

Kinetics, isothermal and thermodynamic studies of the adsorption of Acid Blue 113 dye from aqueous solution onto dried tea waste as natural adsorbent

R. Aziam*, S. Nouaa, A. Aboussabek, L. Boukarma, E. Eddaoudi, M. Zerbet, F. Sinan, M. Chiban*

Lab. LACAPE, Department of Chemistry, Faculty of Science, Ibn Zohr University, Agadir, Morocco, Tel.: +212627-39-19-35; email: rac.aziam@gmail.com (R. Aziam), Tel.: +212661-24-16-39; emails: m.chiban@uiz.ac.ma/mmchiban@gmail.com (M. Chiban), nouaasafa.pro@gmail.com (S. Nouaa), a.aboussabek@uiz.ac.ma (A. Aboussabek), latifaboukarma@gmail.com (L. Boukarma), heddaoudi@hotmail.fr (E. Eddaoudi), zerbetmohamed@gmail.com (M. Zerbet), f.sinan@uiz.ac.ma (F. Sinan)

Received 25 June 2023; Accepted 15 November 2023

ABSTRACT

In the current study, we have aimed to investigate the potential of dried tea waste as a low-cost adsorbent for removing Acid Blue 113 from aqueous solutions using the batch equilibration technique. Scanning electron microscopy, energy-dispersive X-ray spectroscopy, and zero charge point examined the textural property of the material studied and its morphology. The effect of adsorbent dose, contact time, solution pH, and temperature on the adsorption of the anionic dye onto dried tea waste microparticles was evaluated. The adsorption kinetics were tested and illustrated using pseudo-first-order, pseudo-second-order, intraparticle diffusion, and Elovich models. The adsorption process follows second-order kinetics, and the corresponding rate constants are provided. The adsorption equilibrium using Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich isotherm models was also studied, and the Langmuir isotherm model was found to be the most appropriate for the adsorption of Acid Blue 113 dye using dried tea waste. The thermodynamic parameters suggest that the adsorption process is spontaneous and exothermic in nature. The results demonstrate that the tea waste microparticles show good adsorption of Acid Blue 113 dye from aqueous solutions.

Keywords: Adsorption; Anionic dye; Acid Blue 113; Low-cost; Tea waste

1. Introduction

In recent decades, wastewater contaminated with dyes deserves special importance, because of the many dye chemicals that are discharged into the environment, especially into water systems. Industrial wastewater containing organic pollutants has been extensively studied for treatment before discharge into the environment. These toxic colorful discharges pose an aesthetic and health problem. Several techniques have been used for the removal of dyes from industrial effluents [1,2].

including precipitation, coagulation, flocculation, reverse osmosis, filtration, ozonation, and adsorption process [3–7]. The adsorption is one of the most widely used treatment technologies for textile wastewater due to its availability, highest profit, ease of disposal and highest efficiency [8–10].

Research was then directed towards treatment processes using cheap adsorbent materials. A number of natural materials have been evaluated for their ability to remove dyes from aqueous solutions, such as charcoal, newspaper waste, banana peel, orange peel, sawdust, fly ash, tea waste, etc. [11–18]. The Acid Blue 113 dye chosen as the model

* Corresponding authors.

compound for this study has wide applications as a coloring agent in the textile industry.

In this study, we aimed to evaluate the suitability of dry tea waste as a low-cost adsorbent for the removal of Acid Blue 113 from aqueous solutions using the batch equilibrium technique. Scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS) and zero charge point (pH_{PZC}) examined the textural property of the material studied and its morphology. The effects of adsorbent dosage, contact time, initial dye concentration, solution pH and temperature on the adsorption rate of anionic dyes on dried tea waste particles were studied. Studies of adsorption equilibria, isotherms, and kinetics are essential to provide the basic information needed for the design and operation of adsorption for wastewater treatment. This work aims to investigate the adsorption of Acid Blue 113 from aqueous solution onto dried tea waste as a cost-effective bio-adsorbent. Kinetic, isothermal and thermodynamic data were also evaluated.

2. Materials and methods

2.1. Adsorbent preparation

The adsorbent used in this study was obtained from tea waste. The soluble and colored components were removed from the tea by washing it with boiling water. This was repeated until the water was almost colorless. The tea leaves were then washed with distilled water and oven dried for 12 h at 85°C. The microparticles of tea waste were crushed with an electric grinder to obtain fine powders. The microparticles (125 μm) were used as bio-adsorbent materials in batch adsorption experiments.

2.2. Preparation of adsorbent and dye solutions

We start by collecting a quantity of raw material (TW), which is then rinsed multiple times with distilled water to remove impurities and contaminants from its surface. Afterwards, it is reduced into smaller fractions, washed, dried, ground, and sieved before being used as an adsorbent.

A synthetic dye solution of Acid Blue 113 (AB113) was the adsorbent used in this study, and the anionic dye was used without further purification. Table 1 lists the properties

of the AB113 dye. Synthetic dyes used in this study were purchased from Sigma-Aldrich (America). A stock solution of 1,000 mg/L in anionic dye was prepared by dissolving an accurately weighed quantity of AB113 dye in double distilled water.

2.3. Batch adsorption experiments

The adsorption experiments were carried out using a batch technique at room temperature (except when the effect of temperature was studied). The batch mode was chosen because of its simplicity and efficiency. A known amount of tea waste was placed in different stoppered Erlenmeyer glass flasks of 100 mL capacity containing 40 mL of Acid Blue 113 of a known concentration and pH. The stirring speed was kept constant for each cycle to ensure even mixing. After different contact times (t), the resulting solutions were centrifuged at 5,000 rpm for 10 min and the supernatant was filtered through a 0.45 μm membrane filter and the filtrate was evaluated. The residual concentration of dye solution was determined using UV-Visible (Techcomp UV 2300 Spectrophotometer) at the respective λ_{max} value, which is 566 nm for AB113 dye. The concentration of AB113 dye (Cr) removed from the aqueous solution was calculated as the difference between the initial concentration C_0 and the concentration ($\text{Cr} = C_0 - C_t$) at different contact times.

The amount removed per unit mass of bio-adsorbent (q_t , mg/g) at time " t " was calculated as follows:

$$q_t = (C_0 - C_t) \times \frac{V}{m}$$

and the removal Acid Blue 113 percentage was calculated by:

$$\% \text{ adsorption} = \frac{(C_0 - C_t)}{C_0} \times 100$$

where C_0 (mg/L) is the initial concentration of anionic dye in aqueous solution; C_t (mg/L) is the concentration of anionic dye in aqueous solution at time ' t '; q_t (mg/g) is the concentration of anionic dye in aqueous solution at time ' t '; The amount removed per unit mass of bio-adsorbent; C_e (mg/L)

Table 1
Properties of Acid Blue 113 dye

Structure molecular					
Molecular formula	Molar mass (g/mol)	Index code	CAS number	Type	λ_{max} (nm)
$\text{C}_{32}\text{H}_{21}\text{N}_5\text{Na}_2\text{O}_6\text{S}_2$	681.65	26360	3351-05-1	Anionique	566

is the equilibrium concentration of anionic dye in aqueous solution, q_e (mg/g) is the amount removed per unit mass of bio-adsorbent at equilibrium, m (g) is the amount of adsorbent, V (L) is the volume of the solution.

The initial pH of the solution (pH = 6.3), the dose of adsorbent ($R = 5$ g/L) and initial concentration of solution ($C_0 = 20$ mg/L) are the optimal conditions for the adsorption of AB113 dye on dried tea waste in this work. The characterization of the adsorption process of the anionic dye was studied by varying certain parameters such as contact time, initial dye concentration, pH of the initial solution, temperatures and mass/volume ratio of the solution.

