

# **Biosorption of a Leather Dye (Dycem TTO) onto Banana Peel: Characterization, Isotherm, Kinetic, Thermodynamic, and Mechanism Studies**

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Abstract Banana peel (BP), a by-product of the fruit processing industry that is widely available, has been applied in this study as an effective biomaterial for the removal of Black Dycem TTO (DTTO) dye from aqueous solution. X-ray diffraction analysis (XRD), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), Brunauer-Emmett-Teller (BET) surface area analysis, and point of zero charge (pHpzc) have all been used to characterize the biosorbent. Large active groups (like OH, NH, and C=O) on the BP surface are observed by FTIR analysis. It was discovered that BP's BET surface area was 35.4 m<sup>2</sup> g<sup>-1</sup>. SEM results showed a rough and a smoothing surface before and after dye biosorption, respectively. The optimum conditions for pH, BP amount and DTTO concentration were found to be 2, 0.005 g and 10 mg  $L^{-1}$ , respectively. Under these conditions, removal efficiency was found to be 80.8%. The Langmuir isotherm provided a better description of the biosorption of DTTO on BP. The maximum monolayer adsorption capacity was found to be 54.34 mg  $g^{-1}$  at 25 °C. The kinetic

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studies disclosed pseudo-second-order for the studied biomaterial. The thermodynamic studies disclosed favorable, spontaneous, and exothermic processes. Consequently, this work showed that DTTO could be removed using low-cost material waste under appropriate conditions through an environmentally friendly process.

KeywordsBiosorption  $\cdot$  Characterization  $\cdot$  Bananapeel  $\cdot$  Kinetics  $\cdot$  Leather dye

# **1** Introduction

Water is an absolute wealth that is both valuable and brittle, and it is also limited. It must be managed coherently and rationally. This resource has no substitute (Zhao et al., 2015). Unfortunately, due to heavy industrialization, various poisonous chemicals like dye, organic, and metal were released and caused a substantial environmental problem (Tang et al., 2019). The effluents, loaded with pollutants, have been stocked in the collection basins, and their disposal into lakes and rivers without sufficient and proper pretreatment causes severe threats to the ecosystem (Vakili et al., 2014). Dyes are hazardous pollutants; they are very toxic, mutagenic, carcinogenic, and non-biodegradable, damaging living beings (Wang et al., 2019). Many dye molecules in wastewater are derived from numerous manufacturing, like textiles, leather, painting, plastic (Li et al., 2016),

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dyeing, paper, and clothing. Generally, wastewater from these manufacturing processes that contains supportable amounts of coloring materials is very hard to treat.

The Modern Society of Leather and Skins is a tannery industry in Sfax (South of Tunisia). The breakdown of the tannery's production is 57% sheep skins (525 t/year), 10% goat skins (90 t/year), and 33% cattle skins (300 t/year). The product is intended for international and local markets. This industry is a well-known source of groundwater contamination in Sfax. During the dyeing operation, a good deal of Black Dycem TTO dye-contaminated effluent was generated, which accounts for approximately 30% of the tannery effluent and is the origin of environmental problems (Pengthamkeerati et al., 2008). Due to its functional properties, black Dycem, a water-soluble dye, does not quickly deteriorate, and the sewage containing this pollutant must be recycled (Baccar, 2013). Several technologies have been applied for remediation, such as precipitation, membrane filtration, advanced oxidation, coagulation and flocculation, ion exchange, and biosorption (Collivignarelli et al., 2019; Holkar et al., 2016). Yet, the essential impediment to treating dye-containing wastes and wastewater is the excessive fee and the low performance of a few methods. Contrariwise, the elimination of dye from the effluent by a biosorption process presents an appealing opportunity for therapy, especially when the sorbent is inexpensive and readily available. Waste agricultural materials may constitute a substantial source of this sort of adsorbent. They include pine cones (Bagherian et al., 2021), pomegranate peels (Ghibate et al., 2021), and pistachio shells (Armagan & Toprak, 2014; Nejadshafiee & Islami, 2020). A further waste substance that could be very powerful as a biosorbent for dye removal is banana peel. Banana is a vital fruit consumed as food or to be employed for manufacturing a wide diversity of products (cosmetics, textile industry, etc.). Banana is an essential fruit consumed as food or used to manufacture various of products (cosmetics, textile industry, etc.). In its constitution, BP contains high quantities of cellulose, lignocellulose, protein, lipid, and polysaccharides that bear carboxyl (-COOH), hydroxyl (-OH), amine (-NH<sub>2</sub>), and carbonyl (C=O) functional groups that can bind ionic species (Mohapatra et al., 2010; Oyewo et al., 2016). The banana peel was employed as a renewable precursor to synthesize nanocomposite BPAC/ZnO (Ahmadi & Ganjidoust, 2021), mesoporous silica nanoparticles (Mohamad et al., 2019), and activated carbon (Thuan et al., 2017; Hashem et al., 2020). However, the retention of dyes by raw BP powder has not been sufficiently studied. For example, Khalfaoui et al. (2012) investigated raw BP for MB adsorption. Results displayed that the maximum value of adsorption capacity was 18.47 mg  $g^{-1}$ . Annadurai et al. (2002) have studied the removal of heavy metals using BP from water. Therefore, this study's main objective is to assess BP's bioadsorption potential for a leather dye removal.

