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Kinetic modeling, equilibrium isotherm and thermodynamic studies on a batch adsorption of anionic dye onto eco-friendly dried *Carpobrotus edulis* plant

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Abstract. In the present study, a low-cost bio-adsorbent is developed from the naturally and abundantly available dried Mediterranean plant which is biodegradable. The bio-adsorbent was characterized by Fourier transform infrared spectroscopy (FTIR) and point of zero charge (PZC). A study on the adsorption kinetics and isotherms was performed applying the optimized conditions. The equilibrium data for the adsorption of acid blue 113 on dried plant is tested with various adsorption isotherm models such as Langmuir, Freundlich, Temkin and Dubinin–Radushkevich equation. The Langmuir isotherm model is found to be the most suitable one for the acid blue 113 (AB113) adsorption using dried *C. edulis* plant and the theoretical maximum adsorption capacity obtained with the application of Langmuir isotherm model is 8.2 mg.g^{-1} at room temperature. The adsorption process follows the second-order kinetics and the corresponding rate constants are obtained. The thermodynamic parameters suggest that the adsorption process is spontaneous and exothermic nature. It can be concluded that the dried *C. edulis* adsorbent studied has good perspective to be used as adsorbent material in anionic dyes removal from industry effluents.

1 Introduction

Dyes are an important class of organic pollutants and are well known for their hazardous effects on aquatic life in general and human beings in particular [1]. In order to reduce the negative effects of dye contaminated wastewater on humans and the environment, the wastewater must be treated carefully before discharge into main streams. Currently, much attention has been paid to the removal of dyes from industrial wastewater [2]. Various chemical, physical and biological treatment methods have been developed for the removal of dyes from aqueous solution, including precipitation, coagulation, flocculation, reverse osmosis, degradation, anion exchanging,

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membrane separation and bacterial cells application [3–7]. Adsorption has proven to be a reliable treatment methodology due to its low capital investment cost, simplicity of design, ease of operation and insensitivity to toxic substances, but its application is limited by the high price of some adsorbent and the large amount of wastewater normally involved. Activated carbon and clay minerals are among the adsorptive materials that have been tested for the decolourization of dye effluents [8,9]. In the last few years agricultural solid wastes have been used intensely as low-cost, available adsorbents for the adsorption of anionic dyes such as mango seed [10], soy meal [11], bagasse [12,13], bamboo [14], by palm kernel fibre [15], tea waste [16] red mud [17] and dried *Lemna minor* biomass [18] and potato peel waste [19]. In this regard, much attention has recently been also paid to dried plants as low cost adsorbents for the removal of industrial dyes in liquid-solid interface. The water-soluble anionic dyes are commonly used to dye fabrics like wool, nylon and silk. Due to the weak interactions between the negatively charged surface in biomaterial and anionic dyes, a few studies on the adsorption of acid blue 113 dye has been carried out using natural biomaterial as an adsorbent [18–27] but none of them has investigated the kinetics, isotherms and thermodynamics of adsorption of Acid Blue 113 onto dried *C. edulis* Mediterranean plant. The choice of *C. edulis* plant is based on their relative abundance in various zones of Morocco and their abundance without any commercial importance. The study of adsorption equilibrium, isotherms and kinetics is essential in supplying the basic information required for the design and operation of adsorption equipments for wastewater treatment. Various models have been put forward to describe or predict the adsorption kinetics. The resistance models, such as the pseudo-first-order, pseudo-second-order, Elovich and intraparticle diffusion models and the adsorption isotherms including Langmuir, Freundlich, Temkin and Dubinin-Radushkevich (D-R) provide a detailed description of the adsorption. The objective of this work is to study the adsorption of Acid Blue 113 (AB113) from aqueous solutions onto dried *C. edulis* plant as low-cost bio-adsorbent. The kinetic, isotherm and thermodynamic data were also evaluated.

2 Experimental

2.1 Reagents and materials

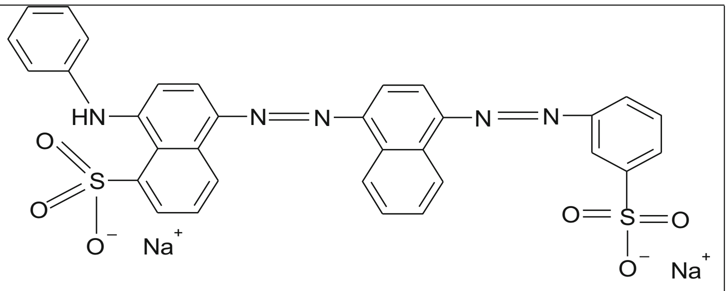
All chemical reagents were of analytical degree and were used without further purifications. The stock solution of acid blue 113 containing 500 mg.l^{-1} was prepared by double distilled water. The synthetic dye used in this study was purchased from Sigma-Aldrich. Properties of acid blue 113 dye are presented in Table 1. The working solutions were obtained by diluting the stock solution with double distilled water. The initial pH value of work solutions was found to be 6.3.