3. Results and discussion

3.1. Characterization of dried tea waste used

The point of zero charge of dried tea waste was determined using the solid addition method. In this method, six bottles were prepared with 50 mL of 0.01 M NaCl

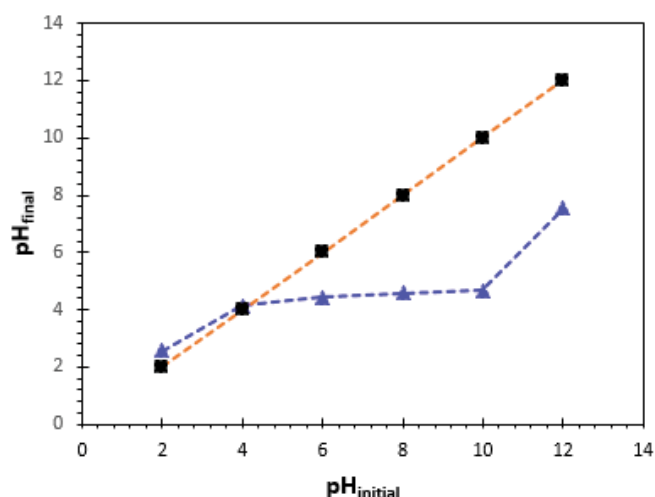


Fig. 1. pH at the point of zero charge of dried tea waste used.

solutions, each maintained at a pH range of 2–12. To each bottle, 0.5 g of dried tea waste used material developed was added. The pH of the solutions was adjusted using 0.1 M HCl/NaOH solutions. The bottles were then shaken for 48 h at room temperature, and the final pH of the solutions was measured [19]. These solutions were stirred for 48 h at room temperature and the final pH of the solutions was measured. The point of intersection between the initial pH and the final pH was taken as the zero charge point (Fig. 1). The pH_{PZC} values for the dried tea waste used are equal to 4.4. This shows that at pH below pH_{PZC} (pH < 4.4), the adsorbent surface studied is positively charged, while at pH above pH_{PZC} (pH > 4.4), the surface is dominated by negative charges.

SEM allows for detailed observation of grain morphology, including estimating their approximate diameter and the arrangement of the sample grains. Texture analyses were conducted using a scanning electron microscope (SEM, TESCAN VEGA3, Cadi Ayyad University) with an acceleration voltage of 20 kV. Fig. 2 displays the SEM images of dried tea waste and the corresponding EDS spectrum.

From the SEM image, we observe that its morphology exhibits a wide distribution of differently sized grains, which helps explain the adsorption of molecules on the surface of this biomaterial. The energy-dispersive X-ray spectroscopy results of the adsorbent used indicated a high presence of the chemical elements carbon, oxygen, and calcium (C, O, and Ca). Based on the analyses, it can be inferred that the average fraction of light carbon atoms is around 99.1%, with the presence of small quantities of oxygen and calcium (1.65%) in atomic percentage.

The X-ray powder diffraction analysis of green tea waste, as depicted in Fig. 3, reveals a distinctive peak at $2\theta = 22^\circ$ (002 plane) related to the amorphous structure of the tea powder [20]. This matrix exhibits superimposed peaks in shifted positions, suggesting that the material is partially crystallized [21].

The Fourier-transform infrared spectrum of the tea waste sample is depicted in Fig. 4. The prominent and wide peak observed at approximately 3480 cm^{-1} can be attributed to

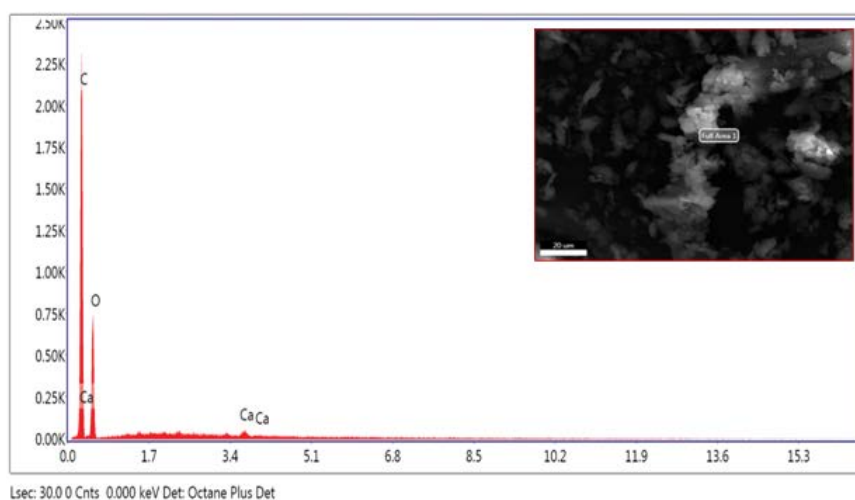


Fig. 2. Scanning electron microscopy-energy-dispersive X-ray spectroscopy patterns of dried tea waste used.

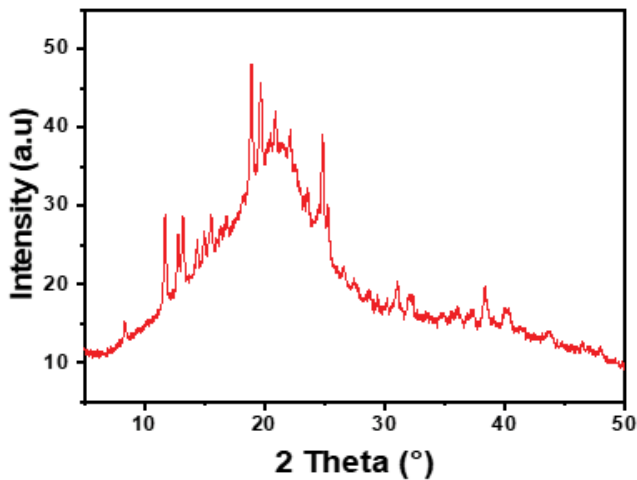


Fig. 3. X-ray diffraction pattern of dried tea waste.

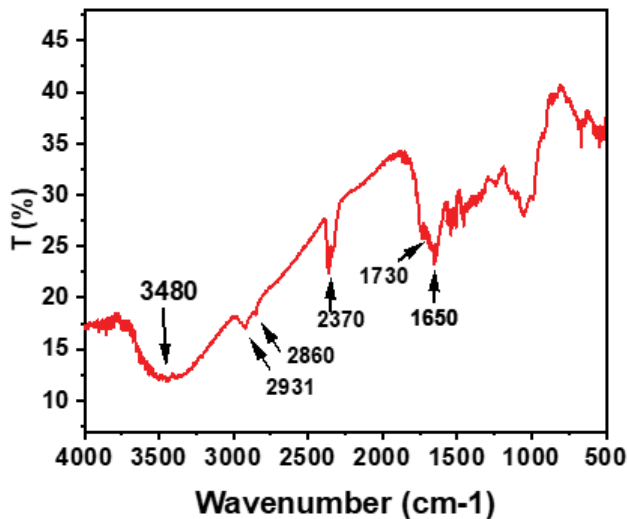


Fig. 4. Fourier-transform infrared spectra of dried tea waste.

the presence of the hydroxyl functional group (O–H). This interpretation is further supported by the elevated bands at 1,080 and 1,020 cm^{-1} , which correspond to deformations of the C and C–O bonds in single bonds found in primary and secondary alcohols. The bands located at 2,931 and 2,860 cm^{-1} are associated with the stretching vibrations of the C–H single bond. However, identifying specific structural components is challenging due to the presence of minor peaks, notably at 1,220 cm^{-1} , primarily stemming from phenolic, ether, and epoxide structures. The intense and prominent peak occurring at around 1,650 cm^{-1} is attributed to the stretching vibration of the C=C bond. In contrast, a shoulder band at approximately 1,730 cm^{-1} indicates the vibration of the C=O bond [22].

3.2. Effect of adsorbent dosage

The adsorbent dosage is a crucial parameter as it defines the capacity of an adsorbent for a given initial concentration of the adsorbate [2,23]. The effect of adsorbent dosage on the

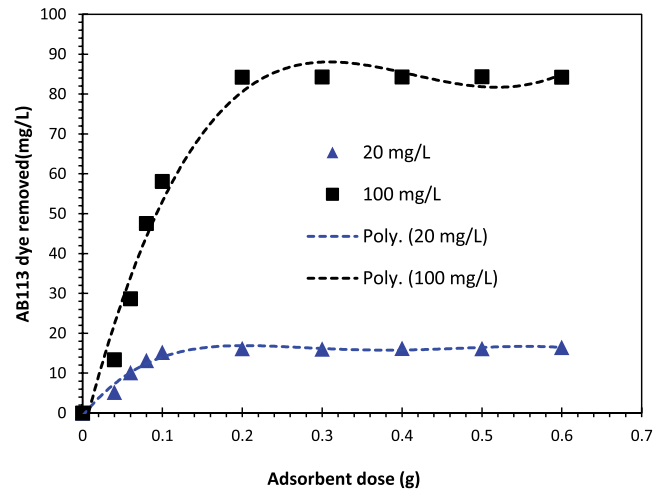


Fig. 5. Effect of dried tea waste amount on the removal of Acid Blue 113 dye: $C_0 = 20 \text{ mg/L}$, $T = 23^\circ\text{C} \pm 2^\circ\text{C}$, $\text{pH} = 6.3$ and $t_c = 12 \text{ h}$.

removal of AB113 at $C_0 = 20 \text{ mg/L}$ was studied by stirring in different masses at 25°C . Fig. 5 illustrates the adsorption of AB113 as a consequence of the adsorbent dosage. The removal of dye used increases with the adsorbent dose, which could be explained by the increase in the number of available adsorption sites [24]. The dye removed remains almost unchanged when the concentration of the adsorbent used is higher than 5 g/L (0.2/40 mL). For an adsorbent dosage of 5 g/L, the increase in Acid Blue 113 removal becomes very low on the adsorbent surface, and the dye concentration reaches equilibrium. For a higher adsorbent concentration of 5 g/L, the removal efficiency becomes almost constant for the removal of AB113 from tea waste microparticles. To achieve the maximum adsorption of Acid Blue 113, an m/V ratio of 5 g/L was chosen for subsequent studies.

