Kalipci, 2020), waste tea (Cherdchoo et al., 2019), cotton stalk (Deng et al., 2011) were used as adsorbent and their adsorption capacities were investigated.

Waste green tea, a type of agricultural waste, is an alternative low-cost adsorbent for dye removal from wastewater. The green tea plant, called Camellia sinensis, is native to South-East Asia. They are pale-colored, unfermented leaves with a slightly bitter flavor. It has beneficial effects on health such as anticancer, antibacterial, anti-inflammatory, lowering cholesterol level and also helps to lose weight. Extracts from it are utilized in a variety of beverages, cosmetic products, nutritional supplements and health foods. Also, the green tea plant is a species of plant whose leaves are used to make tea, and after making tea, the leaves are considered waste and thrown away (Jeyaseelan and

Gupta, 2016). Therefore, it is important to use such wastes as adsorbents, which causes disposal problems (Burca et al., 2016; Indolean et al., 2017).

In this study, waste green tea leaves were used for dye removal from aqueous solutions by the adsorption method. Adsorption studies were carried out using crystal violet, a cationic dye. The effect of contact time, dye concentration, adsorbent amount, temperature, initial pH and stirring speed on dye removal has been studied and optimized.

MATERIALS AND METHODS

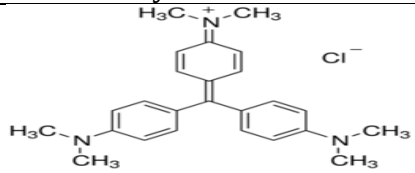
Preparation of The Adsorbent

Waste green tea was used as an adsorbent in the study. The green tea leaves were purchased at a local market. Typically, green tea leaves were steeped in 100 °C boiled water for 5 minutes. After being used as the tea, the waste leaves were washed until a colorless filtrate was obtained and rinsed with distilled water. It was then dried in an oven at 105 °C for 24 hours. Finally, dried green tea leaves were ground in a grinder and passed through sieves of various grain sizes to obtain adsorbents with different particle sizes ranged from 75 to 500 µm.

Chemicals

In the study, crystal violet (Sigma Aldrich), a cationic dye was used as adsorbate. The characteristic properties and molecular structure of CV is given in Table 1.

Table 1. Characteristics of crystal violet

Name	Crystal Violet
Structural formula	
Molecular formula	$C_{24}H_{28}N_3Cl$
Molecular weight	393.95 g/mol
CAS Number	122965-43-9
Dye class	Trietilmetan
$\lambda_{max\ (nm)}$	579

1000 mg L^{-1} CV stock solution was prepared and then the desired concentrations were obtained by diluting this solution with distilled water in the experiments. 0.1 N HCl (Sigma Aldrich, 36-38%) and 0.1 N NaOH (Sigma Aldrich) were used to adjust the pH of the solutions. The chemicals used are of analytical purity.

Point of zero charge (pH_{pzc})

The point of zero charge (pH_{pzc}) of the waste green tea leave was determined using 0.01M NaCl concentration series (50 mL). 0.1M NaOH or 0.1M HCl were used to adjust the pH between 2.0 and 12.0. After that, 0.15 g of waste green tea leaves was added to the solutions and shaken at 200 rpm for 48 hours. The final pH values of the samples were measured. The initial pH has been plotted versus the ΔpH (initial pH-final pH). The pH_{pzc} was determined by intersecting the resulting curve with the abscissa (Degermenci et al. 2019).

Experimental procedure

Adsorption experiments were carried out with 100 mL dye solution in 250 mL flasks. In the study, contact time (3-120 min), initial dye concentration (25-150 mg L^{-1}), pH (2-12), amount of adsorbent (0.1-5 g L^{-1}), size of adsorbent (75-125, 125-180, 180-500 and >500 µm), temperature (25-

55 °C) and stirring speed (100-400 rpm) were optimized. 50 mg L^{-1} dye solution was mixed at natural pH, 25 ºC and 200 rpm constant stirring speed for equilibrium time after adding 2.5 g L^{-1} biosorbent. The pH measurements of the samples were performed with pH meter (WTW Multi 3620 IDS SET C) electrometrically according to TS EN ISO 10523 standard. The samples taken at certain time intervals were filtered with filter paper and the absorbance values were determined with a spectrophotometer at the wavelength where the dyes showed maximum absorbance (at the wavelengths of 579 nm for CV). After determining the optimum operating parameters at which the maximum removal efficiency is achieved, isotherm, kinetic and thermodynamic studies were carried out with the obtained data.

RESULTS AND DISCUSSION

pH_{pzc}, which expresses the pH value at which the electrical charge density on the adsorbent surface is zero, is an important parameter for the adsorption process as it determines the charge of the active sites interacting with organic molecules. If the pH value of the solution is greater than pH_{pzc} ($pH>pH_{pzc}$), the adsorbent surface is negatively charged and cationic dyes are retained while anionic dyes are pushed from the surface due to electrostatic interaction. On the contrary, if the pH value of the solution is lower than pH_{pzc} ($pH<pH_{pzc}$), the adsorbent surface is positively charged and while the anionic dyestuffs containing the carboxyl functional group are kept on the surface very effectively, the cationic dyestuffs are repelled (Stavrinou et al., 2018). In the study, the pH_{pzc} of waste green tea leaves used as adsorbent, was read as 5.511 from the X-axis cut-off point of the drawn curve (Figure 1).

