Assessment of Brilliant Green and Eriochrome Black T dyes adsorption onto fava bean peels: kinetics, isotherms and regeneration study

Loubna Nahali[a,*], Youssef Miyah[a], Fatiha Mejbar[a], Mohammed Benjelloun[a], Ouissal Assila[a], Youssef Fahoul[a], Valentin Nenov[b], Farid Zerrouq[a]

[a]Laboratory of Materials, Processes, Catalysis, and Environment, University Sidi Mohamed Ben Abdellah, School of Technology, P.O. Box: 2427 Fez, Morocco, emails: Nahali.loubna@gmail.com/Loubna.nahali@usmba.ac.ma (L. Nahali), youssef.miyah@gmail.com (Y. Miyah), fatihamejbar2@yahoo.fr (F. Mejbar), mohammed.benjelloun94@gmail.com (M. Benjelloun), ouissal.assila@usmba.ac.ma (O. Assila), fahoulyoussef@gmail.com (Y. Fahoul), zerrouq1959@gmail.com (F. Zerrouq)
[b]Department of Chemical Technologies, Burgas "Asen Zlatarov" University, 1 Yakim Yakimov Blvd, Burgas 8010, Bulgaria, email: nenov@yvn-bg.com (V. Nenov)

A B S T R A C T

This research aims to assess the employability of fava bean peels (FBP) as low-cost adsorbents in the removal of Brilliant Green (BG) and Eriochrome Black T (EBT) from aqueous solutions and therefore in colored wastewater treatment. Scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR), and pH_{PZC} were used to characterize these materials. The constants of Langmuir, Freundlich, and Dubinin-Radushkevich have all been determined. The adsorption capacity of BG and EBT was 28.14 and 7.91 mg g^{-1}, respectively, at 5 g L^{-1} FBP dose, 40 mg L^{-1} initial dye concentration, temperature 20°C, and contact time BG (80 min) and EBT (40 min). The calculated thermodynamic parameters indicated that adsorption of BG was endothermic and exothermic for EBT. The isotherm studies show that the adsorption experimental data of both dyes are fitted well by the Freundlich isotherm model. The adsorption of the two dyes studied on fava bean peels is perfectly described by a pseudo-second-order kinetic model. Cyclic experiments have indicated that the current bio-adsorbent can be effectively reused to remove BG and EBT from aqueous solutions. Removal efficiencies remained above 84% and 10% for BG and EBT respectively even after four adsorption–desorption cycles. As a consequence of these relevant results, our inexpensive and environmentally friendly material could provide enormous application prospects in large-scale wastewater treatment in the industrial level.

Keywords: Adsorption; Fava bean peels; Isotherms; Kinetics; Regeneration

1. Introduction

Today, the biggest problem for the environment and ecosystems is water pollution, which is considered an indispensable element of all socio-economic activities, regardless of the degree of the country's development. Industries often produce liquid pollutants loaded with mixtures of dyes, acids, bases, and soluble solids [1]. The textile industry is the most important in terms of using dyes to color fibers out of all the industries [2]. Some dyes have been mutagenic and carcinogenic [3,4]. Alteration of kidney, liver, brain, reproductive and central nervous system functions are among the effects of dyes in humans [5]. Brilliant green is a very controversial dye due to its negative effects on the immune and reproductive systems [6]. When consuming the dye orally, it may cause nausea, coughing and shortness

* Corresponding author.

of breath, diarrhea, and vomiting and brilliant green can also cause eye burns responsible for permanent eye damage in humans and animals [7,8]. It is also considered highly toxic to the lungs when inhaled [9]. Furthermore, the color of BG in wastewater reduces light penetration [10], preventing aquatic plants from photosynthesis, which can be hazardous to the environment. Eriochrome Black T is commonly used as a complex metric detector to determine water hardness [11]. Its release into water resources has affected aquatic life by limiting the reoxygenation capacity of water bodies and the photosynthetic capacity of aquatic plants [12,13]. Thus, human exposure to EBT dye is harmful and can cause serious health problems [14].

Therefore, to protect human public health and the receiving ecosystem, the effluent must be adequately treated before its release into the environment. It is, therefore, necessary to reduce pollution by setting up an appropriate treatment system including a discoloration unit. A wide variety of physicochemical and biological techniques have been developed and have shown great discoloration efficiency [15], in particular coagulation-flocculation [16], oxidation [17,18], membrane filtration [19], and aerobic and anaerobic biological treatment [20]. However, there are several technical and economic constraints to these procedures, such as cost, sludge generation, and low biodegradability [21].

Adsorption has gained importance as the most desirable technique for the treatment of wastewater loaded with organic and inorganic substances [22,23], due to its low cost of operation and maintenance, ease of handling, simplicity of design, its profitability, its large adaptability and its excellent performance [24,25]. As well as the adsorption process does not cause any side effects or toxicity to the water [26]. However, the efficiency of adsorption depends on adsorbents which have high adsorption capacity, selectivity and are efficient, economical, and robust which can be recycled many times [27,28]. Bio-adsorbents from residual biomass sources are economical, renewable, and environmentally friendly for wastewater treatment. Therefore they have attracted attention in recent years, with an accentuation on the use of crude lignocellulosic biomass as raw materials for the production of new adsorbents [29]. Several authors are directed to the study of dye adsorption over various natural materials such as clays [30–37], bagasse agricultural materials of sugarcane [38], corn cobs [39], coconut shell [40], potato peels [41], industrial wool waste [42], fly ash [43], blast furnace sludge [44], etc.

The adsorptive removal of BG and EBT dye using locally available and modified adsorbents has been described by several authors among which manganese oxide-coated zeolite [45], Acid modified grapheme [46], the yellow passion fruit peel '*Passifora edulis f. Flavicarpa*' [47], orange peel and orange peel-modified chemically [48], clay [49,50], *Pinus roxburghii* leaves [51], Sandpaper wastes [52], Bambusa Tulda [53], *lawsonia inermis* seed powder [9], Ferroferric oxide/polypyrrole composites [23], Limestone chitosan alginate nanocomposite [54], etc.

The originality of this study is justified by the fact that it is an integrated part of the agri-food waste recovering process in an experimental project exploiting the adsorption phenomenon, to propose a contribution to the

total or partial elimination of a dissolved dye with ratio cost-effectiveness. For that, we used fava bean peels (FBP) as an inexpensive and very abundant adsorbent material in North Africa, especially in Morocco for the removal of the basic dye Brilliant Green (BG) and the acidic dye Black Eriochrome T (EBT).

The main purpose of our work is to evaluate the fava bean peel's adsorption capacity concerning two organic dyes, namely Eriochrome Black T (EBT) with anionic character and Brilliant Green (BG) with a cationic character. Scanning electron microscopy-energy dispersive X-ray (SEM-EDX), Fourier transform infrared (FTIR), and point of zero charges (pH_{pzc}) measurements were used to characterize the adsorbent. Various experimental parameters were analyzed such as the effect of the dye initial concentration, temperature, contact time, adsorbent dose, pH solution, and ionic strength. The adsorption capacity of the fava bean peels was studied using the isotherms of Langmuir, Freundlich, and Dubinin–Radushkevich. The pseudo-first-order, pseudo-second-order, and intraparticle diffusion models were used to study adsorption kinetics. Also, that thermodynamic study and regeneration were evaluated.

2. Materials and methods

2.1. Preparation of adsorbed solution

We investigated two dyes; Brilliant Green (cationic) and Eriochrome Black T (anionic) were used without purification in this study. The stock solution was prepared by dissolving a quantity of the two dyes weighed accurately to obtain a concentration of 100 mg L^{-1}. Diluting the stock solution with distilled water yielded the required concentration experimental solutions.

2.2. Preparation of the adsorbent

The fava bean peels were collected and washed with tap water many times to remove any dust or adherent impurities, then it was rinsed with distilled water three times, air-dried, and put in an oven at 60°C/24H. The material has been crushed and sieved to a particle size of less than 250 μm. Finally; the material was stored and preserved to be used later on.

2.3. Characterization technique

The chemical structure of FBP was analyzed using the KBr pellet method onto a BRUKER (Vertex70) Fourier Transform Infrared (FTIR) spectrometer, in the wavelength range 4,000–400 cm^{-1}. The surface morphology of FBP was analyzed using scanning electron microscopy (SEM) coupled with energy-dispersive X-ray spectroscopy (EDX). The use of these approaches allowed researchers to see the surface morphology of adsorbents. The SEM observation was carried out at the UATRS Materials platform.

The point of zero charge pH_{pzc} is a very important character of the surface; it corresponds to the pH value for which the surface charge of the adsorbents is zero. So this parameter characterizes the alkalinity or the acidity of the surface.

At pH below pH$_{pzc}$, the surface charge is positive and, at pH above pH$_{pzc}$, it is negative. A very simple method was applied to determine the pH$_{pzc}$ in beakers of 200 mL one introduces 100 mL of NaCl (0.01 M) by adjusting the pH to the desired value by adding NaOH or HCl (0.1 M). Then 0.2 g of the material to be characterized is added to each beaker. The set was left under constant stirring for 24 h, and the final pH is then determined. By plotting ΔpH (pH$_f$ – pH$_i$) as a function of the adjusted pH$_i$, the intersection of the curve with the axis that passes through zero gives the isoelectric point.

2.4. Adsorption procedure

All adsorption experiments were performed in a batch system: the objective is to study the effect of the initial dye concentration (20–30–40 mg L^{-1}), the dose of the fava bean peels powder (1–5 g L^{-1}), the contact time (0–120 min), the solution temperature (20°C–60°C) and the pH (2–12). Adsorption tests were performed in beakers containing 200 mL of the colored solution with constant stirring. The samples were taken every 5 min, subsequently, the adsorbent was separated from the stained solution by filtration in a centrifuge at 60 rpm for 3 min, and then the concentration of Brilliant Green and Black Eriochrome T dyes was then evaluated using a UV-visible spectrophotometer (Selecta Vr-2000 spectrophotometer) to measure the absorbance of the solution at the maximum wavelengths of 625 and 520 nm, respectively. All experiments were performed in duplicate.

The following equation is applied for calculating the adsorption quantities from the change in solution concentration:

$$q\left(\mathrm{mg/g}\right) = \frac{\left(C_0 - C\right)V}{m} \tag{1}$$

where q is the adsorption amount (mg g^{-1}), V is the solution's volume (L) and m is the adsorbent mass (g), C_0 is the initial concentration of dye (mg L^{-1}), and C is the final dye's concentration in an aqueous solution after phase separation (mg L^{-1}).

3. Results and discussion

3.1. Characterization of the adsorbent

The presence of the bond characterizing fava bean peel powder is confirmed by the absorption bands observed (Fig. 1). We focus on a few of these groups: the intense absorption band at 3,289 cm^{-1} can be attributed to the O–H stretching vibration of the water of constitution [55], the band 1,698 cm^{-1} shows a C–C symmetric plane [56]. The band at 1,607.21 cm^{-1} is attributed to the stretching vibration of the (C=O) and (C=C) bonds [57]. The bands 1,520 and 1,427 cm^{-1} are assigned to the C=C stretching of the lignin [58,59]. The band 1,314 cm^{-1} corresponds to the C–H stretch of cellulose [58]. The bands observed at 1,155, 1,022, and 927 cm^{-1} could represent the C–O–C of cellulose [58,60]. Also, the presence of absorption band assigned to of plane bending vibration of O–H is located at 765 cm^{-1} [61].