3.3. Effect of contact time

Equilibrium time is another important operational parameter for an economical wastewater treatment process. The impact of contact time on the batch adsorption of the dye solution is shown in Fig. 6. The adsorption rate is fast in the first steps, decreases gradually and becomes constant when equilibrium is reached. This result could be due to the high availability of free active sites at the beginning of the adsorption process. In general, the percentage values of dye adsorption increase with increasing contact time. Taking these results into account, the contact time was set at 90 min for the remaining batch experiments. In conclusion, the equilibrium adsorption time of the studied azo dye AB113 on the used adsorbent micro-particles is approximately 90 min of contact. For the continuation of this work, we have chosen a time of 90 min, which is more than sufficient for the establishment of equilibrium to study the parameters influencing the retention of the azo dye AB113. The rapid adsorption observed during the initial minutes of the reaction can be attributed to the abundance of available active sites on the surface of the adsorbent [7,25]. As the contact time increases, organic molecules require more time to penetrate and diffuse into the pores of the adsorbent.

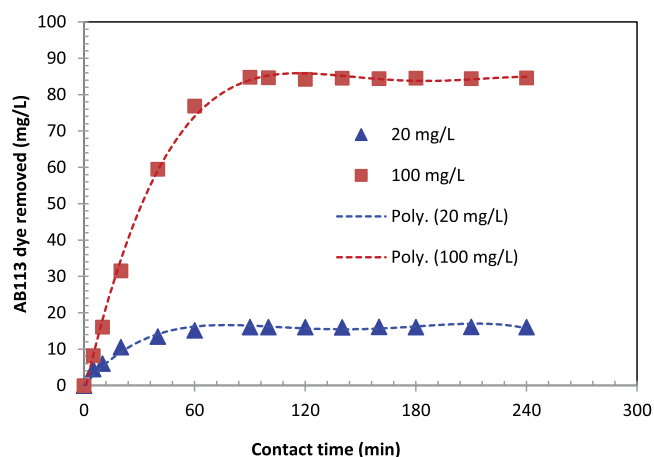


Fig. 6. Effect of contact time on the removal of Acid Blue 113 onto dried tea waste ($m/V = 5$ g/L, $pH_i = 6.3$ and $T = 23^\circ\text{C}$).

Similarly, Jain et al. [26] conducted a study on the removal of an anionic dye (Acid Blue 25) using a tea waste-based biomaterial. This study indicates faster removal in the initial stage, which is attributed to the abundant availability of free sites, resulting in a higher probability of adsorption.

The second slow stage is attributed to a decrease in the availability of free sites as most of the active sites are already occupied by adsorbed molecules [27]. Parvin et al. [27], demonstrated that the adsorption process consists of two stages, namely a rapid stage and a slow stage.

3.4. Effect of initial pH

Typically, the initial pH value can either enhance or reduce the rate at which dyes are taken up, which is closely related to changes in the surface of the adsorbent and the chemistry of the dyes [28]. The effect of solution pH was investigated according to the following procedure: A mass of 0.2 g of dried tea waste was added to a number of glass bottles containing 40 mL of dye solution. The pH of the dye solutions was adjusted over the range of pH 2 to pH 10 using 0.1 M HCl or 0.1 M NaOH solutions. The results presented in Fig. 5 reveal that the removal of Acid Blue 113 is significantly influenced by the initial pH of the solution. Based on these results, the uptake of Acid Blue 113 increased slightly from pH 2 to 8 and then decreased with increasing pH until 12. The maximum dye removal for the adsorbent was observed at pH₂.

The effect of pH on dye removal may be due to chemical and electrostatic interactions between the adsorbent surface and the dye molecules. This result demonstrates that the adsorption of AB113 is lower at higher pH values [7] (Fig. 7). We can see that at pH values below the pH of the zero charge point ($pH < pH_{pzc}$), the removed amount of AB113 dye is significant. The surface of dried tea waste used at $pH < pH_{pzc}$ is positively charged, which favors AB113 dye adsorption. This can be explained by the electrostatic attraction between the anionic dye and the positively charged adsorbent surface. At pH values above pH_{pzc} , the adsorption capacity is low, due to the presence of hydroxide ions

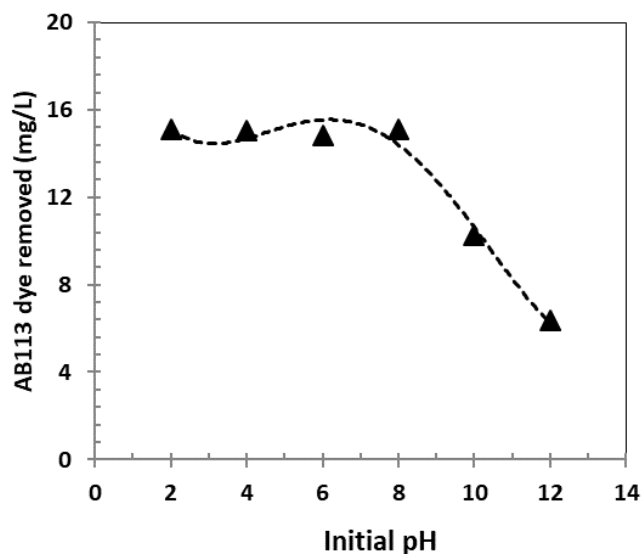


Fig. 7. Effect of initial pH on adsorption of Acid Blue 113: $C_0 = 20$ mg/L, $m/V = 5$ g/L, $T = 23^\circ\text{C} \pm 2^\circ\text{C}$, and $t_c = 90$ min.

(OH⁻). For the adsorption of AB113 dye, the surface of the dried tea waste must be positively charged [29,30].

3.5. Adsorption kinetic models

The experimental data on adsorption kinetics were examined using a variety of kinetic models, pseudo-first-order model, pseudo-second-order model, Elovich model and intraparticle diffusion model [7,31–35].

3.5.1. Pseudo-first-order kinetics model

The kinetics equation of pseudo-first-order model and its linearized form may be represented by Eq. (1):

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (\text{non-linear form}) \quad (1)$$

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (\text{linear form}) \quad (2)$$

where k_1 (min^{-1}) is the rate constant for the pseudo-first-order kinetics model, q_e (mg/g), q_t (mg/g) are the amounts of AB113 retained on weight unit of adsorbent at equilibrium and at any time t (min), respectively.

The plot of $\ln(q_e - q_t)$ vs. contact time t for dried tea waste gives a straight line of slope $-k_1$ and intercepts $\ln q_e$ (Fig. 8). The values of the theoretical adsorption capacity ($q_{e,cal}$), the rate constant for the pseudo-first-order kinetics model (k_1) and the correlation coefficient (R^2) were presented in Table 2. Table 2 shows that the value of q_e is not quite similar to the experimental value ($q_{cal} = 2.72$ mg/g $<$ $q_{exp} = 3.218$ mg/g), suggesting the insufficiency of pseudo-first-order model.

We find that under these conditions, the pseudo-first-order model is not adequate to describe the adsorption kinetics of AB113 from aqueous solutions onto dried tea waste as a natural adsorbent.

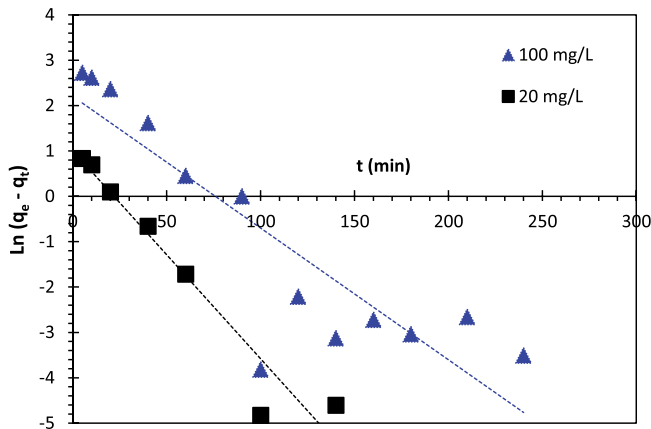


Fig. 8. Pseudo-first-order adsorption kinetics of Acid Blue 113 onto dried tea waste at different dye concentration.