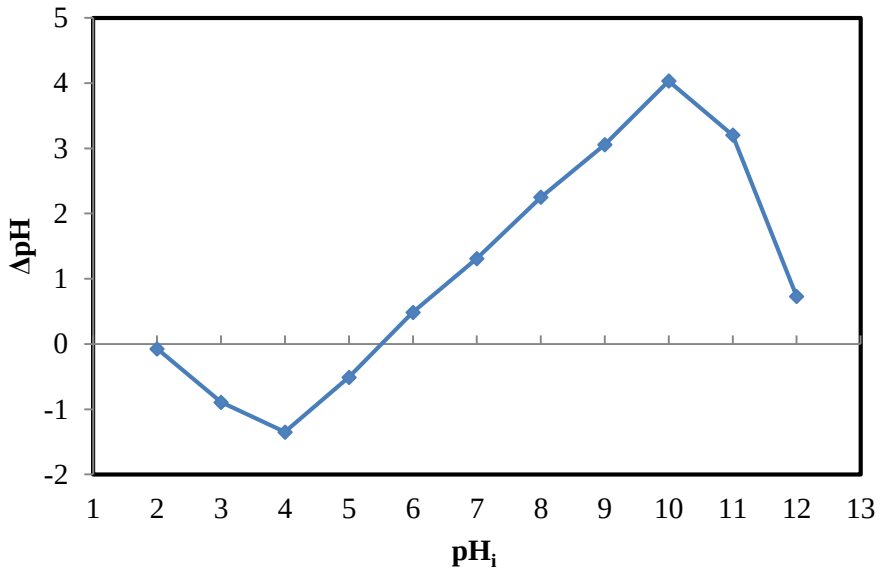


Figure 1. Zero load point of waste green tea leaves

pH is an important parameter that has an effect on dye solubility in solution and adsorbent surface charge (Kazemia and Javanbakht, 2020). In the study, the effect of initial pH on adsorption of CV dye was investigated by changing the initial pH between 2-12 for dye concentration of 50 mg L^{-1} and adsorbent dose of 2.5 g L^{-1}. The dye removal efficiencies obtained are shown graphically in Figure 2. The CV removal efficiency from the aqueous solution is 40.71% at pH 2, 70.39% at pH 4, 80.33% at pH 10 and 85.69% at natural pH (5.58). The results show that the removal efficiency of CV, which is a cationic dye, is low at acidic pH and increases with increasing pH. Also, pH_{pzc} of waste green tea leaves was read as 5.511 from Figure 1. When $pH>pH_{pzc}$, the adsorbent surface is negatively charged. As a result of the electrostatic interaction between the negatively charged surface and the positively

charged organic molecules, CV adsorption was more efficient at pH>5.511. The results are also supported by the results obtained in the study by Silva et al (2020).

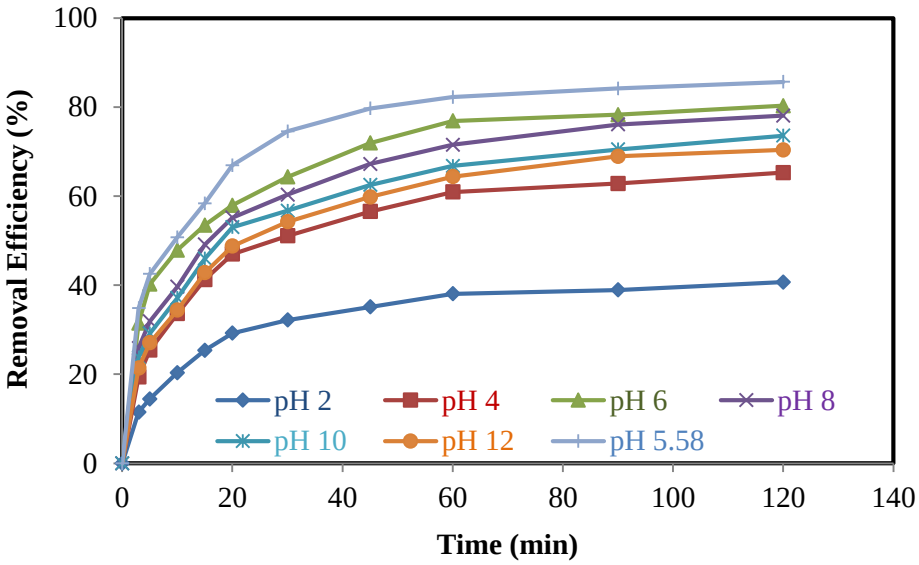


Figure 2. Change of CV removal efficiency with initial pH as a function of time

The stirring speed of the adsorbent/adsorbate system is a factor that affects the adsorption process as it reduces the surface film resistance of the adsorbent particle. The effect of stirring speed on the adsorption of CV was examined for 100, 200, 300 and 400 rpm stirring speeds and the removal efficiencies obtained are shown in Figure 3.

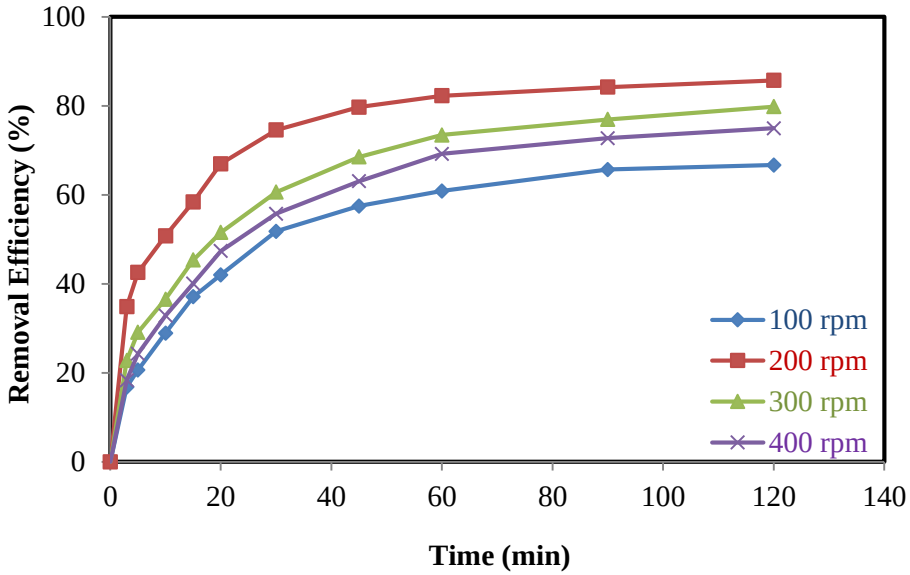


Figure 3. Change of CV removal efficiency with stirring speed as a function of time

While the dye removal efficiency is 66,67% at 100 rpm stirring speed, it is 85.69% at 200 rpm stirring speed. When the mixing speed was increased from 100 rpm to 200 rpm, the adsorbent showed a more homogeneous distribution in the solution and the mass transfer rate of dye molecules on waste green tea leaves increased (Harrache et al., 2019). When the mixing speed is increased to 300 and 400 rpm, a vortex has formed in the suspension and the homogeneity has deteriorated (Tang et al., 2017). Similar results were also obtained in the study conducted by Kul (2021).

Particle size is an important parameter in the diffusion of solutes to adsorbents, as it affects the available surface area for adsorption and the mass transfer rate. The effect of adsorbent particle size on

the adsorption of CV dyestuff was investigated for particle sizes of 75, 125, 180 and >500 µm. The dye removal efficiencies obtained in the experiments are given in Figure 4. The crystal violet removal efficiencies at 75, 125, 180 and >500 µm particle sizes were 69.21%, 65.42%; 59.91% and 49.99%, respectively. As the particle size decreased, the dye removal efficiency showed an increasing trend. This is because the adsorption process is controlled by the surface area available for adsorption. In this case, the adsorption capacity is low as the larger particles have a smaller surface area. Small particles, on the other hand, have a large surface area, and therefore their adsorption capacity is high (Felista et al., 2020).