Any change in BP was used. The physicochemical features of the BP, including XRD, FTIR, SEM, BET, and PZC, are determined. The impact of multiple parameters on DTTO adsorption, such as the pH solution, the time, the biosorbent amount, and the temperature, has been examined. The obtained experimental data were analyzed using equilibrium isotherms and kinetic models.

# 2 Materials and Methods

# 2.1 Materials

A supermarket provided banana fruits, and their peels were employed as inexpensive biosorbents. The waste peels were rinsed with distilled water, then subjected to air-drying for 4 days and oven-drying at 105 °C to remove moisture content. Then, it was crushed with a stainless grinder, and the fine powder was sieved on a mechanical shaker (Retsch AS 200) to obtain a sample between 200 and 500  $\mu$ m.

DTTO was furnished by the modern society of leather and skins. 100 mg  $L^{-1}$  of DTTO solution was prepared by dissolving DTTO in 1000 ml of distilled water; desired concentrations were obtained by diluting the solution.

DTTO is an acidic dye, and the main chemical categories of anthraquinone, nitro, nitroso, triphenylmethane, azo, and azine. Because of its sulphonate groups, this dye is soluble in water. The maximum biosorption wavelength of DTTO is 462 nm.

## 2.2 Methods

The crystallinity of materials was identified by X-ray diffraction (PANalytical X0 Pert High Score

Plus diffractometer using CuKα radiation). The surface chemistry of the BP was performed by Fourier transform infrared (FTIR, Perkin-Elmer 783 spectrophotometer) using the KBr pellets. To evaluate the zero charge point (PZC), the experimental test consisted of preparing ten flasks filled with 25 mL of a 0.1 mol L<sup>-1</sup> NaCl solution. Then, 1.0 g of BP was added, and everything was stirred for 48 h at 25 °C. Finally, the final pH was determined. Results were plotted as pH<sub>f</sub> vs. pH<sub>i</sub>. The specific surface area (SSA) of the solid was determined by Brunauer-Emmett-Teller (BET) method.

#### 2.3 Biosorption Studies

Batch adsorption tests were performed in a 250-mL shaking flask containing 20 mL of dye solution with a known concentration of 10 mg  $L^{-1}$  using a rotary shaker at 200-rpm min<sup>-1</sup> at 25 °C

The pH (2.0–10), contact time (5–120 min), and biosorbent amount (0.005–0.1 g) effects on the biosorption of DTTO were studied. Solutions of HCl and NaOH (0.1N) were used to adjust the initial pH.

After attaining equilibrium, the biosorbent was separated by centrifugation at 4500 rpm for 4 min, and the remaining dye concentration was determined by a UV-vis spectrophotometer (Shimadzu 1650 UV-vis spectrophotometer model). The biosorbed capacity of DTTO on BP was described as follows:

$$q = \frac{\left(C_0 - C_e\right)V}{m}$$
(Equation 1)

With V is the solution volume (L), m is the biosorbent mass (g),  $C_0$  is the initial concentration of DTTO in solution, and  $C_e$  is its concentration at time  $t \pmod{L^{-1}}$ .

