Adsorbent materials obtained from palm waste and its potential use for contaminants removal from aqueous solutions

S Giraldo¹, A P Ramírez¹, E Flórez¹ and N Y Acelas¹
¹ Grupo de Investigación Materiales con Impacto, Universidad de Medellín, Medellín, Colombia
E-mail: nyacelas@udem.edu.co

Abstract. This work reports the production of an adsorbent material obtained by H₃PO₄ chemical activation of oil palm waste (fiber). The experiments were carried out to explore methylene blue uptake by this adsorbent. The influence of initial dye concentration and adsorbent dosage was investigated. The adsorption equilibrium data of methylene blue onto the adsorbent material were best fitted to the Langmuir model. The maximum adsorption capacity monolayer was of 20.85 mg g⁻¹, which showed to be high compared to other adsorbent materials reported in the literature. Adsorption of methylene blue onto adsorbent material followed pseudo-second order model. The structural and chemical characterization of the adsorbent material was carried out by using various analytical techniques. FTIR showed the formation of oxygenated functional groups on the surface, which are very important for adsorption applications because they act as active sites capable of interacting with dye molecules.

1. Introduction

Agro-industry is an economic activity that combines agricultural and industrial production to develop food products. As a byproduct of this activity, agro-industrial wastes are generated since the raw material plantation to its commercialization. These wastes become an environmental and also, an economic problem due the high costs of final disposal. In Colombia, every year approximately 72 million of tons of agro-industrial wastes are generated, among which palm oil residues stand out [1]. In palm industry, from total weight of bunch fresh fruit, 17% corresponds to residues of fiber (~ 500 t/year) without any use [2]. A typical use given to fiber (F) is the production of adsorbent materials.

These materials are characterized by having low production costs and being highly efficient for the adsorption of environmental contaminants [3-5]. For example, carbonaceous materials obtained from oil palm residues exhibit good adsorption capacities for methylene blue (MB) [6]. Methylene blue (MB), a cationic dye, was selected herein because of its widespread application in textile dyeing, paper, plastic, food [7,8] and therefore it is present in wastewater generating contamination of rivers and lakes [5].

Therefore, the objective of this study was to evaluate the possibility of using fiber to develop a new low cost adsorbent material and study its application to remove methylene blue dye from aqueous solution. The physicochemical and morphological characterization of the produced material were made by using scanning electron microscope (SEM), Fourier transform infrared spectroscopy (FTIR), specific surface area of Brunauer, Emmett and Teller (BET). Kinetics studies and adsorption isotherm models were investigated to evaluate experimental data.
2. Methodology

2.1. Preparation and material characterization
Fiber (F) a residue of the oil palm industry was provided by a palm oil processing located in Villavicencio, Colombia. Fiber was washed with distilled water and oven dry during 12 hours at 105°C. In the next step, F was placed in contact during 5 hours with H₃PO₄, and subjected to a heat treatment at 110°C for 12 hours and then 1 hour at 300°C. Then the sample was washed with hot distilled water and subsequently the pH was stabilized between 6 and 7. Finally, the activated material (AF) was filtered under vacuum, oven dry for 12 hours at 105°C and macerated (< 0.15 mm). The material obtained was characterized by several analysis techniques for adsorbent materials.

2.2. Adsorption experiments
Batch adsorption experiments were performed in a set of Erlenmeyer flasks (250 mL), each of which contained 100 mL of different MB concentrations (50 mg L⁻¹ y 100 mg L⁻¹) along with a fix adsorbent dose. The temperature of the adsorbate-adsorbent solution during adsorption experiment was maintained at room temperatures (23°C) and shaking speed 150 rpm using a shaker HD-3000 (Actum). After the adsorption process, the residual concentrations of methylene blue were measured by using VIS-DR 3900 spectrophotometer at wavelength of 665 nm. With kinetic studies it is possible to find the optimum contact time and with the isotherms, the adsorption capacity of the material.

2.3. Adsorption kinetics
Kinetic studies allow to identify the type of adsorption mechanism and predict the removal speed of a contaminant from aqueous solutions [10]. To determine the optimum contact time and adjust experimental data to the various kinetic models, several erlenmeyer flasks were taken with 50 mL of MB solution and 0.05 g of the adsorbent material and shaken at 150 rpm. Subsequently, several samples were taken between 5 min and 540 min and the absorbance of each sample was measured. The MB adsorbed at a given time (t) was calculated from the mass balance between the initial concentration and the concentration at time t, according to the Equation (1).

\[ q_t = \frac{(C_i - C_f)}{w} \times V \]  

Where \( q_t \) is the adsorption capacity at time (mg g⁻¹), \( C_i \) is the initial MB concentration in liquid phase (mg L⁻¹), \( C_f \) is the MB concentration in liquid phase at time “t” (mg L⁻¹), \( V \) is the volume of solution (L) and \( w \) is the adsorbent amount (g). Each experiment was performed at least in duplicate under identical conditions. For this study, the kinetic models of pseudo-first order, pseudo-second order and intra-particular diffusion for adsorption of MB at different concentrations were taken into account.