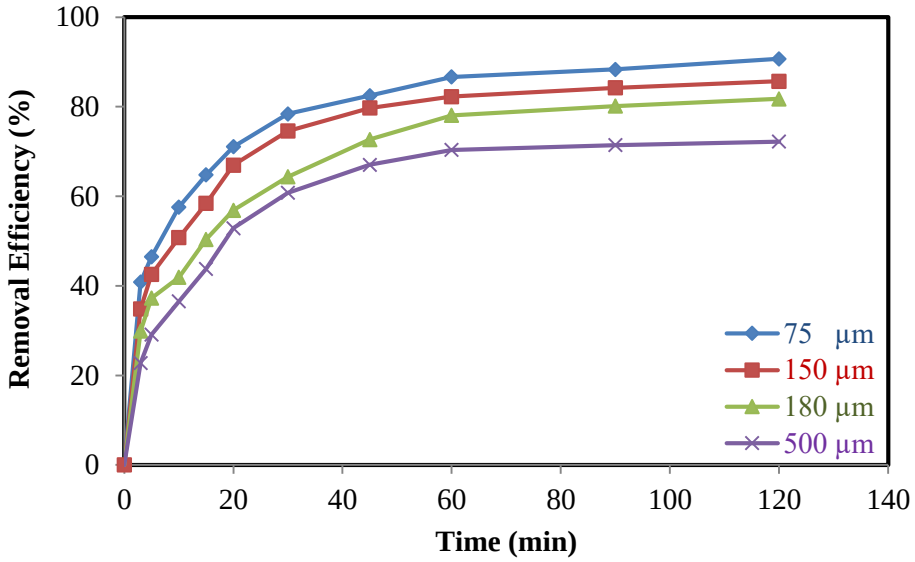


Figure 4. Change of CV removal efficiency with adsorbent particle size as a function of time

The amount of adsorbent is an important variable in the adsorption process since it increases the total surface area and active sorption sites. In the study, the effect of the amount of adsorbent on the adsorption of CV dyestuff was investigated for five different adsorbent amounts of 0.25, 0.5, 1, 1.5, 2 and 3 g L^{-1}. The experiments were carried out at 25 °C, 200 rpm stirring speed, initial dye concentration of 50 mg L^{-1} and natural pH (5.58) conditions. The obtained dye removal efficiencies and the amount of dye adsorbed per unit adsorbent is shown in Figure 5.

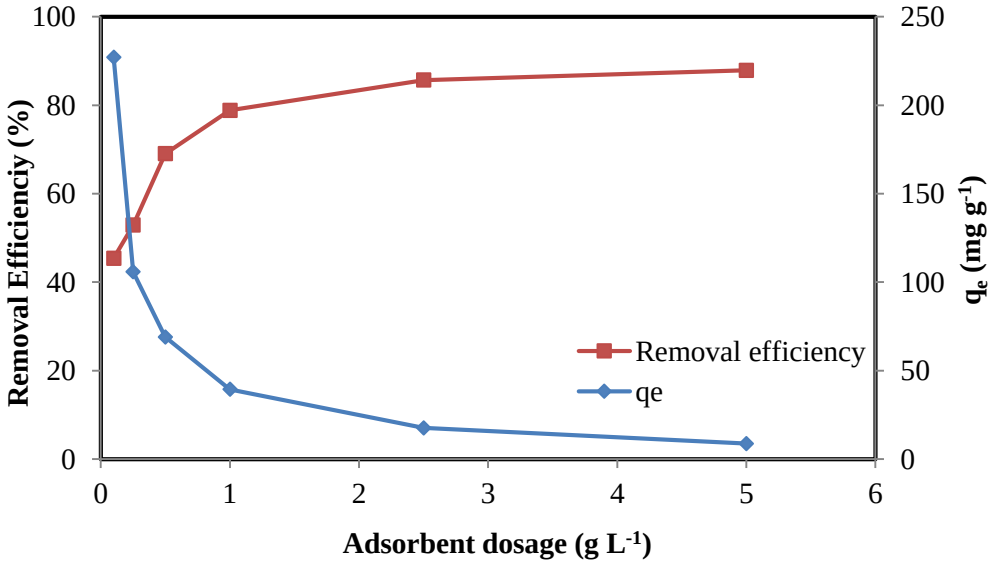


Figure 5. Change of removal efficiency and q_t versus adsorbent concentration in CV adsorption

When the amount of adsorbent was increased from 0.1 g to 5 g, the dye removal efficiency increased from 45.40% to 87.88%, while the amount of dye adsorbed per unit adsorbent decreased from 227.049 mg g^{-1} to 8.788 mg g^{-1}. The higher percentage of dye adsorption with the increase in the amount of adsorbent is attributed to the availability of more binding sites for adsorption. Similar results have been found in adsorption of methylene blue on kaolin (Mouni et al., 2018).

The initial dye concentration is the driving force for the mass transfer that occurs in the adsorption process. The effect of the initial dye concentration on adsorption of CV dyestuff was investigated at dye concentrations ranging from 25 to150 mg L^{-1}. The results obtained are shown in Figure 6.

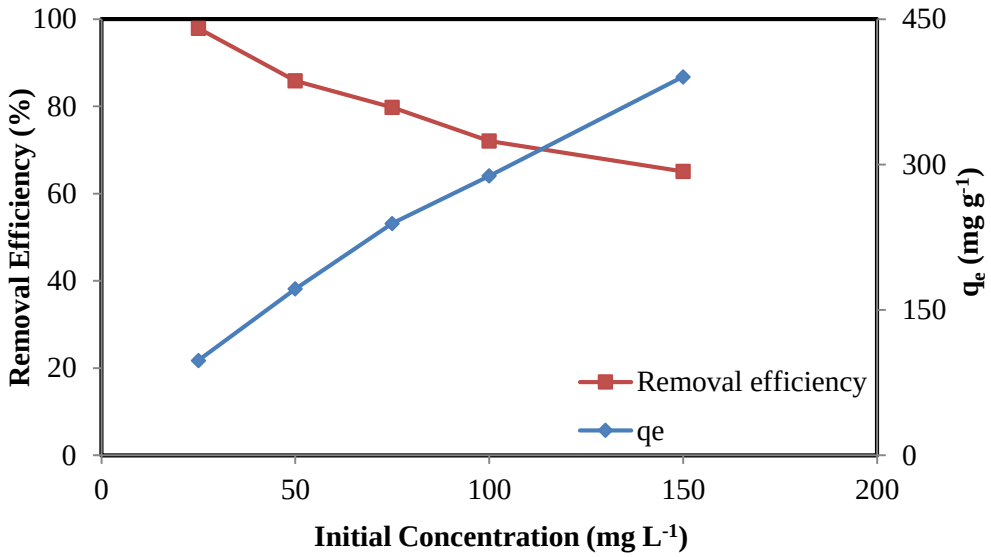


Figure 6. Change of q_t and dyestuff removal efficiencies versus initial CV concentration

While the dye removal efficiency was 97.88% at 25 mg L^{-1}, it decreased to 79.76% at 75 mg L^{-1} and to 65.07% at 150 mg L^{-1}. While the amount of dye adsorbed per unit adsorbent was 97.876 mg g^{-1} at 25 mg L^{-1}, it increased to 239.273 mg g^{-1} at 75 mg L^{-1} and to 390.438 mg g^{-1} at 150 mg L^{-1}. As the initial concentration increased, the dye removal efficiency decreased, while the amount of dye adsorbed per unit adsorbent increased. The reason for this is that the number of active sites that will hold the dye molecules does not change as the dye concentration increases (Birhanu et al., 2020). At low initial concentrations, the ratio of active sites on the adsorbent surface to dye molecules is high, and therefore the interaction of dye molecules with the adsorbent is higher (Bingul et al., 2016; Hamzezadeh et al., 2020). Therefore, the removal percentage is higher at low dyestuff concentrations. At high initial concentrations, the removal efficiency decreases as the active sites on the adsorbent surface reach saturation. A similar trend was reported by Nuhoğlu et al. (2021).