Table 2

Parameters of four kinetic models for Acid Blue 113 dye adsorption onto dried tea waste at different initial dye concentrations

Kinetic models	Parameters	Acid Blue 113 dye concentration	
		20 mg/L	100 mg/L
Pseudo-first-order			
	k_1 (min ⁻¹)	0.046	0.049
	$q_{e,cal}$ (mg/g)	2.728	9.057
	R^2	0.934	0.778
Pseudo-second-order			
	k_2 (g/mg·min)	0.026	0.001
	$q_{e,cal}$ (mg/g)	3.432	20.618
	R^2	0.998	0.971
Elovich			
	α	0.905	0.286
	β	1.565	0.220
	R^2	0.911	0.925
Intraparticle diffusion			
Region I	k_{PI} (mg/g·min ^{1/2})	0.402	2.570
	c_I	0.069	-4.618
	R^2	0.967	0.994
Region II	k_{PII} (mg/g·min ^{1/2})	0.004	0.010
	c_{II}	3.170	16.754
	R^2	0.291	0.413
Exp. adsorption capacity ($q_{e,exp}$, mg/g)		3.218	16.956

3.5.2. Pseudo-second-order kinetics model

In case of pseudo-second-order kinetics model, the rate equation and its linearized form may be formulated by Eq. (3):

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (\text{non-linear form}) \quad (3)$$

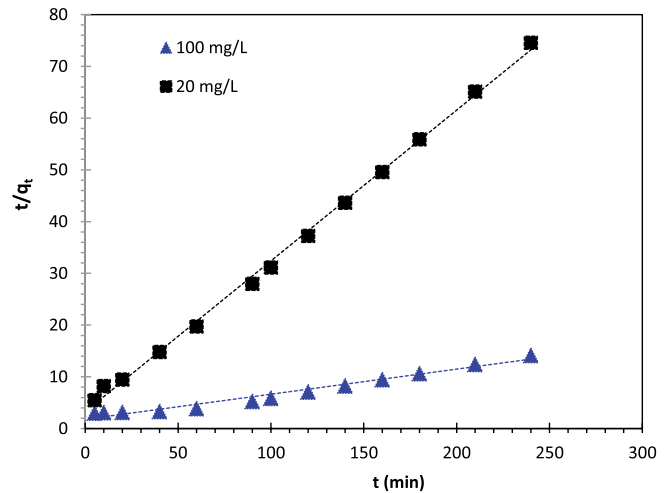


Fig. 9. Pseudo-second-order adsorption kinetics of Acid Blue 113 onto dried tea waste at different dye concentrations.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e}\right)t \quad (\text{linear form}) \quad (4)$$

where k_2 (g/mg·min) is the rate constant for the pseudo-second-order kinetics model, q_e (mg/g), q_t (mg/g) are the amounts of AB113 retained on weight unit of adsorbent at equilibrium and at any contact time t (min), respectively. The pseudo-second-order plots for AB113 adsorption system at different initial concentrations are presented in Fig. 9 and the kinetic parameters are given in Table 2. The correlation coefficient for the pseudo-second-order kinetic model is nearly equal to 1 and the value of calculated amount adsorbed $q_{e,cal}$ is comparable to the experimental one ($q_{e,cal} = 3.432$ mg/g).

Therefore, it was concluded that the pseudo-second-order adsorption model is more appropriate to describe the adsorption kinetics of AB113 dye on dried tea waste.

3.5.3. Elovich kinetics model

The Elovich model is valid for systems with heterogeneous surface and it is suitable for chemisorption kinetics. The kinetics equation Elovich model and its linearized form may be expressed as:

$$\frac{dq_t}{dt} = \alpha e^{-\beta q_t} \quad (\text{non-linear form}) \quad (5)$$

$$q_t = \frac{\ln(\alpha\beta)}{\beta} + \frac{1}{\beta} \ln(t) \quad (\text{linear form}) \quad (6)$$

where q_e (mg/g) and q_t (mg/g) are the amounts of AB113 dye adsorbed at equilibrium and at any contact time t (min), respectively. α (mg/g·min) is the initial adsorption rate and β (g/mg) is the desorption constant related to the extent of the surface coverage and activation energy for chemisorption. The Elovich kinetic constants α and β are obtained from the intercept and the slope, respectively (Fig. 10). The correlation coefficient indicates that the Elovich model is

not adequate to characterize the AB113 adsorption on dried tea waste.

3.5.4. Intraparticle diffusion kinetics model

The intraparticle diffusion model is of significant interest because internal diffusion determines the adsorption rate in most liquid systems. The initial rate of intraparticle diffusion is calculated by linearization of Eq. (7) [36]:

$$q_t = k_p t^{1/2} + c \quad (\text{linear form}) \quad (7)$$

where k_p (mg/g·min^{1/2}) is the intraparticle diffusion rate constant, c (mg/g) is the concentration of AB113 from solution at equilibrium and q_t (mg/g) is the amount of AB113 retained on weight unit of adsorbent at contact time t (min). The graphical representation is given in Fig. 11.

The intraparticle diffusion, k_p , values were obtained from the slope of the straight-line portions of plot of q_t vs. $t^{1/2}$ for various solutions temperature. The correlation coefficients (R^2) indicates that the intraparticle diffusion model

is not suitable to describe the kinetics of AB113 adsorption from aqueous solutions on dried tea waste as natural adsorbent. The values of k_p and c , calculated from the slopes and intercepts are summarized in Table 2.

3.6. Adsorption isotherm models

Adsorption isotherms are mathematical models that describe the distribution of adsorbed species between the solid and liquid phases, and are significant data for studying the adsorption mechanism. In this study, the Langmuir, Freundlich, Temkin and Dubinin–Radushkevich equations were used to describe the relationship between the adsorption of AB113 dye on dried tea waste and its equilibrium concentration in solution. This study was performed by ranging the initial ion concentration from 20 to 200 mg/L at different temperatures and a natural pH of 6.3.

3.6.1. Langmuir adsorption isotherm

The Langmuir adsorption isotherm [7,37,38] supposes that the solid surface has a finite number of identical sites, which shows homogeneous surfaces. The Langmuir equation and its linearized form may be represented by Eqs. (8) and (9):

$$q_e = q_L \frac{K_L C_e}{1 + K_L C_e} \quad (\text{non-linear form}) \quad (8)$$

$$\frac{1}{q_e} = \frac{1}{q_L} + \frac{1}{q_L K_L C_e} \quad (\text{linear form}) \quad (9)$$

where q_e (mg/g) is the amount adsorbed at equilibrium concentration C_e (mg/L), q_L (mg/g) is the Langmuir constant representing maximum monolayer capacity, and K_L (L/mg) is the Langmuir constant related to energy of adsorption [39]. The plots between $1/q_e$ and $1/C_e$ for the adsorption of AB113 are drawn in Fig. 12. The values of the adsorption capacity (q_L), the Langmuir constant (K_L), and the correlation

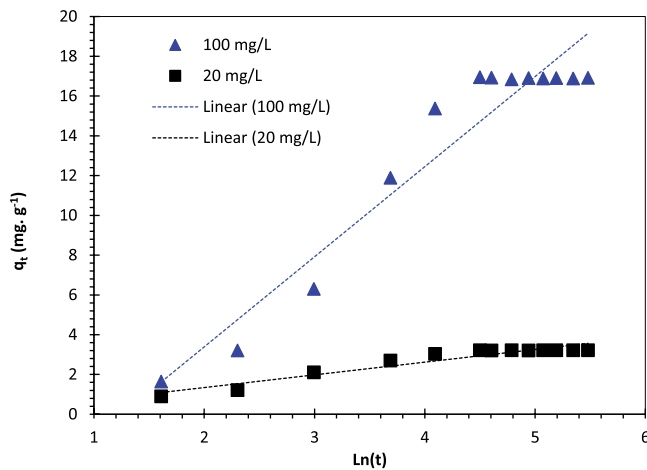


Fig. 10. Elovich adsorption kinetics of Acid Blue 113 dye onto dried tea waste at different dye concentrations.