The removal efficiency (R %) was determined by the subsequent equation:

$$R(\%) = \frac{\left(C_0 - C_e\right)}{C_0} \times 100$$
 (Equation 2)

To obtain the biosorption isotherms, 1 g of biosorbent was added to a set of 20 mL solutions with

different concentrations of dye ions (10, 25, 50, 100,  $300 \text{ mg L}^{-1}$ ).

# **3** Results and Discussion

## 3.1 Biosorbent Characterization

Three peaks could be seen in the BP XRD pattern (Fig. 1):

- (i) A sharp peak at around  $2\theta = 14^{\circ}$  (d = 5.27), which corresponds to the (101) crystal plane of cellulose;
- (ii) A broad peak at around  $2\theta = 15-25^{\circ}$  (d = 4.13), which corresponds to the amorphous material (Bediako et al., 2019);
- (iii) The presence of lignin and hemicellulose in the banana peel powder may be the cause of a prominent peak at  $35^{\circ}$  (d = 2.48).

The FTIR spectrum of BP is displayed in Fig. 2. The band at 3400 cm<sup>-1</sup> was due to the (-OH) and (-NH) groups (Abdel-khalek et al., 2017; Piol et al., 2021). Furthermore, a peak at 2850 cm<sup>-1</sup> corresponds to the C-H stretch (Mondal & Roy, 2018). Bands at 2300 cm<sup>-1</sup> reflect C=C. The C=O group can be identified by the bands at 1700 and 1400 cm<sup>-1</sup> (Munagapati et al., 2018a). According to Khalfaoui (2012), the C-O stretching vibration of carboxylic acids and alcohols is responsible for the bands in the 1050–1450 cm<sup>-1</sup> range.

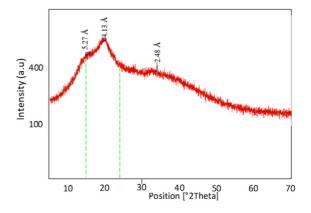


Fig. 1 XRD patterns of the banana peel

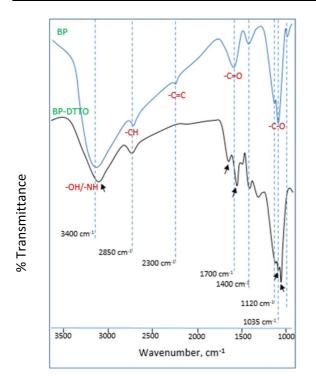


Fig. 2 FTIR spectra of BP and BP-DTTO (after DTTO biosorption)

The band around 1120 cm<sup>-1</sup> is attributed to the C-O vibration of carboxylic acids and alcohols. Some substantial modifications can be noticed by examining the IR spectrum of BP after biosorption (Fig. 2) and comparing it with the ones before biosorption. The movements from the peaks at 3400 to 3358 cm<sup>-1</sup>, and 1035 to 1014 cm<sup>-1</sup>, are enclosed by change in structures containing hydroxyl -OH. Besides, there is an alteration in the -COOH vibrations after DTTO biosorption. So, it is likely to be verified that the adsorptive process of DTTO dye took place in the hydroxyl, amine, and carboxyl groups, which coexist in the BP structure. Moreover, a new band appeared after biosorption at 1095 cm<sup>-1</sup>, related to the common group in acid dye.

The SEM results of BP are displayed in Fig. 3. In the micrographs (Fig. 3a), the rough surface can be seen before biosorption, indicating a porous-looking form of the BP that serves as a biosorption site for DTTO. Figure 3b reveals the smoothing surface of the BP after removing DTTO. The outcomes agree with those obtained for the same biomaterial by Thomas et al. (2021) and Afolabi et al. (2021). The investigated biosorbent's BET surface area was found to be  $35.4 \text{ m}^2$  $g^{-1}$ . After the biosorption process, this surface decreases to 17 m<sup>2</sup> g<sup>-1</sup>. This decrease was essentially attributed to the biosorption within the pores, their filling, and their blocking because of the very large size of the dye molecule.

The  $pH_{pzc}$  is found to be 6.8. Thus, the BP surface is positively charged for pH values below 6.8 and negatively charged for pH values higher than 6.8.