The bioadsorbent used in this study was obtained from dried plant of *Carpobrotus edulis* which is a Mediteranean plant. The microparticles of *C. edulis* plant were dried in oven at 35 °C during 24 hours and crushed with an electric grinder to get fine powders. The obtained micro-particles ($< 250\,\mu$m) were used as bio-adsorbent material in batch experiments without any other pre-treatment.

2.2 Methods

The adsorption experiments were performed by batch technique, at room temperature ($23 \pm 2\,°$C). Well established amounts of dried *C. edulis* plant were placed in Erlenmeyer glass flasks of 100 ml containing 40 ml of dye solution of known concentration

Table 1. Main properties of acid blue 113 dye.

Molecular structure	
Molecular formula	$C_{32}H_{21}N_5O_6S_2Na_2$
IUPAC name	Disodium8-anilino-5-[[4-(3-sulfonatophenyl)azo-1-naphthyl]azo]naphthalene-1-sulfonate
Synonyms	1-Napthalenesulfonic acid,8-(phenylamino)-5-[[4-[(3-sulfophenyl)azo]-1-napthalenyl]azo]-disodium salt, Acid Blue 113, Acid Fast Blue 5R
Chemical class	Anionic, Azo
Molar mass	681.65 g/mol
Solubility in water	40 g/L
Absorption maxima ($\lambda_{\max}$)	566 nm
Color index number	26360
Appearance	Dark blue powder
Nature	Was purple when dissolved in water, violet blue when dissolved in ethanol, did not dissolve in organic solvents
Uses	Used for dyeing wool, nylon and silk fabric, rayon blended fabric, and leather; also used for biological coloring of paper

and pH. The solutions were vigorously stirred for a given time period to reach equilibrium. The agitation speed was kept constant for each run to ensure equal mixing. After different contact times (t), the resulting solutions were centrifuged at 5000 rpm for 10 min and the supernatant was filtered through a 0.45 μm membrane filter and the filtrate was analyzed. The determination of acid blue 113 dye was done spectrophotometrically on a TechComp UV 2300 Spectrophotometer at the respective $\lambda_{\max}$ value, which is 566 nm for AB113. The amount of the adsorbed dye onto natural adsorbent was determined by the difference between the initial and remaining concentrations of dye solution.

The pH at the point of zero charge (pH_{pzc}) was determined by batch equilibrium method described by Abidar et al. [28]. The Fourier transform infrared (FTIR) analysis in solid phase using an infrared spectrometer (Spectrum 100 Perkin Elmer, Jasco, Japan) between wavenumbers of 4000 and 400 cm^{-1} was performed on the dried plant prepared in a KBr disk.

All experiments were conducted in duplicates and the results are reported as average (Error: ±1–2% for percentage removal and ±0.005–0.01 mg/g for amount adsorbed).

3 Results and discussion

In a previous study [29–31] it has shown that the *C. edulis* plant can be successfully used for heavy metals and dyes removal from aqueous solutions, and the efficiency of

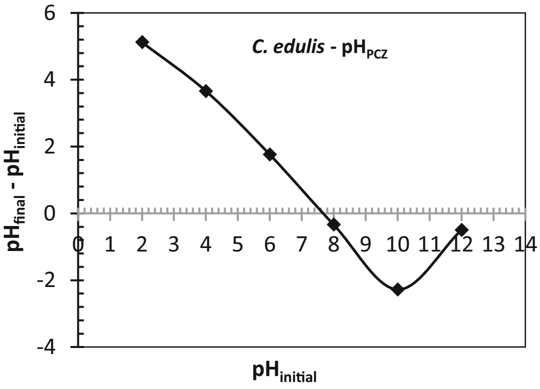


Fig. 1. pH at the point of zero charge (pH_{pzc}) of dried *C. edulis* plant.

adsorption process depends by various parameters such as the initial solution pH and adsorbent dose. On the basis of these experimental results we have considered that the optimum conditions for AB113 adsorption on dried plant are an initial solution pH = 6.3 and an adsorbent dose of 20 g.l^{-1} (0.8/40 ml).