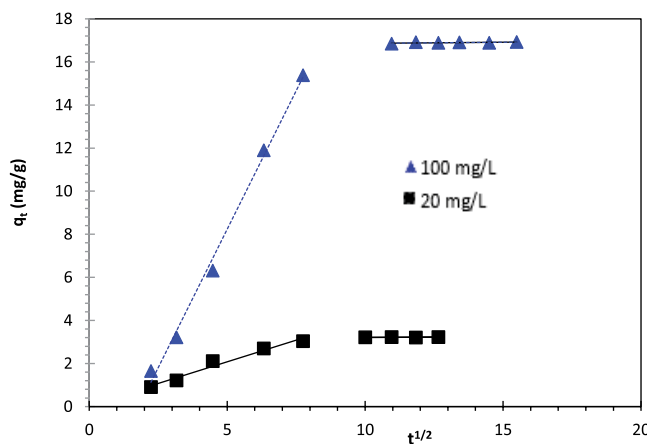


Fig. 11. Intraparticle diffusion kinetics model of Acid Blue 113 dye onto dried tea waste at different dye concentrations.

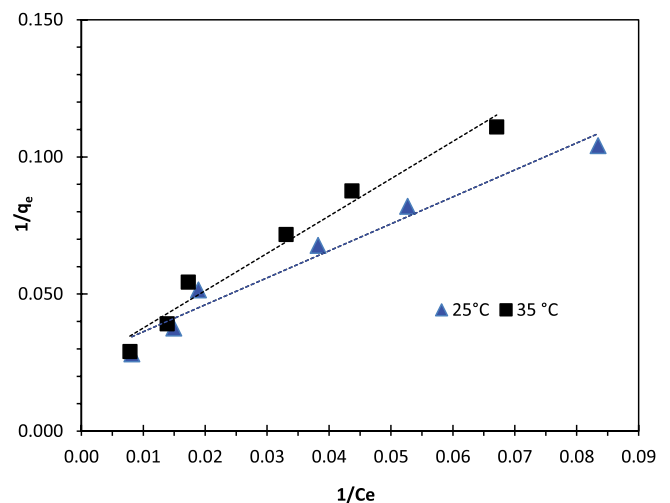


Fig. 12. Langmuir adsorption isotherm of Acid Blue 113 onto dried tea waste at different temperatures.

coefficient (R^2) are presented in Table 3. The Langmuir model is an indication of surface homogeneity of the adsorbent.

The basic assumption of Langmuir adsorption isotherm is also based on monolayer coverage of the adsorbate on the surface of adsorbent. The adsorption capacity of adsorbent decreased on increasing the temperature. The highest value of q_L obtained at 25°C was 37.87 mg/g (Table 3).

The essential feature of the Langmuir isotherm can be expressed by means of ' R_L ', a dimensionless constant referred to as separation factor or equilibrium parameter to predicting whether an adsorption system is favorable or unfavorable. R_L is calculated using Eq. (10) [40]:

$$R_L = \frac{1}{1 + K_L C_0} \tag{10}$$

where K_L (L/mol) is Langmuir constant and C_0 (mol/L) the highest initial anionic dye concentration. According to the value of R_L , the isotherm shape may be interpreted as shown in Table 4 [41].

The calculated values of parameter R_L for this study was found to be 0.11 and 0.16 for 25°C and 35°C (between 0 and 1), indicating that the adsorption of AB113 dye onto dried tea waste particles was favourable.

3.6.2. Freundlich adsorption isotherm

The Freundlich equation provides the most suitable adsorption data for heterogeneous natural adsorbent s. The Freundlich adsorption isotherm equation and its linear form can be written by Eqs. (11) and (12) [42]:

$$q_e = K_F C_e^{1/n} \quad (\text{non-linear form}) \tag{11}$$

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (\text{linear form}) \tag{12}$$

where q_e (mg/g) is the amount of AB113 adsorbed per unit weight of adsorbent; C_e (mg/L) is the equilibrium concentration of solute in the bulk solution; K_F (mg/g) is the Freundlich constant, which is a comparative measure of the adsorption capacity of the adsorbent, and n is an empirical constant related to heterogeneity of the adsorbent surface. The parameter n also indicates the nature of the adsorption process. The value of n lies between 0 and 1 for a favorable adsorption, while $n > 1$ represents an unfavorable adsorption, and $n = 1$ represents the linear adsorption, while the adsorption operation is irreversible if $n = 0$. The isotherm constants n and K_F were calculated from the slope and intercept of the plot $\ln q_e$ vs. $\ln C_e$ (Fig. 13). The values for Freundlich constants and correlation coefficients (R^2) for both temperatures are also presented in Table 3.

The Freundlich isotherm constants K_F and n are constants incorporating all factors affecting the adsorption process such as of adsorption capacity and intensity of adsorption.

The constants K_F and n were calculated from Eq. (12). These experiments confirm the efficiency of the dried tea waste to remove acid dyes from aqueous solutions.

3.6.3. Temkin isotherm

The Temkin adsorption isotherm model is based on the heat of pollutant adsorption, which is due to the

Table 3
Parameters of four isotherms for Acid Blue 113 dye adsorption onto dried tea waste at different temperatures

Isotherms	Parameters	Temperature	
		298 K	308 K
Langmuir			
	K_L (L/mg)	0.027	0.017
	$q_{e,cal}$ (mg/g)	37.87	41.66
	R^2	0.965	0.971
Freundlich			
	K_F (mg/g)	2.34	1.525
	n	1.781	1.55
	R^2	0.985	0.976
Temkin			
	K_T (L/mg)	0.916	0.851
	b_T (J/mol)	227.05	194.09
	R^2	0.935	0.942
Dubinin–Radushkevich			
	K_D (mol ² /J ²)	3×10^{-5}	4×10^{-5}
	q_m (mg/g)	9.676	8.623
	E (J/mol)	129.09	111.80
	R^2	0.711	0.729

Table 4
Type of isotherm for different values of R_L

Value of R_L	Type of isotherm
$R_L > 1$	Unfavourable
$R_L = 1$	Linear
$0 < R_L < 1$	Favourable
$R_L = 0$	Irreversible

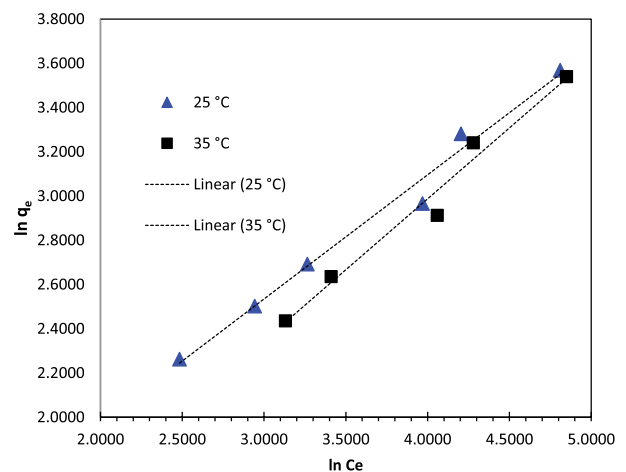


Fig. 13. Freundlich adsorption isotherm of Acid Blue 113 dye onto dried tea waste at different temperatures.

interactions between the adsorbate and the adsorbent [7,31]. The Temkin isotherm equation is given by Eqs. (13) and (14):

$$q_e = \frac{RT}{b_T} \ln K_T C_e \quad (\text{non-linear form}) \quad (13)$$

$$q_e = \frac{RT}{b_T} \ln K_T + \frac{RT}{b_T} C_e \quad (\text{linear form}) \quad (14)$$

where T is absolute temperature in Kelvin and R the universal gas constant (8.314 J/mol·K). b_T (J/mol) is Temkin isotherm constant related to the heat of adsorption. K_T (L/mg) is the equilibrium binding constant corresponding to the maximum binding energy. The Temkin isotherm plot for dye-dried tea waste system at different temperatures are presented in Fig. 14 and the isotherm parameters are given in Table 3. The Temkin constants b_T related to heat of adsorption for both temperatures were found to be 227.05 and 194.09 J/mol for 25°C and 35°C, respectively.

Linear regression of the data points showed rather low R^2 values ranging from 0.93 to 0.926, indicating that the adsorption of AB113 dye did not fully follow the Temkin isotherm.