Temperature is a parameter affecting the adsorption capacity and diffusion rate of dye molecules (Bingul and Adar, 2021). The effect of temperature on the adsorption of CV dyestuff was investigated at different temperatures between 25°C and 55°C and the results are presented in Figure 7. The percentage of dye removal decreased from 85.69% to 68.69% when the temperature increased from 25 °C to 55 °C. The decreasing trend of CV adsorption with increasing temperature indicates that the bonding forces on the surface deteriorate at high temperature and the adsorption is exothermic. The solubility of the dye increased as the temperature increased, causing the interaction between the solute and the solvent to be stronger than the interaction between the solute and the adsorbent, making adsorption of the solute more difficult (Alshabanat et al., 2013; Shoukat et al., 2017). A similar trend was reported by Kumari et al. (2017).

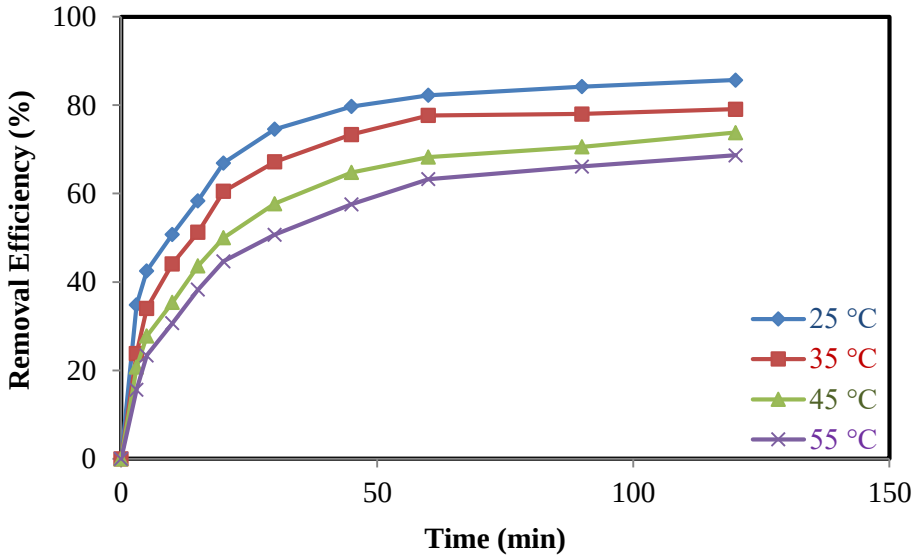


Figure 7. Change of CV removal efficiency with temperature as a function of time

Adsorption isotherms

In adsorption studies, mathematical equations of adsorption isotherm models are used to provide a connection between the dye molecules adsorbed and the dye molecules in the solution at equilibrium (Shanmugaprakash et al., 2014). In this study, Freundlich, Langmuir, Halsey, and Dubinin–Radushkevich isotherm models were used to describe experimental data obtained in adsorption of CV on waste green tea leaves at different initial dye concentrations ranging from 25 to 150 mg L^{-1}. The results are shown in Table 2 and Fig. 8.

Langmuir, Freundlich, Halsey and Dubinin–Radushkevich isotherm models are given in Eq. 1-4, respectively.

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m K_L C_e} \qquad R_L = \frac{1}{1 + K_L C_0} \tag{1}$$

$$log\ q_e = log\ K_F + \frac{1}{n} log C_e \tag{2}$$

$$lnq_e = \frac{1}{n_H} lnK_H - \frac{1}{n_H} lnC_e \tag{3}$$

$$lnq_e = \ln q_m - \beta\varepsilon^2 \qquad \varepsilon = RTln\left(1 + \frac{1}{C_e}\right) \qquad E = \frac{1}{\sqrt{2B}} \tag{4}$$

Where, q_e is amount of dye adsorbed per unit adsorbent at equilibrium (mg g^{-1}), K_L is Langmuir isotherm constant (L mg^{-1}), C_e is concentration of dye in solution at equilibrium (mg L^{-1}), q_m is the maximum monolayer adsorption capacity (mg g^{-1}), K_F is the Freundlich adsorption constant, n is heterogeneity factor, β is Dubinin-Radushkevich isotherm constant ($mol^2\ kJ^{-2}$), ε is potential energy, E is adsorption energy (kJ mol^{-1}), T is temperature (K), R is gas constant (J $mol^{-1}\ K^{-1}$), K_H is Halsey isotherm constant and n_H is the Halsey exponent.

The degree of suitability of isotherms for CV is Freundlich=Halsey>Langmuir>Dubinin-Radushkevich, respectively. The Freundlich isotherm is an empirical relationship that demonstrates the interaction between adsorbate molecules and heterogeneous surfaces (Safa and Bhatti, 2011). The smaller $1/n$, the greater the expected heterogeneity. If 1<n<10, it indicates a suitable sorption process (Liu and Wang, 2013). If the n value is also below one (n<1), the adsorption is chemical, if the value is above one (n>1), the adsorption is physical (Ajenifuja et al., 2017). The 1/n value was computed as

0.2929 using the data in Table 2, and the fact that it is close to 0 shows that the adsorbent is heterogeneous. The n value was calculated to be 3.4141, indicating a physical adsorption process.

