Adsorptive removal of direct red 80 and methylene blue from aqueous solution by potato peels: a comparison of anionic and cationic dyes
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ABSTRACT
Adsorption of direct red 80 (DR 80) and methylene blue (MB) from aqueous solutions on potato peels (PP) has been compared. The use of peels in decontamination technology is very promising given the near zero-cost for the synthesis of those adsorbents. The selected potato peels were first analyzed by scanning using electron microscopy (SEM) and Fourier transforms infrared spectroscopy (FTIR). Then the adsorption behavior was studied in a batch system. The adsorption process is affected by various parameters such as the solution pH (2–11), the initial concentration of the dye (20, 50, 100, 150 and 200 mg L⁻¹), the adsorbent dose (0.1–3%), the temperature (303.16 K, 313.16 K, and 323.16 K), agitation (up to 250 rpm), as well as the contact time. Adsorption isotherms of the studied dye on the adsorbent were determined and compared with the Langmiur, Freundlich and Temkin adsorption models. The results show that the data was most similar to the Freundlich isotherm (R² = 0.99). The maximum adsorption capacities (Qmax) of MB and DR 80 by the PP at temperatures 303.16 K, 313.16 K and 323.16 K were found to be approximately 97.08 mg g⁻¹; 45.87 mg g⁻¹; 61.35 mg g⁻¹ and 27.778 mg g⁻¹; 45.45 mg g⁻¹; and 32.258 mg g⁻¹. The kinetic data was compared to the pseudo-first-order, pseudo-second-order, and intraparticle diffusion models. This revealed that adsorption of methylene blue onto PP abided mostly to the pseudo-second-order kinetic model. Calculations of various thermodynamic parameters such as enthalpy change (ΔH), entropy change (ΔS), and free energy change (ΔG) display the endothermic and spontaneous nature of the adsorption process.

Key words | adsorption isotherm, dye adsorption, potato waste, water treatment

HIGHLIGHTS
• The potato peels waste (PP) was used as adsorbent for the removal of methylene blue (MB) and direct red 80 (DR 80).
• PP can efficiently adsorb high amounts of cationic and anionic dyes from water.
• The adsorption isotherm data were fitted well to Freundlich isotherm.
• The adsorption kinetics described well by the pseudo-second-order model.
• The adsorption of DR80 and MB was spontaneous and endothermic.

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INTRODUCTION

Water pollution has become a major issue in modern times. Increased industrial and agricultural activities have resulted in the increase of various types of toxic pollutants. However, agricultural activities are widely regarded as the main cause of water pollution on a global scale. Polluted wastewater must be filtered, depurated, and returned to water receptors for other uses. An example of a major pollutant that is found in our everyday lives is dye. Dyes are considered to be a major type of pollutants, used in large amounts in textiles, paper and pulp, tannery and paint industries (Gupta & Suhas 2009). The main purpose of dye is to modify the color characteristics of different materials such paper, fabric, leather and others (De Campos Ventura-Camargo & Marin-Morales 2013; Kyzas et al. 2013). It has already been proved that dyes have largely affected the photosynthetic activity of various plants (Ferreira et al. 2014). Moreover, numerous types of dyes have shown to be toxic and carcinogenic, even affecting aquatic biota and human health (Ferreira et al. 2014; Kyzas & Kostoglou 2014). Amongst these dyes, direct red are water-soluble anionic dyes, generally the dyes in this class are polyazo compounds, along with some stilbenes, phthalocyanines and oxazines (Gupta & Suhas 2009). Their discharge into the hydrosphere possesses a significant source of pollution due to their visibility even at very low concentrations and due to their recalcitrance nature, giving undesirable color to the water, reducing sunlight penetration, resisting photochemical and biological attack, and their degradation products being toxic or even mutagenic and carcinogenic (Van der Zee & Villaverde 2005). This has resulted in increased research in innovative technology that could be used for the filtration and removal of dyes from contaminated water. Multiple physical and chemical methods have been experimented with to treat dye wastewater, such as coagulation/flocculation, chemical oxidation, and activated sludge processes. Unfortunately, these processes proved to be difficult, ineffective, and in some cases economically disadvantageous (Aguedach et al. 2005; Mane et al. 2007). The adsorption process is one of the efficient methods to remove contaminants from wastewater. In addition, adsorption is regarded as the simplest, the impactful and the most economical method for dyes treatment in wastewater (Abussaud et al. 2016). Adsorption is a surface phenomenon and defined as the increase in the concentration of a particular component at the surface or interface between two phases (Saleh & Gupta 2014). It is used for source reduction, wastewater treatment and reclamation for potable, industrial and other purposes (Saleh 2015). Thus, in recent decades, the search for cheap adsorbent materials with an efficiency comparable to that of commercially activated carbon has been a prioritized research topic. Scientists have discovered alternatives such as eucalyptus bark (Morais et al. 1999), orange peel (Namasiyavam et al. 1996), and date dierts (Nassar 1999). Research has largely yielded bio-adsorbents as substitutes or complements to commercially activated carbon for wastewater treatment, which is affordable and preferable to economies of developing countries.

