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Valorization of Mango Peels as Low-Cost Biosorbent in Methylene Blue Adsorption: Kinetic and Equilibrium Study

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Abstract: Mango peels, which constitute a significant proportion of urban waste, have been modified with phosphoric acid for use as a biosorbent in the removal of methylene blue from wastewater. The characterization of the obtained biosorbent showed that cellulose is the primary constituent followed by lignin and hemicellulose. The high water content and the low value of ash content indicate that the studied biosorbent is a porous material containing a low proportion of inorganic, inert, amorphous and unusable part for biosorbent production. The zero charge point (pHpzc) assessment showed that the overall surface charge of the biosorbent is negative and therefore plays a key role in the adsorption process. The adsorption of methylene blue by mango peels biosorbent is a two-step process: a rapid first step in which over 90% methylene blue is removed in less than 10 min followed by a slowdown of the adsorption rate when approaching the adsorption equilibrium. Among pseudo-first, pseudo-second order and intraparticle diffusion kinetics models studies, pseudo-second order was the best applicable to describe methylene blue adsorption, suggesting a two-step mechanism: the transfer of methylene blue molecules from the solution to the mango peels biosorbent surface, followed by the interaction between adsorbates and surface. The equilibrium adsorption data were analyzed by Langmuir, Freundlich and Temkin isotherms models. Among them, Langmuir was the best model to describe adsorption, indicating the existence of homogeneous distribution of adsorption sites on mango peels biosorbent surface and a mono-layer adsorption of methylene blue molecules. The low value of Temkin's constant B relative to the interaction energy between methylene blue molecules and the surface of the biosorbent shows that the adsorption involved is a physisorption process.

Key words: Mango peels, methylene blue, low-cost biosorbant, adsorption kinetic, adsorption isotherm.

1. Introduction

Textile, tanneries, dyes houses, paper and printing industries are known for their high dyes and water consumption, and also for the production of large quantities of effluents. The effluents of these industries are characterized by high dye contents because it has been shown that in these industries production chain, 1 to 15% dye is lost in the effluents [1, 2]. When these effluents are released into nature without prior treatment, they generate adverse effects on the population's health and also cause aquatic flora and fauna destruction [3]. Because of their synthetic origin, dye molecules are stable to light, heat and oxidizing agents and are therefore resistant to natural degradation [4, 5].

Among physicochemical methods commonly used for the removal of dyes from effluents (e.g. advanced oxidation methods, electrochemical destruction, coagulation-flocculation, membrane filtration, electroflotation and adsorption), adsorption is the most widely used technique because it is easy to implement, less expensive and does not lead to the formation of

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hazardous by-products [6-8].

Adsorbents already used for this purpose include, among others, activated carbon, montmorillonites, smectites, kaolinites, sepiolites and silicon and aluminium gels [9-15]. However, their high production, extraction and regeneration cost and sometimes their low adsorption efficiency increasingly limit their use. Natural lignocellulosic materials such as household waste, agricultural waste therefore appears as an alternative for commonly used adsorbents [11, 16, 17]. The growing interest in these materials is justified by their abundance, their high efficiency and their low acquisition cost. Mango peels are an example of these lignocellulosic residues which constitute a significant proportion of urban waste but which remain poorly valorized.

The objective of this study is to investigate mango peels biosorbent characteristics and evaluate the adsorption potential of mango peels biosorbent for methylene blue in batch mode. Elucidation of adsorption mechanisms was made through the processing of the kinetics and equilibrium data of methylene blue adsorption on the mango peels biosorbent.

2. Material and Methods

2.1 Preparation of Biosorbent

Mango peels used in this work were obtained from mangoes harvested in Ngaoundéré, a locality in the Adamaoua region of Cameroon. Mangoes collected were first washed several times with tap water and then with deionized water to remove any dust and adhering particles. The washed mangoes were peeled and the resulting peels were dried in an air-driven electric dryer at 50 °C until constant mass then grounded into fine particles to pass through 0.25 mm mesh sieve.

The obtained material was activated using 2 N phosphoric acid of analytical grade, for 6 h at room temperature and at a solid to liquid ration of 1:5. After activation, the suspension was filtered and the solid phase was washed several times with ultra-pure water until neutral pH. The obtained biosorbent was oven dried at 105 °C until complete evaporation and stored in an airtight closed glass bottle.