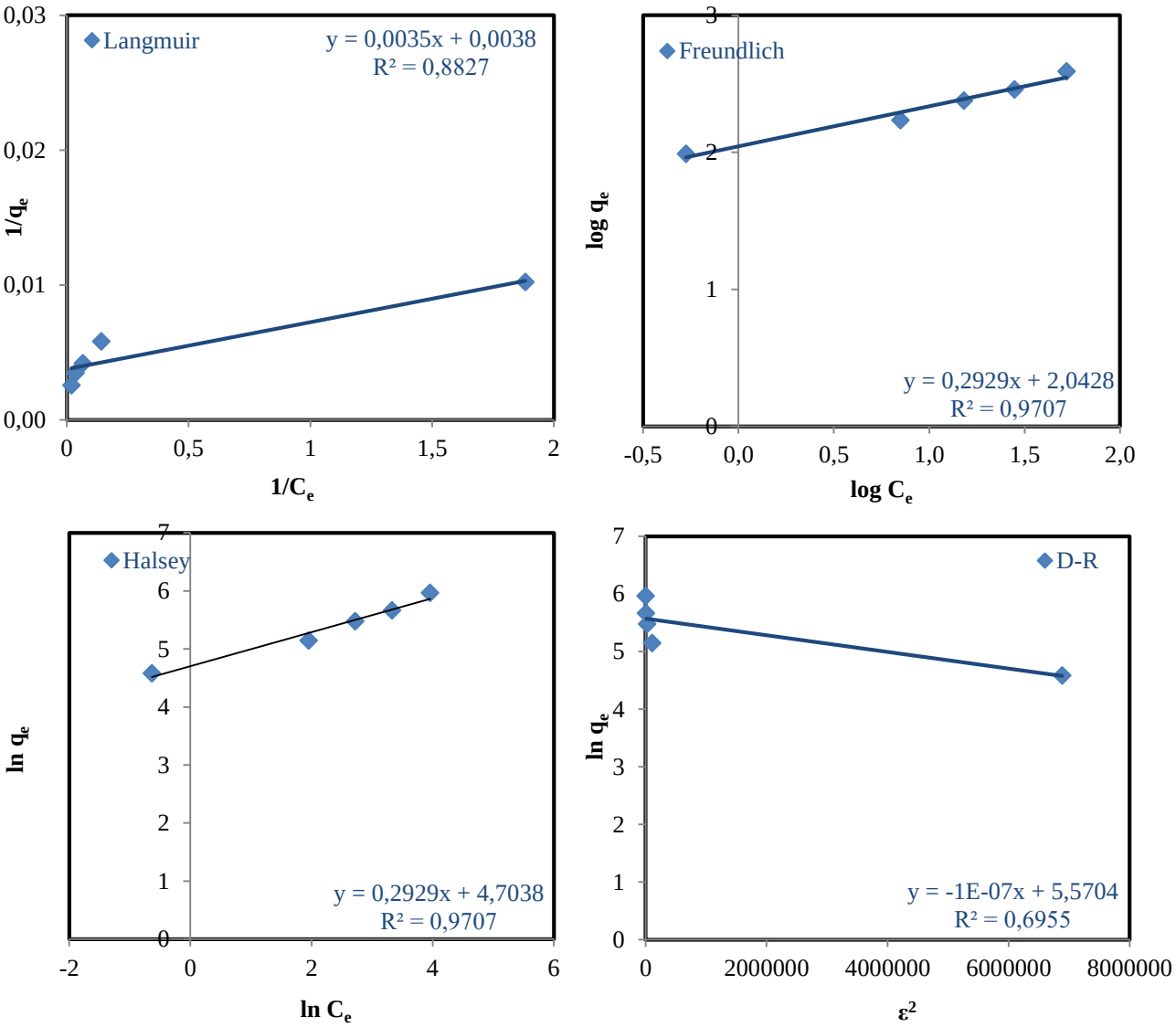


Figure 8. Adsorption isotherm models

Table 2. Isotherm constants

Isotherm constants	Values	Isotherm constant	Values
Langmuir isotherm		**Freundlich isotherm**	
q_m (mg g^{-1})	263.158	n	3.4141
K_L (L mg^{-1})	1.086	K_F	1.963
R^2	0.883	R^2	0.971
Dubinin–Radushkevich isotherm		**Halsey isotherm**	
q_m (mg g^{-1})		K_H	0.213
β (mol^2 kJ^{-2})	1*10^{-7}	n_H	3.4141
E (kJ mol^{-1})	2.236	R^2	0.971
R^2	0.695		

The Langmuir isotherm model is a monolayer adsorption model that determines the equilibrium distribution of contaminants between solid and liquid phases (Miyah et al., 2017). R_L is a dimensionless constant and is an important parameter for the Langmuir isotherm, which shows the suitability of the adsorption process. If $0<R_L<1$, adsorption is suitable, if $R_L>1$ is not suitable, if $R_L=1$

is linear, and if R_L=0, adsorption is irreversible. The R_L value for an initial dye concentration of 50 mg L^{-1} is 0.0181, greater than 0 but less than 1. This value shows that the adsorption process is suitable for CV and the adsorption process occurs spontaneously.

The Halsey isotherm confirms the heterogeneity of the adsorbent structure. It is seen from Figure 8 and Table 2 that the experimental data fit the Halsey isotherm model. Fitting the experimental data to the Halsey isotherm also confirms the heterogeneous nature of waste green tea leaves.

To determine the kind of adsorption process, the Dubinin–Radushkevich (D–R) isotherm is used. If the activation energy value is between 1-8 kJ mol^{-1}, the adsorption is physical, if it is greater than this value, the adsorption is chemical (Amin et al., 2015). The E value calculated in this study is 0.8 kJ mol^{-1} and the adsorption of CV on waste green tea leaves is physical.