Potato peels (PP) are agricultural solid wastes and could be assumed to be below-cost adsorbents since they are abundant in nature, inexpensive, require little processing and are effective materials. In addition, due to its high molecular weight and highly branched molecular structure, PP are insoluble in aqueous solutions, and could be a promising adsorbent for the removal of methylene blue (MB) cationic dye and of direct red 80 (DR 80) anionic dyes from wastewater. Indeed, modified and non-modified PP were used as adsorbent to remove some dyes like for example: MB, Malachite Green (MG), crystal violet (CV), reactive red 198 (RR198) reactive black 5 (RB5) and acid red 37 (AR37) (Anastopoulos & Kyzas 2014). Also sorption potential of chemically treated PP and neem bark is observed on three different synthetic dyes viz. MB, MG and Direct Red 81 (DR 81) (Sharma et al. 2020).

Potato is the most common non-grain food commodity in the world. Its production ranges from 300 to 325 million tons/year. This has resulted in a crisis of the management of PP, raising the concern of the potato industries in Europe. This emphasizes the need to establish an integrated, environmentally-friendly solution. Due to its high molecular weight and highly branched molecular structure, PP could be a key promising adsorbent to remove most pollutants in aqueous solutions. The main focus of this experiment is to observe the efficiency of PP as an effective bio-adsorbent, specifically to remove two dyes, MB and DR 80, from aqueous solutions. The effects of the operating conditions such as contact time, initial dye concentration, mass of the sorbent material, granulometry, pH of the solution, and temperature on the sorption kinetics of the two dyes were examined. The application of different isotherm models to describe the experimental results of the kinetics and the sorption isotherms, makes it possible to understand the validity and the limits of application of the models. This allows us to
generate a database of adsorption defined by the speed and capacity of adsorption. Moreover, using the models as a basis makes it possible to identify the potential mechanisms of adsorption of the two dyes by the PP.

**MATERIALS AND METHODS**

**Substrate preparation**

PP, from the Spunta variety, was obtained from a local market (Sfax, Tunisia). It was first washed using tap water and then in distilled water in order to remove the surface dust particles. It was dried at 50 °C for 48 h, ground using a mixer-grinder (Moulinex) and then sieved to obtain particle sizes below 100 μm, 110–200 μm, and 260–300 μm. It was then stored at room temperature (25 ± 5 °C) until the experiment was conducted.

MB and DR 80 were purchased from Sigma–Aldrich (SdnBhd, Malaysia) and used as adsorbents. A stock solution of 1 g L⁻¹ dye was prepared in deionized water and used to generate the working solutions at different concentrations of MB and DR 80. The structure and characteristics of the dye used here are presented in Table 1. All the remaining reagents were used as received without further purification.

**Characterization of adsorbent**

FTIR spectra of potato peel powder was performed using a spectrophotometer and KBr pellets (Spectrum BX FTIR, USA) as described by Sila et al. (2014). The samples were exposed to radiations in the range of 4,000–500 cm⁻¹ with 2 cm⁻¹ resolution. Scanning electron microscopy experiments were performed after coating samples with gold using a sputter coater (JEOL, JFC-1100 E ion sputtering device, Japan). Pictures were taken by a scanning microscope (JEOL, JSM-5400, Japan) under vacuum at an accelerating voltage of 5 kV. Images were magnified 500x and 1000x fold.

**Adsorption studies**

Prior to the measurements, a calibration curve was prepared using known concentrations of MB and DR 80. Measurements were performed using a UV–vis spectrophotometer (Shimadzu UV 1240, Japan) at 668 and 523 nm; corresponding to the maximum absorption of the MB and DR 80, respectively. Sorption experiments were carried out in a rotary shaker at different temperatures (from 303.16 K to 323.16 K) and rotation speeds (from 100 to 250 rpm), using 250 mL shaking flasks containing 100 mL dye at different concentrations (from 20 mg mL⁻¹ to 200 mg mL⁻¹), and initial pH values (from 2 to 10) were adjusted with either HCl or NaOH, at 0.1 N. Adsorbent doses that were used were fixed in the range of 1–20 g L⁻¹. The values of temperature, time, proportion... were selected by preliminary tests. After shaking for the preselected times, the samples were taken from the flasks and the dye solutions were separated from the adsorbent by centrifugation at 5,000 rpm for 5 min. The MB and DR 80 concentrations in the supernatants were estimated using the calibration curve, after measuring the absorbance at 668 and 523 nm, respectively. All experiments were conducted in duplicate.