In the images Figs. 2a and 2b, we can observe microcavities on the adsorbent surface, which seems to indicate a very porous irregular structure favorable for good diffusion of the dye molecules. The weight percentage of chemical compositions available at the surface was determined employing energy dispersive spectrometer (EDX) analysis. The results grouped in Fig. 2c indicate that the material contains mainly: carbon (35.32 wt%), oxygen (61.40 wt%), and low content of calcium (2.35 wt%) and magnesium (0.93 wt%).

3.2. Effect of initial concentration and contact time

The effect of the initial concentration and the contact time on the biosorption of the two dyes, Eriochrome Black T and Brilliant Green, by fava bean peels were studied, and the results are represented in Fig. 3. The latter shows that the amounts of the dyes' adsorption increased
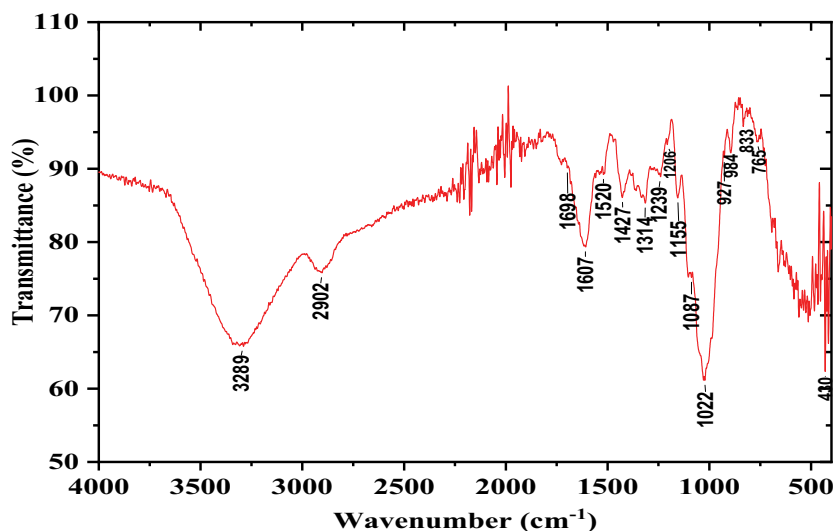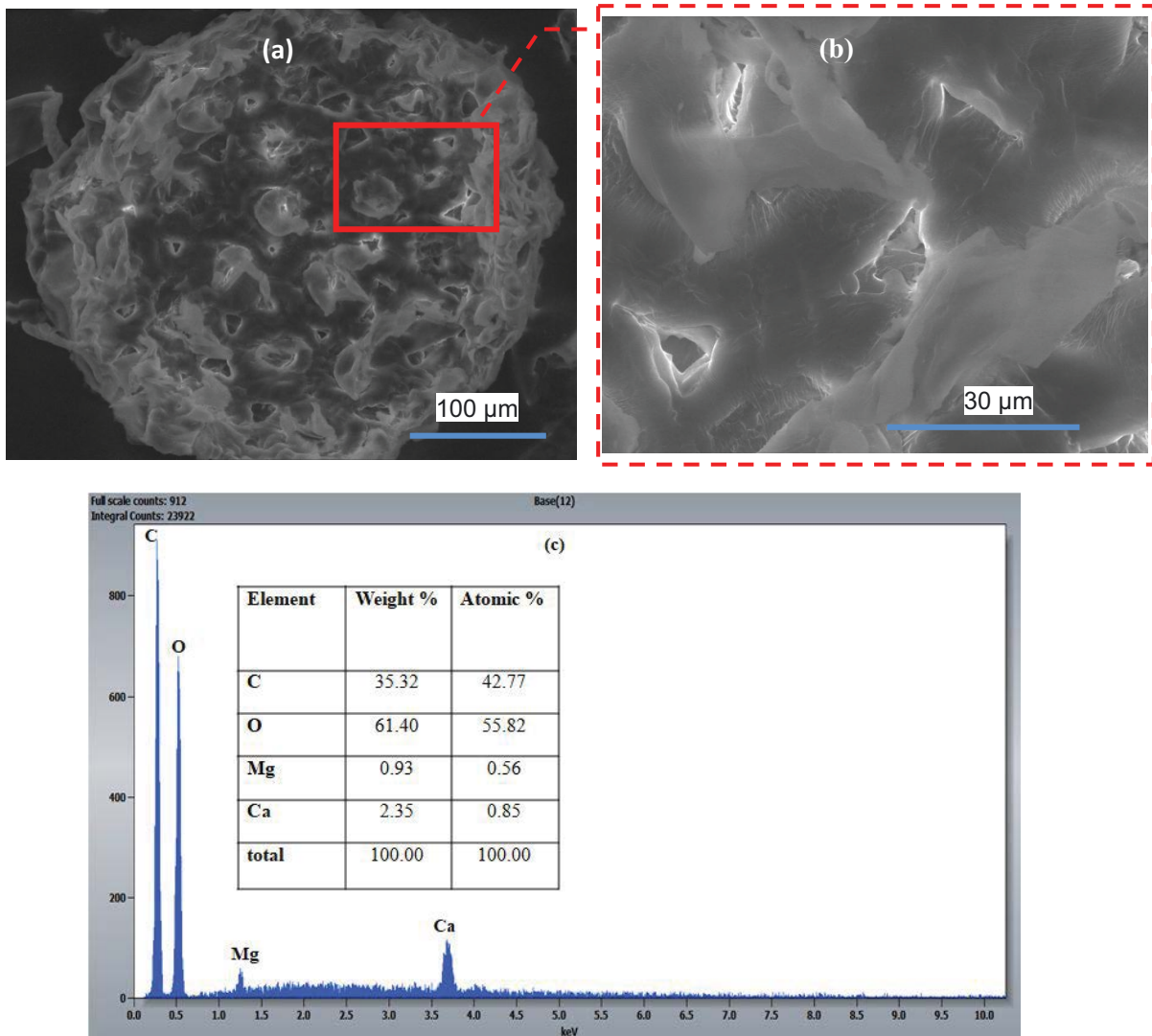

Fig. 1. Fava bean peels powder FTIR.

Fig. 2. SEM microscopy (a and b) coupled by EDX (c), for FBP.

progressively with the two dyes concentration increasing, and the adsorption equilibrium time is reached after 80 min of contact for the adsorption of BG and after 40 min for the adsorption of EBT. This difference is linked to the structure and nature of the molecules. The adsorbent amount at 20, 30, and 40 mg L^{-1} were found to be 14.10, 21.34, and 28.14 mg g^{-1} for BG and 5.40, 7.12, and 7.91 mg g^{-1} for EBT, respectively. Compared to the results of the two dyes, it is found that the adsorbed amount of Brilliant Green was greater than the Eriochrome Black T. This may be due to the reason that since FBP is acid; there may be the presence of certain irremovable acid groups on the surface of the FBP which would have been involved in forming a covalent bond with the basic dye molecules effectively compared to the acidic dye molecules [62].

3.3. Effect of adsorbent dosage

The adsorption capacities of Brilliant Green and Eriochrome Black T on FBP decrease from 14.10 to 3.67 mg g^{-1},

and from 4.56 to 1.32 mg g^{-1}, respectively, in increasing the adsorbent dose from 1 to 5 g L^{-1}. The results, shown in Fig. 4, reveal a considerable decrease in the amount adsorbed as the adsorbent dose is increased. As the amount of adsorbent increases, the number of active sites available for adsorption also increases. In the meantime, the adsorbed amount was reduced by increasing the dosage, because some available sites on the surface adsorbent had not been saturated and the adsorbate/adsorbent ratio decreased [63]. These results indicate that the optimum dose of our FBP biosorbent is on the order of 5 g L^{-1}.

3.4. Effect of temperature

To determine how temperature can affect Brilliant Green and Eriochrome Black T dye biosorption, experiments were conducted from 20°C to 60°C by fixing the initial concentration of the two dyes at 20 mg L^{-1}.

The results presented in Fig. 5 show that temperature has no effect on the amount adsorbed of Brilliant Green, whence
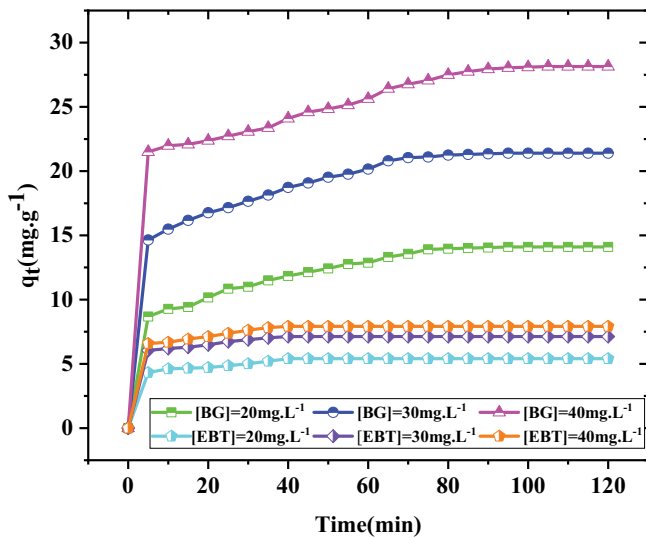
Fig. 3. Effect of contact time, and initial concentration of BG and EBT dyes. Interval C_i = (20–40 mg L^{-1}), w = 0.2 g, V = 200 mL, T = 20°C ± 2°C and stirring time 120 min.

Fig. 4. Effect of adsorbent dose. Interval adsorbent dose (1–5 g L^{-1}), C_0: [BG] = [EBT] = 20 mg L^{-1}, V = 200 mL, T = 20°C ± 2°C.

Fig. 5. Effect of temperature. Interval of temperature (20°C–60°C), w = 1 g, C_0: [BG] = [EBT] = 20 mg L^{-1}, V = 200 mL.

the adsorption capacity remains constant with increasing temperature, while the amount adsorbed of Eriochrome Black T decreases slightly from 1.32 to 0.78 mg g^{-1}. This suggests that the interaction of the adsorbent/adsorbate is endothermic nature for BG and is exothermic nature for EBT.

Güzel et al. [64] have reported that this thermodynamic phenomenon can be explained by the fact that an increase in temperature adds strength to the rate at which the adsorbate molecule diffuses through the outer boundary region, and inner pores of the adsorbent particles, due to the low viscosity of the solution. In general, the higher temperature leads to an enhancement in the amount of adsorption due to the movement of the adsorbate molecule, which also increases with temperature.

3.5. Effect of pH

The solution's pH is an important parameter that conditions the state of the surface charge of both the adsorbent and the adsorbate. Its effect on the adsorption of BG and EBT was examined using the same solid–liquid ratios as in the kinetic study. The initial concentration of the two dyes was set at 20 mg L^{-1}. The explored pH was adjusted from 2 to 12 by adding HCl (0.1 N) and NaOH (0.1 N). The stirring time is that corresponding to the equilibrium time of each dye.

