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Adsorption of Methylene Blue from aqueous solution using Senegal River *Typha australis*

Abdoulaye Demba N'diaye [1, 2,*], Youssef Aoulad El Hadj Ali [1], Mohamed Abdallahi Bollahi [2], Mostafa Stitou [1], Mohamed Sid'Ahmed Kankou [3] and Driss Fahmi [1]

[1] Laboratoire de L'Eau, les Etudes et les Analyses Environnementales, Département de Chimie, Faculté des Sciences, Université Abdelmalek Essadi, B.P. 2121, Mhannech II, 93002 Tétouan, Maroc

[2] Laboratoire de Chimie, Service de Toxicologie et de Contrôle de Qualité, Institut National de Recherches en Santé Publique, BP 695, Nouakchott, Mauritanie

[3] Unité de Recherche Eau, Pollution et Environnement, Département de Chimie, Faculté des Sciences et Technique, Université de Nouakchott Al Aasriya, BP 880, Nouakchott, Mauritanie

Abstract: In this work, batch adsorption experiments were carried out for the removal of Methylene Blue (MB) from aqueous solutions using *Typha australis* leaf as a low cost adsorbent. The effects of some variables governing the efficiency of the process such as adsorbent mass, pH, ionic strength, contact time and temperature were investigated. The adsorption kinetic data were analyzed using the Pseudo First Order (PFO) and Pseudo Second Order (PSO) models. The experimental equilibrium data were analyzed using Langmuir and Freundlich isotherm models. The results show that the PSO model is the best for describing the adsorption of MB by Typha australis for all initial MB concentrations. The equilibrium data fitted well with the Langmuir model with the monolayer adsorption capacity for MB-*Typha australis* leaf system was of 103.12 mg g^{-1}. The values of activation parameters such as free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were also determined as - 4.44 kJ mol^{-1}, 55.13 kJ mol^{-1} and 203.21 J mol^{-1} K^{-1}, respectively. The thermodynamics parameters of MB-Typha australis system indicate spontaneous and endothermic process. These results indicate that the *Typha australis* leaf can be feasibly employed for the eradication of MB from aqueous solution.

Keywords: Methylene Blue, adsorption, *Typha australis*, isotherm, kinetic.

1. Introduction

The textile industry is one of the most water-consuming industries in the world and produces large quantities of wastewaters which contain hazardous compounds such as dyes. These chemical species can have an important ecological impact on ecosystems due to their strong toxicity and environmental persistence [1].

Among the dyes, Methylene Blue (MB) has been widely used as a colorant, an indicator and an antiseptic agent in clinical therapy [2,3].

However, disposal of MB containing waters can cause severe damage to the environment [4,5]. Many human diseases have been reported to be closely related to MB, such as hemolytic anemia and acute renal failure [6]. Hence, the removal of MB is a very important task in the protection of our environment and health.

Some techniques have been applied for the elimination of dyes in aquatic media such as biodegradation [7], electrochemical treatment [8], electrochemical oxidation and aerobic biodegradation [9], nanofiltration and reverse osmosis [10], photo catalytic degradation [11], degradation by Fenton and photo-Fenton processes [12] and adsorption [13].

Solid-phase adsorption is one of the most efficient technologies for the treatment of variety of hazardous compounds in water [14-23]. However, the adsorption of dyes onto activated carbons has attracted many researchers, but its high cost inhibits its application on a large scale [24].

For this reason, researchers have concentrated on finding alternative natural adsorbents to commercial activated carbon. Natural adsorbents are preferred for their biodegradable, non-toxic nature, low commercial value and highly cost-effective nature. A number of non-conventional and low cost agro wastes sorbents have been tried for removing MB from aqueous solution via adsorption process [25-28].

In this work, *Typha australis* an abundant and available plant along the Senegal River was chosen to investigate its adsorption capacity for MB present

*Corresponding author: *Abdoulaye Demba N'diaye*
Email address: abdouldemba@yahoo.fr
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in aqueous solution. The effects of various parameters such as adsorbent mass, pH, ionic strength, contact time and temperature on the adsorption efficiency of MB were studied using the batch technique. The adsorption kinetic data were analyzed by the pseudo-first-order (PFO) and pseudo-second-order (PSO) kinetic models using the nonlinear method. The experimental equilibrium data were examined by Langmuir and Freundlich isotherms using nonlinear method. The thermodynamics parameters, such as ΔG°, ΔH°, ΔS°, have been determined. So, the adsorption parameters obtained using the present *Typha australis* leaf adsorbent will be compared with the ones presented in the literature.