The removal (R) percentage of MB and the amount of adsorbed dye (qₑ(mg g⁻¹)) were calculated as described by Chiou et al. (2004) and Gupta et al. (2006), following these equations:

\[
R = \frac{C₀ - Cₑ}{Cₑ} \times 100 \quad (1)
\]
\[
qₑ = \frac{(C₀ - Cₑ) \times V}{M} \quad (2)
\]

where C₀ and Cₑ represent the initial and equilibrium concentrations of dye solutions (mg L⁻¹), whereas V and M represent the volume of the solution (in L) and the mass of the adsorbent used (in g), respectively.

**Point of zero charge pHₚₑₑ**

The pHₚₑₑ of adsorbent is an important characteristic reported by Faria et al. (2004). 10 mL NaCl solution (0.01 M) with pH value between 2 and 12 (adjusted using either HCl or NaOH, 0.1 N) was added to 30 mg of PP and shaken for 24 h (150 rpm and 25 °C). The pHₚₑₑ value
was determined by plotting the final pH value, versus the initial pH of the solution.

**Adsorption isotherms**

Investigating the isotherms of adsorption provided potent information to describe how adsorbed molecules are distributed between the liquid and solid phases. Several isotherm equations are available in the literature; three of them were selected for this study: the Langmuir, Freundlich, and Temkin equations.

The Langmuir equation (Langmuir 1918):

\[
\frac{C_e}{q_e} = \frac{1}{Q_{max} K_1} + \frac{1}{Q_{max}} C_e
\]

(3)

The Freundlich equation (Freundlich 1906):

\[
\ln q_e = \ln K_f + \ln C_e
\]

(4)

The Temkin equation (Temkin & Pyzhev 1940):

\[
q_e = \beta \ln K_t + \beta \ln C_e
\]

(5)

where

\[
\beta = \frac{RT}{b}
\]

(6)

k_l is the Langmuir constant (L mg\(^{-1}\)) related to the affinity of the binding sites and the free energy of adsorption; Q_{max} (mg g\(^{-1}\)) represents the maximum adsorption capacity when the surface is fully covered with dye molecules that assist in the comparison of sorption performance; q_e is the dye concentration at equilibrium on the adsorbent (mg g\(^{-1}\)); C_e is the equilibrium concentration of the dye (mg L\(^{-1}\)). K_f and n are the Freundlich constants, K_t and b are the Temkin constants, T is the absolute temperature in Kelvin and R is the universal gas constant (8.314 J mol\(^{-1}\) K\(^{-1}\)).

The essential characteristic of the isotherm could be expressed by a dimensionless constant called equilibrium parameter RL, defined by Hameed (2008) as follows:

\[
RL = \frac{1}{1 + K_t C_0}
\]

(7)

where b is the Langmuir constant, and C_0 (mg L\(^{-1}\)) is the highest dye concentration. The value of RL indicates the type of the isotherm. Adsorption isotherm is considered to be favorable when 0 < RL < 1, linear when RL = 1, unfavorable when RL > 1, and irreversible when RL = 0.

**Adsorption kinetics**

The time dependence adsorption process and the mechanism of MB and DR80 adsorptions involved were studied using three kinetic models; Lagergren's pseudo-first order equation, Ho's pseudo-second order equation and the intraparticle diffusion model.

The equations used were as follows:

Pseudo-first-order equation:

\[
\ln (q_e - q_t) = \ln q_e - k_1 t
\]

(8)

Pseudo-second-order equation:

\[
t = \frac{1}{K_2 q_t^2} + \frac{t}{q_e}
\]

(9)

where q_t (mg g\(^{-1}\)) is the amount of dye adsorbed at time t (min), k_1 (min\(^{-1}\)) is the pseudo-first-order rate constant, and k_2 (g mg\(^{-1}\) min\(^{-1}\)) is the pseudo-second-order rate constant.

Intraparticle diffusion equation:

\[
q_t = k_i t^{0.5} + C
\]

(10)

where k_i (mg g\(^{-1}\) min\(^{-1/2}\)) is the intraparticle diffusion rate constant and C (mg g\(^{-1}\)) is the intercept.