The effect of pH on the adsorption of BG and EBT on FBP is studied in Fig. 6a. The adsorption capacity of BG increases slightly with increasing pH and indicates a maximum value of 3.66 mg g^{-1} at pH = 12. On the other hand, a decrease in the adsorbed quantity of EBT is observed, going from 3.06 to 0.73 mg g^{-1} when the pH of the solution increases.

To better illustrate these results, we have determined the point of zero charges (PZC). The FBP's pH$_{pzc}$ is equal to 4, which means that the adsorbent surface is negatively charged at pH > 4 and positively at pH < 4 (Fig. 6b) [65]. When the pH is higher than the pH$_{pzc}$ of our material, its surface is negatively charged, and the cationic dye
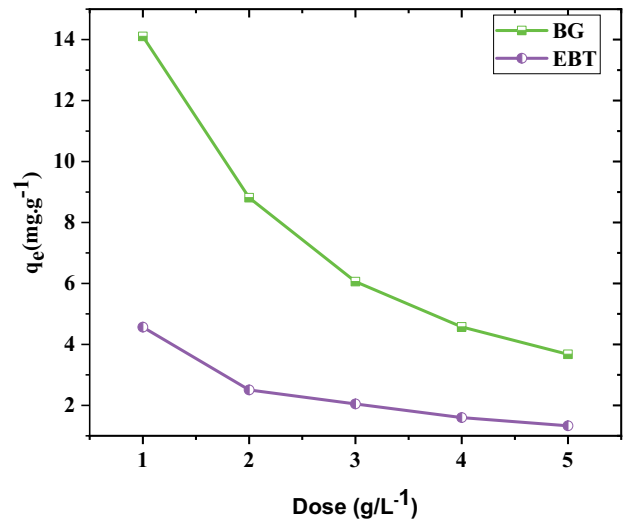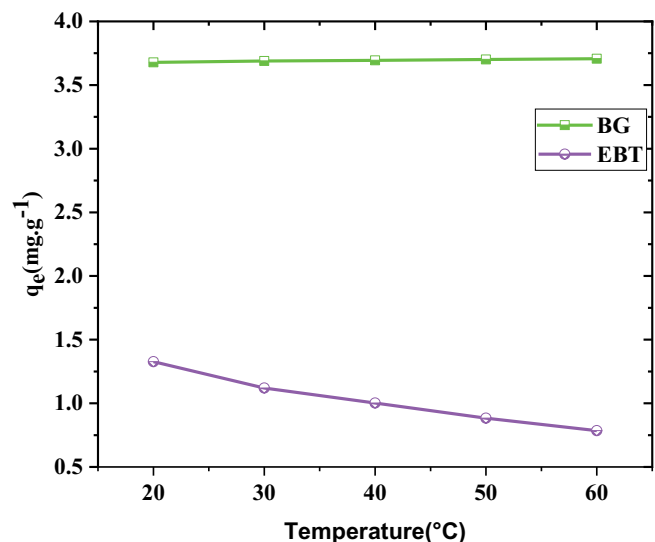
(BG) molecules in the solution are positively charged. Adsorption can therefore be considered through electrostatic interactions between different charges of adsorbent FBP and adsorbate BG. These interactions increase with increasing pH because the FBP surface area loading becomes negative as the solution becomes more and more basic. While the negative charges (OH$^-$) increase as the pH increases, which prevents adsorption of the anionic dye due to the electrostatic repulsion between the surface of the FBP and the Eriochrome Black T molecules [66].

3.6. Adsorption kinetics

The adsorption kinetics studies are performed to provide information on the adsorption amount, to determine the time required to reach the equilibrium state between
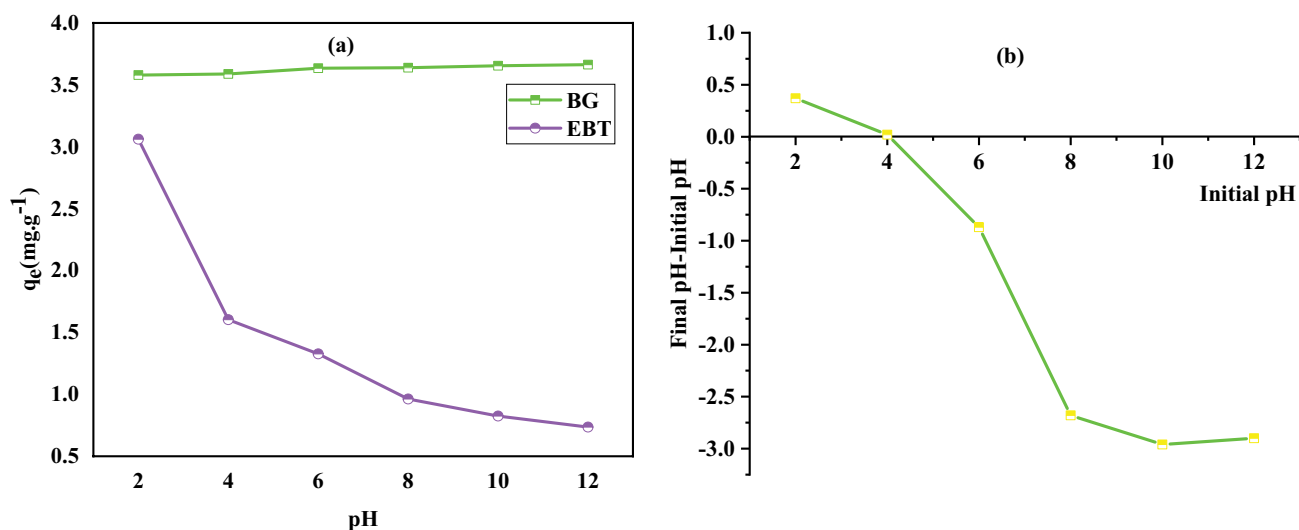
Fig. 6. Effect of pH on adsorbed quantity (a). Interval of pH (2–12), w = 1 g, C_0 = [BG] = [EBT] = 20 mg L^{-1}, V = 200 mL. pH of the point of zero charge pH$_{pzc}$ of the FBP (b).

two phases, as well as the effluent adsorption equilibrium constants.

The kinetics of dye adsorption on adsorbent supports is required for selecting the optimal operating conditions for large-scale processing.

Three classical kinetic models: the pseudo-first-order, the pseudo-second-order, and the intraparticle diffusion models were used to test the experimental data on dye adsorption by fava bean peels.

The first-order model is based on the adsorbed quantity and the first-speed equation, as expressed by Lagergren [67] and cited by Ru-Ling et al [68]. The following relation represents this model [69]:

$$\ln\left(q_e - q_t\right) = \ln q_e - K_1 t \tag{2}$$

where K_1: constant rate of Lagergren's first order (min^{-1}), q_t and q_e: are adsorbent amount at time t and equilibrium (mg g^{-1}), t: time of contact (min).

We can determine the adsorption rate constant K_1 by plotting $\ln(q_e - q_t)$ as a function of time t.

The reaction rate of the pseudo-second-order kinetic model is proportional to the amount adsorbed on the adsorbent's surface and the amount adsorbed at equilibrium. This model can be represented in the following form [70]:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \tag{3}$$

where K_2: constant rate of pseudo-second-order (g^{-1} mg min); q_e: the amount of adsorbate in the adsorbent at equilibrium (mg g^{-1}); q_t: the amount of adsorbate in the adsorbent at time t (mg g^{-1}); t: time of contact (min).

The slope and y-intercept of the line t/q_t as a function of t can be used to determine the adsorbed quantity at equilibrium q_e and the pseudo-second-order constant K_2.

The intra-particle diffusion model or Weber-Morris model assumes that the diffusion process is the only step controlling adsorption [71]. This model can be tested by applying the following equation [67]:

$$q_t = k_p t^{1/2} + I \tag{4}$$

where q_t is the amount of solute on the adsorbent surface at time t (mg g^{-1}), k_p is the intraparticle rate constant (mg g^{-1} min$^{1/2}$), t is the time (min), and I (mg g^{-1}) is a constant that gives an idea about the thickness of the boundary layer.

The intraparticle diffusion rate constant k_p and the constant I were calculated from the slope of the line obtained by plotting q_t and $t^{1/2}$.

Fig. 7 represents the three models of the adsorption kinetics of BG and BET on FBP. The three parameters of the kinetic model have been collected in Table 1, which also shows the determination coefficients and the amount adsorbed by the two dyes studied (BG and EBT). From these results, we can see that in the case of intraparticle diffusion and pseudo-first-order kinetics models, the quantity adsorbed by the experimentally determined equilibrium differs from that calculated, on the other hand, the adsorption quantity values of the two dyes calculated from the pseudo-second-order model are closest to those determined experimentally, indicating the advisability of using this model to describe the adsorption of Brilliant Green and Eriochrome Black T by the FBP material.

The determination coefficients of the pseudo-second-order model are of the order of 0.99. For the pseudo-first-order model, the determination coefficients are between 0.43 and 0.85 for the BG and EBT. These results confirm that the adsorption kinetics of BG and EBT on the fava bean peels obey the pseudo-second-order model. In addition, the equilibrium adsorption capacity (q_e) of the pseudo-second-order closely corresponded to the experimental values ($q_{e,exp}$). These results indicate that the limiting step of this adsorption could be chemisorption.
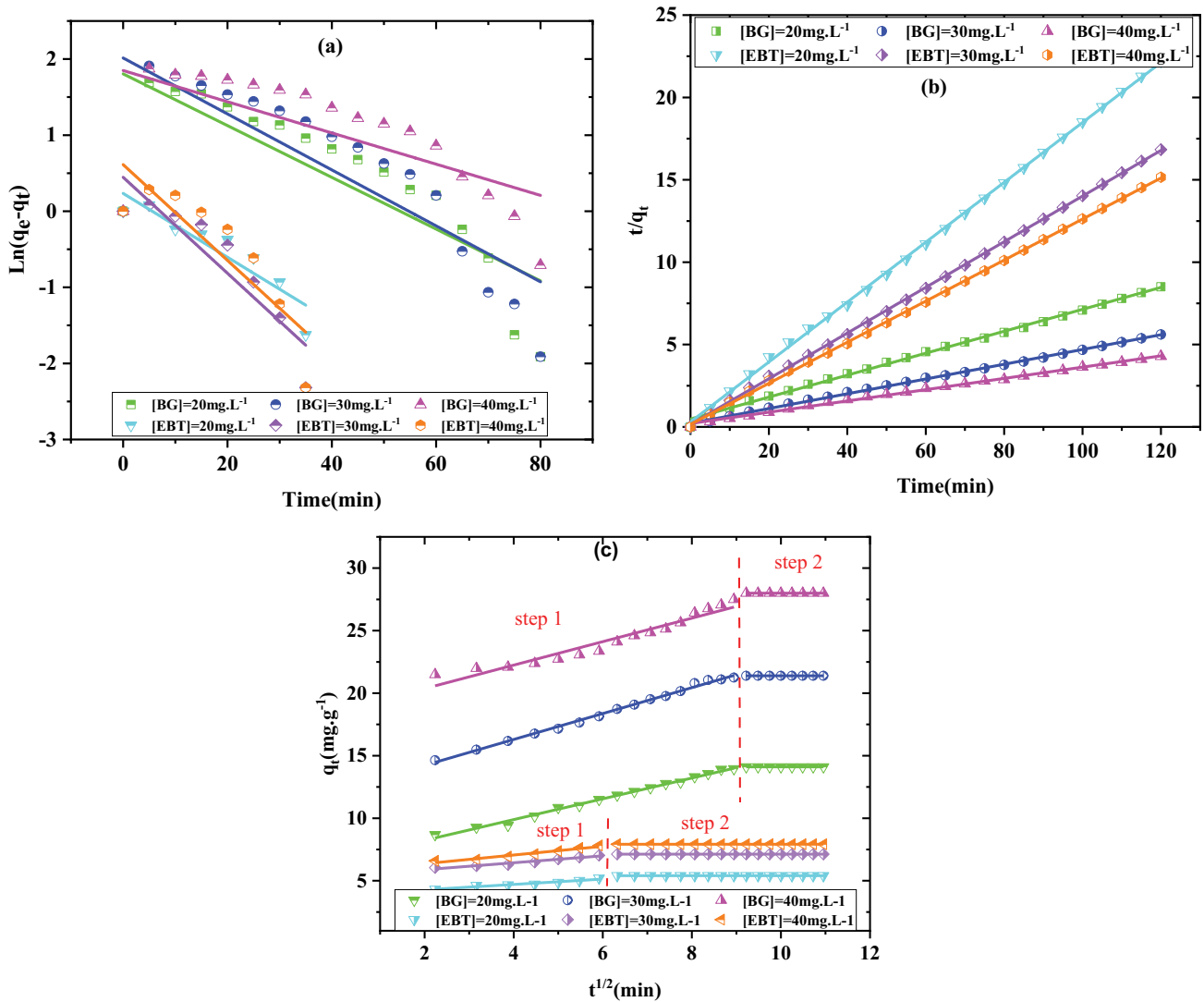
Fig. 7. Pseudo-first-order (a), pseudo-second-order (b) and intraparticle diffusion (c) of adsorption kinetics models.