2.2 Characterization of Biosorbent

Analysis of components was done by the determination of cellulose, hemicellulose and lignin content which form essential components of plant biomass apart from extractives. Thorough analysis of these structural components in mango peels biosorbent was conducted following the procedures of Li et al. [18]. Moisture and ash contents were analyzed according to Zainuddin et al. [19]. The point of zero charge (pHpzc) which corresponds to the pH for which the sum of the charges on the surface of the solid is zero was determined by the method described by Faria et al. [20]. The specific surface was determined by adsorption of nitrogen at 77 K in ASAP 2020 Micrometrics Instrument sorptometer, model VEGA 3 from TESCAN, Hitachi-Japan. Sample was out gassed prior to use at 473 K overnight under vacuum.

2.3 Adsorption Studies

Adsorption experiments were carried out in batch mode by adding a fixed amount of sorbent (0.03 g) into 50 mL beaker containing 20 mL of different initial concentrations (5, 10 and 20 mmol/L) of dye solution. The temperature was controlled at 25 ± 2 °C. Agitation was made at 300 rpm for 3 h. The initial and equilibrium dye concentrations were determined by absorbance measurement using a double beam UV-Vis spectrophotometer at 620 nm. It was then calculated to dye concentration using standard calibration curve. The amount of methylene blue adsorbed at time *t*, q_t (mmol/g), was calculated by the equation:

$$q_t = \frac{(C_0 - C)}{m} V \tag{1}$$

where C_0 is the initial methylene blue concentration (mmol/L), C the methylene blue concentration at time t (mmol/L), m the mass of the biosorbent used (g) and V the volume of solution (L).

3. Results and Discussion

3.1 Characteristics of the Biosorbent

Table 1 presents the main characteristics of the mango peels biosorbent.

The analysis revealed that cellulose was the primary constituent of mango peels biosorbent. Lignin and hemicellulose represented secondary and tertiary components respectively.

The high water content value is an indication of the likely high porosity of the mango peels biosorbent. In fact, in lignocellulosic materials, water molecules accumulate in the network of pores and cavities by the phenomenon of capillary condensation. So it is obvious that the more porous a material, the higher the water content will be.

The low ash content of the peelsshows that, this material has a low proportion of inorganic, inert, amorphous and unusable part for biosorbent production.

The value of the point of zero charge (5.01) deduced from Fig. 1 shows that the surface of the biosorbent studied is globally negatively charged. This negative charge could therefore play a determining role in the adsorption process by fixing positively charged molecules.

Textural analysis shows that, the acid treatment applied to the mango peels increases the specific surface from 24 m^2/g for the raw material to 105 m^2/g for the biosorbent. This increase is attributed to the removal of extractives and the expansion of cellulose and hemicellulose that releases pores.

Table 1 Main properties of mango peels biosorbent.

Components (%)	Content (%)
Moisture	74.123 ± 10.43
Ash	2.670 ± 3.29
Hemicellulose*	15.33 ± 3.29
Cellulose	35.07 ± 1.08
Lignin*	27.06 ± 0.19

* Free of extractives matter. All data is presented as dry weight percent.

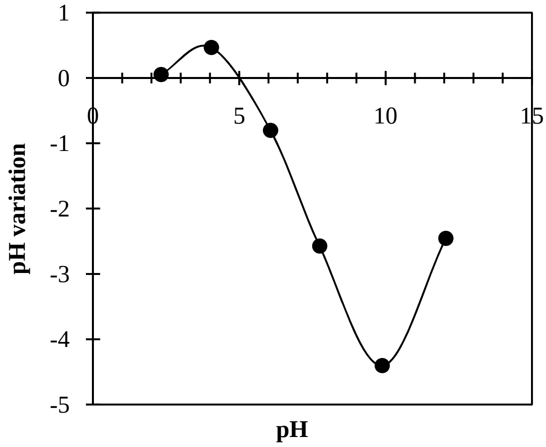

Fig. 1 Variation of pH as a function of pH for mango peels biosorbent.

3.2 Adsorption Studies

In order to evaluate the influence of the initial methylene blue concentration on the adsorption capacities of mango peels biosorbent, the adsorption kinetic at room temperature was carried out from 0 to 100 min on three solutions of concentration 5, 10 and 20 mmol/L. Fig. 2 presents the results obtained.