**Adsorption thermodynamics**

Adsorption thermodynamics were used to identify the affinity of adsorbent for the adsorbate. The thermodynamic parameters reflect the feasibility and spontaneous nature of the process. These parameters include the ΔG, ΔH, and ΔS that were calculated using the following equations (Gupta & Suhas 2009):

\[
\Delta G = \Delta H - T \Delta S
\]

(11)

\[
\ln K_D = \frac{\Delta S}{R} - \frac{\Delta H}{RT}
\]

(12)

The values of ΔH and ΔS are determined from the slope and intercept of the plot ln K_D vs 1/T.

K_D = q_e/C_e and q_e are the dye concentration at equilibrium on the adsorbent (mg L\(^{-1}\)), R is the universal gas constant (8.314 J mol\(^{-1}\) K\(^{-1}\)).
constant \((8.314 \text{ J mol}^{-1} \text{ K}^{-1})\), and \(C_e\) is the concentration of dye at equilibrium \((\text{mg L}^{-1})\).

**Statistical analysis**

Experiments were conducted three times, and results were expressed as the average value. Error bars in the figures represent the standard deviations of replicate values. Differences are considered significant when the probability, \(p\), is below 0.05. Analyses were performed using Microsoft Excel software version 2007.

**RESULTS AND DISCUSSION**

**Fourier transform infrared spectroscopy (FTIR)**

FTIR is an important technique to determine characteristic functional groups that serve as adsorption sites. Figure 1(a) and 1(b) show, respectively, the macroscopic aspects and the FTIR spectra of PP before and after adsorption of MB and DR 80. The infrared spectra revealed the presence of various functional groups detected on the surface of PPs, indicating the complex nature of the material examined.

The peaks detected at 3,434 cm\(^{-1}\) and 3,435 cm\(^{-1}\), were found in both PP spectra before and after dye adsorption, and could be assigned to O-H stretching vibration of hydroxyl groups \(\text{(Davila-Jimenez et al. 2005; Mohanty et al. 2006)}\). After dye adsorption, the intensity of the bands significantly increased, probably indicating the presence of interactions between the functional groups of PPs and dyes (MB and DR80). The peaks 2,852–2,923 cm\(^{-1}\), and 1,602–1,640 cm\(^{-1}\) correspond to C-H stretching vibration and NH\(_2\) deformation, respectively, were found in both PP samples, before and after dye adsorption.

The peaks detected at 1,464 cm\(^{-1}\) and 1,164 cm\(^{-1}\) in PP before MB and DR80 adsorption are assigned to CH\(_2\) deformation and C-N stretching vibration, respectively. However, the peak intensities became higher after dye sorption.

![Figure 1](http://iwaponline.com/wst/article-pdf/83/6/1384/865284/wst083061384.pdf)

**Figure 1** Adsorption effects on potato peel (PP). (a) Pictures of dried and ground PP taken before and after dye adsorption. (b) FTIR spectra of PP before and after dye adsorption.
Microstructure characterization of the adsorbent

SEM has been the primary tool used to characterize the surface morphology and fundamental physical properties of the adsorbent. Pictures of PP surface were taken before and after MB and DR 80 adsorption and are presented in Figure 2(a)–2(c), respectively.

Figure 2(a) shows that the PP has a rough and porous surface, while Figure 2(b) and 2(c) show that the pores on the surface of the PP have been completely filled with MB and RD80, respectively.

Effect of contact time and particle size on dye adsorption

The adsorption of the dyes is directly related to the adsorbent morphology and the contact time. The size of the particle is an important factor, that affects the adsorption capacity. The kinetics of adsorption were studied for the various particle sizes of the powder. Other adsorption parameters such as dye concentration (100 mg L⁻¹), pH (7), adsorbent dose (2%), agitation (150 rpm), and temperature (313.16 K) were kept constant. Figure 3(a) and 3(b) indicate the percentage of dye adsorption as a function of particle size and contact time. The results show that the adsorption equilibrium was reached after a contact time of 10 and 60 min, respectively, for MB and DR 80, and this is whatever the size of the particles. This is mainly due to the saturation of the PP surface by the dye molecules. Although the adsorption equilibrium is reached at the same time irrespective of the particle size tested, the percentage of dye adsorption is higher when using the finest particles (1–100 μm) (Figure 1). This behavior is mainly related to the large contact area of particles of smaller sizes. For larger particles (>100 μm), most of the internal surface of the particles cannot be used for adsorption. As a result, the mass transport diffusion resistance is higher, and the amount of adsorbed dye is reduced. Based on the results obtained, the best size is less than 100 μm for the two dyes studied.

