

Study of the removal of paraquat from aqueous solution by biosorption onto *Ayous* (*Triplochiton schleroxylon*) sawdust

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ABSTRACT

This study concerns the batch biosorption of paraquat on *Ayous* (*Triplochiton schleroxylon*) sawdust; the study centers on the evolution of biosorption parameters during the process. It appears that paraquat forms a monolayer on the sawdust surface as evidenced by the good correlation between the experimental data and the Langmuir model. The biosorption which is rather fast (the equilibrium was reached after ten minutes) follows a pseudo-second-order kinetic model and does not obey to the intra-particle diffusion model. According to the mathematical kinetic modeling, pore and surface mass transfer well describe the phenomenon. NaCl reduces the adsorption capacity of the material but has no significant effect on the kinetics. Alkaline solutions enhance the accumulation of the pollutant, the reverse being observed for acidic media. According to the thermodynamic data, this biosorption is a spontaneous and exothermic process. From these results we concluded that the adsorption of the pollutant is mainly due to cation exchange as indicated by the adsorption energy determined by the Dubinin–Radushkevich model ($E = 12.0736 \text{ kJ mol}^{-1}$); some other interactions resulting from the affinity through organophilic interactions between paraquat and sawdust have also been pointed out. Desorption experiments conducted in HCl and HNO_3 solutions confirmed the proposed mechanism.

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1. Introduction

Paraquat (1,1'-dimethyl-4,4'-bipyridinium) along with glyphosate appears to be among the most widely used herbicides in the world [1]. This compound is a non-selective contact herbicide which destroys plants by inhibiting photosynthesis [1–3]. Because it has no effect on the barks of trees, it is particularly used for weed control in orchards and cocoa or coffee plantations [1]. At the beginning, paraquat was essentially used in very large exploitations, but for the past few years, many African farmers with rather small-sized farms have used it extensively. Unfortunately, paraquat is known to display some harmful effects: upon ingestion by humans, it can damage the digestive apparatus, the kidneys and the lungs, among others. Pulmonary fibrosis however is the most common known disease in the series which results from the transformation by paraquat of the oxygen available in the lungs into free radicals [2]. The risk of contamination by paraquat is enhanced by its high water solubility (620 g L^{-1}) [1,5]. In fact, many studies have revealed its presence in surface and drinking waters [4,6,7], as the consequence of the infiltration in soils of industrial waste contaminated with paraquat or from its application in plantations. Although the lethal dose for human being is 35 mg kg^{-1} [2,4] for

European standards, the maximum permissible concentration for individual pesticides (including paraquat) in drinking water is $0.1 \text{ } \mu\text{g L}^{-1}$ and $1\text{--}3 \text{ } \mu\text{g L}^{-1}$ for surface waters [8]. Thus, the necessity to reduce the concentration of paraquat in water is a worldwide challenge as far as water pollution is concerned.

Classical methods of remediation of pesticides in contaminated waters include oxidation processes (ozonolysis, electro-Fenton process, electro-oxidation), microfiltration and adsorption on porous materials [4]. The latter is particularly attractive because its application is relatively easy and interestingly, it needs rather rudimentary apparatus. In addition, its performance is remarkable both for high and low concentrations [9]. The literature reports many studies on paraquat adsorption on activated carbons, the most common adsorbent used [4]. However, the cost of this material is the main limitation for its intensive use [8]. As substitution materials, clays have been the subject of numerous research studies and the results obtained so far are often comparable to those obtained with activated carbons [7,10].

In recent years, a new class of biosorbents and specifically lignocellulosic materials have been investigated for the same purposes, their attractiveness resulting from their availability, low cost and biodegradability. Some previous studies report their ability to quantitatively accumulate heavy metals and various organic compounds such as dyes and pesticides [8,11–29]. Accumulation of these pollutants on biosorbents is generally achieved through interactions with the hydroxyl and carboxyl groups particularly

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abundant in polysaccharides (cellulose and hemicelluloses) and lignin, both of which constitute about 90% of dry lignocellulosic materials [9]. Furthermore, the functionalization of this material by the grafting of organic molecules bearing active groups was carried out very successfully. Interestingly, the use of the resulting hybrid materials as adsorbents leads to significant increases of adsorption capacity (sometimes greater than that of activated carbons) compared to raw materials [30–33].

Among lignocellulosic materials, sawdust is produced annually in tons by timber industries. However, this large production is mostly either incinerated or dumped in the environment. Yet, studies dealing with the removal of heavy metals and dyes from water by sawdust from various species of wood show that this material is a very promising biosorbent [9,11,15,31,33,34]. However, to the best of our knowledge, none of them deals with the removal of pesticides, particularly paraquat. In addition, only very few studies have reported the use of trees of the African equatorial forest as biosorbents [9,11].

In this work, sawdust from *Ayous* (*Triplochiton schleroxylon*), an abundant wood of the African rainforest has been tested for the uptake of paraquat in aqueous solution. The mechanisms of biosorption as well as the influence of several factors (contact time, biosorbent and pollutant concentration, experimentation temperature, ionic strength and pH of the solution) on the process were thoroughly studied.

2. Materials and methods

2.1. Apparatus and reagents

Stocks solutions of paraquat dichloride were prepared by dissolving in distilled water paraquat dichloride of 98% purity from Aldrich. The other chemicals used in this work were of analytical grade.

Homogenization of the solutions was carried out by using an Edmund Bühler GmbH SM-30 shaking table or a magnetic stirrer. A thermostated cell mgw LAUDA RM6 was used during the thermodynamic studies and pH measurements were carried out with a Multi 340i/SET Weight Watchers International (WTW) pH-meter. The residual concentrations of paraquat after biosorption were measured using a HACH 2500 Odissey spectrophotometer.