3.1 Characteristics of the adsorbent

The point of zero charge of dried *C. edulis* plant was determined by solid addition method. In this method 50 ml of 0.01 M NaCl solutions were taken in six bottles maintained with pH in the range of 2–12 and 0.5 g of dried plant was added to each bottles. These solutions were adjusted by 0.1 M HCl/NaOH solutions. These solutions were shaken for 48 h at room temperature and the final pH of the solutions was measured. The difference between the initial and final pH was measured and the point where $\Delta pH = 0$ was taken as the point of zero charge (Fig. 1). In this study, the pH_{pzc} of dried *C. edulis* plant was found to be 7.6. This shows that at pH less than pH_{pzc} the surface of the dried plant is predominated by positive charges while at pH greater than pH_{pzc} the surface is predominated by negative charges. Thus, at pH <7.6, the surface has a high positive charge density, so the uptake of negatively charged AB113 dye would be high. At pH >7.6, the surface has a high negative charge density, so the uptake of negatively charged AB113 dye would be low.

A detailed characterization of *C. edulis* plant adsorbent has been done by different methods as it was described in our previous reports [32,33]. The result has shown that the major functional groups on *C. edulis* plant are polar hydroxyl, aldehydic and carboxylic groups, which could be responsible to pollutants removal from aqueous solutions. Selected physicochemical properties of dried *C. edulis* plant are listed in Table 2. The elemental analysis showed that the contents of C and O in dried *C. edulis* plant were higher suggesting that the former carbon possessed more oxygen-containing surface functional groups. The presence of surface functional groups was further validated by FTIR spectra (figure not shown). Several bands were associated with oxygen-containing groups. The absorption peaks at 1159.5 cm^{-1} indicates the presence of –COOH group and the peaks appeared at 1318 cm^{-1} corresponds to –OH group. The bands around 1512 cm^{-1} are indicative of amid or sulfamide groups. Moreover, the peak that appears at around 1616 cm^{-1} is due to C=O stretching vibration of a carboxylic acid and strengthening of this peak, in the case of dried plant, may be indicative for increasing number of carboxyl groups on

Table 2. Main characteristic of dried *C. edulis* plant adsorbent.

Parameters	Value
BET surface area ($m^2\,g^{-1}$)	2.6
pH_{pzc}	7.6
Elemental analysis (wt %)	
O	52.25
C	38.52
Si	2.27
Ca	2.09
K + Na + Mg + Cl + Al	3.76

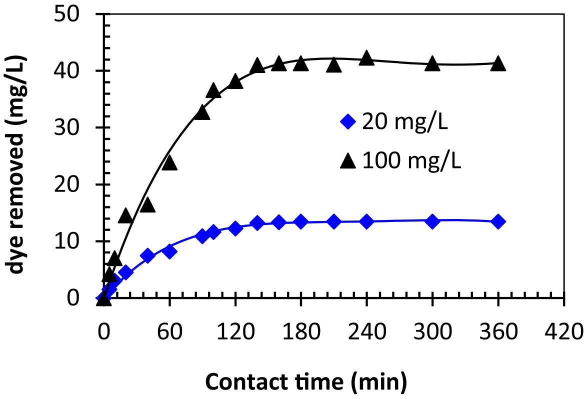


Fig. 2. Effect of contact time and initial dye concentration on the removal of AB113 by *C. edulis* plant.

cellulose or pectin chains. The peaks observed at 2919 can be assigned to the C–H group. The broad peak between 3412 and 3444 cm^{-1} is indicative of the existence of bounded hydroxyl groups of macromolecular association (cellulose, pectin, etc.). In fact, it was shown in the FTIR analysis of the dried *C. edulis* plant that these materials present a heterogeneous surface with different functional groups available to adsorb AB113 dye.

3.2 Effect of contact time and initial dye concentration

Figure 2 shows the effect of contact time on the adsorbed amount of AB113 by dried plant from solutions with different initial concentrations of dye of 20, 100 $mg\,l^{-1}$ at 25 °C. The adsorption capacity of AB113 dye increased sharply with contact time in the first 90 min and attained equilibrium within 140 min. In order to ensure a complete adsorption equilibrium, 3 h was chosen for *C. edulis* adsorbent, in each batch equilibrium adsorption experiment.

It is also clear from Figure 2 that efficiency of adsorption increased with increase in initial concentration of AB113 dye, and then the nitial concentrations of AB113 dye had no significant effect on the equilibrium time. The equilibrium adsorption amount of AB113 dye was found to increase from 0.7 to 2.1 $mg.g^{-1}$ as the initial concentration increased from 20 to 100 $mg.l^{-1}$ for dried *C. edulis* plant. The increase in the adsorption capacity is probably due to greater interaction between the adsorbate and adsorbent. The higher amount of dye adsorption at higher concentrations is probably due to increased diffusion and decreased resistance to dye uptake.