Effect of agitation on dye adsorption

The effect of agitation on dye adsorption was investigated under conditions that were: initial dye concentration = 100 mg/L, contact time = 10 min for MB and 60 min for DR 80, and dose of PPT = 2%. The results obtained (Figure 3(c)) show that up to 200 rpm, adsorption of MB increases with increasing agitation speed, whereas for
Figure 3 | Kinetic study of MB and DR 80 adsorption on PP. (a) Impact of particle size and contact time on MB adsorption on PP. (b) Impact of particle size and contact time on DR 80 adsorption on PP. (c) Effect of agitation on MB and DR 80 adsorption on PP. (d) Effect of adsorbent dosage on MB and DR 80 adsorption on PP (dye concentration: 100 mg L\(^{-1}\); particle size: 100 μm; contact time: 10 min for MB and 60 min for DR80; pH 7). (e) Effect of temperature (298.16 K, 303.16 K, 313.16 K, and 323.16 K) on MB and DR 80 adsorption rate on PP using 0.2 g PP. (f) Effect of initial dye concentration on MB and DR80 adsorption on PP (adsorbent dose: 0.2 g PP; pH 7; particle size: 100 μm). (g) Effect of pH on MB and DR 80 adsorption on PP (adsorbent dose: 0.2 g PP, pH 7; particle size: 100 μm; contact time: 10 min for MB and 60 min for DR 80). (h) pH variation in terms of initial pH of the solution to determine the \( \text{pH}_{\text{pzc}} \).
DR 80 above 100 rpm, the adsorption decreases slightly to 40% at 200 rpm.

**Effect of the adsorbent’s dose on dye adsorption**

The search for the minimum necessary and sufficient mass of material to adsorb a given pollutant is a crucial step in any study on adsorption. This is why we started this step for the two dyes MB and DR 80 on PP. The influence of the mass of the adsorbent was studied while setting an initial concentration of MB at 100 mg/L. Figure 3(d) shows an increase in the adsorption of these two dyes as a function of the mass of peels added to the reaction medium. For these two dyes, the optimal mass of PP is 2%. Beyond 2 g of PP, the percentage of dye removal remains unchanged. The increase in dye retention with increasing adsorbent mass is due to the availability of a large active area in sites. This deduction is reported by different authors (Mane et al. 2007). Our results are in agreement with those reported previously for the adsorption of dyes on seeds of papayas and jackfruit peels (Kallel et al. 2016).

**Effect of temperature on dye uptake**

The effect of temperature on the adsorption rate of MB and DR 80 on PP was investigated using 2% PP. Figure 3(e) shows a decrease in BM retention but essentially RD 80 as a function of the increase in temperature, indicating that the reaction is endothermic. The rise in temperature makes the adsorption phenomenon unfavorable (Aarfane et al. 2014). So the best results are obtained at ambient temperature.

**Effect of initial dye concentration**

The initial concentration provides an important driving force to overcome any transfer resistance of molecules between the aqueous and solid phases (Ho et al. 2005; Dogan et al. 2006). Figure 3(e) shows the effect of the initial concentration of MB and DR 80 on the percentage of dye adsorption. The results obtained show that the adsorption of MB remains constant until a dye concentration of 100 mg L\(^{-1}\) is reached, and then a slight decrease in the percentage of adsorption is observed. For DR 80, a net decrease is noted when the dye concentration exceeds 50 mg L\(^{-1}\). As a result, for very high concentrations of MB and DR 80, the percentage of adsorption decreased significantly due to the saturation of the surface of the adsorbent by molecules of the dyes.

**Effect of pH on dye uptake**

The pH is a critical parameter to take into account for the removal of dyes from aqueous solutions, as it can affect the charge at the surface of the adsorbent (Abussaud et al. 2016). The effect of pH on the equilibrium uptake capacity of PP was studied at 313.16 K using 100 mgL\(^{-1}\) MB, 50 mg L\(^{-1}\) DR 80 and 2% PP (Figure 3(g)). For DR 80, the results showed that the amount of dye retained by the PP is closely related to the initial pH value of the dye solutions. In fact, at a pH of 2, the adsorption of DR 80 is the best (92.86%) and then decreases slightly to a pH of 4. Above this pH, the adsorption remains constant until a pH of 8 with a DR 80 adsorption rate of 61.48% is reached, then this rate decreases again to a pH of 11. For MB, the results showed that the initial pH of the dye solutions does not affect the rate of MB elimination. Indeed, this cationic dye shows maximum adsorption at both acidic and basic pH (91.57%). Therefore, it can be considered that PP are recommended for the treatment of industrial effluents since the pH of these effluents can be acidic or basic. The point of zero charge for PP was equal to 6 (Figure 3(h)). Thus, the overall surface charge of PP is positive for pH solutions lower than the pH\(_{\text{PZC}}\) value and it is negative when the pH is higher than pH\(_{\text{PZC}}\).