Fig. 7c shows the plot of the intraparticle diffusion model applied to the system studied. It can be observed that the linear traces did not go through the origin, indicating that the intraparticle diffusion was not the only step that controls the rate of adsorption of the two dyes on FBP [72]. The graphs demonstrate that in the adsorption process, there are two stages of diffusion: the first is due to external diffusion of BG and EBT molecules on the surface of FBP, and the second is due to intraparticle diffusion, which is a delayed process due to the low dye concentration in the solution.

3.7. Adsorption isotherms

Isothermal models are generally used to describe the relationship between the adsorbed amount and the solute concentration in a given solution at adsorption equilibrium and constant temperature [73].

The study of the two dyes' adsorption isotherms on our material is carried out using different concentrations of adsorbate and an adsorbent dose of 5 g L^{-1}. In a beaker containing 200 mL of solution, the experiments were carried out. To ensure that the adsorption/desorption equilibrium was established, the adsorbent and adsorbate were in contact for 120 min with constant agitation.

The fixation data of the two dyes on FBP are processed using Langmuir, Freundlich, and Dubinin–Radushkevich linear equations.

The Langmuir model is a very simple mono-layer adsorption model. It assumes that adsorption occurs at specific and homogeneous adsorption sites within the adsorbent. Langmuir's linear form is expressed by the following equation [71,74]:

$$\frac{C_e}{Q_e} = \frac{1}{K_L Q_{max}} + \frac{C_e}{Q_{max}} \tag{5}$$

where C_e: Equilibrium concentration (mg L^{-1}), Q_e: adsorption capacity at equilibrium (mg g^{-1}), Q_{max}: is the maximum

Table 1
Comparison between the intraparticle diffusion model, pseudo-first-order and pseudo-second-order adsorption constant rate, calculated and experimental q_e values for different initial BG and EBT concentrations

|	C_0 (mg L^{-1})	$q_{e,\exp}$ (mg g^{-1})	Pseudo-first-order			Pseudo-second-order			Intraparticle diffusion		
			q_e (mg g^{-1})	K (min^{-1})	R^2	q_e(cal) (mg g^{-1})	K_2 (g mg^{-1} min^{-1})	R^2	K_{p1} (mg g^{-1} min$^{1/2}$)	I (mg g^{-1})	R^2
BG	20	16.69	6.079	0.034	0.65	15.15	0.009	0.99	0.83	6.57	0.99
	30	21.69	7.493	0.036	0.65	22.72	0.008	0.99	1.035	12.156	0.99
	40	28.83	6.353	0.02	0.43	29.41	0.005	0.99	0.938	18.489	0.94
EBT	20	5.40	1.263	0.041	0.85	5.524	0.106	0.99	0.213	3.85	0.94
	30	7.12	1.562	0.063	0.83	7.246	0.124	0.99	0.277	5.327	0.95
	40	7.91	1.844	0.062	0.75	8.064	0.098	0.99	0.348	5.663	0.95
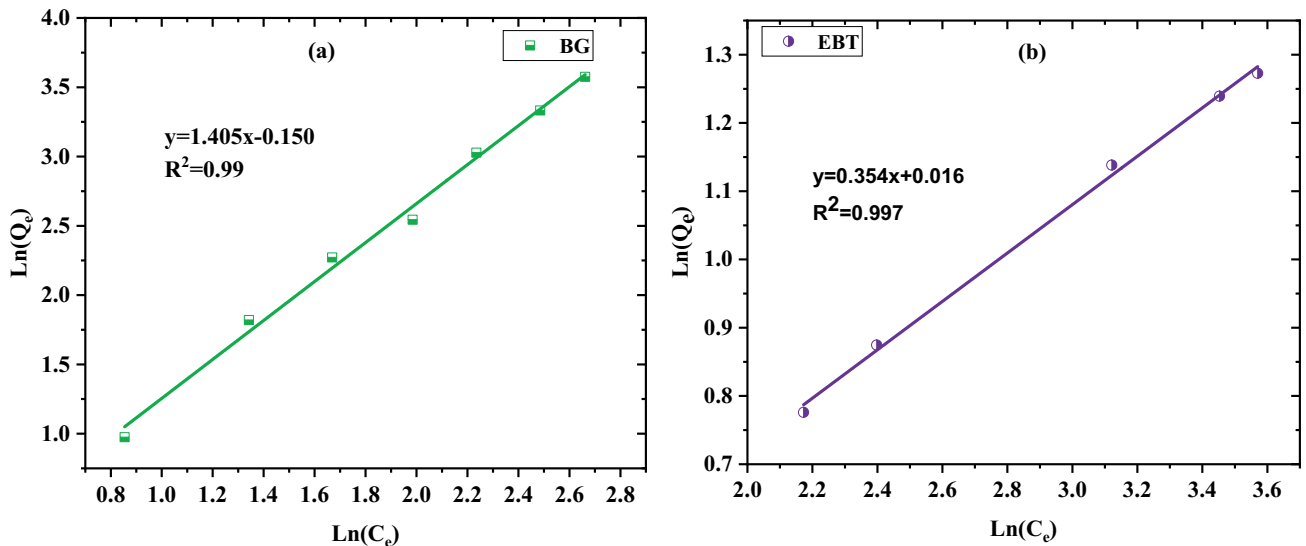
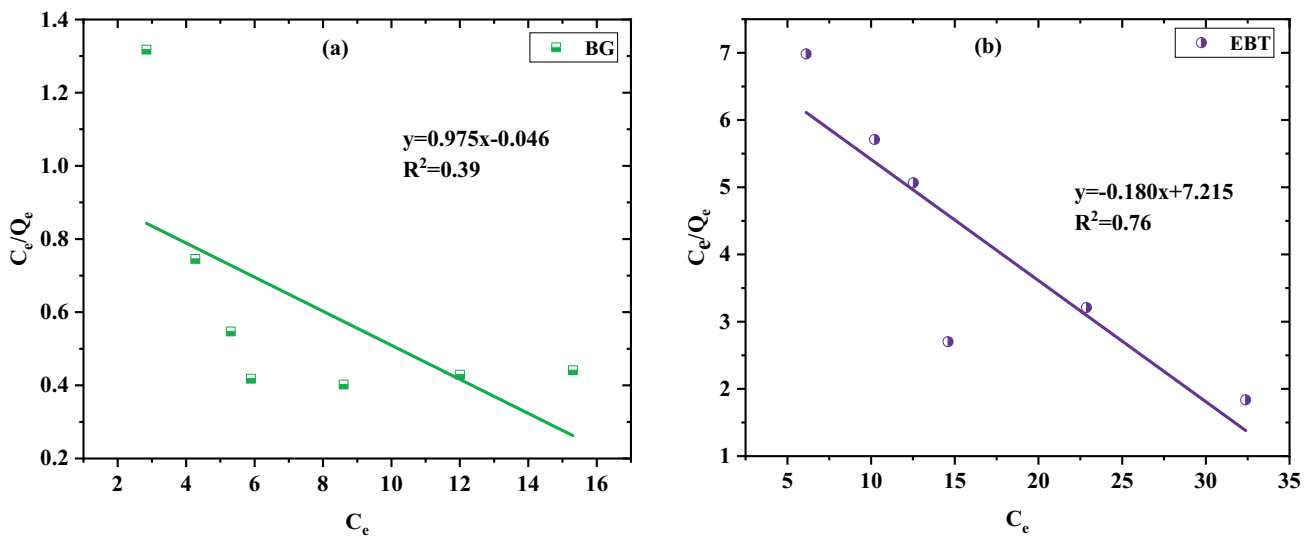Fig. 8. Isotherm of Freundlich of BG adsorption (a) of EBT adsorption.

Fig. 9. Isotherm of Langmuir of BG adsorption (a) of EBT adsorption (b).

adsorption capacity (mg g^{-1}), and K_L: is the equilibrium constant related to the affinity between adsorbent and adsorbate (L mg^{-1}).

The line is obtained by plotting C_e/Q_e as a function of C_e.

The Freundlich isothermal model suggests that the adsorption surface is heterogeneous with sites of different adsorption energies. The following equation expresses the linear Freundlich form [75]:

$$\ln Q_e = \ln K_f + \frac{1}{n_f}\ln C_e \qquad (6)$$

where K_f: is the Freundlich constant and $1/n_f$ is the adsorption intensity. If $1/n < 1$, the process is favorable and if $1/n > 1$, it represents unfavorable conditions [76]. Q_e: the capacity of adsorption at equilibrium (mg g^{-1}), C_e: equilibrium concentration (mg L^{-1}).

The graphical representation of $\ln(Q_e)$ as a function of $\ln(C_e)$ is a line with directing coefficient $1/n$ and y-intercept $\ln(K_f)$.

The Dubinin–Radushkevich isothermal model is a model generally applied to express the adsorption mechanism by distributing Gaussian energy over a non-homogeneous surface. The isothermal model for D–R is expressed by the following equation [77].

$$\ln q_e = \ln q_{mDR} - K_{DR}\varepsilon^2 \qquad (7)$$

where q_e: the amount of adsorbate in the adsorbent at equilibrium (mg g^{-1}), q_{mDR} theoretical isotherm saturation capacity (mg g^{-1}), K_{DR}: Dubinin–Radushkevich isotherm constant; and ε: potential of Polanyi.