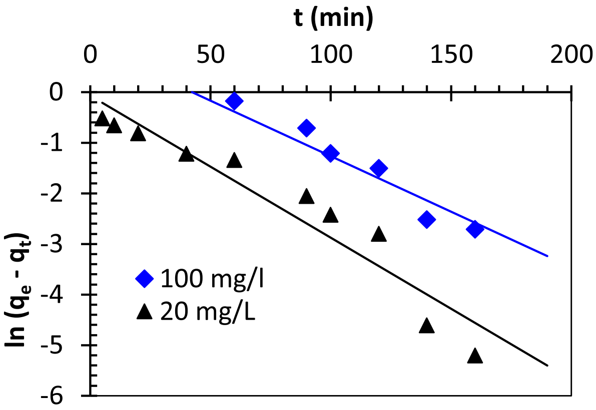


Fig. 3. Pseudo-first order adsorption kinetics of AB113 onto *C. edulis* plant at different dye concentrations.

3.3 Adsorption kinetic models

Designing of adsorption treatment systems requires knowledge of kinetic processes due to the many varied chemical systems, the nature of different adsorbents, and the different designs of contacting systems. For that reason, four liquid-phase adsorption kinetic models, pseudo-first-order model [34], pseudo-second-order model [35], Elovich model [36] and intraparticle diffusion model [37], were used in this study to analyze the adsorption kinetic experimental data.

3.3.1 Pseudo-first order kinetics model

The kinetics equation of pseudo-first order model and its linearized form may be represented as:

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

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

where, $k_1\,(\mathrm{min}^{-1})$ 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 $\ln(q_e - q_t)$ versus contact time t for dried *C. edulis* plant gives a straight line of slope $-k_1$ and intercepts $\ln q_e$ (Fig. 3). 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 3.

It can be observed from Figure 3 and Table 3, that in case of pseudo-first order kinetics model utilization, the values of correlation coefficient is lower and the value of equilibrium adsorption capacity ($q_{e,cal}$, mg.g^{-1}) calculated from this equation is much lower that the experimental value ($q_{e\ exp}$, mg.g^{-1}). Under these conditions, the pseudo-first order model is not suitable for to describe the kinetics of

Table 3. Parameters of four kinetic models for AB113 dye adsorption onto dried *C. edulis* plant at different initial dye concentrations.

Kinetic models	Parameters	AB113 concentration	
		20 mg.l^{-1}	100 mg.l^{-1}
Pseudo-first-order	$k_1 (\text{min}^{-1})$	0.028	0.022
	$q_{e\,cal}$ (mg.g^{-1})	0.93	2.53
	R^2	0.913	0.970
Pseudo-second-order	k_2 (g.mg^{-1}min^{-1})	0.019	0.004
	$q_{e\,cal}$ (mg.g^{-1})	0.906	3.115
	R^2	0.988	0.990
Elovich	α	0.041	0.114
	β	5.549	1.713
	R^2	0.973	0.964
Intraparticle diffusion	k_{PI} (mg.g^{-1}min$^{1/2}$)	0.062	0.199
Region I	$c_{I\,(\text{mg/g})}$	−0.051	−0.250
	R^2	0.979	0.988
Region II	k_{PII} (mg.g^{-1}min$^{1/2}$)	0.032	0.095
	c_{II}	0.257	0.878
	R^2	0.910	0.935
Exp. adsorption capacity ($q_{e\ exp}$, mg/g)		0.67	2.01

AB113 adsorption from aqueous solutions on dried plant as natural adsorbent. A similar phenomenon has been observed in the adsorption of acid blue 193 and acid blue 294 onto natural sepiolite [38,39] and Acid Red 57 onto surfactant modified sepiolite [40].

3.3.2 Pseudo-second order kinetics model

In case of pseudo-second order kinetics model, the rate equation and its linearized form may be formulated as:

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

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

where, k_2 (g.mg^{-1} min^{-1}) 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- adsorbent system at different initial concentrations are presented in Figure 4 and the kinetic parameters are given in Table 3. The value of correlation coefficient (R^2) for the pseudo-second-order adsorption model for both initial concentration is relatively high (> 0.99), and the adsorption capacities calculated by the model are also close to those determined by experiments. Therefore, it has been concluded that the pseudo-second-order adsorption model is more suitable to describe the adsorption kinetics of AB113 dye onto dried *C. edulis* plant.