3.6.4. Dubinin–Radushkevich isotherm

Dubinin–Radushkevich isotherm is commonly used to express the adsorption mechanism with a Gaussian energy distribution onto a heterogeneous surface [43]. It is not based on the assumption of homogeneous surface or constant adsorption potential, but it is applied to estimate the mean free energy of adsorption (E). The non-linear and linear forms of Dubinin–Radushkevich equation can be written by Eqs. (15) and (16) [44]:

$$q_e = q_m e^{-K_D \varepsilon^2} \quad (\text{non-linear form}) \quad (15)$$

$$\ln q_e = \ln q_m - K_D \varepsilon^2 \quad (\text{linear form}) \quad (16)$$

where q_m (mg/g) is the theoretical saturation capacity and ε is the Polanyi potential that can be calculated from Eq. (17):

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (17)$$

The constant K_D (mol²/J²) gives an idea about the mean free energy E (kJ/mol) of adsorption per molecule of the adsorbate when it is transferred to the surface of the solid from infinity in the solution and can be calculated from the K_D value using Eq. 18:

$$E = \frac{1}{(2K_D)^{1/2}} \quad (18)$$

This parameter gives information on the adsorption mechanism if it is a chemical ion exchange or a physical adsorption. If the value of E is between 8 and 16 kJ/mol, the adsorption process is expected to be chemisorption, while for values of $E < 8$ kJ/mol, the adsorption process is physical in nature [44]. The results are illustrated in Table 3.

The slope of the plot of $\ln q_e$ vs. ε^2 gives K_D and the intercept yields the adsorption capacity q_m . As can be seen in Fig 15 and Table 3, the correlation coefficient values are 0.968 and 0.878 for 25°C and 35°C, respectively. The numerical value of adsorption of the mean free energy is 129.09 and 111.80 J/mol for 25°C and 35°C, respectively (Table 3) corresponds to a physisorption and the predominance of van der Waals forces.

3.7. Adsorption thermodynamic study

The thermodynamic parameters such as standard Gibbs free energy change (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) were calculated from Eqs. (19)–(21) [45]:

$$\Delta G^\circ = -RT \ln(K_d) \quad (19)$$

$$\ln(K_d) = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (20)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (21)$$

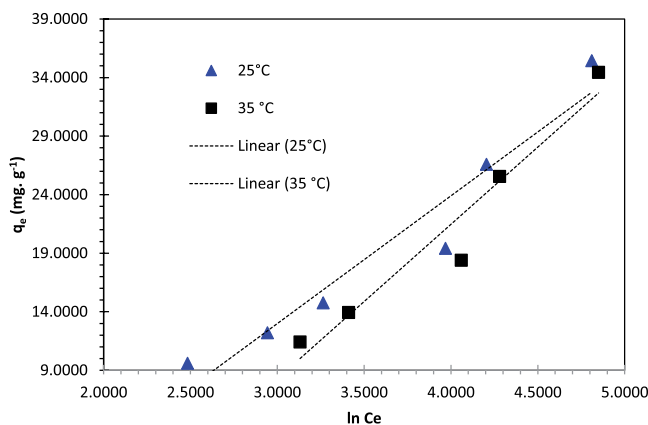


Fig. 14. Temkin adsorption isotherm of Acid Blue 113 dye onto dried tea waste at different temperatures.

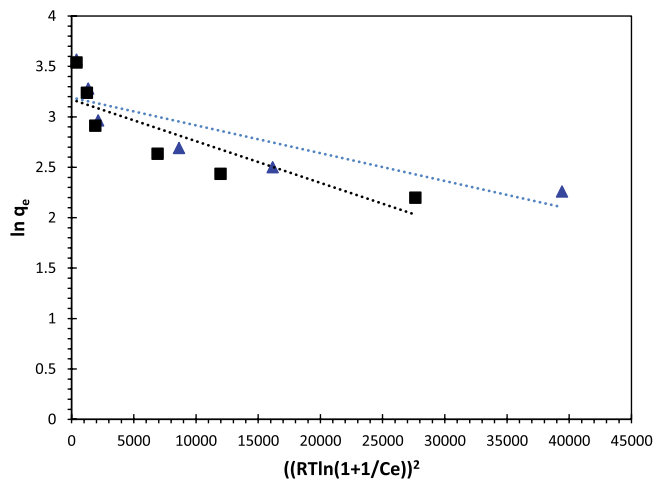


Fig. 15. Dubinin–Radushkevich adsorption isotherm of Acid Blue 113 dye onto dried tea waste at different temperatures.

Table 5
Thermodynamic parameters for Acid Blue 113 dye adsorption onto dried tea waste

T (K)	K_d (L/mol)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/K·mol)
298	5.95	-14.75		
303	5.83	-14.69	-14.67	0.178
308	5.74	-14.73		
313	5.66	-14.74		

where T is the absolute temperature in K and R the universal gas constant (8.314 J/mol·K). K_d (L/mol) is the distribution coefficient. The obtained results for thermodynamic parameters are reported in Table 5. The negative value of ΔH° suggests the adsorption to be physical and exothermic process which is consistent with experimental observations [46]. The negative ΔG° values show spontaneous nature of adsorption process and the positive value of entropy (ΔS°) revealed that the degrees of free active sites increased at the solid–liquid interface during the adsorption of anionic dye onto dried tea waste [47,48].

3.7.1. Desorption and regeneration studies

In order to consider the practical usefulness of the adsorbent, desorption experiment as performed. After the adsorption test in optimal conditions. Desorption of AB113 dye was carried out as follows: a series of an Erlenmeyer that contained 0.2 g of adsorbent were treated with 40 mL of solution dye (100 mg/L). AB113 dye loaded adsorbent was filtered after optimal condition of contact time and washed gently several times with double distilled water to remove any excess of un-adsorbed AB113 dye. It was then treated with 20 mL of hydroxide solution at different concentrations (0.01–0.07 M) for a period equal to the adsorption time and then filtered. The volumes used for adsorption and for desorption were, respectively, $V_a = 40$ mL and $V_d = 20$ mL and the ratio V_d/V_a equaled 0.5. The amounts desorbed of AB113 are calculated by the following equation [49]:

$$\% \text{ Desorption} = \frac{C_a}{C_d} \times 100$$

where C_a (mg/L) and C_d (mg/L) are concentrations adsorbed and desorbed of AB113 dye, respectively.

Regeneration of dried tea waste is an important step in order to check in economic the feasibility of adsorption process. Desorption of AB113 dye from dried tea waste using NaOH as an eluent at concentration from 0.01 to 0.07 M, as indicated in Table 6.

The results show that the maximum desorption of AB113 dye (82.345%), was obtained with 0.07 M of NaOH. After each test of desorption using NaOH (0.07 M), the support washed with distilled water several times to remove traces of NaOH, then dried in an oven for 24 h. After drying tea waste reuse for the adsorption of AB113 in optimal conditions. The results obtained are presented in Fig. 16. The result that tea waste are employed at least 4 cycles desorption–adsorption without losing their desorption efficiency of AB113 dye.

Table 6
Desorption of Acid Blue 113 from tea waste using NaOH

Concentration of NaOH (M)	0.01	0.02	0.03	0.05	0.07
% Desorption	61.554	66.541	76.887	80.354	82.345

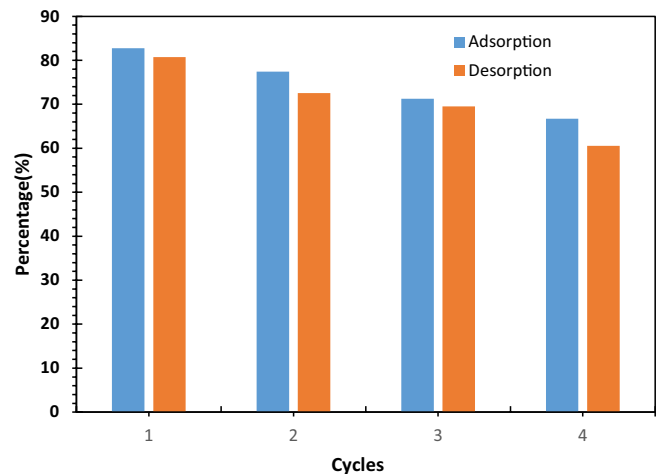


Fig. 16. Regeneration of dried tea waste using NaOH (0.07 M).