2.2. Biosorbent

Ayous is a fast growing tree of many African forests; it produces soft and porous wood widely used in light carpentry [35]. Given its low durability, it is less valuable compared to other African species such as Moabi (*Baillonella toxisperma*) and Iroko (*Chlorophora excelsia*) [35]. For these reasons, *Ayous* sawdust is a common waste of little value. Like the majority of wood species of this area, it contains about 98% of cellulose, lignins and hemicelluloses, the rest being made of extractives (tannins, pectins, polymers of low degree of polymerization) and minerals (Ca^{2+} , Na^+ , Cl^- , SO_4^{2-}) [31,36].

For this study, *Ayous* sawdust was collected from a sawmill, sun dried until a fixed mass is obtained and then grounded and sieved after passing through different mesh size sieves. The fraction used in this study consists of particles between 100 and 160 μm . To remove the extractives which may reduce the adsorption capacity, the sawdust was washed several times with distilled water and then soaked for two hours in a solution of methanol (water/methanol ratio of 9/1). After washing again thoroughly with distilled water, the sawdust was again sun dried for two days and then in an oven at 105 °C for two hours. The biosorbent obtained at the end of this process was used without further treatment for the biosorption of paraquat. Compared with the thermal treatment

applied for adsorption purposes to activated carbon or clays, the present treatment of the sawdust with methanol (which can also be achieved with ethanol) is by far less expensive.

2.3. Determination of point of zero charge (PZC)

The point of zero charge of *Ayous* sawdust was determined using the method described by Ofomaja and Ho for the determination of *Mansonia* sawdust PZC [11].

In different flasks, an equal volume of solution (50 mL of NaNO_3 0.1 mol L^{-1}) is introduced and the pH of each solution is adjusted with molar solutions of NaOH or HCl to obtain a given value denoted pH_i between 2 and 12. 0.1 g of the sawdust treated with methanol is then introduced in each of these flasks which are covered and allowed to rest for some 48 h during which they are manually stirred from time to time. After this period, the pH of the solution (pH_f) is measured. pH_{PZC} is derived from the curve $\Delta\text{pH} = \text{pH}_i - \text{pH}_f = f(\text{pH}_i)$ as the intercept of the abscissa.

2.4. Paraquat biosorption

The biosorbent treated as indicated above was weighed and introduced into a 50-mL flask containing 25 mL of a solution of a given concentration of paraquat. A series of flasks were prepared by varying the different parameters to be investigated. The pH was pre-adjusted with molar solutions of NaOH and HCl. The flasks were then capped and stirred with the shaking table for one hour at a speed of 200 rpm. A flask without sawdust was stirred under the same conditions as a control. After filtration, the residual concentrations of paraquat were determined. In the first series of experiments, the samples were triplicated and it was noticed that there was less than 5% variability in the results. It was then useless to triplicate the experiments throughout the study.

The conditioning of the samples was varied depending on the study undertaken:

- for thermodynamics studies, a paraquat solution containing 6 g L^{-1} of sawdust was stirred in a thermostated cell in the temperature range of 30–55 °C.
- for kinetic studies, the solution of paraquat was stirred in a beaker with a biosorbent concentration of 6 g L^{-1} . About 2 mL of this solution was collected with a syringe after a precise period of time, filtered and analyzed.

The determination of the quantity of paraquat remaining in solution after adsorption proceeded as follows: paraquat is reduced in an alkaline medium to a stable radical cation by ascorbic acid to yield a solution which is blue colored and whose concentration can be determined by spectrophotometry at 600 nm [37,38]. A calibration curve is plotted before each series of experiments so that the concentration of paraquat in the samples can be obtained directly by interpolation. The accuracy of this method was proven by the reproducibility of the titrations and by the fact that the correlation coefficients of the different calibrations curve were very close to unity.

The amount of paraquat adsorbed at equilibrium per unit mass of biosorbent (q_e (mol g^{-1})) and the percentage adsorbed ($\%_{\text{ads}}$) were determined using Eqs. (1) and (2):

$$q_e = \frac{(C_i - C_e)}{m} V_S \quad (1)$$

$$\%_{\text{ads}} = \frac{(C_i - C_e)}{C_i} 100 \quad (2)$$

where C_i ($\mu\text{mol L}^{-1}$) is the initial concentration of paraquat, C_e ($\mu\text{mol L}^{-1}$) the equilibrium concentration of paraquat after adsorp-

Table 1
Langmuir, Freundlich and Dubinin–Radushkevich constants.

Langmuir			Freundlich			Dubinin–Radushkevich		
q_m ($\mu\text{mol g}^{-1}$)	K_L ($\text{L } \mu\text{mol}^{-1}$)	R^2	$1/n$	K_F	R^2	q_m ($\mu\text{mol g}^{-1}$)	E (kJ mol^{-1})	R^2
36.8324	0.0135	0.993	0.3879	2.9733	0.970	110.7460	12.0736	0.986

tion, V_S (L) the volume of the solution and m (g) the mass of the sawdust.