## 3.2 Biosorption Studies

# 3.2.1 Effect of pH

According to Wawrzkiewicz and Hubicki (2009), the final pH of the solution affects the biosorption

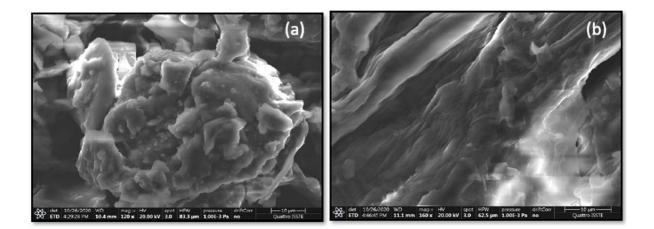


Fig. 3 SEM images of BP a before and b after DTTO biosorption

mechanisms on the BP surface as well as the kind of physicochemical interactions between the species in solution and the biosorbent's adsorptive sites. The removal effectiveness decreased from 80.8 to 38% when the solution pH varied from 2 to 10 (Fig. 4a). As it is well established, pH affects the degree of ionization of the Dycem TTO. Banana peel biomaterial is composed of various functional groups, such as amino and carboxyl, which could also be affected by pH. From these results, it was concluded that the biosorption of dye is dependent on the biosorbent surface. As a result, the BP surface is negatively charged in a basic solution (pH> pH<sub>PZC</sub>). Electrostatic repulsion between the negatively charged DTTO and the deprotonated OH<sup>-</sup> and COO<sup>-</sup> groups on the BP surface explains the low removal efficiency. Additionally, at a basic pH, the high concentration  $OH^-$  in the solution and the negatively charged dye molecules compete for biosorption onto the BP active sites, which explains the low removal of acid dye. As the pH of the aqueous solution decreases (pH<pH<sub>PZC</sub>), the density of the positively charged BP surface groups increases, which promotes the biosorption of the anionic dye through attractive interactions. On the other hand, when the pH of the solution decreases, the BP surface charge becomes positive due to the protonation of the surface groups (OH<sub>2</sub><sup>+</sup>, COOH), promoting the biosorption of DTTO due to the electrostatic attraction between the negative sulfonate groups of the dye and the positive BP surface charge. The optimal pH value where the removal efficiency reaches its maximum is pH =2.

The specific interaction banana peel-Dycem TTO dye under acidic conditions is performed due to:

 $dye - SO_3Na \longrightarrow dye - SO_3^- + Na^+(DTTO dye is a water - soluble acidic dye that exists in a dissociated form in water)$ 

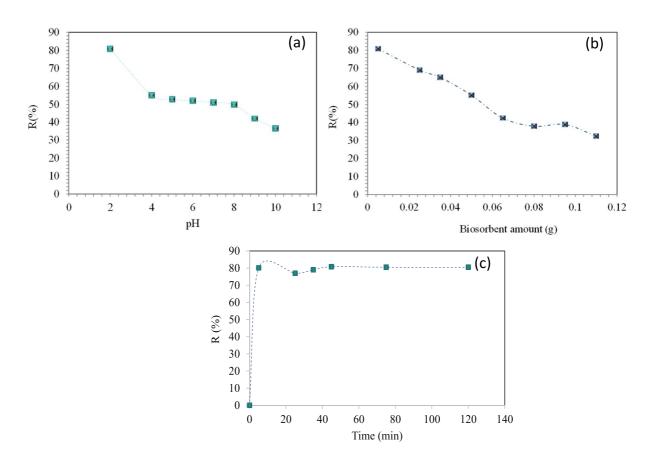


Fig. 4 a Effect of pH, b biosorbent amount, and c time at a constant temperature of 25 °C

$$-\text{COOH} / - \text{OH}_2^+ + \text{SO}_3^- \longrightarrow -\text{COO} - \text{Na}^+ / - \text{OH} - \text{Na}^+$$

#### 3.2.2 Effect of Biosorbent Amount

The biosorbent amount effect on DTTO removal is exhibited in Fig. 4b. The outcomes displayed that as the BP quantity was enhanced from 0.005 to 0.1 g, DTTO dye retention decreased from 80.8 to 32%. The decrease in removal efficiency with an increase in biosorbent amount is mainly attributed to the fact that at higher amounts, active sites of the biomaterial were reduced due to aggregation (Han et al., 2008). Based on the study above, an optimum amount chosen for further experiments is 0.005 g because of the availability of binding sites to bind to DTTO in agreement with earlier studies (Cardoso et al., 2011).