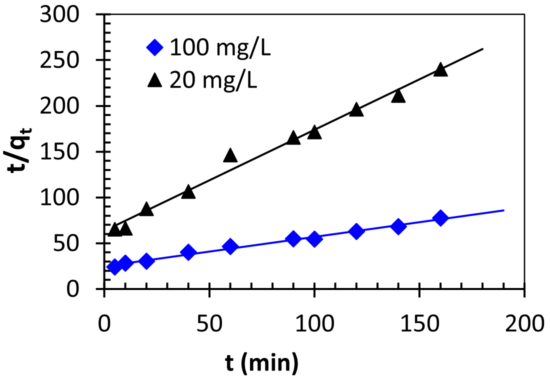


Fig. 4. Pseudo-second order adsorption kinetics of AB113 onto *C. edulis* plant at different dye concentrations.

3.3.3 Elovich kinetics model

The kinetics equation Elovich model and its linearized form may be expressed as:

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

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

where, q_e (mg/g) and q_t (mg/g) are the amounts of AB113 adsorbed at equilibrium and at any contact time t (min), respectively. α (mg.g^{-1}.min^{-1}) is the initial adsorption rate and β (g.mg^{-1}) 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. 5). The correlation coefficient values (R^2) are obtained in the range of 0.964–0.973 for both values of initial dye concentration which are found to be less than the values calculated using pseudo second-order kinetic model as shown in Table 3. Therefore, the Elovich model is not suitable for modeling the adsorption of AB113 dye onto dried plant.

3.3.4 Intra-particle diffusion kinetics model

The kinetics equation of intra-particle diffusion model is:

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

where k_p (mg.g^{-1}min$^{1/2}$) is the intra-particle diffusion rate constant, c (mg.g^{-1}) 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).

If the intra-particle diffusion is the rate-limiting elementary process, the amount of dye retained on weight unit of adsorbent varies with the square root of time. The graphical representation of dependence q_t versus $t^{1/2}$, obtained in case of AB113 adsorption on dried plant (Fig. 6) does not go through the origin, and two separated regions were obtained. Both separately regions were separately evaluated using equation (7), and the values of k_p and c, calculated from the slopes and intercepts are summarized in Table 3.

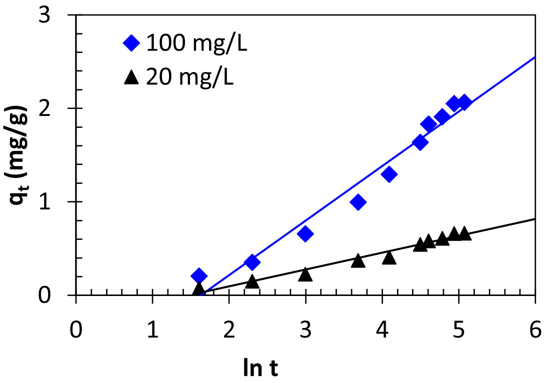


Fig. 5. Elovich adsorption kinetics of AB113 onto *C. edulis* plant at different dye concentrations.

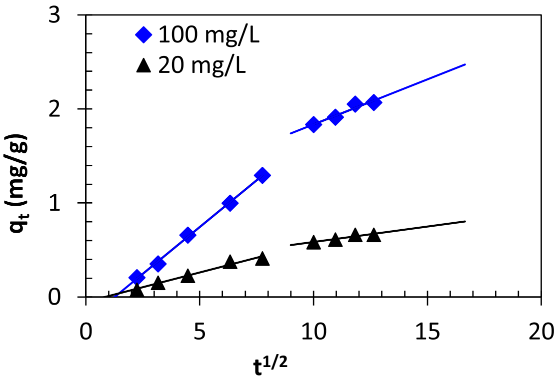


Fig. 6. Intra-particle diffusion kinetics of AB113 onto *C. edulis* plant at different dye concentrations.

The deviation of the straight lines from origin indicates that the intra-particle diffusion process is not the rate controlling step, but the boundary layer diffusion controls the adsorption in some degree. In addition, the higher values of rate constants obtained from this model (in comparison with the pseudo-second order model) is another argument which sustain that the intra-particle diffusion process not limited the rate of AB113 adsorption on dried plant.

The multi-linearity obtained in this case indicated that two or more elementary steps occur in the adsorption process. The first region is attributed to the fast transfer of AB113 from bulk solution to the adsorbent surface, and the second region to the intra-particle diffusion on adsorbent.