2.5. Desorption

For the desorption studies, the sawdust is loaded with paraquat. The loading proceeds as follows: a mixture of sawdust and paraquat is shaken during 1 h in a beaker, and the modified sawdust is then recovered by filtration and air dried for 48 h. The loaded biosorbent is introduced in a flask containing the desorption solution (H_2O , HCl or HNO_3). The mixture is then stirred at 200 rpm with a shaking table for one hour. After filtration, the concentration of the desorbed paraquat in the filtrate is determined by spectrophotometry as previously described above. The desorption percentage ($\%_{\text{des}}$) expressed by Eq. (3) stands for the fraction of paraquat released by the material:

$$\%_{\text{des}} = \frac{q_e \cdot m_c}{C_{\text{ed}} \cdot V_{\text{sd}}} 100 \quad (3)$$

where q_e ($\mu\text{mol g}^{-1}$) represents the quantity of paraquat in one gram of sawdust, m_c (g) the mass of the sawdust loaded by paraquat, C_{ed} ($\mu\text{mol L}^{-1}$) the equilibrium concentration of paraquat in solution after desorption and V_{sd} the volume of the desorption solution.

3. Results and discussion

3.1. Point of zero charge

The PZC of a material in a solution is the pH value at which the net surface charge of this material is equal to zero. At this value, the adsorbent is neutral, while it turns positively charged at lower pH values or negatively charged at higher pH values [11]. Hence, by plotting the difference $\Delta\text{pH} = \text{pH}_i - \text{pH}_f$ as a function of pH_i , it can be observed that ΔpH values are positive for the pH_i values below 6.5 and negative when these values are above 6.5. This can be explained by the fact that for initial pH values below 6.5, the protons in solution migrate into the sawdust and settle on the carboxylate and hydroxyl functions with which they interact; this protonated material is positively charged. As a consequence, an increase of the solution pH after equilibrium was observed. However, for initial pH above 6.5, protons are released from sawdust into the solution, resulting in sawdust bearing an overall negative charge. The decrease of the pH of the solution in this domain is indicated by negative variations of the pH. From these observations, we can conclude that the pH_{PZC} of methanol treated *Ayous* sawdust is 6.5. This value is close to the PZC of *Mansonia* sawdust (6.91) determined by a similar method [11].

3.2. Effect of the amount of biosorbent

The maximum amount of the biosorbent to be used for an optimum removal of paraquat was investigated. For this to be achieved, increasing amounts of *Ayous* sawdust were introduced in a solution with a given amount of paraquat. The variation of the removal percentage of this analyte versus the biosorbent concentration shows that the amount of the adsorbed pollutant increases significantly with the quantity of biosorbent. A plateau is observed above 16 g L^{-1} revealing that for higher values of the adsorbent concentration, equilibrium arises between the pollutant and the

adsorbent (results not shown). Indeed, in this domain where significant amounts of biosorbent are present in solution, adsorption sites may interact each other, thus inducing the decrease of the active sites available for the sorption of the pollutant, a behavior that has already been observed by many other authors on various adsorbents [4,24,39]. In order to minimize the interactions between active sites for the biosorption of paraquat for the rest of this work, a biosorbent concentration of 6 g L^{-1} was used i.e. far below the plateau obtained here.

3.3. Sorption isotherms

In biosorption studies, the biosorbate concentration is a key parameter that must be monitored precisely in order (i) to optimize the pollutant removal process and (ii) to establish isotherms. In Fig. 1(A), the efficiency of the adsorption of paraquat was plotted against its quantity in solution. It can be observed that for a

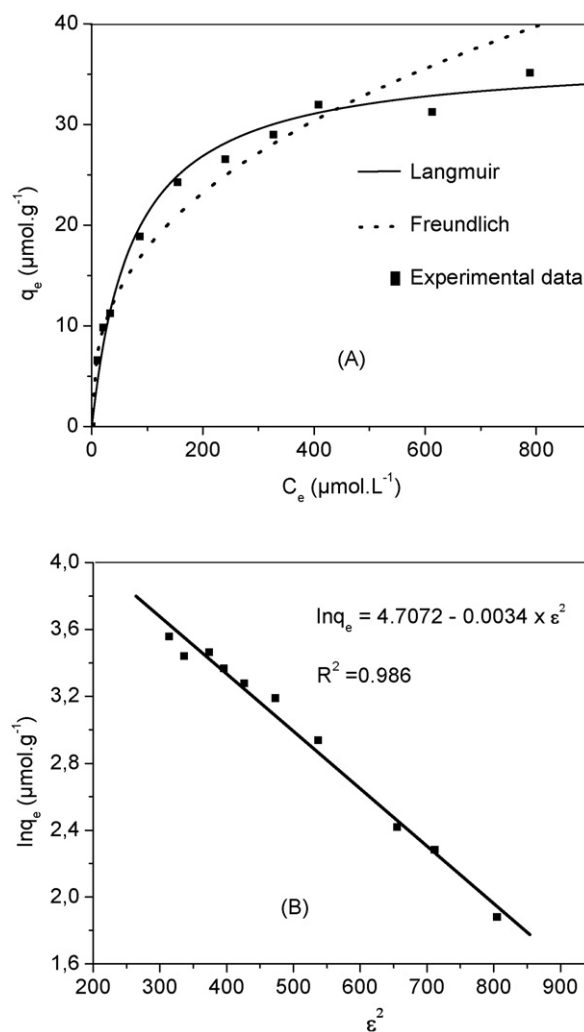


Fig. 1. (A) Effect of the variation of the adsorbed amount of paraquat on the equilibrium concentration in solution; (B) linear form of Dubinin–Radushkevich isotherm. Experimental conditions: 6 g L^{-1} of sawdust in 25 mL of paraquat, pH not adjusted, 200 rpm shaking speed on a shaking table during 1 h at ambient temperature (25°C).

given solution, the amount of paraquat adsorbed at equilibrium per unit of sorbent mass (q_e) increases with its initial concentration. An easier accumulation of the biosorbate onto the biosorbent seems to result from the increase of the concentration gradient of paraquat i.e. between the solution and the sawdust. The increase in the amount of adsorbed pollutant becomes less important when the initial concentration of paraquat is raised, due to the reduction of binding sites. The plateau which appeared for initial concentrations above $600 \mu\text{mol L}^{-1}$ indicates that the biosorption process reached equilibrium and that all adsorption sites are occupied. These observations are very common during adsorption studies [6–34].