2. Material and Methods

2.1 Adsorbate preparation and analysis

All chemicals used in this study were of analytical reagent grade. All the solutions are prepared using pure MB and distilled water. The stock solution is prepared by adding 1 g of the MB to 1 L of distilled water. Other concentrations are prepared by dilutions of the stock solution and used to develop the standard curves using the Spectrophotometer UV1800 Ray Leigh.

2.2. Collection, preparation and characterization of Typha australis

Biomass of *Typha australis* growing along the Senegal River was collected from the city of Rosso, Wilaya of Trarza, from the south of Mauritania. The collected materials were washed thoroughly with distilled water to remove dirt. The biomass was then air dried for 3 days followed by drying in an oven at 105°C for 24 h. The dried biomass was ground, sieved to obtain particle sizes below 0.5 mm and stored in a dessicator before use. The physicochemical characteristics of the *Typha australis* leaf are given in Table 1 [29].

Table 1. Physicochemical characteristics of *Typha australis* leaf.

Parameters	Mean
pHpzc	6.36
Bulk density (g mL^{-1})	0.48
Moisture (%)	3.9
Ash (%)	9.9
Total surface acidity (meq g^{-1})	0.744
Total surface basicity (meq g^{-1})	0.376

The Brunauer- Emmett-Teller (BET) surface of the *Typha australis* was obtained using a micromeritics® TriStar II Plus device, based on N_2 adsorption isotherms determination. The BET surface for *Typha australis* was found to be 0.91 $m^2 g^{-1}$. The value of the surface area of Typha Australis without any thermal or chemical process is satisfactory when compared with other species of Typha studied in the literature whose preparations required excessive heat and chemical inputs and especially with the use of toxic acids and corrosive [30].

2.3. Batch adsorption studies

MB batch adsorption using *Typha australis* leaf as adsorbent was conducted in batch experiments. In all sets of experiments, fixed concentrations of MB (5 and 10 mg L^{-1}) were stirred (150 rpm) with varying adsorbent mass for different time periods. The effect of ionic strength was investigated in 2 steps: in lower NaCl salt concentrations (0.001-0.006 mol L^{-1}) and higher of NaCl salt concentrations (0.05-2 mol L^{-1}). The effects of process conditions and contact time (5–180 min) were evaluated for *Typha australis* leaf adsorbent. The effect of pH on the amount of MB removed was studied at pH of 2.5, 7 and 11.5. The pH of the solutions was adjusted using a pH-meter to constant values by addition of 0.1 M HCl or 0.1 M NaOH solutions. The effect of temperature on the amount of MB removed was studied at temperature of 20, 25 and 30°C. The adsorption isotherms were obtained by varying the initial MB concentrations from 5 to 100 mg L^{-1}.

At the end of each experiment, the stirred solution mixture was centrifuged and the residual concentration of MB was analyzed by Spectrophotometer UV1800 Ray Leigh at 655 nm wavelength. The adsorption uptake at equilibrium time q_e (mg g^{-1}), is expressed by following equation (1):

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

The percentage of the MB removed (%) from the solution was calculated using the equation (2):

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

Where q_e is the MB concentration in adsorbent (mg g^{-1}), C_i is the initial MB concentration (mg L^{-1}); C_e is the MB concentration at equilibrium (mg L^{-1}); V is the solution volume (L) and m is the mass of the *Typha australis* leaf as adsorbent used (g). All batch experiments were conducted in triplicate and the average values are reported.

2.4. Kinetics and equilibrium adsorption modelling

The mechanism of the adsorption process was evaluated using PFO and PSO models. We used a PFO equation of Lagregren, based on solid capacity with the assumption that the adsorption mechanism is rate limiting [31]. The non-linear kinetic PFO model may be expressed by equation (3):

$$q_t = q_e(1-\exp^{-k_1 t}) \quad (3)$$

Where q_t is the amount of MB adsorbed per unit mass of *Typha australis* leaf adsorbent (mg g^{-1}) at time t, k_1 is the PFO rate constant (L min^{-1}), and t is the contact time (min). PSO equation based on solid phase adsorption was used with the assumption that the rate limiting step may be chemical sorption (chemisorptions) involving valence forces through sharing or exchange of electrons between adsorbent and the adsorbate [32]. The non-linear kinetic PSO model may be expressed as in equation (4):

$$q_t = \frac{k_2 q_e^2 t}{1+k_2 q_e t} \quad (4)$$

Where k_2 ($gmg^{-1}min^{-1}$) is the rate constant for adsorption, q_e (mg g^{-1}) the amount of MB adsorbed at equilibrium and q_t (mg g^{-1}) is the amount of MB adsorbed at time t.