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \qquad (8)$$

The adsorption energy constant E is calculated as follows:

$$E = \frac{1}{\sqrt{2K_{DR}}} \qquad (9)$$

The relative adsorption isotherms parameters of Langmuir, Freundlich, and Dubinin-Radushkevich were calculated and illustrated in Table 2. The graphical representations of the linear models are shown in Figs. 8–10. Based on the values of the maximum adsorption quantity and the calculated Langmuir equilibrium constants and determination coefficients, that $R^2 = 0.39$, $R^2 = 0.76$ are very far from 1. Therefore the studied process is not described by the Langmuir isotherm for the two dyes studied. Thus, the adsorption of BG and BET on the surface of the FBP material is multilayer. Whereas the adsorption of BG and EBT is satisfactorily described by the Freundlich model $R^2 = 0.99$. This isotherm indicates that the two dyes were adsorbing on heterogeneous surfaces and that it was a multi-layered

Table 2
Isotherm constants for dye adsorption

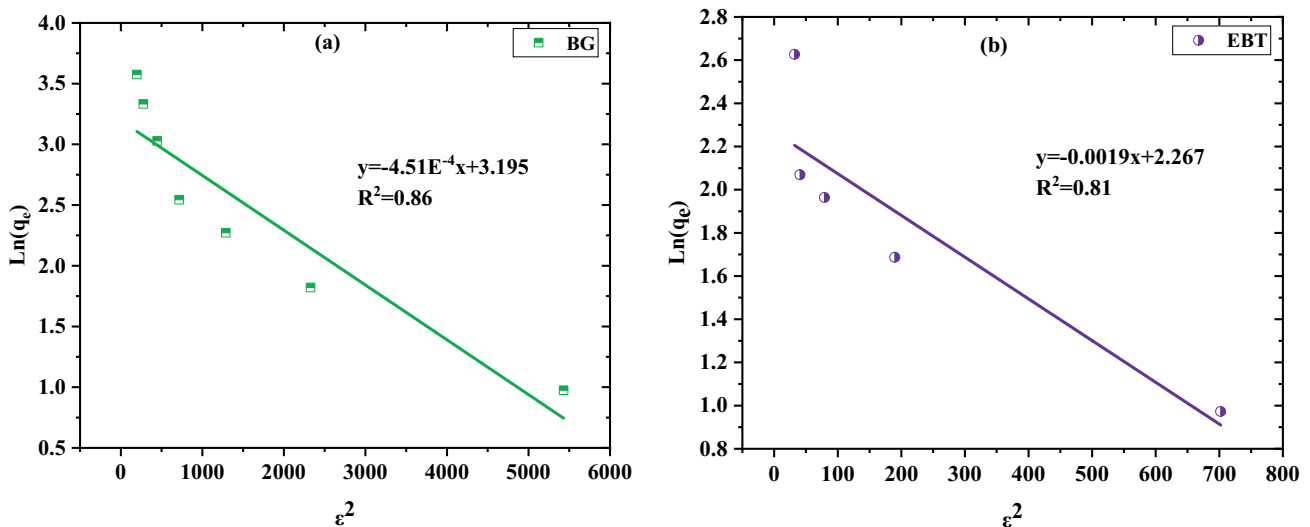|	Langmuir			Freundlich			Dubinin–Radushkevich			
	Q_{max} (mg g^{-1})	K_L (L mg^{-1})	R^2	K_f (mg g^{-1})	n_f	R^2	q_m (mol g^{-1})	K_{ad} (mol^{-2} J^{-2})	E (kJ mol^{-1})	R^2
BG	21.73	0.04	0.39	1.16	0.71	0.99	24.41	4.51·10^{-4}	33.3	0.86
EBT	5.55	0.02	0.76	1.01	2.82	0.99	9.65	1.9·10^{-3}	16.22	0.81

Fig. 10. Isotherm of D–R of BG adsorption (a) of EBT adsorption (b).

process. In this study, the value of *n* is 0.71, which means that the process is unfavorable for the adsorption of BG on FBP. On the other hand, the value of *n* is greater than unity (2.82), implying that the adsorption process to be favorable for EBT.

For the Dubinin-Radushkevich model, the average free energy was determined from the line graph of the D_{RK} model, *E* = 16.22 and 33.3 kJ mol^{-1} for BG and EBT respectively, this value is greater than 8 k mol^{-1} which explains that the adsorption process is of ion exchange type. As well as the determination coefficients of Brilliant Green and Eriochrome Black T are of the order R^2 = 0.86 and 0.81, respectively.

3.8. Thermodynamics of adsorption

The study of the influence of temperature on the adsorption of the two dyes on the substrate studied makes it possible to determine thermodynamic parameters such as the variation of the standard entropy $\Delta S°$, the variation of standard enthalpy $\Delta H°$ and Gibbs free energy variation of $\Delta G°$. These standard thermodynamic adsorption quantities are related to the dissolved body distribution coefficient (K_d) by the following equations [78]:

$$K_d = \frac{Q_e}{C_e} \tag{10}$$

$$\Delta G° = -RT \cdot \ln K_d \tag{11}$$

$$\ln K_d = \frac{\Delta S°}{R} - \frac{\Delta H°}{R} \cdot \frac{1}{T} \tag{12}$$

$$\Delta S° = \frac{\Delta H° - \Delta G°}{T} \tag{13}$$

where *R*: the perfect gas constant (*R* = 8.314 J mol^{-1} K^{-1}), *T*: the absolute temperature of the solution (K), K_d: the partition coefficient, Q_e: the amount of adsorbate in the adsorbent at equilibrium (mg g^{-1}), and C_e: equilibrium concentration (mg L^{-1}).

Plotting the $\ln K_d$ curve as a function of (1/*T*) allows you to calculate ΔH (slope of the line) and ΔS (y-intercept). Fig. 11 shows the $\ln K_d = f(1/T)$ curve for the adsorption of BG and EBT by fava bean peels. The thermodynamic parameters of this process are shown in Table 3.

The results grouped in Table 3 show that the enthalpy ΔH values of BG adsorption are positive. Thus, we can confirm that the adsorption process is endothermic, while for EBT, the values are negative so, the adsorption process is exothermic. The negative values of free enthalpy ΔG shows that the adsorption process is feasible and thermodynamically spontaneous for Eriochrome Black T, while the positive $\Delta G°$ values suggesting that the sorption process of BG on FBP was unspontaneous. Generally, the binding energies of physical adsorption are in general <80 kJ mol^{-1}, while the energies of a chemical bond are between 80 and 400 kJ mol^{-1} [79,80]. In our case, the enthalpy values are between

Table 3
Equilibrium constant and thermodynamic parameters for the adsorption of BG and EBT onto FBP biosorbent

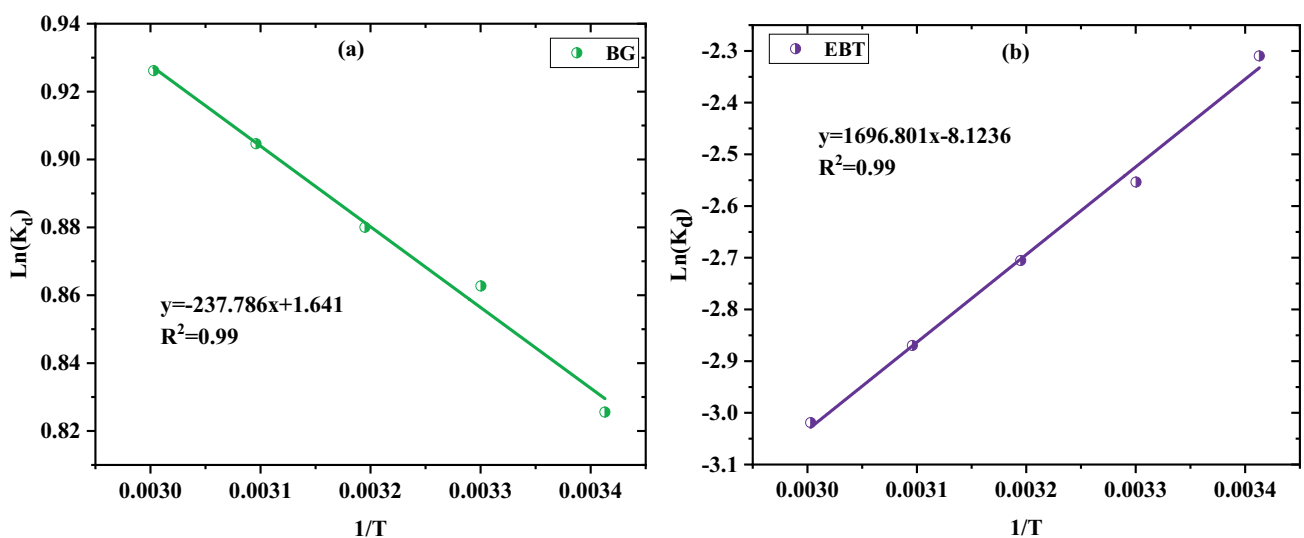|	$\Delta H°$ (kJ mol^{-1})	$\Delta S°$ (J mol^{-1} K^{-1})	$\Delta G°$ (kJ mol^{-1})				
			20°C	30°C	40°C	50°C	60°C
BG	1.976	−0.985	2.011	2.173	2.290	2.429	2.564
EBT	−14.107	−22.786	−5.626	−6.433	−7.040	−7.706	−8.358

Fig. 11. Trace of $\ln K_d$ as a function of 1/*T*.

–8.358 and 2.564 kJ mol^{-1}, which means that the adsorption of BG and EBT by FBPs is physical in nature. On the other hand, the entropy ΔS negative values of the two dyes reflect the increased disorder at the solid/liquid interface.

3.9. Effect of ionic strength

Wastewater comes from textile industries; water contains various concentrations of organic and inorganic ions and usually cations [81].

One of the factors controlling the electrostatic and non-electrostatic interactions between the adsorbate and the adsorbent surface is the ionic strength due to the presence of salts in the solution [82]. To understand the impact of this parameter on the adsorption process of the two anionic and cationic dyes on FBP, different concentrations of sodium chloride (NaCl) and potassium chloride (KCl) (0.1–0.4 g L^{-1}); were added to the dyes at high concentrations initial 20 mg L^{-1} and an FBP ratio of 5 g L^{-1} at residual pH of the solution.

The results have shown that increasing the ionic strength from 0.1 to 0.4 g L^{-1} of NaCl and KCl resulted in a slight decrease in the adsorbed amount of BG, which is consistent with the conclusions of Hai Nguyen Tran et al. They reported that the amount of basic dye adsorbed only showed a small change. Therefore, they concluded that electrostatic screening does not affect the adsorption of cationic BG. For EBT, the amount adsorbed also decreased with increasing salt concentration. This decrease is explained either by the competition between the ions Cl$^-$ and anionic EBT [83], or by the protective effect of Cl$^-$ for the ammonium groups on the bio-adsorbents is increased and consequently, the adsorption of the Anionic EBT is limited due to the repulsive force between Cl$^-$ and anionic EBT [84].

3.10. Desorption reaction and adsorbents regeneration

Desorption studies were conducted; with Distilled Water. All the experiments were performed; after saturation of FBP at 5 g L^{-1}, with an initial 20 mg L^{-1} solution of BG and EBT separately. The concentrations of desorbed dye were determined; from their absorbance characteristics in the UV-visible range. To verify the economic viability of the adsorption process, the regeneration of the adsorbents is an essential step.