In order to get more insight into the adsorption process, a check was carried out to verify which of the three widely used models for solid–liquid systems: Langmuir, Freundlich and Dubinin–Raduschkevich (DR) isotherms matched the results. This study aimed at predicting the distribution of the particles adsorbed on the biosorbent surface as well as the distribution of the adsorption sites and the nature of the interactions between the adsorbate and the adsorbent.

(i) The Freundlich model is known to characterize the adsorption on heterogeneous surfaces; its logarithmic form is given by Eq. (4):

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (4)$$

where q_e (mol g^{-1}) represents the amount of the adsorbate per unit mass, C_e (mol L^{-1}) its concentration in solution at the equilibrium, K_F the Freundlich constant and n a constant related to the intensity of adsorption;

(ii) The Langmuir model which characterizes monolayer's adsorptions is expressed in its linear form by Eq. (5):

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m K_L} \quad (5)$$

where q_m (mol g^{-1}) represents the maximum adsorption capacity, and K_L (L mol^{-1}) the Langmuir constant.

(iii) The Dubinin–Raduschkevich (DR) model is used to describe gas adsorption onto non-energetically uniform surfaces of microporous solids. It should be noted that this model has also been successfully applied to many biosorption processes [16]. Its linear form is given by Eq. (6):

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \quad (6)$$

where ε , the Polanyi potential i.e. the energy required to move a particle from its adsorption site to infinity, is determined from Eq. (7):

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (7)$$

R ($8.314 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1}$) being the ideal gas constant, T (298 K in our case) the experimental temperature and β ($\text{kJ}^2 \text{ mol}^{-2}$) a constant related to the adsorption energy E (kJ mol^{-1}) obtained from Eq. (8):

$$E = \frac{1}{\sqrt{-2\beta}} \quad (8)$$

The models of the Langmuir and the Freundlich isotherms are plotted in Fig. 1(A) and the DR linear isotherms in Fig. 1(B); the corresponding constants are given in Table 1. The correlation coefficients obtained (0.993 for Langmuir, 0.970 for Freundlich and 0.986 for DR models) tend to show that the process is best described by the Langmuir model. This implies that the *Ayous* sawdust adsorption sites display an equivalent energy and are uniformly distributed so that paraquat fixation proceeds by a monolayer type. The maximum adsorption capacity determined by the Langmuir model is $36.8324 \mu\text{mol g}^{-1}$. Although this model is rather common for the biosorption of organic pollutants [4,11,31,39], it is difficult to

Table 2

Maximum adsorption capacities obtained for the adsorption of paraquat onto various adsorbents.

Adsorbents	q_m (mg g^{-1})	References
Regenerated clay mineral from bleaching earth waste	24.80	[10]
Activated carbon derived from used tires	33.70	[4]
Commercial activated carbon	75.80	[4]
Methacrylic acid-modified rice husk	317.70	[30]
Activated clay	58.48	[7]
<i>Ayous</i> sawdust	9.47	This work

compare the q_m values of the various adsorbents because the experimental conditions have to be identical which is not the case, the various studies having been carried out independently. However, we have gathered in Table 2 the values of maximum adsorption capacities obtained for the adsorption of paraquat onto various adsorbents. We can observe that, compared to the other adsorbents, the adsorption capacity of *Ayous* sawdust is relatively low. Nevertheless, an optimization of the experimental parameters (which is not the case in this work) should significantly increase this value. Indeed, if we consider the value of the PZC of the biosorbent (6.5), alkaline solutions should increase the biosorption of paraquat since this compound is a cation.

The $1/n$ value (0.3879) determined by the Freundlich model lies between 0 and 1 which shows that paraquat has a good affinity for *Ayous* sawdust [7]. The adsorption energy determined from the DR model is $12.0736 \text{ kJ mol}^{-1}$. Hence, biosorption proceeds through a cation exchange mechanism since this value is in the interval $8\text{--}16 \text{ kJ mol}^{-1}$ expected for such a mechanism [4,41]. This also implies that electrostatic interactions are involved during the process [16]. This mechanism has been experienced on studies of the adsorption of paraquat on clay and lignocellulosic materials [7,10,30]. However, in our case, the wide gap between the value of the maximum adsorption capacity determined ($110.7460 \mu\text{mol g}^{-1}$) and the one obtained from the Langmuir model is surprising.

3.4. Effect of the pH

Since the adsorbent charge is closely dependent on the acidity of the solution [4,6,10], the pH is a key factor as far as adsorption of cationic compounds is concerned. We have thus studied the efficiency of the adsorption when the pH is varied. As shown in Fig. 2, the adsorption percentage increases when the pH is raised, this effect being more pronounced in the pH ranges of 3–4 and 9–11. This result which is also in accordance with previous work on paraquat adsorption [4,6,10] can be explained by the fact that for pH values below 6.5, the biosorbent is positively charged due to the protonation of carboxylate groups present in the sawdust and interactions between hydroxyl functions and protons. Electrostatic repulsions then prevent the protonated sawdust and paraquat (positively charged) to interact efficiently. For high value of pH however, the deprotonation of the material occurs which favors attraction between the sawdust and the pollutant [11,31]. The rather high removal percentage obtained in alkaline media is consistent with the value of the PZC (6.5).