The Langmuir and Freundlich isotherms had been used to evaluate the equilibrium characteristics of the adsorption processes. The Langmuir isotherm model assumes that the adsorption is localized on a monolayer and all adsorption sites at the adsorbent are structurally homogeneous [33]. The non-linear Langmuir isotherm model may be expressed as in equation (5):

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

Where q_m and K_L are Langmuir constants related to adsorption capacity and affinity of the binding sites, respectively. The factor of separation of Langmuir, R_L, which is an essential factor characteristic of this isotherm is calculated by using the relation (6):

$$R_L = \frac{1}{(1+k_L C_0)} \quad (6)$$

Where C_o refers to the initial concentration of the MB. The R_L value implies the adsorption to be defavourable (R_L>1), linear (R_L=1), favourable (0<R_L<1), or irreversible (R_L=0).

The Freundlich adsorption isotherm is based on the assumption that the adsorption occurs on heterogeneous surfaces of non-identical sites with different energy of adsorption. The Freundlich isotherm model employed to describe multilayer adsorption with interaction between the adsorbed molecules [34]. The non-linear Freundlich isotherm model may be expressed as in equation (7):

$$q_e = K_F C_e^{1/n} \quad (7)$$

Where K_F and n are Freundlich constants representing adsorption capacity and the energy of adsorption effectiveness, respectively.

The R^2 analysis was used to fit experimental data with adsorption kinetic and isotherm. The fit appreciation was assessed by the coefficient of determination R^2 which is given by the expression (8):

$$R^2 = 100\left(1-\frac{\left\|q_{exp}-q_{mod}\right\|^2}{\left\|q_{exp}-q_{avr}\right\|^2}\right) \quad (8)$$

Where q_{exp} (mg g^{-1}) is equilibrium capacity from the experimental data, q_{avr} is equilibrium average capacity from the experimental data and q_{mod} is equilibrium from model. So that $R^2 \leq 100$ – the closer the value is to 100, the more perfect is the fit.

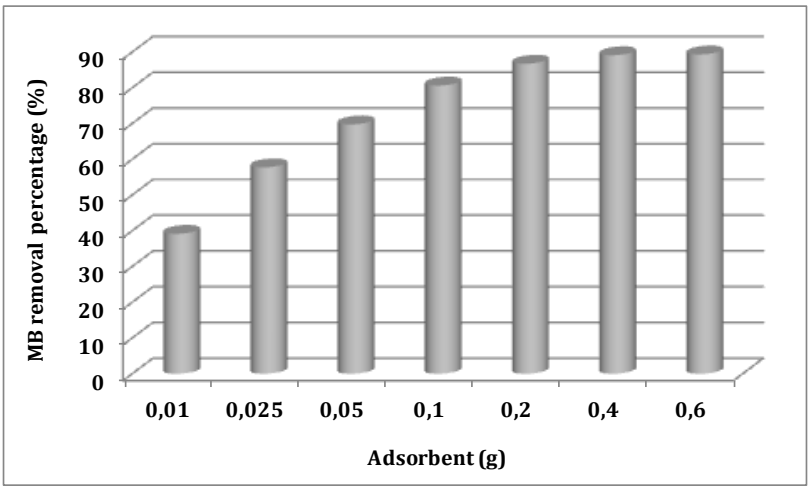

Figure 1. Effect of *Typha australis* mass on MB removal (%) at $[MB]_o$ = 10 mg L^{-1}, V = 100 mL, pH= 6.9, T = 20.9°C, shaking speed = 150 rpm and contact time = 120 min.

3. Results and Discussion

3.1. Effect of adsorbent mass

Biomass dosage is an important parameter in adsorption studies, as it gives the optimum mass at which maximum adsorption occurs. The effect of the amount of adsorbent on the efficiency of adsorption was studied. Variation of mass in the range 0.01-0.6 g at a fixed MB concentration (10 mg L^{-1}) for MB removal by *Typha australis* leaf adsorbent is shown in Figure 1.