3.4 Adsorption isotherm models

Adsorption isotherms describe qualitative information on the nature of the solute-surface interaction as well as the specific relation between the concentration of adsorbate and its degree of accumulation onto adsorbent surface at constant temperature [41–43]. Adsorption isotherms are critical in optimizing the use of adsorbents, and the analysis of the isotherm data by fitting them to different isotherm models is an important step to find the suitable model that can be used for design purposes

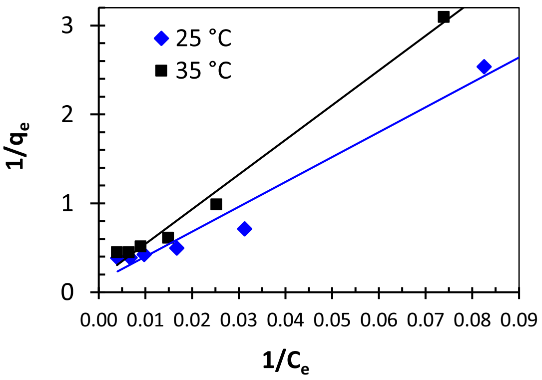


Fig. 7. Langmuir adsorption isotherm of AB113 onto *C. edulis* plant at different temperatures.

[41–43]. In this study, the Langmuir, Freundlich, Temkin and Dubinin-Radushkevvich (D-R) equations were used to describe the relationship between the adsorbed AB113 dye uptake onto dried *C. edulis* plant and its equilibrium concentration in solution. This study was carried out by varying initial ion concentration from 20 to 300 mg/L at different temperatures and natural pH 6.3.

3.4.1 Langmuir adsorption isotherm

The Langmuir adsorption isotherm [44] assumes that solid surface has a finite number of identical sites which shows homogeneous surfaces. The Langmuir equation and its linearized form may be represented as:

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

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

where q_e (mg/g) is the amount of dye adsorbed per unit weight of the dried plant adsorbent at equilibrium, C_e (g/l) is the equilibrium concentration of dye in the solution, q_L (mg/g) is the Langmuir maximum adsorption capacity and K_L (l/mg) is the Langmuir constant related to free energy of adsorption. The isotherm constants q_L and K_L were calculated from the slope and intercept of plot between *1*/q_e and $1/C_e$, as shown in Figure 7.

The values of the adsorption capacity q_L, the Langmuir constant K_L and the correlation coefficient R^2 were presented in Table 4. The values of the correlation coefficient for both temperatures was 96% and 99% for 25 °C and 35 °C, respectively, indicating also a good fit of the Langmuir model to the adsorption of AB113 on dried plant. 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 8.2 mg/g (Tab. 4).

Table 4. Parameters of four isotherms for AB113 dye adsorption onto dried *C. edulis* plant at different temperatures.

Isotherms	Parameters	Temperature	
		298 K	308 K
Langmuir	K_L(L.mg^{-1})	4.4×10^{-3}	3.9×10^{-3}
	$q_{e\,cal}$(mg.g^{-1})	8.18	6.48
	R^2	0.964	0.988
Freundlich	K_F (mg.g^{-1})	0.113	0.066
	n	1.484	1.393
	R^2	0.990	0.991
Temkin	K_T (L.mg^{-1})	0.181	0.125
	b_T (J.mol^{-1})	3282.4	3659.2
	R^2	0.947	0.962
Dubinin-Radushkevvich	B_D (mol^2.J^{-2})	2×10^{-6}	2×10^{-6}
	q_D (mg.g^{-1})	5.5×10^4	290.5×10^4
	E (J.mol^{-1})	5×10^2	5×10^2
	R^2	0.926	0.952

3.4.2 Freundlich adsorption isotherm

The Freundlich equation shows best fittings to adsorption data for natural heterogeneous adsorbents. The Freundlich adsorption isotherm equation and its linear form can be written as follows [45]:

$$q_e = K_F C_e^{1/n} \quad \text{(non-linear form)} \tag{10}$$

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad \text{(linearform)} \tag{11}$$

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^{-1}) 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 lnq_e versus lnC_e (Fig. 8). The values for Freundlich constants and correlation coefficients (R^2) for both temperatures are also presented in Table 4. The numerical values of $n$at both temperatures are between 1 and 10 (i.e., $1/n$ less than 1), indicating that AB113 dye is favourably adsorbed by dried plant bio-adsorbent. In general, both Freundlich and Langmuir models had a good agreement with the experimental data for anionic acid blue 113 dye adsorption, evidenced by the high R^2 values (all greater than 0.97) (Tab. 4). These experiments confirm the efficiency of the dried *C. edulis* plant to remove acid dyes from aqueous solutions.