3.5. Kinetic studies

In this section, we were interested in the kinetic aspect of the adsorption of paraquat by the *Ayous* sawdust. The experiment consists of determining the time necessary for the adsorption process to reach the equilibrium. The results are presented in Fig. 3(A) from

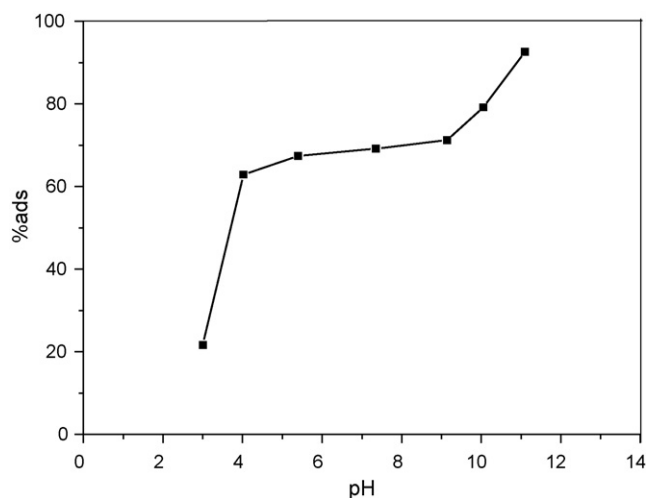


Fig. 2. Effect of pH on the paraquat biosorption. Experimental conditions: 6 g L⁻¹ of sawdust in 25 mL of paraquat 10⁻⁴ M, 200 rpm shaking speed on a shaking table during 1 h at ambient temperature (25 °C).

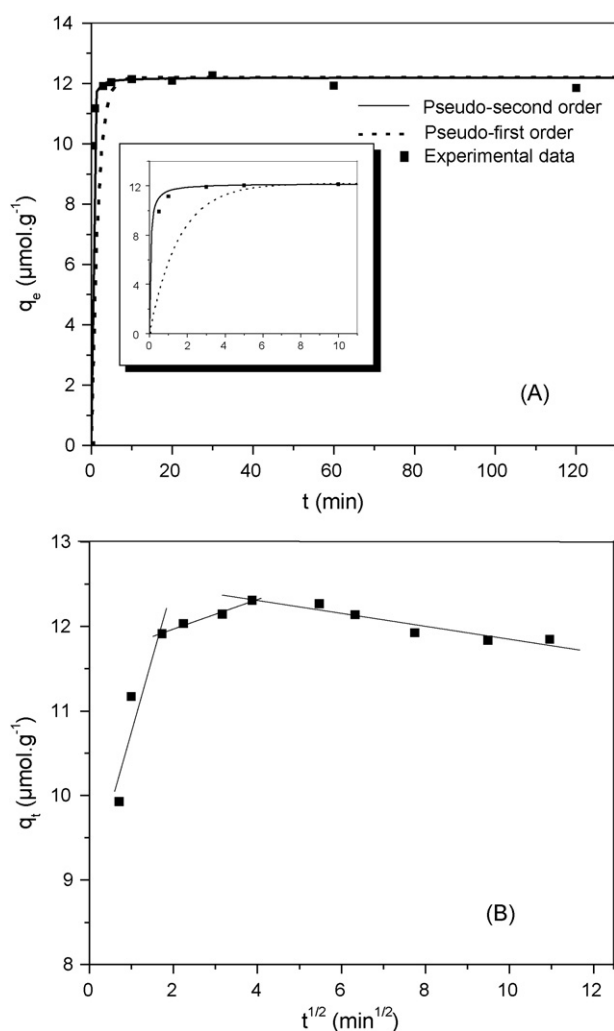


Fig. 3. (A) Effect of contact time on the paraquat biosorption; (B) intra-particle diffusion model. Experimental conditions: 6 g L⁻¹ of sawdust in 400 mL of paraquat 10⁻⁴ M, pH not adjusted and stirred at ambient temperature (25 °C).

which it can be seen that the kinetics of the adsorption is rather fast since 10 min is sufficient for the phenomenon to go to completion. This observation which is in agreement with previous other work on the adsorption of paraquat on lignocellulosic materials or clays [4,7,10,30] is typical of macro-porous adsorbents. Indeed, the large pore size, in addition to the hydrophilic nature of sawdust (due to the presence of hydroxyl groups), promotes accessibility to the adsorption sites.

In order to shed more light on this kinetic process, two kinetic models which are commonly used to study the kinetic of biosorption processes: the pseudo-first order (Eq. (9)) and the pseudo-second order models (Eq. (10)) were applied to the experimental data obtained in Fig. 3(A)

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (9)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (10)$$

$$t_{1/2} = \frac{1}{k_2 q_e} \quad (11)$$

In the above equations, k_1 (min⁻¹) is the rate constant of pseudo-first order, k_2 (g μmol⁻¹ min⁻¹) the rate constant of pseudo-second order, q_t (μmol g⁻¹) the amount of paraquat adsorbed at time t (min) and q_e (μmol g⁻¹) the amount adsorbed at equilibrium.

From Fig. 3(A), it can be noted that the process matches the pseudo-second order model better compared to that of pseudo-first order. This is also confirmed by the value of the adsorption capacity evaluated from the pseudo-second order model (12.1951 μmol g⁻¹) which is close to the experimental value (12.3105 μmol g⁻¹). This implies that the limiting step of the paraquat biosorption on *Ayous* sawdust is governed by chemisorption [14,42]. On the other hand, the reaction half time ($t_{1/2} = 0.0524$ min) determined from Eq. (11) confirms that the biosorption of paraquat is very fast compared to the value ($t_{1/2} = 1.084$ min) obtained for adsorption of this pollutant on activated clay [7].