Table 7
Comparison of maximum uptakes (q_m , mg/g) of various adsorbents to remove Acid Blue 113 anionic dye

Adsorbent	q_m (mg/g)	References
Rubber tire activated carbon	9.20	[50]
Commercial activated carbon	7.19	[50]
Potato peel waste biomass	11.71	[51]
<i>Carpobrotus edulis</i> plant	8.20	[2]
<i>Corallina officinalis</i> alga	11.79	[52]
Tea waste	37.87	This study

3.7.2. Comparison with published data

In order to situate our adsorbent among those used to remove AB113 dye from aqueous solutions, the maximum experimental adsorption capacity of tea waste adsorbent was compared to the maximum uptakes (q_m , mg/g) of other adsorbents reported in literature. The adsorption of AB113 anionic dye on different adsorbents reported in the literature are presented in Table 7. The q_m of this study was found to be comparable with those of other adsorbents. The results indicated that tea waste adsorbent has a great potential to be used in the treatment of dye-contaminated wastewater.

4. Conclusions

This study explored the equilibrium and adsorption dynamics of industrial Acid Blue 113 dye from aqueous solutions using the batch equilibration technique. Adsorption is significantly dependent on pH, contact time,

and temperature. The adsorption of AB113 was exothermic in nature, with the removal capacity of the dye decreasing with increasing temperature due to the increasing mobility of the dye molecules. The pseudo-second-order kinetic model fits very well with the kinetic behavior of the adsorption of AB113 on dried tea waste at different values of the initial dye concentration. The Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich adsorption models were employed for the mathematical description of the adsorption equilibrium of this dye. The experimental data fitted well to the Langmuir adsorption isotherm. The kinetics of adsorption of AB113 on dried tea waste was studied by using four kinetic models. The adsorption occurs according to the pseudo-second-order model which provides the best correlation of the data in all cases and the experimental values of $q_{e,exp}$ are in accordance with those calculated. The negative values of ΔG° demonstrate the spontaneous nature of the adsorption process and the positive value of entropy (ΔS°) revealed that the degrees of free active sites increased at the solid–liquid interface during the adsorption of the anionic dye onto the dried tea waste.

Symbols

AB113	—	Acid Blue 113 dye
C_0	—	Initial dye concentration, mg/L
C_e	—	Equilibrium dye concentration, mg/L
q_e	—	Equilibrium uptake of Acid Blue 113 dye adsorbed, mg/g
q_m	—	Maximum adsorption capacity, mg/g
T	—	Absolute temperature, K
R	—	Universal gas constant, 8.314 J/(mol·K)
K_L	—	Langmuir constant related to the free adsorption energy, L/mg
R_L	—	Separation factor in Langmuir isotherm model
K_F	—	Freundlich constant indicative of the relative adsorption capacity of the adsorbent, mg/g
ΔH°	—	Enthalpy change
ΔS°	—	Entropy change
ΔG°	—	Gibbs free energy change

References

- [1] M.T. Uddin, M.A. Islam, S. Mahmud, M. Rukanuzzaman, Adsorptive removal of methylene blue by tea waste, *J. Hazard. Mater.*, 164 (2009) 53–60.
- [2] R. Aziam, M. Chiban, E. Eddaoudi, A. Soudani, M. Zerbet, F. Sinan, Factors controlling the adsorption of Acid Blue 113 dye from aqueous solution by dried *C. edulis* plant as natural adsorbent, *Arabian J. Geosci.*, 9 (2016) 659, doi: 10.1007/s12517-016-2675-4.
- [3] T. Akar, T.A. Demir, I. Kiran, A. Ozcan, A.S. Ozcan, S. Tunali, Biosorption potential of *Neurospora crassa* cells for decolorization of Acid Red 57 (AR57) dye, *J. Chem. Technol. Biotechnol.*, 81 (2006) 1100–1106.
- [4] M. Ghaedi, B. Sadeghian, A.A. Pebdani, R. Sahraei, A. Daneshfar, C.E.L.A.L. Duran, Kinetics, thermodynamics and equilibrium evaluation of Direct Yellow 12 removal by adsorption onto silver nanoparticles loaded activated carbon, *Chem. Eng. J.*, 187 (2012) 133–141.
- [5] M. Chiban, A. Soudani, M. Zerbet, F. Sinan, Chapter 10 – Wastewater Treatment Processes, J. Valdez, E.M. Maradona, Eds., *Handbook of Wastewater Treatment: Biological Methods, Technology and Environmental Impact*, Nova Science Publishers, USA, 2013, pp. 249–262.
- [6] V.K. Gupta, I. Tyagi, S. Agarwal, R. Singh, M. Chaudhary, A. Harit, S. Kushwaha, Column operation studies for the removal of dyes and phenols using a low-cost adsorbent, *Global J. Environ. Sci. Manage.*, 2 (2016) 1–10, doi: 10.7508/gjesm.2016.01.001.
- [7] R. Aziam, M. Chiban, E. Eddaoudi, A. Soudani, M. Zerbet, F. Sinan, Kinetic modeling, equilibrium isotherm and thermodynamic studies on a batch adsorption of anionic dye onto eco-friendly dried *Carpobrotus edulis* plant, *Eur. Phys. J. Spec. Top.*, 226 (2017) 977–992.
- [8] A.A. Adeyemo, I.O. Adeoye, O.S. Bello, Adsorption of dyes using different types of clay: a review, *Appl. Water Sci.*, 7 (2017) 543–568.
- [9] K. Ravikumar, B. Deebika, K. Balu, Decolourization of aqueous dye solutions by a novel adsorbent: application of statistical designs and surface plots for the optimization and regression analysis, *J. Hazard. Mater.*, 122 (2005) 75–83.
- [10] M. Arami, N.Y. Limaee, N.M. Mahmoodi, N.S. Tabrizi, Removal of dyes from colored textile wastewater by orange peel adsorbent: equilibrium and kinetic studies, *J. Colloid Interface Sci.*, 288 (2005) 371–376.
- [11] G. McKay, J.F. Porter, G.R. Prasad, The removal of dye colours from aqueous solutions by adsorption on low-cost materials, *Water Air Soil Pollut.*, 114 (1999) 423–438.
- [12] K. Okada, N. Yamamoto, Y. Kameshima, A. Yasumori, Adsorption properties of activated carbon from waste newspaper prepared by chemical and physical activation, *J. Colloid Interface Sci.*, 262 (2003) 194–199.
- [13] K.G. Akpomie, J. Conradie, Banana peel as a biosorbent for the decontamination of water pollutants. A review, *Environ. Chem. Lett.*, 18 (2020) 1085–1112.
- [14] A.D. Rosanti, Y. Kusumawati, F. Hidayat, A. Fadlan, A.R. Wardani, H.A. Anggraeni, Adsorption of Methylene Blue and Methyl Orange from aqueous solution using orange peel and CTAB-modified orange peel, *J. Turk. Chem. Soc. Sect. A Chem.*, 9 (2022) 237–246.
- [15] G. Annadurai, R.S. Juang, D.J. Lee, Use of cellulose-based wastes for adsorption of dyes from aqueous solutions, *J. Hazard. Mater.*, 92 (2002) 263–274.
- [16] Y.S. Ho, G. McKay, Kinetic models for the sorption of dye from aqueous solution by wood, *Process Safety Environ. Prot.*, 76 (1998) 183–191.
- [17] C.D. Woolard, J. Strong, C.R. Erasmus, Evaluation of the use of modified coal ash as a potential sorbent for organic waste streams, *Appl. Geochem.*, 17 (2002) 1159–1164.
- [18] R. Sadki, M. Dalimi, N. Labjar, G.A. Benabdallah, S. El Hajjaji, Adsorptive removal of Methylene Blue, from aqueous solution using tea waste as a low-cost indigenous biosorbent: mechanism of adsorption, equilibrium study, kinetics and isotherms, *Moroccan J. Chem.*, 11 (2023), doi: 10.48317/IMIST.PRSM/morjchem-v11i03.38683.
- [19] M. El Alouani, S. Alehyen, B. Aouan, J. Mabrouki, H. Saufi, Application of mesoporous fly ash as a low-cost adsorbent for effective removal and immobilization of hazardous pollutants in aqueous environments, *Model. Earth Syst. Environ.*, 9 (2023) 3539–3552.
- [20] P. Babaei, J. Safaei-Ghomi, Engineered N-doped graphene quantum dots/CoFe₂O₄ spherical composites as a robust and retrievable catalyst: fabrication, characterization, and catalytic performance investigation in microwave-assisted synthesis of quinoline-3-carbonitrile derivatives, *RSC Adv.*, 11 (2021) 34724–34734.
- [21] Y. Wei, X. Yin, H. Wu, M. Zhao, J. Huang, J. Zhang, T. Li, J. Ning, Improving the flavor of summer green tea (*Camellia sinensis* L.) using the yellowing process, *Food Chem.*, 388 (2022) 132982, doi: 10.1016/j.foodchem.2022.132982.
- [22] M.H. Tahir, T. Mubashir, M.B. Hussain, X. Cheng, A. Karim, N. Ali, M. Jamil, A.M. Khan, R.M. Irfan, Selective catalytic conversion of tea waste biomass into phenolic-rich bio-oil and subsequent extraction, *J. Anal. Appl. Pyrolysis*, 159 (2021) 105315, doi: 10.1016/j.jaap.2021.105315.
- [23] A. Ullah, M. Zahoor, W.U. Din, M. Muhammad, F.A. Khan, A. Sohail, R. Ullah, E.A. Ali, H.A. Murthy, Removal of