Therefore, the removal efficiency increases from pH2 to pH3 because the attraction forces between the cationic dyes and the negative surface charge increase. Up to pH3, the adsorption of MB remains unchanged because the charge of the negative surfaces remains constant. Therefore, the optimum pH for higher removal from aqueous solution is 6.

On the other hand, a low pH leads to an increase in the concentration of H\(^+\) in solution, which gives the material a positive surface charge, strong electrostatic attractions then appear between the positive surface sites and the anionic charges of the molecules of the DR 80. In fact, the removal efficiency increases when the pH < pH\(_{\text{PZC}}\) due to attractive forces that occur between the anionic dye and the positively charged surface of PPs. This is confirmed by the low binding of the DR 80 molecules to a strongly basic medium due to the repulsion of the DR 80 anionic molecules, resulting in the reduction of dye adsorption. This behavior has been observed during direct red adsorption by orange peels (Arami et al. 2005) and almond shells (Ardejani et al. 2008).

**Adsorption isotherms**

The adsorbent-adsorbate interaction can be easily predicted by plotting the adsorption data into equilibrium isotherm...
models and the model helps in ascertaining the designing of single batch adsorption system.

**Langmuir’s isotherm**

This is the most frequently used model to comment on the results found during the adsorption of dyes in aqueous solution. Among the characteristics of the Langmuir isotherm is its simplicity and the fact that the parameters Qmax and KL have a physical meaning (Table 2). The value of KL is related to the interaction force between the adsorbed molecule and the surface of the solid. The value of Qmax expresses the amount of solute bound per gram of solid whose surface is considered to be completely covered by a mono-molecular layer. This simplicity is a consequence of the restrictive assumptions that make it possible to establish this model. The plots of Ce/qe vs Ce of the three chosen temperatures are presented in Figure 4. The Langmuir constants Qmax and KL are calculated at each temperature from the slope for the two dyes BM and DR80.

The maximum adsorptions capacities (Qmax) of MB and DR80 by the PP at 303.16 K, 313.16 K and 323.16 K are respectively 97.08 mg g⁻¹; 45.87 mg g⁻¹; 61.35 mg g⁻¹ and 27.778 mg g⁻¹; 45.45 mg g⁻¹; 32.258 mg g⁻¹. For the MB and compared to other biosorbents (Table 3), the maximum adsorption capacity of PP at 303.16 K is higher than that of orange peel (13.9 mg/g), banana peel (15.9 mg/g), wheat shells (16.56 mg·g⁻¹), or rice peel (41 mg/g). However, the Qmax of PP was similar to that of peanut shells (68 mg/g) and lower than that of grass waste (457.64 mg/g) and peach gum (298 mg/g). For DR80, the maximum adsorption capacity of PP at 303.16 K is higher than that of almond shell (22.42 mg/g), orange peel (21.05 mg/g) and residue of *Mabeafistuliferz Mart* seed (4.92 mg/g). However, Qmax of PP was lower than that of soy shell flour (178.57 mg/g).

The correlation coefficients of these lines were 0.506; 0.784 and 0.705 for MB and 0.629; 0.844 and 0.854 for the DR 80, for the respective temperatures of 303.16 K, 313.16 K and 323.16 K. The values of the dimensionless separation constants (RL) calculated from the Langmuir constant (KL) were 0.526; 0.28 and 0.41 for MB and 0.04; 0.102 and 0.08 for DR 80 at temperatures of 303, 313 and 323 K. The RL constants ranged from 0 to 1 at all temperatures tested, which shows that the adsorption of MB and DR80 by PP are favorable.