## 3.2.3 Effect of Contact Time

The time between pollutant and solid is a significant factor for wastewater purification; therefore, we also verified the decontamination period of the biosorbent, as it is feasible to observe from Fig. 4. According to the time study, 80.8% of DTTO was removed within 5 min (Fig. 4c). This dye uptake trend results from the strong electrostatic interactions between DTTO and the predominant groups present on the outer surface of the biosorbent (Liu et al., 2014). After this time, the removal efficiency decreases slightly to 77% at 25 min. At 40 min, it rises to 79%. This is why a 45-min biosorption equilibrium was selected to avoid biosorption error. At this time, the biosorbent surface becomes saturated. The test was pursued further for 120 min, but no significant increment was noted in dye adsorption after 45 min of shaking time. Therefore, the remaining experiments were determined at 45 min.

#### 3.3 Biosorption Kinetics Study

To explore the rate of DTTO adsorption by the BP, pseudo-first-order (Lagergren, 1898), the pseudo-second-order (Ho & McKay, 1998), and intra-particle diffusion (Weber & Morriss, 1963) models were adopted to correlate the time-dependent biosorption data.

$$\ln\left(q_{eq} - q_t\right) = \ln q_{eq} - \frac{K_1}{2.303}t \qquad (\text{Equation 3})$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_{eq}^2} + \frac{1}{q_{eq}}t$$
 (Equation 4)

$$q_t = k_i t^{1/2} + C$$
 (Equation 5)

With  $q_{eq}$  is the amount of DTTO adsorbed at equilibrium (mg g<sup>-1</sup>);  $q_t$  is the amount of DTTO adsorbed on BP (mg g<sup>-1</sup>) at the instant t;  $k_1$  (min<sup>-1</sup>) and  $k_2$  (g mg<sup>-1</sup> min<sup>-1</sup>) are pseudo-first and pseudosecond rate constants;  $k_{int}$  (mg g<sup>-1</sup> min<sup>1/2</sup>) is the constant of intra-particle diffusion; and X is the boundary layer thickness. Figure 5a–c by adopting first-order, second-order, and diffusion models, respectively. Table 1 includes a summary of the kinetic model's parameters.

As seen from this table, the lowest reduced chisquare ( $\chi^2$ ), the highest correlation ( $R^2$ ), and good conformity between the  $q_{eq,exp}$  and  $q_{eq,cal}$  values exhibited that the biosorption of DTTO onto BP could be well modeled with the pseudo-secondorder, which is similar to the outcomes found by some other researchers for dye biosorption (Munagapati et al., 2018b). The curve of  $q_t$  vs.  $t^{0.5}$  indicates two different straight lines (Fig. 5c). This may suggest that two steps control the DTTO sorption on BP : the first was ascribed to the biosorption of DTTO onto the external surface of BP, whereas the second step depicts the diffusion of DTTO into the pores of BP (Yao et al., 2020).

#### 3.4 Biosorption Isotherms

The experimental outcomes were fitted with the classic models, which are demonstrated as follows:

Langmuir model (Langmuir, 1918):

$$q_{eq} = \frac{Q_m K_L C_{eq}}{1 + K_L C_{eq}}$$
(Equation 6)

Freundlich model (Freundlich, 1906):

$$q_{eq} = K_F C_{eq}^{-1/n}$$
 (Equation 7)

With  $q_{eq}$  (mg g<sup>-1</sup>) and  $C_{eq}$  (mg L<sup>-1</sup>) are the quantity of DTTO biosorbed and the DTTO concentration at equilibrium, respectively;  $Q_m$  is a quantity of DTTO fixed per gram of BP (mg g<sup>-1</sup>); and  $K_F$  (mg g<sup>-1</sup>)/(L mg<sup>-1</sup>)<sup>n</sup> is the biosorption capability.