- methylene blue from aqueous solution using black tea wastes: used as efficient adsorbent, *Adsorpt. Sci. Technol.*, 2022 (2022) 5713077, doi: 10.1155/2022/5713077.
- [24] K.S. Hameed, P. Muthirulan, M.M. Sundaram, Adsorption of chromotrope dye onto activated carbons obtained from the seeds of various plants: equilibrium and kinetics studies, *Arabian J. Chem.*, 10 (2017) S2225–S2233.
- [25] A.R. Dinçer, Y. Güneş, N. Karakaya, Coal-based bottom ash (CBBA) waste material as adsorbent for removal of textile dyestuffs from aqueous solution, *J. Hazard. Mater.*, 141 (2007) 529–535.
- [26] S.N. Jain, S.R. Tamboli, D.S. Sutar, S.R. Jadhav, J.V. Marathe, A.A. Shaikh, A.A. Prajapati, Batch and continuous studies for adsorption of anionic dye onto waste tea residue: kinetic, equilibrium, breakthrough and reusability studies, *J. Cleaner Prod.*, 252 (2020) 119778, doi: 10.1016/j.jclepro.2019.119778.
- [27] S. Parvin, B.K. Biswas, Md.A. Rahman, Md.H. Rahman, Md.S. Anik, Md.R. Uddin, Study on adsorption of Congo red onto chemically modified egg shell membrane, *Chemosphere*, 236 (2019) 124326, doi: 10.1016/j.chemosphere.2019.07.057.
- [28] E.N. El Qada, S.J. Allen, G.M. Walker, Adsorption of basic dyes from aqueous solution onto activated carbons, *Chem. Eng. J.*, 135 (2008) 174–184.
- [29] S. Mandal, J. Calderon, S.B. Marpu, M.A. Omary, S.Q. Shi, Mesoporous activated carbon as a green adsorbent for the removal of heavy metals and Congo red: characterization, adsorption kinetics, and isotherm studies, *J. Contam. Hydrol.*, 243 (2021) 103869, doi: 10.1016/j.jconhyd.2021.103869.
- [30] M. Morghi, F. Abidar, A. Soudani, M. Zerbet, M. Chiban, H. Kabli, F. Sinan, Removal of nitrate ions from aqueous solution using chitin as natural adsorbent, *Int. J. Res. Environ. Stud.*, 2 (2015) 8–20.
- [31] K.Y. Foo, B.H. Hameed, An overview of dye removal via activated carbon adsorption process, *Desal. Water Treat.*, 19 (2010) 255–274.
- [32] J. Wang, X. Guo, Adsorption kinetic models: physical meanings, applications, and solving methods, *J. Hazard. Mater.*, 390 (2020) 122156, doi: 10.1016/j.jhazmat.2020.122156.
- [33] S. Lagergren, Zur theorie der sogenannten adsorption gelöster stoffe, *Kungliga Svenska Vetenskapsakademiens Handlingar*, 24 (1898) 1–39.
- [34] W.J. Weber Jr., J.C. Morris, Kinetics of adsorption on carbon from solution, *J. Sanit. Eng. Div.*, 89 (1963) 31–59.
- [35] Y.S. Ho, Review of second-order models for adsorption systems, *J. Hazard. Mater.*, 136 (2006) 681–689.
- [36] R. Shokoohi, H. Farji, S.A. Ghiasian, J. Faradmal, S. Azizi, M. Salari, Evaluation of ability of *Aspergillus terreus* fungi in removal of cadmium from aquatic solutions: isotherm and kinetic studies, *J. Res. Environ. Health*, 3 (2017) 126–135.
- [37] I. Langmuir, The constitution and fundamental properties of solids and liquids. Part I. Solids, *J. Am. Chem. Soc.*, 38 (1916) 2221–2295.
- [38] M.M. Majd, V. Kordzadeh-Kermani, V. Ghalandari, A. Askari, M. Sillanpää, Adsorption isotherm models: a comprehensive and systematic review (2010–2020), *Sci. Total Environ.*, 812 (2022) 151334, doi: 10.1016/j.scitotenv.2021.151334.
- [39] Y.N. Chen, L.Y. Chai, Y.D. Shu, Study of arsenic(V) adsorption on bone char from aqueous solution, *J. Hazard. Mater.*, 160 (2008) 168–172.
- [40] T.W. Weber, R.K. Chakravorty, Pore and solid diffusion models for fixed-bed adsorbers, *AIChE J.*, 20 (1974) 228–238.
- [41] Y. Bulut, N. Gözübenli, H. Aydın, Equilibrium and kinetics studies for adsorption of Direct Blue 71 from aqueous solution by wheat shells, *J. Hazard. Mater.*, 144 (2007) 300–306.
- [42] H. Freundlich, Over the adsorption in solution, *J. Phys. Chem.*, 57 (1906) 1100–1107.
- [43] A. Günay, E. Arslankaya, I. Tosun, Lead removal from aqueous solution by natural and pretreated clinoptilolite: adsorption equilibrium and kinetics, *J. Hazard. Mater.*, 146 (2007) 362–371.
- [44] B. Mahanty, S.K. Behera, N.K. Sahoo, Misinterpretation of Dubinin–Radushkevich isotherm and its implications on adsorption parameter estimates, *Sep. Sci. Technol.*, 58 (2023) 1275–1282.
- [45] M.S. Gohr, A.I. Abd-Elhamid, A.A. El-Shanshory, H.M. Soliman, Adsorption of cationic dyes onto chemically modified activated carbon: kinetics and thermodynamic study, *J. Mol. Liq.*, 346 (2022) 118227, doi: 10.1016/j.molliq.2021.118227.
- [46] V. Gunasekar, V. Ponnusami, Kinetics, equilibrium, and thermodynamic studies on adsorption of methylene blue by carbonized plant leaf powder, *J. Chem.*, 2013 (2013) 415280, doi: 10.1155/2013/415280.
- [47] K. Polipalli, K. Pulipati, Equilibrium, kinetic and thermodynamic studies of biosorption of methylene blue dye using plant biomass as biosorbent: optimization using response surface methodology (RSM), *Int. J. Sci. Eng. Res.*, 4 (2013) 1244–1252.
- [48] S. Sahu, S. Pahi, S. Tripathy, S.K. Singh, A. Behera, U.K. Sahu, R.K. Patel, Adsorption of methylene blue on chemically modified lychee seed biochar: dynamic, equilibrium, and thermodynamic study, *J. Mol. Liq.*, 315 (2020) 113743, doi: 10.1016/j.molliq.2020.113743.
- [49] M. Chiban, G. Carja, G. Lehutu, F. Sinan, Equilibrium and thermodynamic studies for the removal of As(V) ions from aqueous solution using dried plants as adsorbents, *Arabian J. Chem.*, 9 (2016) S988–S999.
- [50] V.K. Gupta, B. Gupta, A. Rastogi, S. Agarwal, A. Nayak, A comparative investigation on adsorption performances of mesoporous activated carbon prepared from waste rubber tire and activated carbon for a hazardous azo dye—Acid Blue 113, *J. Hazard. Mater.*, 186 (2011) 891–901.
- [51] E. Hoseinzadeh, M.R. Samarghandi, G. McKay, N. Rahimi, J. Jafari, Removal of acid dyes from aqueous solution using potato peel waste biomass: a kinetic and equilibrium study, *Desal. Water Treat.*, 52 (2014) 4999–5006.
- [52] L. Boukarma, R. Aziam, S. Baroud, E. Eddaoudi, F. Sinan, I. Sadki, S. Tahrouch, M. Chiban, (2021). Kinetic and equilibrium isotherm studies for the removal of Acid Blue 113 dye by dried *Corallina officinalis* alga as a novel eco-friendly adsorbent, *E3S Web Conf.*, 240 (2021) 02004, doi: 10.1051/e3sconf/202124002004.