3.4.3 Temkin isotherm

The Temkin adsorption isotherm model based on the heat of pollutant adsorption, which is due to the adsorbate and adsorbent interactions taken [46]. The Temkin

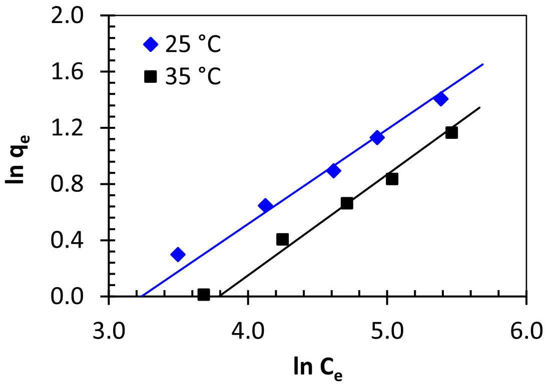


Fig. 8. Freundlich adsorption isotherm of AB113 onto *C. edulis* plant at different temperatures.

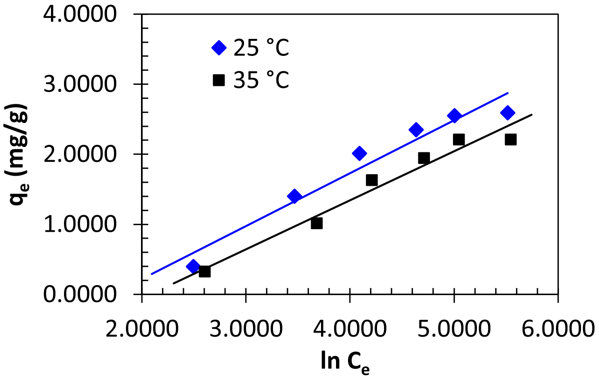


Fig. 9. Temkin adsorption isotherm of AB113 onto *C. edulis* plant at different temperatures.

isotherm equation and its linearized form may be expressed as:

$$q_e = \frac{RT}{b_T}\ln K_T C_e \quad \text{(non-linear form)} \tag{12}$$

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

where T is absolute temperature in Kelvin and R the universal gas constant (8.314 J.mol^{-1} K^{-1}). b_T (J.mol^{-1}) is Temkin isotherm constant related to the heat of adsorption. K_T (L.mg^{-1}) is the equilibrium binding constant corresponding to the maximum binding energy. The Temkin isotherm plot for dye-dried plant system at different temperatures are presented in Figure 9 and the isotherm parameters are given in Table 4. The Temkin constants b_T related to heat of adsorption for both temperatures were found to be 3.3 kJ/mol and 3.7 kJ.mol^{-1} for 25 °C and 35 °C, respectively. It has been reported [47] that the typical range of bonding energy for ion-exchange mechanism is 8–16 kJ.mol^{-1}. The low values in this study indicate a weak interaction between adsorbate and adsorbent, supporting an ion-exchange mechanism for the present study. From linear regression of the data points, the R^2 values range from 0.95 to 0.96 is rather low indicating that the adsorption of AB113 did not follow the Temkin isotherm closely.

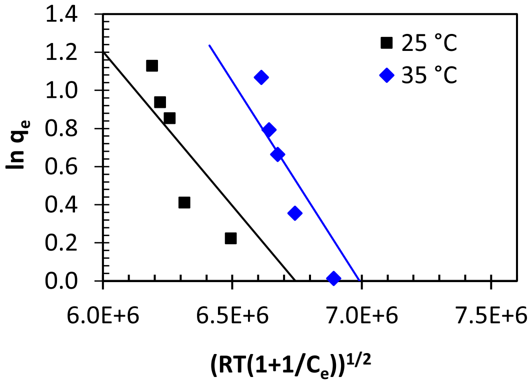


Fig. 10. Dubinin-Radushkevvich (D-R) adsorption isotherm of AB113 onto *C. edulis* plant at different temperatures.