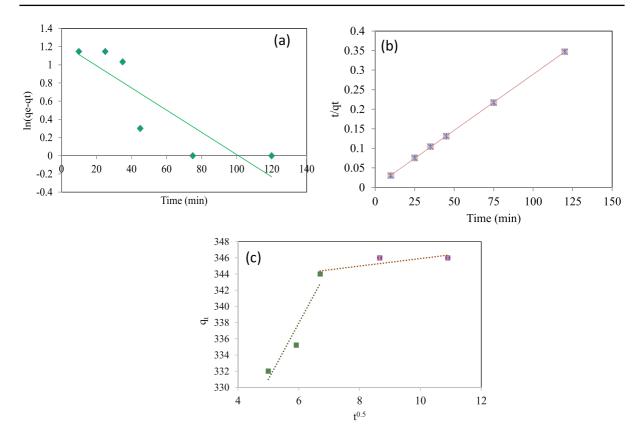


Fig. 5 a Pseudo-first-order kinetics, b pseudo-second-order kinetics and c intra-particle diffusion model of DTTO onto BP

 Table 1
 Estimated parameters of the kinetic models for the DTTO dye biosorption onto BP

| Models type              | Parameters  | Values |
|--------------------------|---|--------|
| Pseudo-first order       | $K_1 ({\rm min}^{-1})$                            | 0.02   |
|                          | $q_{e,\text{cal}} (\text{mg g}^{-1})$             | 344    |
|                          | $q_{e,\exp} (\mathrm{mg \ g^{-1}})$               | 17.28  |
|                          | $R^2$   | 0.75   |
|                          | $X^2$   | 0.98   |
| Pseudo-second order      | $K_2 ({\rm min}^{-1})$                            | 3.23   |
|                          | $q_{e,\text{cal}} (\text{mg g}^{-1})$             | 345    |
|                          | $q_{e,\exp} (\mathrm{mg \ g^{-1}})$               | 344    |
|                          | $R^2$   | 0.99   |
|                          | $X^2$   | 0.22   |
| Intra-particle diffusion | $K_{idl} \ (\text{mg g}^{-1} \ \text{min}^{1/2})$ | 6.95   |
|                          | $R_1^2$   | 0.90   |
|                          | $X^2$   | 0.45   |
|                          | $K_{id2} (\mathrm{mg g}^{-1} \mathrm{min}^{1/2})$ | 0.56   |
|                          | $R_2^2$   | 0.84   |
|                          | $X^2$   | 0.68   |

The chi-square  $(\chi^2)$  test was also assessed to discover the best fit among mg g<sup>-1</sup> the used models. The equivalent mathematical statement of  $\chi^2$  test can be expressed as:

$$X^{2} = \sum \frac{\left(q_{eq} \exp - q_{eq} \, cal\right)^{2}}{q_{eq} \, cal}$$
(Equation 8)

where  $q_{eq, \exp}$  and  $q_{eq, cal}$  are the equilibrium abilities obtained by calculating experimental and theoretical data, respectively.

 $C_e$  vs  $C_e/q_e$  in the Langmuir model is shown in Fig. 6b.  $Q_m$  and  $K_L$  values were found from the intercept and slope of the plot respectively. The values of  $K_F$  and 1/n were found from the intercept and the slope of the straight line in Freundlich model.  $\ln C_e$  was plotted against  $\ln q_e$  as shown in Fig. 6c.

The best model is the one characterized by the lowest  $X^2$  value. The different parameters are presented in Table 2. According to this table, the  $R^2$ 

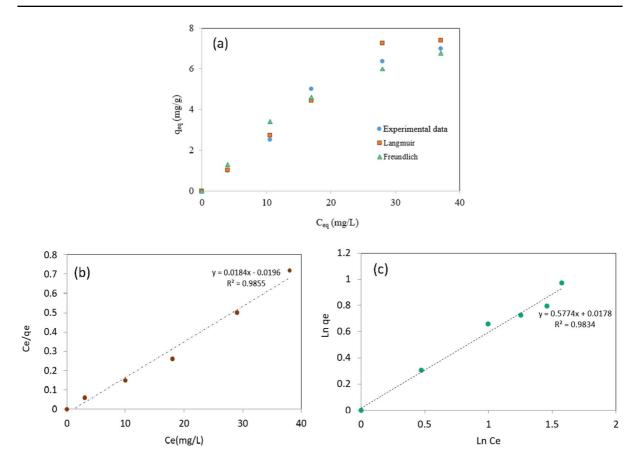


Fig. 6 a Comparison of the experimental data and model fits of the Langmuir and Freundlich isotherms for the adsorption of DTTO onto BP. b Langmuir isotherm plot. c Freundlich isotherm plot