The results suggest that the increase in the mass of *Typha australis* results in an increase in adsorption, probably due to increase in the retention surface area. However, further increase after a certain mass does not improve the adsorption; perhaps due to the interference between binding sites of the *Typha australis* at different mass. The optimal *Typha australis* adsorbent mass obtained is 0.2 g.

3.2. Effect of pH

In biosorption, pH is an important parameter as it affects both the ionization degree of the adsorbate and the surface charge of the adsorbent during the biosorption process [35].

The adsorption of MB under different pH (2.5, 7 and 11.5) is determined for 10 mg L^{-1} of MB solution as shown in Figure 2.

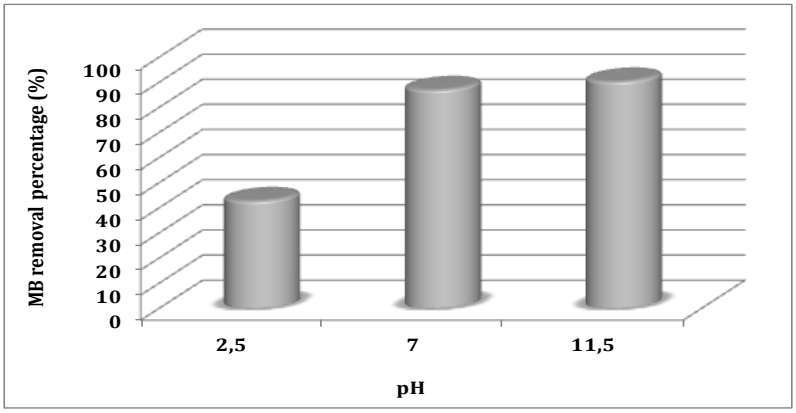

Figure 2. Effect of pH on MB removal (%) using 0.2 g of *Typha australis*, $[MB]_o$ = 10 mg L^{-1}, V = 100 mL, T = 21.3°C, shaking speed = 150 rpm and contact time = 120 min.

The highest removal efficiency of MB adsorption obtained at pH 11.5 is evaluated at 92 %. In addition, the pH_{PZC} of the *Typha australis* adsorbent was found to be 6.36. For values less than pH_{PZC}, the *Typha australis* surface was positively charged, which would result in an electrostatic repulsion and therefore a decrease in MB adsorption (42.55 % at pH 4). At pH > pH_{PZC} the *Typha australis* surface was negatively charged, which would cause an electrostatic attraction and therefore an increase in MB adsorption. Some authors have reported that MB adsorption usually increases as the pH is increased [36-38].

3.3. Effect of ionic strength

The effect of inorganic salt (NaCl) on adsorption of MB on *Typha australis* is presented in Figure 3. As seen in Figure 3, the presence of inorganic salt has influenced the percentage of the MB removed. The MB adsorption increases with the increasing NaCl concentration.

Our results show that higher concentration of salts promotes the adsorption of MB on *Typha australis* leaf. Similar results have been reported for MB adsorption onto hazelnut shell [36].

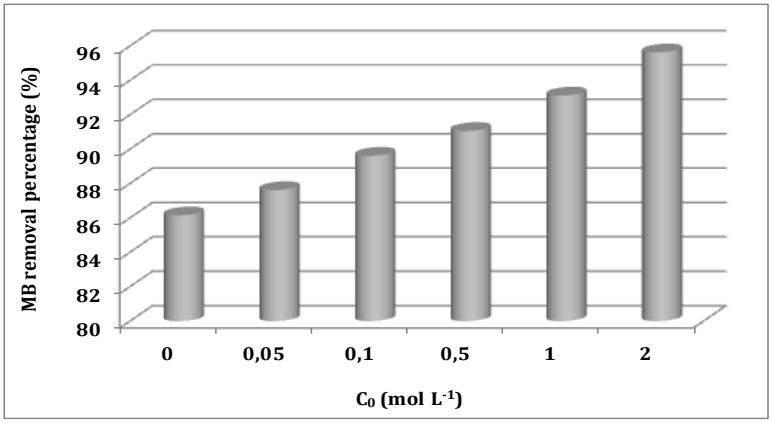

Figure 3. The effect of ionic strength on MB removal (%) using 0.2 g of *Typha australis*, $[MB]_o$ = 10 mg L^{-1}, V = 100 mL, T = 21.9°C, shaking speed = 150 rpm and contact time = 120 min.