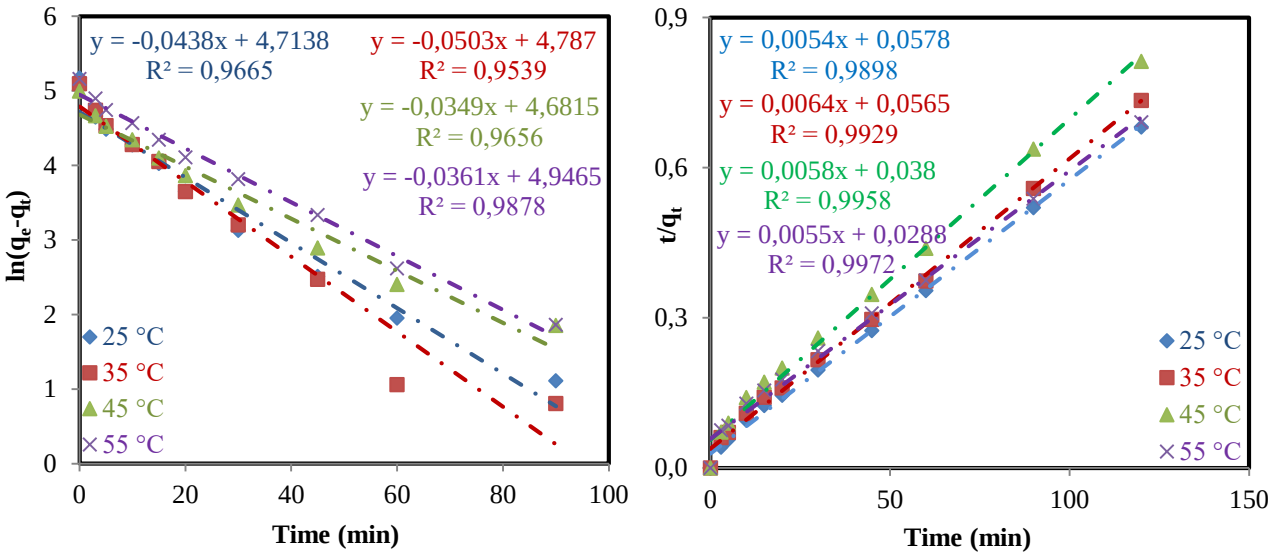
Adsorption kinetics

Adsorption kinetics is a critical factor in determining optimum operating conditions (Akram et al., 2017). The pseudo-first-order and pseudo-second-order kinetics were used in order to investigate the mechanism of CV adsorption onto waste green tea leaves and the results are shown in Fig. 9 and Table 3. The pseudo-first-order is given in Eq. 5 and pseudo-second-order kinetic is given in Eq 6.

$$\ln(q_e - q_t) = lnq_e - \frac{k_1 t}{2.303} \quad (5)$$

$$\frac{1}{q_t} = \frac{1}{k_2 q_e^2}\frac{1}{q_e} \quad (6)$$

Where, k_1 is the pseudo-first-order rate constant (min^{-1}), q_t is amount of dye adsorbed at any time t (mg g^{-1}), k_2 is the pseudo-second-order rate constant (g mg^{-1} min^{-1}) and t is adsorption time (min.). According to Figure 9 and Table 3, the pseudo-second-order kinetic model was determined to be more suitable to explain the adsorption.



(a) **(b)**

Figure 9. (a) First-order plot (b) Second-order plot for the adsorption of CV on waste green tea

Table 3. Kinetic parameters for adsorption of CV on waste green tea

	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
T (K)	k_1 (min^{-1})	q_e (mg g^{-1})	R^2	k_2 (g mg^{-1} min^{-1})	q_e (mg g^{-1})	R^2
298	0.0438	111.475	0.9665	0.0005045	185.18500	0.9898
308	0.0503	119.941	0.9539	0.0007250	156.25000	0.9929
318	0.0349	107.932	0.9656	0.0008850	172.41400	0.9958
328	0.0361	140.682	0.9878	0.0010500	181.81800	0.9972

Adsorption thermodynamics

Thermodynamic calculations are made to understand the nature of the adsorption process (Akram et al., 2017). Gibbs free energy (ΔG^0), enthalpy (ΔH^0), and entropy (ΔS^0) change are calculated according to Equations 7 and 8, respectively. Figure 10 shows graphs of Ln (k_2) and Ln (K_C) as a function of time. The enthalpy, entropy and activation energy values found from these graphs are given in Table 4. Where K_c is the equilibrium constant of adsorption

$$\Delta G^0 = -RTlnK_c \quad (7)$$

$$lnK_c = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (8)$$

The negative ΔGº value indicates that the adsorption is spontaneous, and the negative ΔH° value indicates that the adsorption is exothermic (İrdemez et al., 2021). The negative value of ΔS° indicates that the randomness at the solid/solution interface has reduced. In the study, ΔG° values for 298, 308, 318 and 328 K temperatures were calculated as -4.435, -3.409, -2.738 and -2.142 kJ mol^{-1}, respectively. The ΔH° value was found to be -26.798 kJ mol^{-1} and the ΔS° value as -0.076 kJ mol^{-1}. Changes in entropy, enthalpy and free energy indicated that the adsorption of CV was exothermic and spontaneous.

Activation energy is important in determining whether the adsorption process is physical or chemical. If the activation energy is between 5-40 kJ mol^{-1}, adsorption indicates physical adsorption, and if this value is between 40-800 kJ mol^{-1}, adsorption indicates chemical adsorption. The Arrhenius equation given in Equation 9 is used to calculate the activation energy. The E_a value was also calculated as 19.5790 kJ mol^{-1}, which is an indication that the adsorption of CV on waste green tea leaves is physical. Where A is Arrhenius constant (g $mol^{-1}h^{-1}$), E_a is activation energy (j mol^{-1})

$$lnk_2 = lnA - \frac{E_a}{RT} \quad (9)$$

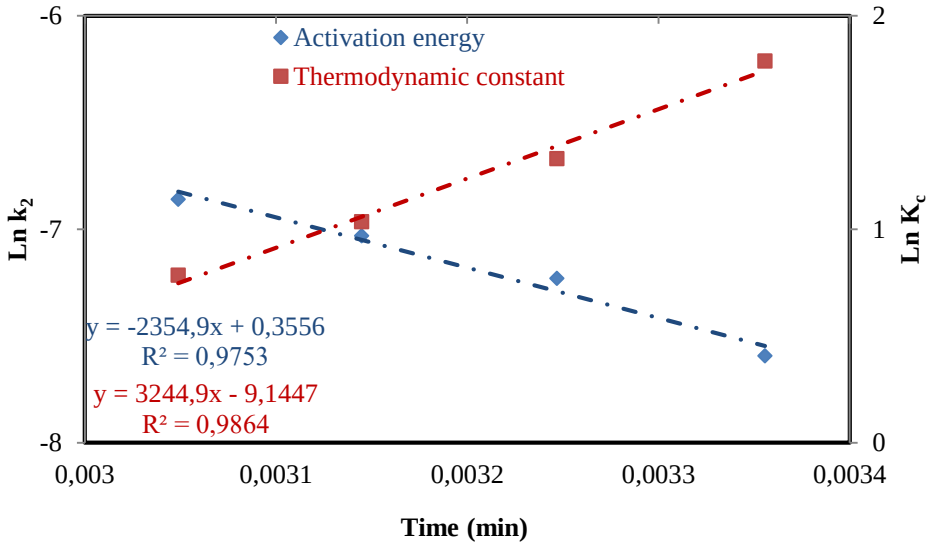


Figure 10. The graphs drawn to find activation energy and thermodynamic constants

Table 4. Thermodynamic parameters

T (K)	ΔG (Kj mol^{-1})	ΔS (Kj mol^{-1} K^{-1})	ΔH (kJ mol^{-1})	E_a (kJ mol^{-1})
298	-4.43472			
308	-3.40855	-0,0760	-26.9780	19.5790
318	-2.73820			
328	-2.14237			

CONCLUSIONS

In this study; the adsorption capacity of waste green tea leaves and their use as an adsorbent in the removal of dyestuffs from aqueous solutions were investigated. Natural pH (5.58), the particle size of 75 μm, stirring speed of 200 rpm and 25 Cº were determined as optimum conditions. It was observed that dye removal efficiency increased as contact time, pH and adsorbent dose were increased. Conversely, adsorption of CV dye decreased with increasing initial dye concentration, stirring speed, temperature, and particle size. Adsorption of CV dye on waste green tea leaves fitted the Freundlich and Halsey isotherm models better than the others. According to kinetic studies, the experimental findings fit well on the pseudo-second-order kinetic model. Changes in entropy, enthalpy and free energy, indicated that the adsorption of CV dyes was exothermic, spontaneous and physisorption. The obtained results showed that waste green tea leaves can be used as a low-cost adsorbent for dye removal from wastewater.