**Freundlich’s isotherm**

It is an empirical equation widely used for the practical representation of the adsorption equilibrium which assumes that adsorption occurs on a heterogeneous surface by a multi layer adsorption mechanism. The calculated Freundlich constants KF and n were determined from the linear plot of ln qe vs ln Ce (Figure 4). The values of KF and n of the three temperatures tested are shown in Table 2. The KF values are 0.46, 0.63 and 0.47 mg g⁻¹(L/mg)⁻¹/n (L/mg)⁻¹/n for MB and 2.38, 1.95 and 1.81 mg g⁻¹ (L/mg)⁻¹/n for DR80 at temperatures 303,16 K, 313,16 K and 323,16 K, respectively. Freundlich constants (n) between 1.08 and 1.19 for DR80 and between 1.05 and 1.11 for MB indicate favorable adsorption for these two dyes by PPs. The values of n obtained satisfy the condition of heterogeneity (1 < n < 10 and 0 < 1/n < 1) required by the model. Similar results

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**Table 2** Isotherm parameters for MB and DR80 removal by PP at different temperatures

| Temperature (K) | 303  | 313  | 323  | 303  | 313  | 323  |
|----------------|------|------|------|------|------|------|
| MB Qmax (mg/g)| 97.08| 45.87| 61.35| 27.778| 45.45| 32.258|
| Langmuir KL (L/mg)| 0.0045| 0.0125| 0.007| 0.104| 0.044| 0.0573|
| | 0.526| 0.28| 0.41| 0.045| 0.102| 0.08|
| | 0.506| 0.784| 0.705| 0.629| 0.844| 0.854|
| Freundlich KF (mg/g(L/mg)¹/n)| 0.462| 0.63| 0.47| 2.381| 1.946| 1.818|
| | 1.05| 1.11| 1.07| 1.075| 1.122| 1.189|
| | 0.9989| 0.998| 0.998| 0.998| 0.997| 0.990|
| Tempkin Kt (L/mg)| 0.374| 0.48| 0.368| 5.340| 4.222| 4.008|
| | 3.705| 3.586| 3.614| 1.221| 1.337| 1.358|
| | 0.920| 0.927| 0.980| 0.987| 0.948| 0.962|
have been found in the literature (Albadarin et al. 2013; Araújo et al. 2013). The correlation coefficients of these lines were 0.99 (very close to 1) for all temperatures (303.16 K, 313.16 K and 323.16 K). Therefore, the adsorption of MB and DR 80 on PPs follows the Freundlich model. This result suggests that these dyes are adsorbed on
the surface of PPs in different ways. Generally, this type of adsorption isotherm results from the predominance of strong ionic interactions between the adsorbent and the adsorbate (Giles et al. 1974).

**Tempkin’s isotherm**

The Tempkin isotherm takes into account the interaction between the adsorbate and the adsorbent and assumes that the fall in heat of adsorption is linear, rather than logarithmic. The Tempkin constants $b$ and $K_t$ were computed from the slope and the intercept of the plot $q_e$ versus $\ln C_e$ (Figure 4). $K_t$ is the binding equilibrium constant (L mg$^{-1}$) corresponding to the maximum binding energy, while $b$ is the constant related to the heat of adsorption.

Based on $R^2$ values of 0.92; 0.92 and 0.98 for the MB and 0.99; 0.95 and 0.97 for DR 80 at temperatures of 303.16 K; 313.16 K and 323.16 K respectively, the experimental data for the adsorption of MB and DR 80 do not follow perfectly the Tempkin isotherm (Table 2).

**Adsorption kinetics**

Several models are given in the literature to describe adsorption kinetics. Experimental adsorption data of MB and DR 80 on PPs were studied using pseudo-first-order (Lagergren 1898) and pseudo-second-order (Ho & McKay 1998) kinetic models.

The constants of the pseudo-first-order model are $q_{e\text{cal}}$, $q_t$ and $K_1$ which correspond respectively to the quantity of dye adsorbed at equilibrium, to the amount of dye adsorbed at a given time (t), and to the constant of kinetics adsorption. The values of $K_1$ were calculated from the slopes and intercept of the plot $\ln (q_e-q_t)$ vs $t$ (Figure 5(a) and 5(c)). For the pseudo-second-order kinetics model, the constants $q_{e\text{cal}}$, $q_t$ and $K_2$ were determined from the slope and the intercept of the representations $t/q_t$ vs $t$ (Figure 5(b) and 5(d)). All these kinetic parameters are listed in Table 4. This table indicates that the values of the correlation coefficient ($R^2$) of the second-order model are closer to 1 than those of the first-order model, whatever the initial concentration of the dye. It can be concluded that the second-order model can give a better description of the kinetics of the adsorption reaction.
of MB and DR 80 with respect to the first-order model. From these results, the chemisorption might be the rate-limiting step controlling the adsorption process.