In other hand, we have tested the effect of NaCl on adsorption of MB on *Typha australis* in the low concentrations (Figure 4). The results show that the increasing of salts decreases the adsorption of MB on *Typha australis* leaf. Similar results have been observed for MB adsorption onto orange peel [39].

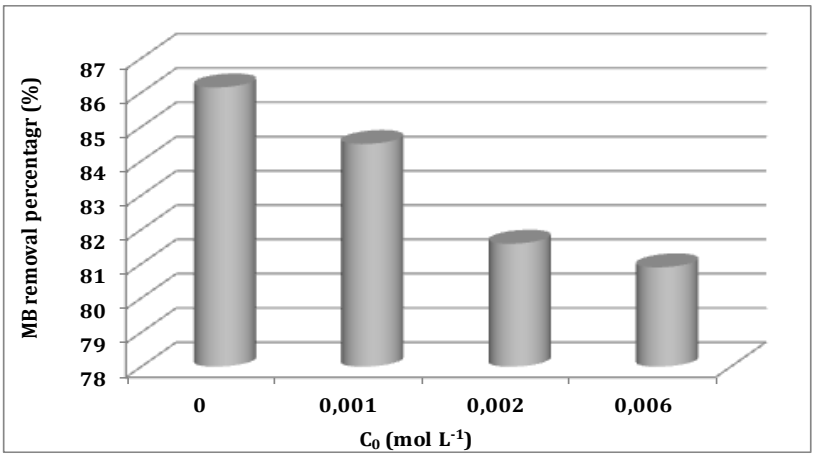

Figure 4. The effect of ionic strength on MB removal (%) using 0.2 g of *Typha australis*, $[MB]_o$ = 10 mg L^{-1}, V = 100 mL, T = 21.9°C, shaking speed = 150 rpm and contact time = 120 min.

The results obtained from Figures 3 and 4 confirm that the presence of NaCl in the solution may have two opposite effects are in agreement with the bibliographic works [36].

3.4. Effect of temperature on MB adsorption

Temperature is anticipated to have an influence on the dye adsorption properties of *Typha australis* leaf adsorbent with MB. Figure 5 shows the effect of temperature on MB removal by varying the temperature in the range 20–30°C at MB concentration of 10 mg L^{-1}. The observed results in Figure 5 indicate that the adsorption process of MB onto *Typha australis* leaf was favoured at higher temperature, in agreement with an endothermic adsorption process [40].

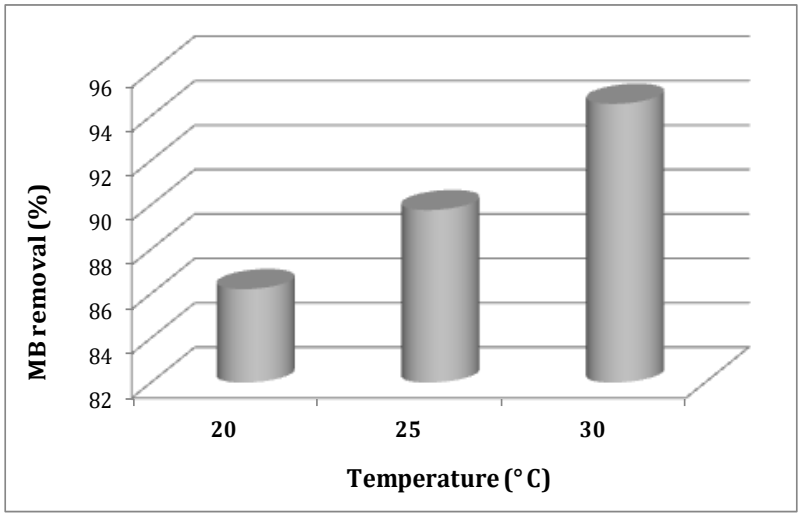

Figure 5. Effect of temperature on MB removal (%) using 0.2 g of *Typha australis*, $[MB]_o$ = 10 mg L^{-1}, V = 100 mL, shaking speed = 150 rpm and contact time = 120 min.