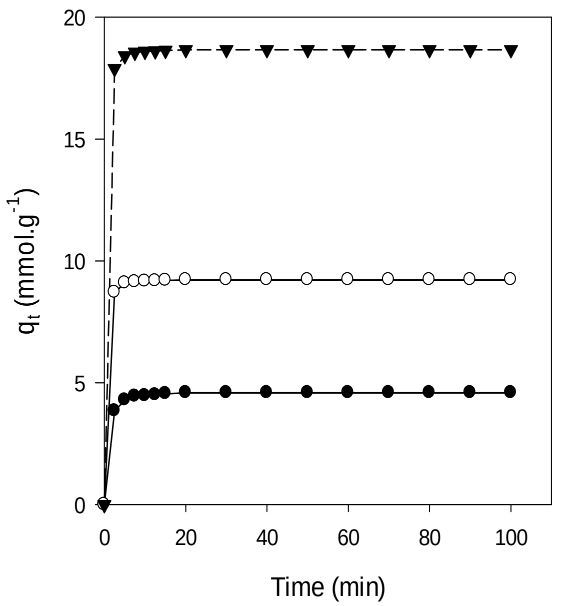

Fig. 2 Kinetics of methylene blue adsorption on mango peels at different initial concentrations (●: 5 mmol/L,○: 10 mmol/L, ▼: 20 mmol/L).

Regardless of the initial methylene blue concentration, all the kinetics curves followed the same trend: a speedy initial step followed by a sluggish step when the adsorption is approaching equilibrium. This result can be explained by the fact that the high availability of active sites on the biosorbent makes the first moments of adsorption very fast. On the other hand, the progressive saturation of the sites over time leads to a reduction in the rate till the absorption equilibrium. This behavior specific to biosorbents is linked to their nature rich in lignin and cellulose as shown by biochemical analyzes. Similar results have also been observed by some authors [21-23].

It should also be noted that, the speedy initial step is accompanied by the removal of more than 90% of methylene blue during the first 10 min of adsorption and the time required to reach adsorption equilibrium was attained before 15 min for all the three concentrations (Fig. 1). This significant elimination rate in a relatively short time is an indication that mango peels biosorbent is an effective adsorbent that can be implemented at low cost in small and medium enterprises.

In order to elucidate the mechanism of adsorption, kinetic data obtained were analyzed in accordance with the theoretical models of intraparticle diffusion, pseudo-first order and pseudo-second order (Eqs. (1)-(3)).

$$q_t = k_{\text{int}}\sqrt{t} + \lambda \tag{2}$$

$$log(q_e - q_t) = log\, q_e - \frac{k_1}{2.303}t \tag{3}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \tag{4}$$

where q_e and q_t (mmol·g^{-1}) are the uptake of methylene blue per gram of biosorbent at equilibrium and at time t (min) respectively and k_{int} (mmol·g^{-1}·min$^{-1/2}$), k_1 (min^{-1}) and k_2 (mmol·g^{-1}·min^{-1}) the respective intraparticle, pseudo-firstorder and pseudo-secondorder rates constants.

The kinetic constants are determined from the plotting of experimental data by the equations q_t versus $t^{1/2}$ for the intraparticle diffusion model, $log(q_e - q_t)$ versus t for the pseudo-first order model and $\frac{t}{q_t}$ versus t for the pseudo-secondorder model (Fig. 3).

The determination coefficient R^2, the amount of methylene blue adsorbed at equilibrium and the rate constants of different kinetic models (intraparticle diffusion, pseudo-first and pseudo-second order) are calculated and reported in Table 2.

It comes out from Table 2 that determination coefficients (R^2) obtained for the pseudo-first order model are all less than 0.159 independently of the initial methylene blue concentration. This model is therefore not suitable for describing the adsorption of methylene blue on mango peels biosorbent.

The application of pseudo-second order kinetic model to experimental data yielded straight regression lines passing through origin for all the studied concentrations (Fig. 3c) with determination coefficient values (R^2) greater than 0.995. The pseudo-second order model can therefore be used to explain the adsorption mechanism in the present study. The adsorption of methylene blue is described by a two-step mechanismas postulated by this model: The first step is the diffusion of methylene blue molecules from solution to the surface of the biosorbent followed by the interaction between molecules and the surface. Similar results have also been found in previous work [24-26].

The high value of determination coefficient (R^2) for the intraparticle diffusion model shows the important role of intraparticle diffusion in the present adsorption process. This result is a strong indication that methylene blue adsorption onto mango peels biosorbent is controlled by external mass transfer, diffusion through pores and bulk transportation of solute molecules [27].