The desorption efficiency and the desorption elimination of the dye are given below (Eqs. (14) and (15)) [85]:

$$Q_{e,\text{desorption}}\left(\text{mg/g}\right) = V\left(\frac{C_f}{M}\right) \tag{14}$$

$$Q_{c\%} = \left(\frac{Q_{e,\text{desorption}}}{q_{e,\text{sorption}}}\right) \times 100 \tag{15}$$

where M is the weight of spent adsorbent (g), V is the volume of the solvent (L), C_f is the dye concentration in the solvent (mg L^{-1}).

Regeneration experiments were performed using 200 mL of the colored solution for four successive cycles. There was a gradual decrease in the desorption and removal efficiencies of BG and EBT with the increasing number of cycles as shown in Figs. 12a and 12b, respectively. For BG, desorption efficiencies of the four cycles decreased from 17.56% to 11.42%. However, there is a slight decrease in the elimination efficiencies of Cycles 1, 2, 3, and 4 with 90.84%, 89.43%, 85.91%, and 84.61%, respectively, as shown in Fig. 12a. While in Fig. 12b, BET desorption efficiencies for cycles 1, 2, 3, and 4 were 26.9%, 21.01%, 15.81%, and 10.62%, respectively. While the elimination efficiencies of the four cycles decreased from 31.7% to 11.26%. The regeneration experiments presented in Fig. 12 showed that the fava bean peels could be reused repeatedly in the adsorption and recovery of Brilliant Green and Eriochrome Black T dyes without significantly losing their adsorption properties.

3.11. Comparison with other adsorbents

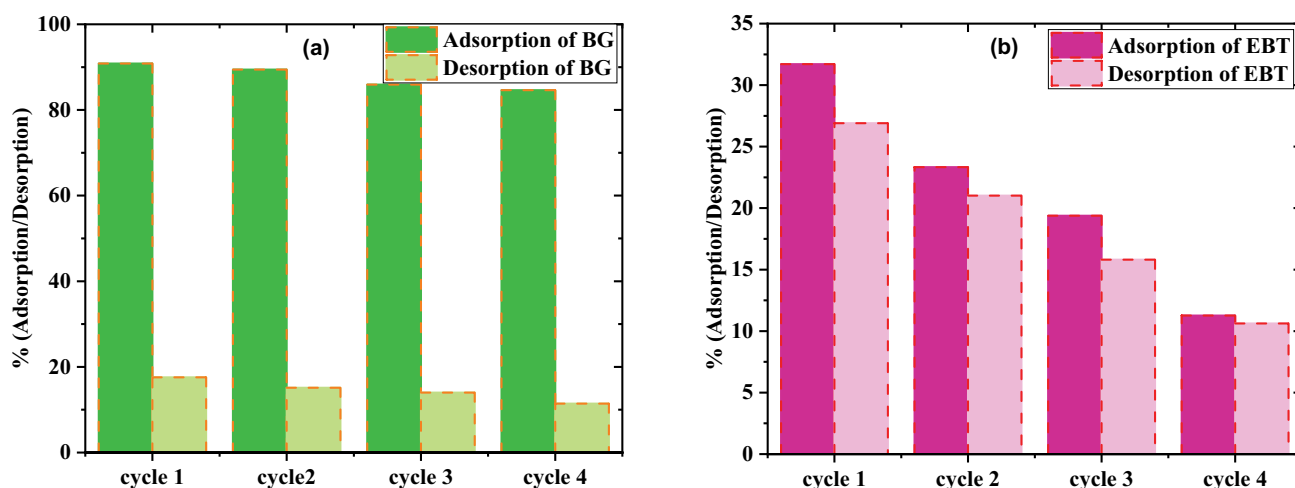The efficiency of the adsorption of brilliant green and Eriochrome Black T for various adsorbent materials

Fig. 12. Regeneration study of FBP saturated with BG (a) and with EBT (b). Initial dye concentration 20 mg L^{-1}, adsorbent amount: 5 g L^{-1}.

Table 4
Comparison of capacity and parameters of various adsorbents for BG and EBT adsorption

Adsorbate	Adsorbent	Operatory conditions	Equilibrium time (min)	Kinetic model	Isotherm model	Equilibrium adsorption amount (mg g^{-1})	References
	Salix alba leaves	$C_i = 50$ mg L^{-1} Mass = 0.15 g pH = 6 $T = 25°C$	210	Pseudo-second-order	Langmuir	15.89	[86]
	Guava seeds activated carbon	–	–	Pseudo-second-order	Langmuir	80.5	[87]
	Guava tree wood activated carbon	pH = 7		Pseudo-second-order	Freundlich	90	[88]
Brilliant Green	Date pits activated carbon	Mass = 0.06 g $T = 25°C$ pH = 8	55	Pseudo-second-order	Freundlich	77.8	[89]
	Sugarcane bagasse	$T = 50°C$	–	Pseudo-second-order	Langmuir	24.32	[90]
	Areca nut husk	pH = 7 Adsorbent dose = 10 g L^{-1} $C_i = 100$ mg L^{-1} $T = 25°C$	–	Pseudo-second-order	Langmuir	18.21	[91]
	Fava bean peels	Mass = 0.2 g $C_i = 40$ mg L^{-1} $T = 20°C$	80	Pseudo-second-order	Freundlich	7.91	This work
	Fucus vesiculosus (brown algae)	pH = 6 $T = 30°C$	17	–	Langmuir	21.26	[92]
	Eucalyptus bark	pH = 2 $T = 30°C$	–	–		52.36	[93]
	Date palm ash/MgAl	pH = 2 $T = 25°C$	180	Pseudo-second-order	Langmuir	167.84	[94]
Eriochrome Black T	Green coffee residue	pH = 6	–	Pseudo-second-order	Freundlich	60.60	[95]
	Fatted jojoba residues	pH = 2	600	Pseudo-second-order	Freundlich	88.96	[96]
	Defatted jojoba residues	pH = 2	600	Pseudo-second-order	Freundlich	113.50	
	Fava bean peels	Mass = 0.2 g $C_i = 40$ mg L^{-1} $T = 20°C$	40	Pseudo-second-order	Freundlich	7.91	This work

according to studies in the literature is presented in Table 1 in which we have gathered the results of this work as well as the conditions necessary for making comparisons. Table 4 confirms that, in comparison to other research, the adsorption processes of Eriochrome Black T and Brilliant Green on the fava bean peels surface show relatively shorter equilibrium times but very lower adsorption capacities. Despite these results, we can still qualify the bean peels by their efficiency since they are a valuable agri-food waste due to their abundance in all regions of Moroccan territory and that there is always the possibility of making it more promising especially by activating more sites in its specific adsorption surface via experimental protocols that can be applied in the scale of our research laboratory.

4. Conclusion

The novelty of this study is the use of an abundant and inexpensive adsorbent (bean peels) for the efficient removal of two different dangerous dyes, Erichrome Black T (anionic dye) and Brilliant Green (cationic dye). The maximum amount of dye adsorbed is estimated at 21.73 and 5.55 mg g^{-1} for BG and EBT, respectively. The adsorption of the two dyes followed the Freundlich isotherm, and therefore the fava bean peels had heterogeneous surfaces. Kinetic studies have revealed that the adsorption process of the two dyes follows the pseudo-second-order model. The processes of adsorption were endothermic for Brilliant Green and exothermic for Eriochrome Black T, according to thermodynamic analyses. It was also found that the adsorption of the BG dye was a much more efficient process than the adsorption of the EBT dye on FBP. From this study, it can be concluded that the use of bean peels as a natural adsorbent, without pretreatment or activation, is effective for the adsorption of cationic dyes compared to anionic dyes. In addition to the advantage of their availability in large quantities, it presents an ecological alternative to traditional wastewater treatment processes. It would be interesting to continue testing on real wastewater and not just on batch processes but also pilot-scale column processes.

References

[1] G.M. Al-Senani, N.S. Al-Kadhi, Studies on adsorption of fluorescein dye from aqueous solutions using wild herbs, Int. J. Anal. Chem., 2020 (2020) 1–9, doi: 10.1155/2020/8019274.

[2] R.V. Kandisa, N. Saibaba, Dye removal by adsorption: a review, J. Biorem. Biodegrad., 7 (2016) 1000371, doi: 10.4172/2155-6199.1000371.

[3] K. Golka, S. Kopps, Z.W. Myslak, Carcinogenicity of azo colorants: influence of solubility and bioavailability, Toxicol. Lett., 151 (2004) 203–210.

[4] S. Shojaei, S. Khammarnia, S. Shojaei, M. Sasani, Removal of Reactive Red 198 by nanoparticle zero valent iron in the presence of hydrogen peroxide, J. Water Environ. Nanotechnol., 2 (2017), doi: 10.22090/jwent.2017.02.008.

[5] K. Kadirvelu, M. Kavipriya, C. Karthika, M. Radhika, N. Vennilamani, S. Pattabhi, Utilization of various agricultural wastes for activated carbon preparation and application for the removal of dyes and metal ions from aqueous solutions, Bioresour. Technol., 87 (2003) 129–132.

[6] A.T. Shah, M.I. Din, F.N. Kanwal, M.L. Mirza, Direct synthesis of mesoporous molecular sieves of Ni-SBA-16 by internal pH adjustment method and its performance for adsorption of toxic Brilliant Green dye, Arabian J. Chem., 8 (2015) 579–586.

[7] A. Mittal, D. Kaur, J. Mittal, Applicability of waste materials—bottom ash and deoiled soya—as adsorbents for the removal and recovery of a hazardous dye, brilliant green, J. Colloid Interface Sci., 326 (2008) 8–17.

[8] B.K. Nandi, A. Goswami, M.K. Purkait, Adsorption characteristics of brilliant green dye on kaolin, J. Hazard. Mater., 161 (2009) 387–395.

[9] R. Ahmad, K. Ansari, Chemically treated *Lawsonia inermis* seeds powder (CTLISP): an eco-friendly adsorbent for the removal of brilliant green dye from aqueous solution, Groundwater Sustainable Dev., 11 (2020) 100417, doi: 10.1016/j.gsd.2020.100417.

[10] E.A. Moawed, A.E. Wahba, R.A. Gabr, Synthesis and application of LGB/St/Al$_2$O$_3$ biocomposite for sensitive detection and efficient removal of brilliant green dye from wastewater, J. Environ. Chem. Eng., 6 (2018) 7225–7232.

[11] V. Javanbakht, R. Shafiei, Preparation and performance of alginate/basil seed mucilage biocomposite for removal of eriochrome black T dye from aqueous solution, Int. J. Biol. Macromol., 152 (2020) 990–1001.

[12] A. Gogoi, M. Navgire, K.C. Sarma, P. Gogoi, Highly efficient heterogeneous Fenton activities of magnetic β-cyclodextrin (Fe) framework for Eriochrome black T degradation, Mater. Chem. Phys., 231 (2019) 233–243.

[13] Y. Kaur, T. Jasrotia, R. Kumar, G.R. Chaudhary, S. Chaudhary, Adsorptive removal of eriochrome black T (EBT) dye by using surface active low cost zinc oxide nanoparticles: a comparative overview, Chemosphere, 278 (2021) 130366, doi: 10.1016/j.chemosphere.2021.130366.