3.5. Kinetic and thermodynamic study

Contact time is an important issue in adsorption and determining the equilibrium time is of real importance. The sorbed MB (5 and 10 mgL^{-1}) at equilibrium q_e was plotted against time for the *Typha australis* (Figures 6 and 7).

The removal of MB by adsorption on *Typha australis* was found to be rapid at the initial period of contact time and then to slow down with increasing in contact time. At equilibrium, 2.22 and 4.34 mg g^{-1} for 5 and 10 mg L^{-1} respectively are obtained with a contact time of 120 min for *Typha australis*.

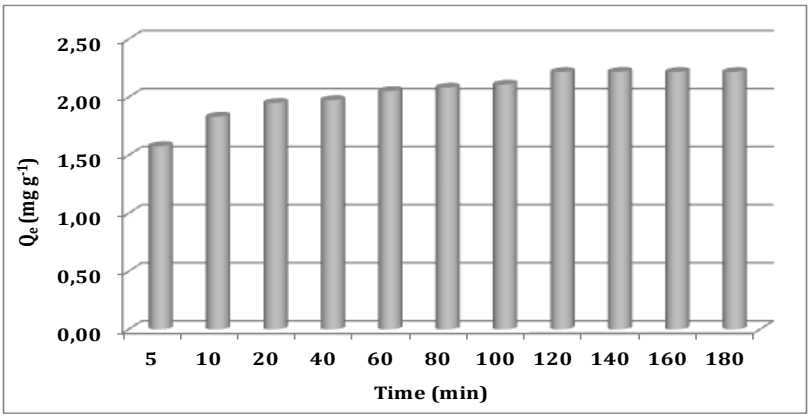

Figure 6. Effect of contact time on the adsorption of MB (5 mg L^{-1}) by *Typha australis* (V = 100 mL, T = 21.9°C, shaking speed = 150 rpm and *Typha australis* mass = 0.20 g).

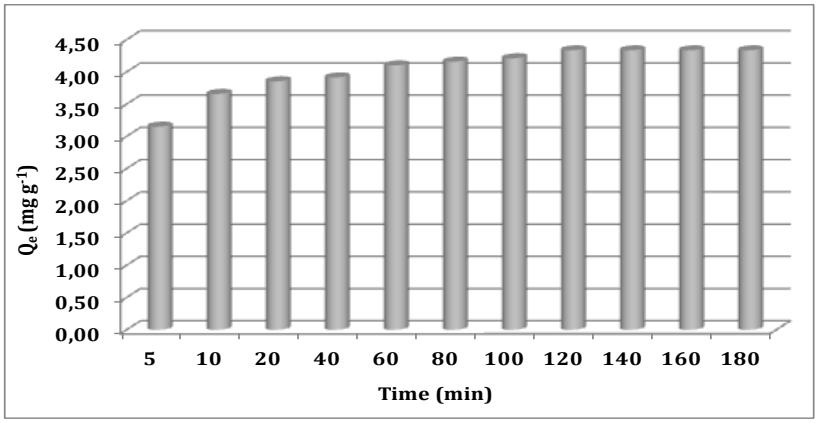

Figure 7. Effect of contact time on the adsorption of MB (10 mg L^{-1}) by *Typha australis* (V = 100 mL, T = 21.9°C, shaking speed = 150 rpm and *Typha australis* mass = 0.20 g).

Figures 8 and 9 show the experimental equilibrium data and the predicted theoretical kinetics for the sorption of MB onto Typha australis for 5 and 10 mg L^{-1}, respectively. The values of model parameters q_e, k_1, k_2 and the correlation coefficient R^2 are presented in Table 2.

The correlation coefficient R^2 showed that the PSO model was the more suitable for sorption MB behaviour onto the *Typha australis* adsorbent. In addition, the q_e calculated by the PSO kinetic model are close to those obtained from the experiments at all initial MB concentrations, indicating that the PFO kinetic model did not properly describe the adsorption process of MB on Typha australis adsorbent.

These results suggest that the adsorption data are well represented by PSO and the rate-limiting step of MB onto *Typha australis* leaf adsorbent may be chemisorption. Similar phenomena have been described for MB adsorption on wheat shells [41], perlite [42], cedar sawdust and crushed brick [43], sepiolite [44] and coir pith carbon [45].

Table 2. Non-linear kinetic model parameters.