Conflict of Interest

The article authors declare that there is no conflict of interest between them.

Author's Contributions

The authors declare that they have contributed equally to the article.

REFERENCES

Afroze S, Sen TK, 2018. A review on heavy metal ions and dye adsorption from water by agricultural solid waste adsorbents. Water Air Soil Pollution, 229(225).

Ajenifuja E, Ajao JA, Ajayi EOB, 2017. Adsorption isotherm studies of Cu (II) and Co (II) in high concentration aqueous solutions on photocatalytically modified diatomaceous ceramic adsorbents. Applied Water Science, 7: 3793–3801.

Akram M, Bhatti NH, Iqbal M, Noreen S, Sadaf S, 2017. Biocomposite efficiency for Cr(VI) adsorption: Kinetic, equilibrium and thermodynamics studies. Journal of Environmental Chemical Engineering, 5(1): 400-411.

Alshabanat M, Alsenani G, Almufarij R, 2013. Removal of crystal violet dye from aqueous solutions onto date palm fiber by adsorption technique. Journal of Chemistry.

Altun T, 2019. Chitosan-coated sour cherry kernel shell beads: an adsorbent for removal of Cr(VI) from acidic solutions. Journal of Analytical Science and Technology, 10: 14.

Amin MT, Alazba AA, Shafiq M, 2015. Adsorptive removal of reactive black 5 from wastewater using bentonite clay: Isotherms, kinetics and thermodynamics. Sustainability, 7(11): 15302-15318.

Arslan R, Tozluoğlu A, Sertkaya S, Fidan H, Küçük S, 2021. Functionalized nanocellulose based adsorbents for dye removal from wastewater. Artvin Coruh University Journal of Forestry Faculty, 22(1): 148-160.

Ayub S, Changani F, 2014. Adsorption process for wastewater treatment by using coconut shell. International Journal of Civil, Structural, Environmental and Infrastructure Engineering Research and Development, 4(3): 21-34.

Bingul Z, Adar E, 2021. Usability of spent Salvia officinalis as a low-cost adsorbent in the removal of toxic dyes: waste assessment and circular economy. International Journal of Environmental Analytical Chemistry.

Bingul Z, Gurbuz H, Aslan A, Ercisli S, 2016. Biosorption of zinc (II) from aqueous solutions by nonliving lichen biomass of Xanthoria parietina (L.) Th. Fr. Environmental Engineering and Management Journal, 15(12): 2733-2740.

Birhanu Y, Leta S, Adam G, 2020. Removal of chromium from synthetic wastewater by adsorption onto Ethiopian low-cost Odaracha adsorbent. Applied Water Science, 10(11): 1-11.

Burca S, Maicaneanu A, Indolean C, 2016. A green approach: Malachite green adsorption onto waste green tea biomass. Isotherm and kinetic studies. Academia Romana, Revue Roumaine de Chimie, 61: 541-547.

Chakraborty S, Chowdhury S, Saha PD, 2011. Adsorption of crystal violet from aqueous solution ontonaoh-modified rice husk. Carbohydrate Polymers, 86: 1533–1541.

Cherdchoo W, Nithettham S, Charoenpanich J, 2019. Removal of Cr(VI) from synthetic wastewater by adsorption onto coffee ground and mixed waste tea. Chemosphere, 221: 758-767.

Degermenci GD, Degermenci N, Ayvaoglu V, Durmaz E, Çakır D, Akan E, 2019. Adsorption of reactive dyes on lignocellulosic waste; Characterization, equilibrium, kinetic and thermodynamic studies. Journal of Cleaner Production, 225: 1220-1229.

Deng H, Lu J, Li G, Zhang G, Wang X, 2011. Adsorption of methylene blue on adsorbent materials produced from cotton stalk. Chemical Engineering Journal, 172(1): 326-334.

Duran C, Ozdes D, Gundogdu A, Senturk HB, 2011. Kinetics and isotherm analysis of basic dyes adsorption onto almond shell (prunus dulcis) as a low cost adsorbent. Journal of Chemical & Engineering Data, 56: 2136–2147.

Farizoglu B, Fil BA, Sozudogru O, Aladag E, Kul S, 2019. Comparison of cationic dyes (Basic Orange 2, Basic Yellow 2 and Basic Violet 3) removal from aqueous solution using clay as an adsorbent. Fresenius Environmental Bulletin, 28(5): 3658-3666.

Felista MM, Wanyonyi WC, Ongera G, 2020. Adsorption of anionic dye (Reactive black 5) using macadamia seed Husks: Kinetics and equilibrium studies. Scientific African, 7.

Güzel F, Sayğılı H, Sayğılı Akkaya G, Koyuncu F, Yılmaz C, 2017. Optimal oxidation with nitric acid of biochar derived from pyrolysis of weeds and its application in removal of hazardous dye methylene blue from aqueous solution. Journal of Cleaner Production, 144: 260-265.

Hamzezadeh A, Rashtbari Y, Afshin S, Morovati M, Vosoughi M, 2020. Application of low-cost material for adsorption of dye from aqueous solution. International Journal of Environmental Analytical Chemistry, 1-16.

Harrache Z, Abbas M, Aksil T, Trari M, 2019. Thermodynamic and kinetics studies on adsorption of Indigo Carmine from aqueous solution by activated carbon. Microchemical Journal, 144: 180-189.

Hasan MM, Shenashen MA, Hasan MN, Znad H, Salman MS, Awual MR, 2021. Natural biodegradable polymeric bioadsorbents for efficient cationic dye encapsulation from wastewater. Journal of Molecular Liquids, 323.

Hasanzadeh M, Simchi A, Fard HS, 2020. Nanoporous composites of activated carbon-metal organic frameworks for organic dye adsorption: Synthesis, adsorption mechanism and kinetics studies. Journal of Industrial and Engineering Chemistry, 81: 405-414.

Indolean C, Burca S, Maicaneanu A, 2017. Adsorptive removal of malachite green from model aqueous solutions by chemically modified waste green tea biomass. Acta Chimica Slovenica, 513(64): 513–521.

İrdemez Ş, Durmuş G, Kul S, Torun FE, Bingül Z, 2021. Comparison of kinetics of Cr (III) ions removal from wastewater using raw and activated montmorillonite minerals. EQA - International Journal of Environmental Quality, 45: 17-26.