**Table 2** Estimated parameter values and correlation coefficients of Langmuir and Freundlich models for the biosorption of DTTO

| Isotherms  | Parameters  | Values |
|------------|---|--------|
| Langmuir   | $Q_m (\mathrm{mg \ g}^{-1})$                          | 54.34  |
|            | $K_L$ (L mg <sup>-1</sup> )                           | 0.04   |
|            | $R^2$   | 0.98   |
|            | $X^2$   | 0.23   |
| Freundlich | $K_F (\mathrm{mg \ g^{-1}})/(\mathrm{L \ mg^{-1}})^n$ | 8.31   |
|            | n   | 1.08   |
|            | $R^2$   | 0.98   |
|            | $X^2$   | 0.58   |

values are 0.98 for both models. Compared to the chi-square  $(\chi^2)$  test (Table 2) and the experimental results (Fig. 6a, b, c), Langmuir was a good-fit model. This exhibited that the retention of DTTO

dye onto BP was monolayer and that the biosorbent has an energetically homogeneous surface.

The maximum adsorption capacity  $(Q_m)$  of BP for DTTO dye is 54.34 mg g<sup>-1</sup>.

## 3.5 Comparison of Anionic Dye Removal by BP

The maximum biosorption capacities,  $Q_m$ , of the investigated banana peel as biosorbent materials are compared in Table 3 with the corresponding values of earlier studies for the anionic dyes (acid and reactive dyes). In this study, the  $Q_m$  value of BP used for the removal of DTTO from aqueous solution was a little higher than those reported in the literature. It is worth mentioning that an important advantage of the studied biomaterial is its significant specific surface area (35.4 m<sup>2</sup> g<sup>-1</sup>) compared to that of other biosorbents. This surface area is largely dependent on the preparation technique of the BP.

 Table 3 Comparison of maximum monolayer biosorption capacities of different dye onto BP

| Dyes | $Q_m (\mathrm{mg g}^{-1})$ | <b>SBET</b> $(m^2 g^{-1})$ | References                  |
|------|----------------------------|----------------------------|-----------------------------|
| MO   | 21                         | 20.6                       | Annadurai et al., 2002      |
| RGY  | 14.7                       | 18.6                       | do Nascimento et al., 2015  |
| RG   | 15.5                       | 18.6                       | do Nascimento et al., 2015  |
| OG   | 20.9                       | -                          | Stavrinou et al., 2018      |
| RB5  | 49.2                       | -                          | Munagapati et al.,<br>2018a |
| DTTO | 54.34                      | 35.4                       | This study                  |

-, not analyzed

#### 3.6 Thermodynamic Study

Twenty milliliters of DTTO (10 mg  $L^{-1}$ ) and 0.005 g of BP were used to study the thermodynamic behavior. The biosorption thermodynamic parameters of BP for dye are calculated by Eq. (9), Eq. (10), and Eq. (11).

 $\Delta G^0 = -RT \ln k_d \tag{Equation 9}$ 

$$k_d = \frac{q_{eq}}{C_{eq}}$$
(Equation 10)

$$\ln k_d = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}$$
 (Equation 11)

where  $\Delta H^{\circ}$  (kj mol<sup>-1</sup>) is enthalpy change,  $\Delta G^{\circ}$  (kj mol<sup>-1</sup>) is Gibbs free energy,  $\Delta S^{\circ}$  (J K<sup>-1</sup> mol<sup>-1</sup>) is entropy,  $K_d$  (L g<sup>-1</sup>) is balance parameter, R (J mol<sup>-1</sup> K<sup>-1</sup>) is the gas parameter, and T (K) is the biosorption temperature.

The positive values of  $\Delta H^{\circ}$  confirm the endothermic nature of the biosorption process (Table 4) and the possibility of physical adsorption (Scheufele et al., 2020). The positive values of  $\Delta S^{\circ}$  suggest the enhancement in randomness at the BP/liquid

 Table 4
 Thermodynamic parameters for DTTO biosorption using BP at different temperatures

| $\Delta H^{\circ}$ (kj mol <sup>-1</sup> ) | $\Delta S^{\circ} (\mathrm{J} \mathrm{K}^{-1} \mathrm{mol}^{-1})$ | $-\Delta G^{\circ} (\text{KJ mol}^{-1})$ |       |       |
|--|---|--|-------|-------|
| 13.34                                      | 0.09  | 298 K                                    | 308 K | 318 K |
|  |   | 14.37                                    | 15.30 | 16.23 |

interface with some structural modifications in the solute and material, as well as the good affinity of BP for the DTTO.