The amount of methylene blue adsorbed, deuced from the pseudo-second order and intra-particle

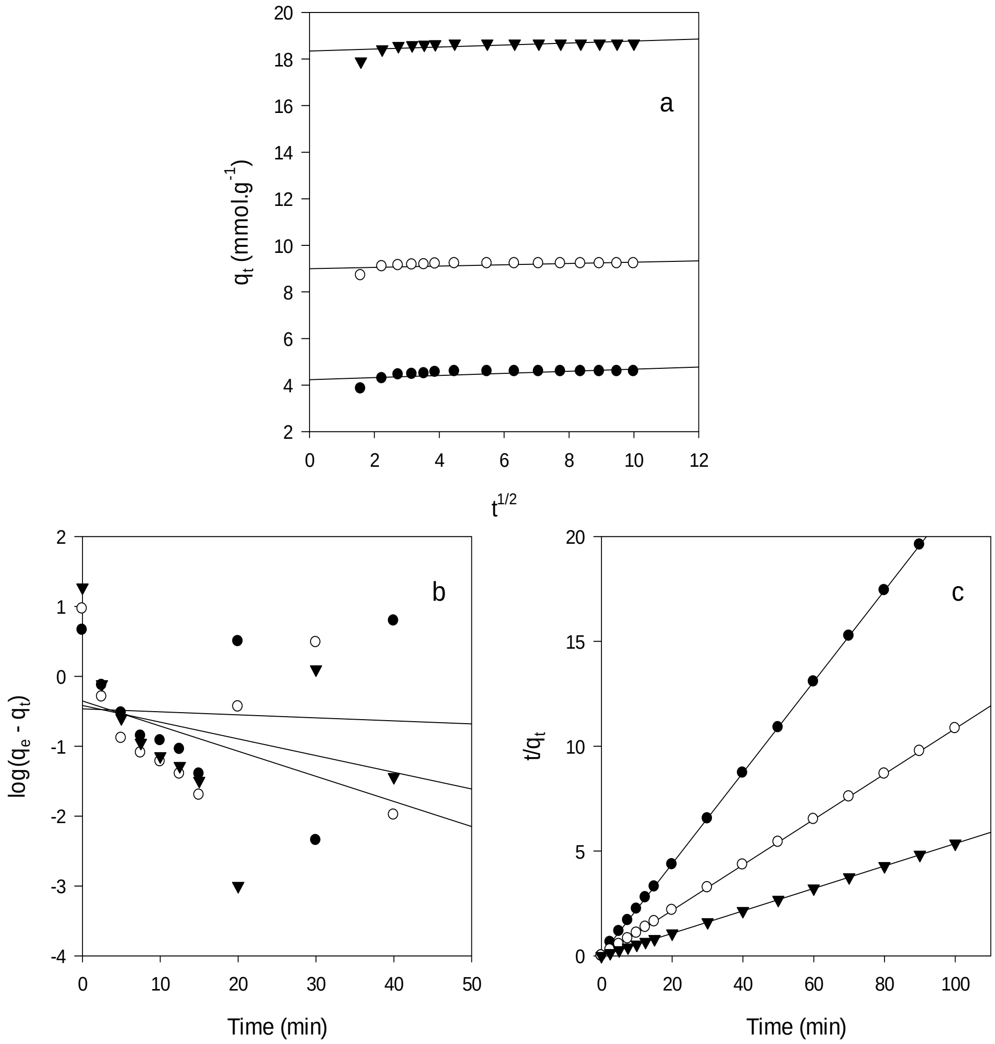

Fig. 3 Intraparticle diffusion model plots: (a) pseudo-first order kinetic plots, (b) pseudo-second order kinetic plots, (c) for the methylene blue adsorption at different concentrations. (●) 5 mmol/L; (○) 10 mmol/L; (▼) 20 mmol/L.

Table 2 Pseudo-first order,pseudo-second order and intraparticle diffusion kinetic constants for the adsorption of methylene blue on mango peels biosorbent.

Parameters	Concentrations (mmol·g^{-1})		
	5	10	20
q_{exp} (mmol·g^{-1})	4.591	9.220	18.671
Pseudo-first order model constants			
q_e (mmol·g^{-1})	0.629	0.659	0.702
k_1 (min^{-1})	0.010	0.055	0.083
R^2	0.003	0.103	0.159
Pseudo-second order model constants			
q_e (mmol·g^{-1})	4.604	9.225	18.692
k_2 (mmol·g^{-1}·min^{-1})	0.991	1.895	1.301
R^2	0.998	0.997	0.999
Intraparticle diffusion model constants			
λ (mmol·g^{-1})	4.237	9.008	18.345
k_{int} (mmol·g^{-1}·min$^{-1/2}$)	0.045	0.028	0.043
R^2	0.946	0.929	0.941

diffusion models, increases with initial methylene blue concentration. This result confirms the observations made during the analysis of the kinetic experimental data.