**Intraparticle diffusion study**

The transfer of a solute from an aqueous phase (the dye in our case) to a solid phase generally follows four steps. The first represents the migration of the solute from the aqueous phase to the surface of the solid. The second step represents diffusion through interparticle spaces (external diffusion). The third concerns the intraparticle diffusion and, finally, the surface chemical reaction between the surface functions of the adsorbent and the active groups of the dye. A plot of $q_t$ vs $t^{0.5}$ was made at initial dye concentrations ranging from 20 to 200 mg/L. These representations give a linear curve for the two dyes tested (Figure 6). The constants of the intraparticle diffusion equation $k_i$ and $C$ calculated from the slope and intercept of these lines are presented in Table 5.

Generally, to predict that the intraparticle diffusion is the step limiting adsorption, it is necessary to check that the plot $(q_t$ vs $t^{0.5})$ passes through the origin. However, for the adsorption of MB and DR 80 by PP, the plot $(q_t$ vs $t^{0.5})$ does not pass through the origin. Thus, intraparticle diffusion is not the limiting step in this case. Otherwise, other mechanisms along with intraparticle diffusion are also involved (Cheung et al. 2007). The result obtained is similar to that of Wu (2007).

**Adsorption thermodynamics**

To identify the biosorption process nature of MB and DR 80 dyes on the surface of PPs (endothermic or exothermic and spontaneous), it is necessary to determine the various thermodynamic parameters such as $\Delta G^\circ$ (J/mol), $\Delta S^\circ$ (J/mol/K) and $\Delta H^\circ$ (kJ/mol) (Figure 7).

Standard free enthalpy values are negative for both dyes (Table 6), indicating that adsorption is a spontaneous
mechanism. For MB, the increase in $\Delta G^\circ$ values with the increase in temperature justifies favorable adsorption at high temperature. Similar results have been reported (Tazerouti & Amrani 2010; Al-Othman et al. 2012). The positive values of $\Delta S^\circ$ and $\Delta H^\circ$ confirm the endothermic nature of the adsorption process and that the order of distribution of the dye molecules on the adsorbent increases relative to that in the solution. The positive value of the entropy changes, $\Delta S$ indicates that the adsorption occurs due to the redistribution of energy between the adsorbate and the adsorbent. It also reflects the affinity of the adsorbent for the adsorbate, mainly taking place based on electrostatic interactions.

### CONCLUSION

The results show the effectiveness of PP, as a low cost adsorbent, in the adsorption of MB or DR 80 dissolved in aqueous solutions. Thus, the adsorption of the two dyes with the PP follows the Freundlich isotherm ($R^2 = 0.99$) and the maximum adsorption capacity obtained is 97.08 and 27.778 mg g$^{-1}$ at 303.3 K for MB and DR 80, respectively. The rate of adsorption was found to follow the pseudo-second-order model with a good correlation coefficient. The determination of the thermodynamic parameters ($\Delta G$, $\Delta H$, $\Delta S$) indicates a spontaneous and endothermic nature of the adsorption process. So, PP can be applied for dye wastewater remediation and it can substitute activated carbon which is a commonly used adsorbent despite its high cost.

### Table 5 | Interparticle diffusion rate constants

| $C_0$ (mg/L) | $K_i$ (mg/g.min$^{-0.5}$) | $C$ (mg/g) | $R^2$ |
|--------------|--------------------------|---------|-------|
| MB 20        | 0.014                    | 0.858   | 0.838 |
| 50           | 0.055                    | 2.066   | 0.705 |
| 100          | 0.043                    | 4.462   | 0.907 |
| 150          | 0.029                    | 6.820   | 0.807 |
| 200          | 0.029                    | 9.192   | 0.734 |
| RD 80 20     | 0.017                    | 0.726   | 0.555 |
| 50           | 0.027                    | 2.326   | 0.522 |
| 100          | -0.014                   | 4.927   | 0.378 |
| 150          | 0.015                    | 7.304   | 0.190 |
| 200          | 0.064                    | 9.573   | 0.663 |

### Table 6 | Thermodynamic parameter of adsorption of MB and DR80 on PPT

| Temperature (K) | MB | DR 80 |
|-----------------|----|-------|
|                 | 303 | 313   | 323   | 303 | 313 | 323 |
| $\Delta G^\circ$ (kJ/mol) | -2,642.89 | -2,996.79 | -3,350.69 | -5,513.844 | -6,047.544 | -6,581.244 |
| $\Delta S^\circ$ (J/mol/k) | 35.39 | 53.37 |
| $\Delta H^\circ$ (kJ/mol) | 8,085.94 | 10,657.266 |

### Figure 7 | Plot of ln KD vs 1/T for MB and DR80 adsorption into PP.
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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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