Models	Parameters	5 mg L^{-1}	10 mg L^{-1}
	q_{exp}	2.22	4.34
PFO	q_e	2 .11	4.14
	K_1	0.24	0.47
	R^2 (%)	73.68	67.98
PSO	q_e	2.19	4.31
	K_2	0.22	0.12
	R^2 (%)	91.15	93.93

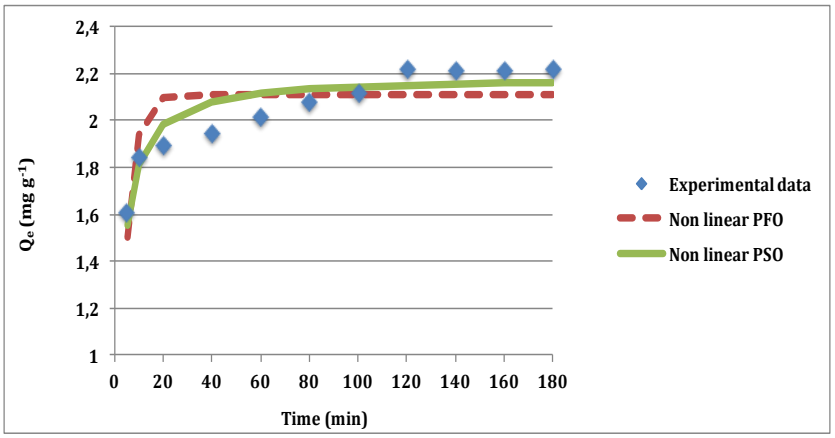

Figure 8. PFO and PSO non linear for *Typha australis* with initial MB concentration of 5 mg L^{-1}

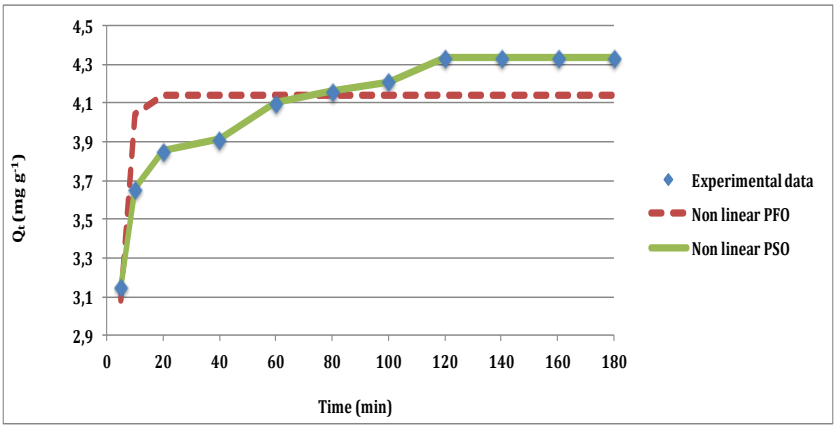

Figure 9. PFO and PSO non linear for *Typha australis* with initial MB concentration of 10 mg L^{-1}

From the thermodynamic calculations ΔG° values for *Typha australis* (-4.44 kJ mol^{-1}) being negative revealed that the mechanism of MB adsorption from the aqueous solution is feasible and shows spontaneity. The positive value of ΔH° (55.13 kJ mol^{-1}) confirms the endothermic process. Similar results for endothermic adsorption were observed on adsorption on carbon nanotubes [46] and carbonaceous particles prepared from Juglans regia shell biomass [47]. The positive value of ΔS° (203.21 J mol^{-1}) showed the increased randomness of the adsorbate molecules on the solid surfaces than in the solution for MB [38].

3.6. Sorption isotherms

Figure 10 shows the experimental equilibrium data and the predicted theorical isotherms for the sorption of MB onto Typha australis leaf. The calculated adsorption parameters and the correlation coefficient R^2 for Langmuir and Freundlich for the adsorption of MB onto *Typha australis* are summarized in Table 3.

The results compiled in Table 3 shows that Langmuir model fitted very well to the experimental data, showing the highest R^2 value compared to Freundlich isotherm. It should be noted that most of the isotherm adsorption studies of MB on various adsorbents follow the Langmuir isotherm model [25-28].

Table 3. Analysis of Langmuir and Freundlich adsorption isotherm parameters for *Typha australis* by non-linear method.