In order to evaluate the contribution of the diffusion of paraquat within the sawdust in the whole biosorption process, the intra-particle diffusion model defined by Eq. (12) (where k_{ip} (μmol g⁻¹ min^{-1/2}) is the intra-particle diffusion constant) was applied to the experimental data and the results obtained are given in Fig. 3(B) where the variation of the amount of paraquat adsorbed is plotted against the square root of time; the related constants obtained are presented in Table 3.

$$q_t = k_{ip} t^{1/2} \quad (12)$$

This curve presents three linear portions. The first one located at the beginning of the process, reflects the easy diffusion of paraquat within the macropores of the sawdust with an intra-particle diffusion constant of 1.7594 μmol g⁻¹ min^{-1/2}; the second one which appears between 3 and 15 min with a lower slope (0.1750 μmol g⁻¹ min^{-1/2}) may account for a reduction in the diffusion when part of the macropores are loaded with the pollutant, or when the diffusion occurs in pores with less important diameter. The third portion has a negative slope which implies that part of the paraquat may diffuse from the bulk of the sawdust to the solution when the binding sites within the pores are fully occupied. However, this desorption is not really significant as evidenced by the low value of the intra-particle diffusion constant (-0.0765 μmol g⁻¹ min^{-1/2}). We can also observe that this intra-particle diffusion model curve does not pass through the origin, which is an indication that paraquat diffusion in the bulk of the sawdust is not the only process that governs the biosorption [14,43].

For many authors, diffusion of a compound at the surface and in the porous structure of the adsorbents plays a key role

Table 3
Pseudo-second order, pseudo-first order, intra-particle diffusion kinetics models and mass transfer constants.

q_{exp} ($\mu\text{mol g}^{-1}$)	Pseudo-second order		Pseudo-first order		Intra-particle diffusion			Mass transfer constants			
	q_e ($\mu\text{mol g}^{-1}$)	k_2 ($\text{g } \mu\text{mol}^{-1} \text{ min}^{-1}$)	q_e ($\mu\text{mol g}^{-1}$)	k_1 (min^{-1})	K_{ip1} ($\mu\text{mol g}^{-1} \text{ min}^{-1/2}$)	K_{ip2} ($\mu\text{mol g}^{-1} \text{ min}^{-1/2}$)	K_{ip3} ($\mu\text{mol g}^{-1} \text{ min}^{-1/2}$)	$k_f \times 10^3$ (cm s^{-1})	R^2	$D \times 10^8$ ($\text{cm}^2 \text{ s}^{-1}$)	R^2
12.3105	12.1951	1.5637	4.4224	0.6455	1.7594	0.1750	-0.0765	5.0744	0.939	1.0348	0.995

during adsorption [44–46]. To evaluate the contribution of this phenomenon, two mathematical kinetic models have been used:

(i) external diffusion model characterized by Eq. (13):

$$\ln \frac{C_t}{C_i} = -k_f \frac{S}{V} t \quad (13)$$

where k_f (cm s^{-1}), the initial external mass transfer coefficient is obtained by plotting the graph $\ln(C_t/C_i)$ as a function of time (s), S/V (cm^{-1}) represents the ratio of the total interfacial area of the particles against the total solution volume; this ratio can be determined by Eq. (14) below:

$$\frac{S}{V} = \frac{3L}{\rho\phi} \quad (14)$$

where L is the biosorbent concentration (g cm^{-3}), ϕ the mean particle diameter (cm), and ρ the apparent density of the adsorbent (g cm^{-3}). Since the particles used in this study have a diameter ranging from 100 to 160 μm , the value used for the kinetic modeling was the mean of these extreme values (130 μm).

(ii) pore and surface mass diffusion are well described by Fick's second law of diffusion [44,47] from which Eq. (15) below is derived.

$$-\log \left(1 - \left(\frac{q_t}{q_e} \right)^2 \right) = \left(\frac{4\pi^2 D}{2.3\phi^2} \right) t \quad (15)$$

The value of D ($\text{cm}^2 \text{ s}^{-1}$), the sum of pore and surface diffusion can thus be obtained through a graph derived from Eq. (15).

In order to check if the internal diffusion mechanism is the main process that governs the adsorption of the pollutant, we calculated the Biot number (B_N), according to Eq. (16):

$$B_N = k_f \frac{\phi}{D} \quad (16)$$

It is known that when B_N is greater than 100, the process can be assumed to proceed mainly by internal diffusion mechanism [44].

The values of k_f ($5.0744 \times 10^{-3} \text{ cm s}^{-1}$) and D ($1.0348 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$) calculated from these models are presented in Table 3. It is known that when the value of D lies in the range 10^{-13} to $10^{-5} \text{ cm}^2 \text{ s}^{-1}$ as it is the case here, this is an indication of a chemisorption phenomenon occurring during the biosorption process [44]. This result corroborates what was already noted with the pseudo-second order model which shows that the limiting step of this biosorption is governed by chemisorption (vide supra). Paraquat biosorption is best described by the internal diffusion mechanism rather than the external diffusion one since the value of B_N (6374.8743) is greater than 100. The high correlation coefficient (0.992) obtained with pore and surface mass diffusion model is in agreement with this conclusion.

3.6. Thermodynamic study

In order to evaluate the thermal effect on the biosorption of paraquat, the influence of temperature was carried out between 30 and 55 °C. It was observed that the adsorption capacity of the sawdust decreases when the temperature is raised, which implies that the fixation of paraquat takes place with the release of heat (exothermic process). A temperature increase would cause a reduction in the affinity of paraquat for Ayous sawdust. A previous study using activated carbon as adsorbent showed that the temperature does not influence the process [4]. By contrast on clay, there is rather an increase in the adsorption capacity with temperature [10].