Jamshidi B, Ehrampoush MH, Dehvari M, 2013. Utilization of olive kernel ash in removal of RB19 from synthetic textile wastewater. Journal of Environmental Treatment Techniques, 1(3): 151-157.

Jawad AH, Abdulhameed AS, Mastuli MS, 2020. Mesoporous crosslinked chitosan-activated charcoal composite for the removal of thionine cationic dye: Comprehensive adsorption and mechanism study. Journal of Polymers and the Environment, 28: 1095–1105.

Jeyaseelan C, Gupta A, 2016. Green tea leaves as a natural adsorbent for the removal of Cr(VI) from aqueous solutions. Air, Soil and Water Research, 9: 13-19.

Joseph J, Radhakrishnan RC, Johnson JK, Joy SP, Thomas J, 2020. Ion-exchange mediated removal of cationic dye-stuffs from water using ammonium phosphomolybdate. Materials Chemistry and Physics, 242.

Kazemia J, Javanbakht V, 2020. Alginate beads impregnated with magnetic Chitosan@Zeolite nanocomposite for cationic methylene blue dye removal from aqueous solution. International Journal of Biological Macromolecules, 154: 1426-1437.

Kul S, 2021. Removal of Cu(II) from aqueous solutions using modifed sewage sludge ash. International Journal of Environmental Science and Technology.

Kumari HJ, Krishnamoorthy P, Arumugam TK, Radhakrishnan S, Vasudevan D, 2017. An efficient removal of crystal violet dye from waste water by adsorption onto TLAC/Chitosan composite: A novel low cost adsorbent. International Journal of Biological Macromolecules, 96: 324-333.

Lafi R, Mabrouk W, Hafiane A, 2019. Removal of methylene blue from saline solutions by adsorption and electrodialysis. Membrane and Water Treatment, 10(2): 139-148.

Liu J, Wang X, 2013. Novel silica-based hybrid adsorbents: lead (II) adsorption isotherms. The Scientific World Journal.

Liu L, He D, Pan F, Huang R, Lin H, Zhang X, 2020. Comparative study on treatment of methylene blue dye wastewater by different internal electrolysis systems and COD removal kinetics, thermodynamics and mechanism. Chemosphere, 238.

Liu N, Wu Y, Sha H, 2020. Magnesium oxide modified diatomite waste as an efficient adsorbent for organic dye removal: Adsorption performance and mechanism studies. Separation Science and Technology, 55(2): 234–246.

Markovic S, Stankovic A, Lopicic Z, Lazarevic S, Stojanovic M, Uskokovic D, 2015. Application of raw peach shell particles for removal of methylene blue. Journal of Environmental Chemical Engineering, 3(2): 716-724.

Meghwal K, Kumawat S, Ameta C, Jangid NK, 2020. Effect of dyes on water chemistry, soil quality, and biological properties of water. Impact of Textile Dyes on Public Health and the Environment, 25.

Miyah Y, Lahrichi A, Idrissi M, Boujraf S, Taouda H, Zerrouq F, 2017. Assessment of adsorption kinetics for removal potential of crystal violet dye from aqueous solutions using Moroccan pyrophyllite. Journal of the Association of Arab Universities for Basic and Applied Sciences, 23: 20-28.

Mouni L, Belkhiri L, Bollinger JC, Bouzaza A, Assadi A, Tirri A, Dahmoune F, Madani K, Remini H, 2018. Removal of methylene blue from aqueous solutions by adsorption on Kaolin: Kinetic and equilibrium studies. Applied Clay Science, 153, 38-45.

Namal OO, Kalipci E, 2020. Adsorption kinetics of methylene blue removal from aqueous solutions using potassium hydroxide (KOH) modified apricot kernel shells. International Journal of Environmental Analytical Chemistry, 100(14): 1549–1565.

Nuhoğlu Y, Kul ZE, Kul S, Nuhoğlu Ç, Torun FE, 2021. Pb (II) biosorption from the aqueous solutions by raw and modifed tea factory waste (TFW). International Journal of Environmental Science and Technology, 18: 2975–2986.

Önal ES, Yatkin T, Ergüt M, Özer A, 2017. Green synthesis of ıron nanoparticles by aqueous extract of eriobotrya japonica leaves as a heterogeneous fenton-like catalyst: Degradation of basic red 46. International Journal of Chemical Engineering and Applications, 8(5): 327-333.

Safa Y, Bhatti HN, 2011. Kinetic and thermodynamic modeling for the removal of Direct Red-31 and Direct Orange-26 dyes from aqueous solutions by rice husk. Desalination, 272: 313–322.

Shanmugaprakash M, Sivakumar V, Manimaran M, Aravind J, 2014. Batch and dynamics modeling of the biosorption of Cr (VI) from aqueous solutions by solid biomass waste from the biodiesel production. Environmental Progress & Sustainable Energy, 33(2), 342-352.

Shoukat S, Bhatti HN, Iqbal M, Noreen S, 2017. Mango stone biocomposite preparation and application for crystal violet adsorption: A mechanistic study. Microporous and Mesoporous Materials, 239: 180-189.

Silva CEF, Gama BMV, Gonçalves AHS, Medeiros JA, Abud AKS, 2020. Basic-dye adsorption in albedo residue: Effect of pH, contact time, temperature, dye concentration, biomass dosage, rotatio. Journal of King Saud University-Engineering Sciences, 32(6): 351-359.

Stavrinou A, Aggelopoulos CA, Tsakiroglou CD, 2018. Exploring the adsorption mechanisms of cationic and anionic dyes onto agricultural waste peels of banana, cucumber and potato: Adsorption kinetics and equilibrium isotherms as a tool. Journal of Environmental Chemical Engineering, 6(6): 6958-6970.

Tang J, Li Y, Wang X, Daroch M, 2017. Effective adsorption of aqueous Pb^{2+} by dried biomass of Landoltia punctata and Spirodela polyrhiza. Journal of Cleaner Production, 145: 25-34.

Yang X, You F, Zhao Y, Bai Y, Shao L, 2018. Confinedly assembling surface nanocoating to manipulate nanofiltration membranes for highly-efficient dye removal. ES Energy & Environment, 1: 106-113.

Yu Z, Hu C, Dichiara AB, Jiang W, Gu J, 2020. Cellulose nanofibril/carbon nanomaterial hybrid aerogels for adsorption removal of cationic and anionic organic dyes. Nanomaterials, 10(1): 169.

Zhao X, Wang X, Song G, Lou T, 2020. Microwave assisted copolymerization of sodium alginate and dimethyl diallyl ammonium chloride as flocculant for dye removal. International Journal of Biological Macromolecules, 156(1): 585-590.

Zuorro A, Lavecchia R, 2010. Adsorption of Pb(II) on spent leaves of green and black tea. American Journal of Applied Sciences, 7(2):153-159.