3.4.4 Dubinin–Radushkevich (D–R) isotherm

Dubinin and Radushkevich have proposed another isotherm which can be used to analyze the equilibrium data [48]. 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 D–R equation can be written as [49]:

$$q_e = q_m \mathrm{e}^{-K_p \varepsilon^2} \quad \text{(non-linear form)} \tag{14}$$

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

where q_m (mg/g) is the theoretical saturation capacity and ε is the Polanyi potential that can be calculated from equation (16):

$$\varepsilon = RT \ln\left(1 + \frac{1}{\mathrm{Ce}}\right) \cdot \tag{16}$$

The constant $K_D(\mathrm{mol}^2.\mathrm{J}^{-2})$ gives an idea about the mean free energy E (kJ.mol^{-1}) 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 the following relation (Eq. (17)):

$$E = \frac{1}{(2K_p)^{1/2}} \cdot \tag{17}$$

This parameter gives information about adsorption mechanism is chemical ion-exchange or physical adsorption. If the magnitude of E is between 8 and 16 kJ.mol^{-1}, the adsorption process is supposed to proceed via chemisorption, while for values of $E < 8\,\mathrm{kJ.mol}^{-1}$, the adsorption process is of a physical nature [50].

The slope of the plot of ln q_e versus ε^2 gives K_D and the intercept yields the adsorption capacity q_m. As can be seen in Figure 10 and Table 4, the correlation coefficient values are 0.93 and 0.95 for 25 °C and 35 °C, respectively. This indicates that the Freundlich model still fits the data better. The numerical value of adsorption of the mean free energy is 5×10^2 J.mol^{-1} (Tab. 4) corresponds to a physisorption and the predominance of van der Waals forces.

Table 5. Thermodynamic parameters for AB113 dye adsorption onto dried *C. edulis* plant.

Temperature (°C)	Δ S° (J.K^{-1}.mol^{-1})	Δ G° (kJ.mol^{-1})	Δ H° (kJ.mol^{-1})
25	41.13	−19.82	−7.57
35	38.99	−19.58	

3.5 Adsorption thermodynamic study

In order to describe thermodynamic behavior of the adsorption of AB113 dye onto *C. edulis* plant biomaterial, thermodynamic parameters including the change in free energy ($\Delta G°$), enthalpy change ($\Delta H°$) and entropy change ($\Delta S°$) were calculated from following equations:

$$\Delta G° = -RTLn(K_L) \tag{18}$$

$$Ln\left(\frac{K_2}{K_1}\right) = -\frac{\Delta H°}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{19}$$

$$\Delta G° = \Delta H° - T\Delta S° \tag{20}$$

where, T is absolute temperature in Kelvin and R the universal gas constant (8.314 J.mol^{-1}.K^{-1}). K_L (L.mol^{-1}) is the equilibrium constant obtained from Langmuir isotherm. The obtained results for thermodynamic parameters are reported in Table 5. The small negative value of $\Delta H°$ suggests the adsorption to be physical and exothermic process which is consistent with experimental observations. The negative $\Delta G°$ values show spontaneous nature of adsorption process and the positive value of entropy ($\Delta S°$) revealed that the degrees of free active sites increased at the solid–liquid interface during the adsorption of anionic dye onto dried *C. edulis* plant.

4 Conclusions

This study investigated the equilibrium and the kinetics of the adsorption of an anionic dye, which is namely Acid Blue 113 onto dried *C. edulis* plant as a Mediterranean plant. The adsorption was found to be strongly dependent on contact time and initial acid dye concentrations. The adsorption of AB113 onto dried plant was exothermic in nature with the dye removal capacity decreasing with increasing temperature due to increasing mobility of the dye molecules.

The pseudo-second-order kinetic model agrees very well with the kinetic behavior for the adsorption of AB113 on dried *C. edulis* plant at different values of initial dye concentration. However, the evidence is provided that the adsorption of dye onto dried plant is a complex process, so it cannot be sufficiently described by a single kinetic model throughout the whole process. For example, intraparticle diffusion (up to 120 min) played a significant role, but it was not the main rate determining step during the adsorption. Adsorption kinetic studies also revealed that a contact time of 140 min was enough for attaining equilibrium.

Adsorption isotherms and equilibrium adsorption capacities were determined by the fittings of the experimental data to four well-known isotherm models including Langmuir, Freundlich, Temkin and Dubinin-Radushkevich. The results showed that the Freundlich model appears to fit the adsorption better than other adsorption models for the adsorption of AB113 onto dried *C. edulis* plant, indicating that the surface of *C. edulis* biomaterial was heterogeneous.

The thermodynamic calculations showed the feasibility, exothermic and spontaneous nature of the the adsorption phenomenon of AB113 dye onto *C. edulis* biomaterial. Taking into consideration present findings, it can be concluded that dried *C. edulis* plant is a good bio-adsorbent for acid blue 113 dye removal from aqueous solution. Furthermore, it could be employed for the economic treatment of wastewater containing the acid dyes, as this bio-adsorbent was derived from dried Mediterranean plants and had a considerable high adsorption capacity.

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