Using the experimental data, some thermodynamic parameters were determined with Eqs. (13) and (14) and (15) [8,12,39,40].

$$K = \frac{F_e}{1 - F_e} \quad (17)$$

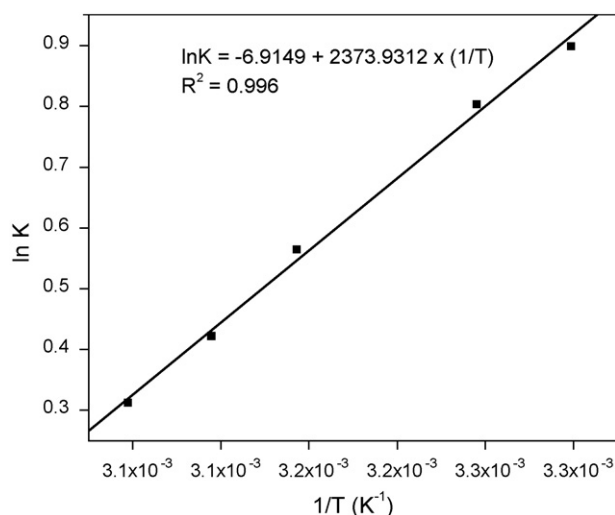


Fig. 4. Effect of temperature on the paraquat biosorption. Experimental conditions: 6 g L⁻¹ of sawdust in 50 mL of paraquat 10⁻⁴ M, pH not adjusted, and stirred at various temperatures (30–55 °C).

$$\ln K = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (18)$$

$$\Delta G = \Delta H - T\Delta S \quad (19)$$

where F_e is the fraction of paraquat adsorbed at equilibrium, ΔH (kJ mol⁻¹) the variation of enthalpy, ΔS (kJ mol⁻¹ K⁻¹) the variation of entropy and ΔG (kJ mol⁻¹) the change in Gibbs free energy.

Fig. 4 presents the graph $\ln K = f(1/T)$ and Table 4 shows the thermodynamic constants determined from this graph.

The value of the correlation coefficient (0.996) shows that the experimental data are very close to the theoretical. The negative value of ΔH (-19.729 kJ mol⁻¹) confirms the exothermic nature of the process. Changes in Gibbs free energies are negative throughout the temperature range studied, indicating that biosorption of paraquat on *Ayous* sawdust is spontaneous. On the other hand, the values of ΔG decrease with the temperature, showing that the process is more favorable at low temperatures, a fact that confirms once more the exothermic nature of the biosorption of paraquat on *Ayous* sawdust.

3.7. Effect of ionic strength

It is well known that the biosorption of a specific ionic compound is often influenced by the interference of the other ions present in solution [6,10,26]. We have thus evaluated the effect of the presence of sodium chloride, on the biosorption process. For this to be achieved, the biosorption was done in a solution without NaCl on one hand and in solutions containing NaCl at 0.01 mol L⁻¹ and 0.1 mol L⁻¹ on the other hand.

It can be seen in Fig. 5 that the presence of NaCl in solution induces a decrease of the paraquat adsorption capacity. A competition occurring between paraquat and Na⁺ for the adsorption sites may explain this behavior, as the biosorption in this case probably proceeds via a cation exchange mechanism as already observed by Larous et al. [26]. However, for NaCl concentration of 0.01 mol L⁻¹ and of paraquat 10⁻⁴ mol L⁻¹, the adsorption capacity is lowered by about 34%. Even when the quantity of Na⁺ is by far larger than that of paraquat, the exchange does not go to completion. Undoubtedly paraquat has a higher affinity compared to Na⁺ ions for the binding sites of *Ayous* sawdust. Indeed, the fact that paraquat is more organophilic than Na⁺ ions can explain this result.

In order to check the effect of the ionic strength on the kinetic of biosorption, the related pseudo-second order constants were

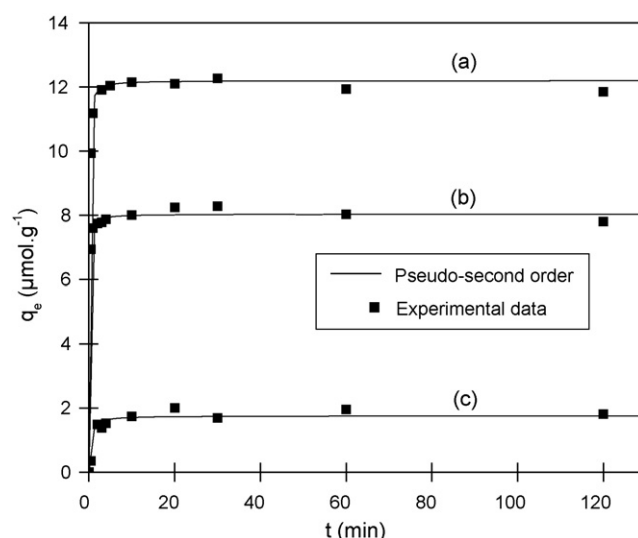


Fig. 5. Effect of ionic strength during the paraquat biosorption. Experimental conditions: 6 g L⁻¹ of sawdust in 400 mL of paraquat 10⁻⁴ M, pH not adjusted and stirred at ambient temperature (25 °C). NaCl concentrations (mol L⁻¹): (a) 0.00, (b) 0.01 and (c) 0.10.

determined from Fig. 5 (constants not presented here). It can be clearly seen that the kinetics follows the pseudo-second order but with a slight decrease in the correlation coefficients when the concentration of NaCl is increased; reaction half times increase slightly in the same time. This again confirms the fact that the presence of Na⁺ cations reduces the number of the active sites for biosorption, but does not change significantly the accessibility of the sites available for paraquat. The high hydrophilic nature of the sawdust may explain this phenomenon. Indeed, the large contact area between the sawdust and the aqueous solution favors interactions between the binding sites available and paraquat.