[14] M. Zubair, H.A. Aziz, M.A. Ahmad, I. Ihsanullah, M.A. Al-Harthi, Adsorption and reusability performance of M-Fe (M = Co, Cu, Zn and Ni) layered double hydroxides for the removal of hazardous Eriochrome Black T dye from different water streams, J. Water Process Eng., 42 (2021) 102060, doi: 10.1016/j.jwpe.2021.102060.

[15] A. Al-Kdasi, A. Idris, K. Saed, C.T. Guan, Treatment of textile wastewater by advanced oxidation processes – a review, Global Nest J., 6 (2004) 222–230, doi: 10.30955/gnj.000288.

[16] B.H. Hameed, A.A. Ahmad, Batch adsorption of methylene blue from aqueous solution by garlic peel, an agricultural waste biomass, J. Hazard. Mater., 164 (2009) 870–875.

[17] N. Modirshahla, A. Hassani, M.A. Behnajady, R. Rahbarfam, Effect of operational parameters on decolorization of Acid Yellow 23 from wastewater by UV irradiation using ZnO and ZnO/SnO$_2$ photocatalysts, Desalination, 271 (2011) 187–192.

[18] N.A. Zubir, C. Yacou, X. Zhang, J.C. Diniz da Costa, Optimisation of graphene oxide–iron oxide nanocomposite in heterogeneous Fenton-like oxidation of Acid Orange 7, J. Environ. Chem. Eng., 2 (2014) 1881–1888.

[19] S. Zinadini, A.A. Zinatizadeh, M. Rahimi, V. Vatanpour, H. Zangeneh, M. Beygzadeh, Novel high flux antifouling nanofiltration membranes for dye removal containing carboxymethyl chitosan coated Fe$_3$O$_4$ nanoparticles, Desalination, 349 (2014) 145–154.

[20] A. Aarfane, S. Tahiri, A. Salhi, G. El Kadiri Boutchich, M. Siniti, M. Bensitel, B. Sabour, M. El Krati, Adsorption of methylene blue and Red195 dyes in aqueous medium by palm bark and sugarcane bagasse: kinetic and thermodynamic study, JMESCN, 6 (2015) 2944–2957.

[21] M. Asgher, H.N. Bhatti, Evaluation of thermodynamics and effect of chemical treatments on sorption potential of *Citrus* waste biomass for removal of anionic dyes from aqueous solutions, Ecol. Eng., 38 (2012) 79–85.

[22] M. Hao, M. Qiu, H. Yang, B. Hu, X. Wang, Recent advances on preparation and environmental applications of MOF-derived carbons in catalysis, Sci. Total Environ., 760 (2021) 143333, doi: 10.1016/j.scitotenv.2020.143333.

[23] M. Zhang, Z. Yu, H. Yu, Adsorption of Eosin Y, methyl orange and brilliant green from aqueous solution using ferroferric oxide/polypyrrole magnetic composite, Polym. Bull., 77 (2020) 1049–1066.

[24] V.K. Gupta, S. Agarwal, R. Ahmad, A. Mirza, J. Mittal, Sequestration of toxic congo red dye from aqueous solution

using ecofriendly guar gum/ activated carbon nanocomposite., Int. J. Biol. Macromol., 158 (2020) 1310–1318.

[25] N.D. Mu'azu, N. Jarrah, T.S. Kazeem, M. Zubair, M. Al-Harthi, Bentonite-layered double hydroxide composite for enhanced aqueous adsorption of Eriochrome Black T, Appl. Clay Sci., 161 (2018) 23–34.

[26] A. Mittal, J. Mittal, Hen Feather: A Remarkable Adsorbent for Dye Removal, S.K. Sharma, Ed., Green Chem. Dyes Remov. Wastewater, John Wiley & Sons, Inc., Hoboken, NJ, USA, 2015, pp. 409–457. Available at: https://doi.org/10.1002/9781118721001. ch11.

[27] S. Samsami, M. Mohamadizaniani, M.-H. Sarrafzadeh, E.R. Rene, M. Firoozbahr, Recent advances in the treatment of dye-containing wastewater from textile industries: overview and perspectives, Process Saf. Environ. Prot., 143 (2020) 138–163.

[28] Y. Xia, Y. Jin, J. Qi, H. Chen, G. Chen, S. Tang, Preparation of biomass carbon material based on Fomes fomentarius via alkali activation and its application for the removal of brilliant green in wastewater, Environ. Technol. Innov., 23 (2021) 101659, doi: 10.1016/j.eti.2021.101659.

[29] L.C. Maia, L.C. Soares, L.V. Alves Gurgel, A review on the use of lignocellulosic materials for arsenic adsorption, J. Environ. Manage., 288 (2021) 112397, doi: 10.1016/j.jenvman.2021. 112397

[30] D. Ghosh, K.G. Bhattacharyya, Adsorption of methylene blue on kaolinite, Appl. Clay Sci., 20 (2002) 295–300.

[31] S. Guiza, M. Bagane, Étude cinétique de l'adsorption du rouge de Congo sur une bentonite, Rev. Sci. L'eau, 26 (2013) 39–50.

[32] R.A. Schoonheydt, C.T. Johnston, The Surface Properties of Clay Minerals, M.F. Brigatti, A. Mottana, Eds., Layer. Miner. Struct. Their Appl. Adv. Technol., Mineralogical Society of Great Britain and Ireland, London, 2011, pp. 335–370. Available at: https://doi.org/10.1180/EMU-notes.11.10

[33] M. Alkan, Ö. Demirbaş, M. Doğan, Adsorption kinetics and thermodynamics of an anionic dye onto sepiolite, Microporous Mesoporous Mater., 101 (2007) 388–396.

[34] E. Bulut, M. Özacar, İ.A. Şengil, Equilibrium and kinetic data and process design for adsorption of Congo Red onto bentonite, J. Hazard. Mater., 154 (2008) 613–622.

[35] L. Lian, L. Guo, C. Guo, Adsorption of Congo red from aqueous solutions onto Ca-bentonite, J. Hazard. Mater., 161 (2009) 126–131.

[36] A. Xue, S. Zhou, Y. Zhao, X. Lu, P. Han, Adsorption of reactive dyes from aqueous solution by silylated palygorskite, Appl. Clay Sci., 48 (2010) 638–640.

[37] Y. Miyah, A. Lahrichi, M. Idrissi, S. Boujraf, H. Taouda, F. Zerrouq, Assessment of adsorption kinetics for removal potential of Crystal Violet dye from aqueous solutions using Moroccan pyrophyllite, J. Assoc. Arab Univ. Basic Appl. Sci., 23 (2017) 20–28.

[38] N. Loubna, M. Youssef, A. Ouissal, E.B. Aziz, K. Bouchta, Z. Farid, Kinetic and thermodynamicstudy of the adsorption of twodyes:brilliant green and eriochrome black T using a natural adsorbent "sugarcane bagasse", Mor. J. Chem., 7 (2019) 652–659.

[39] M. Elgeundi, Colour removal from textile effluents by adsorption techniques, Water Res., 25 (1991) 271–273.

[40] C. Namasivayam, M. Dinesh Kumar, K. Selvi, R. Ashruffunissa Begum, T. Vanathi, R.T. Yamuna, 'Waste' coir pith—a potential biomass for the treatment of dyeing wastewaters, Biomass Bioenergy, 21 (2001) 477–483.

[41] S. Boumchita, A. Lahrichi, Y. Benjelloun, S. Lairini, V. Nenov, F. Zerrouq, Elimination d'un colorant cationique dans une solution aqueuse par un déchet alimentaire: Epluchure de pomme de terre [Removal of cationic dye from aqueous solution by a food waste: potato peel], J. Mater. Environ. Sci., 7 (2016) 9–17.

[42] S. Guiza, M. Bagane, A.H. Al-Soudani, H.B. Amore, Adsorption of basic dyes onto natural clay, Adsorpt. Sci. Technol., 22 (2004) 245–255.

[43] A. Bhatnagar, A.K. Minocha, Conventional and non-conventional adsorbents for removal of pollutants from water – a review, Indian J. Chem. Technol., 13 (2006) 203–217.

[44] S.J. Allen, B. Koumanova, Decolourisation of water/wastewater using adsorption (review), 40 (2005) 175–192.

[45] D.M.M. Aguila, M.V. Ligaray, Ulsan national institute of science and technology, Korea, adsorption of Eriochrome Black T on MnO₂-coated zeolite, Int. J. Environ. Sci. Dev., 6 (2015) 824–827.

[46] A. Khalid, M. Zubair, Ihsanullah, A comparative study on the adsorption of Eriochrome Black T dye from aqueous solution on graphene and acid-modified graphene, Arabian J. Sci. Eng., 43 (2018) 2167–2179.

[47] S.M. de Oliveira Brito, J.L.C. Cordeiro, L. da Cunha Ramalho, J.F.R. Oliveira, Eriochrome black adsorption on yellow passion fruit peel (Passiflora edulis f. Flavicarpa) treated with sodium hydroxide and nitric acid: study of adsorption isotherms, kinetic models and thermodynamic parameters, SN Appl. Sci., 1 (2019) 1226, doi: 10.1007/s42452-019-1266-x.

[48] I. Ali Mayasa, A. Salman Taghried, Eriochrome Black T dye adsorption onto natural and modified orange peel, Res. J. Chem. Environ., 23 (2019) 155–169 Available at: https:// worldresearchersassociations.com/ChemSpecialMay2019/20. pdf

[49] O.C. Elijah, T. Nwabanne Joseph, Adsorption studies on the removal of Eriochrome black-T from aqueous solution using Nteje clay, SOP Trans. Appl. Chem., 1 (2014) 14–25.

[50] G. Zeydouni, M. Kianizadeh, Y. Omidi Khaniabadi, H. Nourmoradi, S. Esmaeili, M.J. Mohammadi, R. Rashidi, Eriochrme black-T removal from aqueous environment by surfactant modified clay: equilibrium, kinetic, isotherm, and thermodynamic studies, Toxin Rev., 38 (2019) 307–317.

[51] R. Rehman, S.J. Muhammad, M. Arshad, Brilliant Green and Acid Orange 74 dyes removal from water by Pinus roxburghii leaves in naturally benign way: an application of green chemistry, J. Chem., 2019 (2019) 1–10, doi: 10.1155/2019/3573704.

[52] Y.İ. Coşkun, N. Aksuner, J. Yanik, Sandpaper wastes as adsorbent for the removal of brilliant green and malachite green dye, Acta Chim. Slov., 66 (2019) 402–413.

[53] N. Laskar, U. Kumar, Removal of Brilliant Green dye from water by modified Bambusa tulda: adsorption isotherm, kinetics and thermodynamics study, Int. J. Environ. Sci. Technol., 16 (2019) 1649–1662.

[54] I.A. Ahmed, A.H. Ragab, M.A. Habila, T.S. Alomar, E.H. Aljuhani, Equilibrium and kinetic study of anionic and cationic pollutants remediation by limestone–chitosan–alginate nanocomposite from aqueous solution, Molecules, 26 (2021) 2586, doi: 10.3390/molecules26092586.

[55] E. Ben Khalifa, B. Rzig, R. Chakroun, H. Nouagui, B. Hamrouni, Application of response surface methodology for chromium removal by adsorption on low-cost biosorbent, Chemom. Intell. Lab. Syst., 189 (2019) 18–26, doi: 10.1016/j. chemolab.2019.03.014.