## 3.7 Biosorption Mechanism

On the basis of the thermodynamic analysis and the physicochemical characterization of BP, the mechanism of DTTO dye biosorption on the surface of BP was inferred. FTIR technique was carried out to uncover the biosorption mechanisms (Fig. 7). The FTIR spectrum of the DTTO-loaded BP indicates that the peaks assigned to hydroxyl (-OH), amine (-NH), and carboxyl functional (-C=O) groups are slightly shifted from their positions and the intensity gets altered. According to these results, these groups may have contributed to the biosorption of DTTO on the surface of BP through weak electrostatic interactions or van der Waals forces (Munagapati et al., 2018a). The  $pH_{PZC}$  of BP was performed in order to further confirm the biosorption mechanisms. In this approach, biosorption of an anionic dye (such DTTO) occurs at pH<pH<sub>PZC</sub> where the surface is positively charged. Subsequently, by controlling the pH value of a wastewater solution, the electrostatic interaction between the BP and the DTTO may be favored.

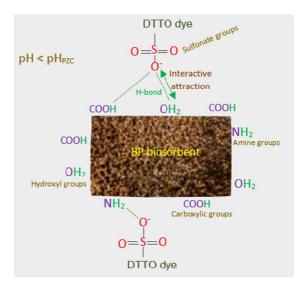


Fig. 7 Possible mechanism of DTTO dye biosorption onto banana peel at pH 2

Thermodynamic study exhibited that the biosorption of DTTO on BP is of the physical type, in which dye molecules from a liquid phase are attracted and held onto the surface of a solid material through weak non-covalent forces like van der Waals forces and hydrogen bonding.

From the above analysis, we can conclude that under acidic conditions, banana peel may contain positively charged groups or surfaces, such as amino  $(-NH_2)$  or carboxyl (-COOH), which can potentially interact with the negatively charged dye (sulfonate ions) through electrostatic interactions.

Additionally, banana peel may contain polar functional groups, such as hydroxyl (-OH) or carbonyl (C=O) groups, which can interact with acid dye through hydrogen bonding.

Hydrogen bonding and electrostatic interactions are generally considered polar interactions as they involve the attraction between charged or polar molecules. If these types of interactions are the dominant forces, the overall biosorption can be considered polar.

However, the complex surface of the BP can also provide many binding sites for anionic dye through van der Waals interactions, which are weak intermolecular forces between nonpolar molecules or functional groups. For this reason, the interaction between sulfonic ions and banana peel at acidic conditions is most likely not primarily through van der Waals forces. Sulfonic acid groups are strongly polar and can form electrostatic interactions with charged or polar functional groups on the surface of the banana peel. At acidic conditions, the banana peel may also contain protonated amino groups or other charged groups that can interact with the sulfonic acid groups through electrostatic interactions.

While van der Waals forces may contribute to the overall interaction between sulfonic ions and banana peel, it is unlikely that they would be the primary mode of interaction at acidic conditions.

# 4 Conclusions

"Dycem TTO" is a leather dye, which is commonly used in SMCP society and has great harmful effects on the groundwater of the Sfax area. This article reports a preliminary study with satisfactory results on the retention of this dye using agricultural waste peels of bananas as a low-cost biomaterial.

The BP was successfully identified by the FTIR: among the several identified functional groups, carboxylic acid, hydroxyl, and amine groups could play a crucial role in the elimination of DTTO. The equilibrium experiments exhibited the pertinence of BP as an environmentally friendly waste. The optimum circumstances for BP biosorption of DTTO were at pH 2, contact time of 45 min. The experimental biosorption performance was 54.34 mg g<sup>-1</sup>. The positive value of enthalpy change denotes that the biosorption favors the endothermic process.

**Data Availability** The authors declare that the data supporting the findings of this study are available within the article, and its supplementary information are available by request.

#### Declarations

**Competing Interests** The authors declare no competing interests.

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