3.8. Desorption study

The possibility to reuse the biosorbent was undertaken by examining the paraquat desorption in nitric and hydrochloric acid at various concentrations. The effect of the acid during desorption was evaluated by performing the same experiment with distilled water. The results are given in Fig. 6 where the variation of desorp-

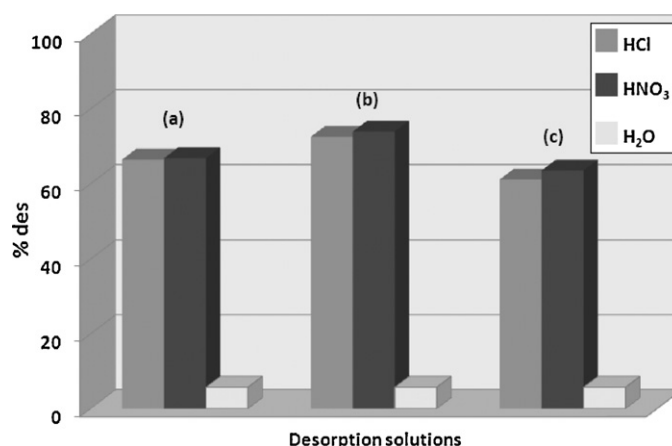


Fig. 6. Effect of the nature of the desorption solution on the recovering of adsorb paraquat. HCl and HNO₃ concentrations: (a) 0.100 mol L⁻¹, (b) 0.010 mol L⁻¹ and (c) 0.001 mol L⁻¹. Experimental conditions: 0.3 g of sawdust (containing paraquat) in 50 mL of desorption solution, 200 rpm shaking speed on a shaking table during 1 h at ambient temperature (25 °C).

Table 4
Thermodynamic constants for the paraquat biosorption onto *Ayous* sawdust.

R^2	ΔH (kJ mol ⁻¹)	ΔS (kJ mol ⁻¹ K ⁻¹)	ΔG (kJ mol ⁻¹)					
			30 °C	35 °C	40 °C	45 °C	50 °C	55 °C
0.996	-19.729	-0.057	-2.266	-2.058	-1.929	-1.493	-1.133	-0.852

Table 5
Characteristics of contaminated river water.

Characteristics	COD (mg L ⁻¹)	Turbidity (NTU)	Conductivity (μS cm ⁻¹)	pH
Value	85	19.2	164	6.44

tion percentage is plotted against the nature and concentration of the desorption solution.

The low desorption percentage obtained with distilled water (approximately 5%) tends to show that interactions between paraquat and sawdust are important. With HCl and HNO₃ 0.001 mol L⁻¹ this percentage rises to 61 and 63.5% respectively and to 72.5 and 74% when the concentrations of desorption solutions are 0.01 mol L⁻¹. So it is clear that desorption results from cation exchange between the protons in solution and the adsorbed paraquat. The undesorbed fraction of paraquat may be bound to the sawdust through a different mechanism from cation exchange. This is why the increase in acidity does not significantly improve desorption. On the contrary, the desorption process even decreases for higher concentrations of HCl and HNO₃: 66.4 and 66.8% respectively for HCl and HNO₃ 0.1 mol L⁻¹. This can be explained by the fact that, for such concentrations, these acids can induce structural changes in the sawdust which may increase its affinity to paraquat. Recent studies have in fact shown that the acidic treatment of sawdust and other lignocellulosic materials alters their structure, particularly through extraction of lignin or modification of some functional groups [48,49]. These modifications increase the adsorption capacity of the biosorbent for some cationic compounds [8,12,39,40].

3.9. Application to real water sample

The efficiency of *Ayous* sawdust to remove paraquat in real water was investigated. A sample of river water was collected and was spiked with 10⁻⁴ mol L⁻¹ of paraquat. Some characteristics of the polluted river water are presented in Table 5. The biosorption procedure was the same as the one described in Sections 2–4 without pre-adjustment of pH or temperature. It appears that the ability of *Ayous* sawdust to adsorb paraquat decreases slightly (67.4240–60.8315% respectively for distilled water and for river water) for identical operating conditions. This decrease can be explained by the interactions between the biosorbent and the cations existing in the river water, leading to less available binding sites for paraquat. This observation matches what was previously noted during the study of the influence of ionic strength (see Sections 3–7).

4. Conclusion

The objective of the present study was to assess the capacity of *Ayous* sawdust to adsorb paraquat and to study the mechanisms of this process. It is noted that *Ayous* sawdust quantitatively adsorbs the pollutant with a very fast kinetics (equilibrium is reached after about 10 min) of the pseudo-second order type. This adsorption seems to proceed by the formation of a monolayer on a uniform surface energy as shown by the good correlation with the Langmuir adsorption model. The energy of adsorption determined from the DR model (12.0247 kJ mol⁻¹) suggests the involvement of the cation exchange mechanism during adsorption. Intra-particle diffusion model reveals that diffusion is not the rate-determining

step of the biosorption of paraquat. The pH has a significant effect on the process: for pH values less than 3, the removal percentage is low (20% at pH 3) whereas at pH of 11 a removal of up to 92.6% is obtained. The thermodynamic study reveals the exothermic nature of the biosorption and the spontaneous fixation of paraquat on *Ayous* sawdust. The presence of NaCl decreases the capacity of the sawdust to uptake paraquat. Desorption with solutions of hydrochloric and nitric acids permits to recover a maximum of 74% of the paraquat.

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