[56] A.H. Hashem, E. Saied, M.S. Hasanin, Green and ecofriendly bio-removal of methylene blue dye from aqueous solution using biologically activated banana peel waste, Sustain. Chem. Pharm., 18 (2020) 100333, doi: 10.1016/j.scp.2020.100333.

[57] S. Ben-Ali, I. Jaouali, S. Souissi-Najar, A. Ouederni, Characterization and adsorption capacity of raw pomegranate peel biosorbent for copper removal, J. Cleaner Prod., 142 (2017) 3809–3821.

[58] M.H.G. Canteri, C.M.G.C. Renard, C. Le Bourvellec, S. Bureau, ATR-FTIR spectroscopy to determine cell wall composition: application on a large diversity of fruits and vegetables, Carbohydr. Polym., 212 (2019) 186–196.

[59] J.-S. Cao, J.-X. Lin, F. Fang, M.-T. Zhang, Z.-R. Hu, A new absorbent by modifying walnut shell for the removal of anionic dye: kinetic and thermodynamic studies, Bioresour. Technol., 163 (2014) 199–205.

[60] A. Fazio, C. La Torre, F. Dalena, P. Plastina, Screening of glucan and pectin contents in broad bean (Vicia faba L.) pods during maturation, Eur. Food Res. Technol., 246 (2020) 333–347.

[61] M.E.M. Ali, H. Abdelsalam, N.S. Ammar, H.S. Ibrahim, Response surface methodology for optimization of the adsorption capability of ball-milled pomegranate peel for different pollutants, J. Mol. Liq., 250 (2018) 433–445.

[62] Z.M. née Benkartoussa, B. Karima, B.L. Mossaab, Adsorption of Eriochrome Black T (EBT) dye using activated carbon prepared from potato peels, J. Dr., 1 (2015). Available at: http://jdoc.sawis.org/wp-content/uploads/sites/12/2015/12/numero-01-JDOC-vf-10-13.pdf

[63] S. Rahdar, A. Rahdar, M. Sattari, L.D. Hafshejani, A.K. Tolkou, G.Z. Kyzas, Barium/cobalt@polyethylene glycol nanocomposites for dye removal from aqueous solutions, Polymers, 13 (2021) 1161, doi: 10.3390/polym13071161.

[64] F. Güzel, H. Sayğılı, G. Akkaya Sayğılı, F. Koyuncu, New low-cost nanoporous carbonaceous adsorbent developed from carob (*Ceratonia siliqua*) processing industry waste for the adsorption of anionic textile dye: characterization, equilibrium and kinetic modeling, J. Mol. Liq., 206 (2015) 244–255.

[65] B.S. Giri, S. Gun, S. Pandey, A. Trivedi, R.T. Kapoor, R.P. Singh, O.M. Abdeldayem, E.R. Rene, S. Yadav, P. Chaturvedi, N. Sharma, R.S. Singh, Reusability of brilliant green dye contaminated wastewater using corncob biochar and *Brevibacillus parabrevis*: hybrid treatment and kinetic studies, Bioengineered, 11 (2020) 743–758.

[66] N.U.M. Nizam, M.M. Hanafiah, E. Mahmoudi, A.A. Halim, A.W. Mohammad, The removal of anionic and cationic dyes from an aqueous solution using biomass-based activated carbon, Sci. Rep., 11 (2021) 8623, doi: 10.1038/s41598-021-88084-z.

[67] M. Benjelloun, Y. Miyah, G. Akdemir Evrendilek, F. Zerrouq, S. Lairini, Recent advances in adsorption kinetic models: their application to dye types, Arabian J. Chem., 14 (2021) 103031, doi: 10.1016/j.arabjc.2021.103031.

[68] R.-L. Tseng, F.-C. Wu, R.-S. Juang, Characteristics and applications of the Lagergren's first-order equation for adsorption kinetics, J. Taiwan Inst. Chem. Eng., 41 (2010) 661–669.

[69] F. Mejbar, Y. Miyah, A.E. Badraoui, L. Nahali, A. Ouissal, A. Khalil, F. Zerrouq, Studies of the adsorption kinetics process for removal of methylene blue dye by residue of grenadine bark extraction, Mor. J. Chem., 6 (2019) 436–443.

[70] Y. Miyah, A. Lahrichi, M. Idrissi, A. Khalil, F. Zerrouq, Adsorption of methylene blue dye from aqueous solutions onto walnut shells powder: equilibrium and kinetic studies, Surf. Interfaces, 11 (2018) 74–81.

[71] W.J. Weber, J.C. Morris, Kinetics of adsorption on carbon from solution, J. Sanit. Eng. Div., 89 (1963) 31–59.

[72] A. Mariyam, J. Mittal, F. Sakina, R.T. Baker, A.K. Sharma, A. Mittal, Efficient batch and fixed-bed sequestration of a basic dye using a novel variant of ordered mesoporous carbon as adsorbent, Arabian J. Chem., 14 (2021) 103186, doi: 10.1016/j.arabjc.2021.103186.

[73] M. Belhachemi, F. Addoun, Comparative adsorption isotherms and modeling of methylene blue onto activated carbons, Appl. Water Sci., 1 (2011) 111–117.

[74] I. Langmuir, The adsorption of gases on plane surfaces of glass, mica and platinum., J. Am. Chem. Soc., 40 (1918) 1361–1403.

[75] O. Assila, K. Tanji, M. Zouheir, A. Arrahli, L. Nahali, F. Zerrouq, A. Kherbeche, Adsorption studies on the removal of textile effluent over two natural eco-friendly adsorbents, J. Chem., 2020 (2020) 1–13, doi: 10.1155/2020/6457825.

[76] N. Fakhar, S. Ayoub Khan, W. Ahmad Siddiqi, T. Alam Khan, Ziziphus jujube waste-derived biomass as cost-effective adsorbent for the sequestration of Cd^{2+} from aqueous solution: Isotherm and kinetics studies, Environ. Nanotechnol. Monit. Manage., 16 (2021) 100570, doi: 10.1016/j.enmm.2021.100570.

[77] N. Ayawei, A.N. Ebelegi, D. Wankasi, Modelling and interpretation of adsorption isotherms, J. Chem., 2017 (2017) 1–11, doi: 10.1155/2017/3039817.

[78] A.E. Badraoui, Y. Miyah, L. Nahali, F. Zerrouq, Fast adsorption for removal of methylene blue from aqueuous solutions using of local clay, Mor. J. Chem., 7 (2019) 416–423.

[79] M. El Haddad, R. Slimani, R. Mamouni, S. El-Antri, S. Lazar, Removal of two textile dyes from aqueous solutions onto calcined bones, J. Assoc. Arab Univ. Basic Appl. Sci., 14 (2013) 51–59.

[80] N.M. Mahmoodi, B. Hayati, M. Arami, C. Lan, Adsorption of textile dyes on Pine Cone from colored wastewater: kinetic,

[81] Y. Miyah, A. Lahrichi, R. Kachkoul, G. El Mouhri, M. Idrissi, S. Iaich, F. Zerrouq, Multi-parametric filtration effect of the dyes mixture removal with the low cost materials, Arabian J. Basic Appl. Sci., 27 (2020) 248–258.

[82] C. Moreno-Castilla, J. Rivera-Utrilla, Carbon materials as adsorbents for the removal of pollutants from the aqueous phase, MRS Bull., 26 (2001) 890–894.

[83] N.S. Maurya, A.K. Mittal, P. Cornel, E. Rother, Biosorption of dyes using dead macro fungi: Effect of dye structure, ionic strength and pH, Bioresour. Technol., 97 (2006) 512–521.

[84] M.K. Dahri, M.R.R. Kooh, L.B.L. Lim, Application of *Casuarina equisetifolia* needle for the removal of methylene blue and malachite green dyes from aqueous solution, Alex. Eng. J., 54 (2015) 1253–1263.

[85] Momina, M. Rafatullah, S. Ismail, A. Ahmad, Optimization study for the desorption of methylene blue dye from clay based adsorbent coating, Water, 11 (2019) 1304, doi: 10.3390/w11061304.

[86] R. Fiaz, M. Hafeez, R. Mahmood, Removal of brilliant green (BG) from aqueous solution by using low cost biomass *Salix alba* leaves (SAL): thermodynamic and kinetic studies, J. Water Reuse Desalination, 10 (2020) 70–81.

[87] R. Mansour, M.G. Simeda, A. Zaatout, Adsorption studies on brilliant green dye in aqueous solutions using activated carbon derived from guava seeds by chemical activation with phosphoric acid, Desal. Water Treat., 202 (2020) 396–409.

[88] R.A. Mansour, A. El Shahawy, A. Attia, M.S. Beheary, Brilliant green dye biosorption using activated carbon derived from guava tree wood, Int. J. Chem. Eng., 2020 (2020) 1–12.

[89] R.A.E.-G. Mansour, M.G. Simeda, A.A. Zaatout, Removal of brilliant green dye from synthetic wastewater under batch mode using chemically activated date pit carbon, RSC Adv., 11 (2021) 7851–7861.

[90] P. Pathak, V.V. Gedam, S. Deokar, S. Bhagat, A. Chahande, P. Raut, Studies on the removal of Brilliant Green dye using low cost agricultural waste, Indian J. Chem. Technol., 27 (2020) 333–339.

[91] K. Sukla Baidya, U. Kumar, Adsorption of brilliant green dye from aqueous solution onto chemically modified areca nut husk, S. Afr. J. Chem. Eng., 35 (2021) 33–43.

[92] Y.A.R. Lebron, V.R. Moreira, L.V. de Souza Santos, Biosorption of methylene blue and eriochrome black T onto the brown macroalgae *Fucus vesiculosus*: equilibrium, kinetics, thermodynamics and optimization, Environ. Technol., 42 (2021) 279–297.

[93] I. Khurana, A.K. Shaw, Bharti, J.M. Khurana, P.K. Rai, Batch and dynamic adsorption of Eriochrome Black T from water on magnetic graphene oxide: experimental and theoretical studies, J. Environ. Chem. Eng., 6 (2018) 468–477.

[94] N.I. Blaisi, M. Zubair, Ihsanullah, S. Ali, T.S. Kazeem, M.S. Manzar, W. Al-Kutti, M.A. Al Harthi, Date palm ash-MgAl-layered double hydroxide composite: sustainable adsorbent for effective removal of methyl orange and eriochrome black-T from aqueous phase, Environ. Sci. Pollut. Res., 25 (2018) 34319–34331.

[95] M.S. Manzar, M. Zubair, N.A. Khan, A. Husain Khan, U. Baig, M.A. Aziz, N.I. Blaisi, H.I.M. Abdel-Magid, Adsorption behaviour of green coffee residues for decolourization of hazardous congo red and eriochrome black T dyes from aqueous solutions, Int. J. Environ. Anal. Chem., (2020) 1–17, doi: 10.1080/03067319.2020.1811260.

[96] H. Al-Zoubi, M. Zubair, M.S. Manzar, A.A. Manda, N.I. Blaisi, A. Qureshi, A. Matani, Comparative adsorption of anionic dyes (Eriochrome Black T and Congo Red) onto Jojoba residues: isotherm, kinetics and thermodynamic studies, Arabian J. Sci. Eng., 45 (2020) 7275–7287.