Models	Parameters	Values
Langmuir	**q_m**	103.12
	K_L	0.034
	R_L	0.23
	R^2 (%)	99.94
Freundlich	**1/n**	0,77
	K_F	4.22
	R^2 (%)	99.81

The values of K_L, R_L and 1/n are in between 0 and 1. This confirms that the adsorption of MB onto *Typha australis* adsorbent is favorable. These results affirmed that the surface binding sites of *Typha australis* leaf adsorbent are homogeneous in nature whereby each MB is attached with similar adsorption energy. The Langmuir model estimated that the monolayer adsorption capacity q_m for MB-*Typha australis* leaf system, herein investigated, was of 103.12 mg g^{-1}.

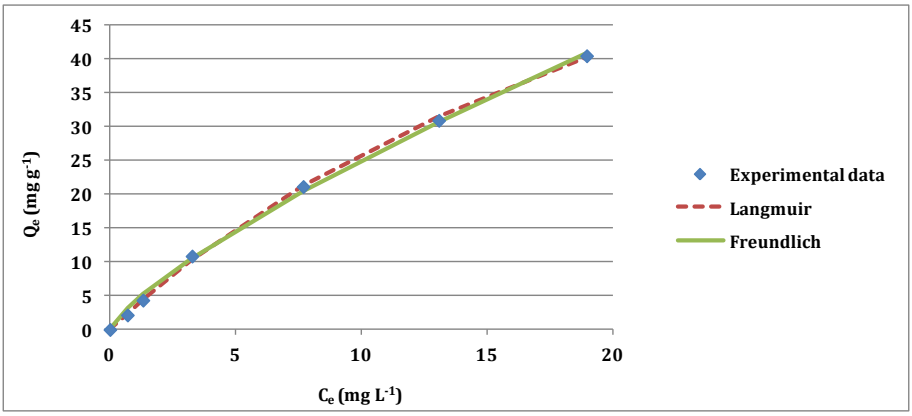

Figure 10. Langmuir and Freundlich non linear for *Typha australis* adsorbent

Values of the adsorption capacities of other adsorbents for MB from the literature are given in Table 4 for comparison. As listed in Table 4, that the adsorption capacity of *Typha australis* adsorbent is found substantially superior or comparable with many reported low-cost adsorbents. This proves the viability of *Typha australis* as one of the most superior adsorbents for removal of MB from aqueous solution.

Table 4. Comparison of adsorption capacity of *Typha australis* adsorbent with other adsorbents for MB sorption.

Adsorbents	Adsorption capacity (mg g^{-1})	References
Wheat shells	16.56	41
Orange peel	18.60	48
Algal waste	104	49
Coffee husks	90.1	50
Rubber seed shell	82.64	51
Coconut bunch waste	70.92	52
Luffa cylindrica fibers	47	53
Yellow passion fruit peel	44.7	54
Tea waste	85.16	55
Banana peel	18.65	56
Banana peel	111.11	57
Typha australis leaves	103.12	Present study

4. Conclusion

The *Typha australis* biomass, collected from Senegal River bank, exhibited great potential as low cost adsorbent for effective removal of MB from aqueous solution. The optimum *Typha australis* mass was 0.2 g and highest removal efficiency of MB adsorption was obtained in solution pH 11.5. A very good agreement with experimental data obtained indicates that a PSO kinetic model is favorable for the MB adsorption on *Typha australis* adsorbent. The equilibrium data fitted well with the Langmuir model with the monolayer adsorption capacity for MB-*Typha australis* leaf system was of 103.12 mg g^{-1}. From the thermodynamic calculations ΔG° values for *Typha australis* leaf (-4.44 kJ mol^{-1}) being negative revealed that the mechanism of MB adsorption from the aqueous solution is feasible and shows spontaneity. The positive value of ΔH° (55.13 kJ mol^{-1}) confirms the endothermic process, meaning the reaction consume energy. The positive value of Δ*S*° (203.21 JK^{-1} mol^{-1}) showed the increased randomness of the adsorbate molecules on the solid surfaces than in the solution for MB. The *Typha australis* showed greater adsorption capacity towards MB than other agro wastes adsorbents and can be easily prepared without any physical and /or chemical treatment. Adsorption of cationic MB dye on *Typha australis* leaf can be considered as a simple, fast and economic method for its removal from aqueous solutions. For future studies, the usability of *Typha australis* for dyes removal from real wastewater will be tested and as comparison, a fixed bed column will be employed to investigate the effect of reactor design.

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