3.3 Equilibrium Studies

The adsorption isotherm studies are of fundamental importance in describing the equilibrium characteristics for the adsorption of a molecule on a solid support. In the present study mango peels biosorbent was put in contact with increasing concentrations of methylene blue and the adsorption isotherm was carried out by plotting the amount of methylene blue adsorbed per gram of biosorbent versus the amount of residual methylene blue at equilibrium C_e (figure not shown).

These adsorption isotherms have shown that the uptake methylene blue increases with the residual concentration at equilibrium and became steady at a certain concentration beyond which no significant adsorption was noted. This result is explained by the fact that at high concentrations the concentration gradient serves as the steering force to overcome resistance to mass transfer leading to increased adsorption with saturation of active sites at higher concentrations [22, 28].

Langmuir, Freundlich and Temkin isotherm models have been used to describe the equilibrium characteristics of the adsorption and Eqs. (5)-(7) present the linearized equations of these different models.

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{1}{q_m} C_e \tag{5}$$

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{6}$$

$$q_e = B \ln A + B \ln C_e \tag{7}$$

where C_e is the residual concentration of methylene blue at equilibrium (mmol/g), q_e the amount of methylene blue adsorbed per gram of mango peels biosorbent. Langmuir constants q_m (mmol/g) and K_L designate the amount of methylene blue adsorbed at the monolayer and the monolayer capacity. K_F and $1/n$ constants of Freundlich indicate respectively the adsorption capacity and the heterogeneity factor. In Temkin isotherm model, $B = \frac{RT}{b}$ is the Temkin constant related to the adsorption energy (J·mol^{-1}), T the absolute temperature (K), A the Temkin isotherm constant and R the gas constant (8.314 J·mol^{-1}·K^{-1}).

The R^2 correlation coefficient, the constants characterizing the adsorption equilibria of methylene blue on the mango peels biosorbent for the different models tested (Langmuir, Freundlich and Temkin) were determined and reported in Table 3.

Analysis of Table 3 data shows that, among the three tested models, Langmuir and Temkin models appropriately illustrated the adsorption of methylene blue on mango peels biosorbent. Validation of the Langmuir model indicates a homogeneous distribution of adsorption sites on the surface of the biosorbent and a single-layer adsorption of methylene blue molecules. There are therefore no interactions between methylene blue molecules and the adsorption of a molecule on a site is independent of the occupation of the neighboring site. Moreover, it also emerges from this table that the quantities of methylene blue necessary for the formation of a monolayer are equivalent to those obtained in the kinetic study.

Table 3 Isotherms models constants and value of linear regression coefficient.

Model and constant	Value
Langmuir isotherm model	
q_{max} (mmol·g^{-1})	19.86
K_L (L·g^{-1})	9.56
R^2	0.999
Freundlich isotherm model	
K_F (L·g^{-1})	0.167
n	1.032
R^2	5.312
Temkin isotherm model	
A (L·g^{-1})	12.05
B (J·mol)	58.13
R^2	0.972

Examination of B constant value of Temkin model shows that the methylene blue-biosorbent interaction energy is low. The overall charge of the surface of mango peels bisorbent being negative and methylene blue a cationic dye, these weak interactions would probably be of the electrostatic type. This result is a strong indication that the adsorption of methylene blue by the mango peel biosorbent is a physical process.

4. Conclusion

The present work studies the valorization of mango peels as a low-cost biosorbent for the removal of methylene blue in wastewater. The characterizations show that, mango peel biosorbent is a porous material in which the main constituents are cellulose, lignin and hemicellulose. The acid treatment of mango peels leads to an increase in the specific surface of the biosorbent obtained by the expansion of the basic constituents and the elimination of extractives. The adsorption of methylene blue molecules is influenced by the overall negative charge of surface of the biosorbent studied. Kinetic studies reveal that more than 90% of methylene blue is eliminated within the first 10 min of treatment. The adsorption process studied reveals a two-step mechanism, as confirmed by the adjustment of the kinetic data to the pseudo-second order model namely: the diffusion of methylene blue molecules from the solution to the surface of the biosorbent followed by the interaction between molecules and the surface. Modeling of adsorption isotherms has shown that there is a homogeneous distribution of adsorption sites on the surface of the biosorbent and that the adsorption process involved is physisorption.Therefore, it can be concluded that mango peels biosorbent fulfils the criteria of an effective adsorbent for the removal of methylene blue.

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