The pseudo-first order kinetic model establishes that, the stage that limits the adsorption process is the physisorption, and it is due to the mass transfer from MB to the adsorbent surface and is based on Equation (2) (Table 1). The plot of \( \log (q_e - q_t) vs t \) should give a linear relationship, from which \( q_e \) and \( k_1 \) can be determined from the intercept and slope, respectively [3].

\[ \frac{t}{q_t} = \frac{1}{k_1 q_e^2} + \frac{t}{q_e} \]

Table 1. Equation kinetic models.

| Kinetic Model                      | Equation                                      |
|-----------------------------------|-----------------------------------------------|
| Pseudo-first order                | \( \log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \) |
| Pseudo-second order               | \( \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \) |
| Intraparticle diffusion           | \( q_t = k_{df} \sqrt{t} + C_i \) |

\( k_i \): pseudo first order adsorption rate constant (min⁻¹); \( q_e \): amount of MB adsorbed in a time t (mg g⁻¹); \( q_t \): amount of MB adsorbed at equilibrium (mg g⁻¹); \( t \): time (min); \( k_2 \): constant speed of pseudo second order (g mg⁻¹ min⁻¹); \( k_{df} \): Intraparticle diffusion rate constant (mg g⁻¹ min⁻¹/2); \( C_i \): constant (mg g⁻¹).
The pseudo-second order model is represented in Equation (3) (Table 1) and assumes that the overall rate of MB adsorption process seems to be controlled by the chemical process through electrons sharing or by covalent forces through exchanging of electrons between adsorbent and adsorbate. $q_f$ and $k_2$ can be determined from the slope and the intercept of the plot of $t/q_f$ Vs $t$ [3].

The effect of diffusion as the rate-controlling step in the adsorption was evaluated according to the intraparticle diffusion model Equation (4) (Table 1). Where $k_{ad}$ is an intraparticle diffusion rate constant, and $C_i$ is related to the thickness of the boundary layer. The intraparticle diffusion parameters could be obtained from the slope and the intercept of the plot of $q_e$ vs $\sqrt{t}$ [11].

2.4. Adsorption isotherms

Langmuir and Freundlich models were tested for equilibrium description at room temperature. The adsorption isotherm can reflect the distribution of adsorption molecules between the liquid and solid phase at the equilibrium state. Langmuir y Freundlich models are characterized by certain constant values which express the surface properties and affinity of the adsorbent and can also be used to compare the adsorptive capacities of the adsorbent for different pollutants. Langmuir is the most utilized, since contains physical assumptions such as: each site can contain only one adsorbate molecule and adsorption occurs in a monolayer. The Langmuir model is represented by Equation (5) (Table 2). A plot of $C_e/Q_e$ vs $C_e$ indicates a straight line of slope $1/Q_mK_L$ and an intercept of $1/ Q_mK_L$. In this model, it can be indicated if the adsorption process is favorable or unfavorable, by means of the dimensionless separation factor, calculated by Equation (7) (Table 2). Freundlich model is an empirical equation based on adsorption on a heterogeneous surface suggesting that binding sites are not equivalent and/or independent. The lineal form of Freundlich isotherm is represent by Equation (6) (Table 2), and from a plot of $\ln q_e$ vs $\ln C_e$, $K_f$ and $1/n$ values can be obtained. $K_f$ is an indicator of the adsorption capacity and $n$ is that of the adsorption intensity [12].

| Table 2. Equations models isotherms. |
|--------------------------------------|
| **Langmuir**                        |
| $\frac{C_e}{Q_e} = \frac{1}{Q_mK_L} + \frac{C_e}{Q_m}$ |
| **Freundlich**                      |
| $\ln Q_e = \ln K_F + \frac{1}{n}\ln C_e$ |
| **Non-dimensional separation factor** |
| $R_L = \frac{1}{1 + K_LC_i}$ |

$c_e$: MB concentration in equilibrium (mg L$^{-1}$); $Q_e$: capability of adsorption at equilibrium (mg g$^{-1}$); $Q_m$: maximum capacity of absorbate (mg g$^{-1}$); $K_L$: constant of Langmuir (L g$^{-1}$); $K_F$: Freundlich constant (mg g$^{-1}$); $1/n$: constant; $R_L$: non-dimensional separation factor; $C_i$: is the initial concentration of MB.

3. Results and discussion

3.1. Material characterization

Biomass characterization has been previously reported in one of our articles [6]. Typical values of moisture, volatile material, fixed carbon and ash can be observed. Figure 1 shows the SEM micrographs, for the unmodified biomass (F) and the modified biomass (AF). The micrographs show a slightly development of the porosity in AF material (surface area of 14.82 m$^2$ g$^{-1}$).

The FTIR analysis (see Figure 2) showed the formation of oxygenated functional groups with the appearance of different bands, such as: the region between 3200 cm$^{-1}$ to 3500 cm$^{-1}$ refers to the hydroxyl functional group (O-H) of alcohols and carboxylic acids. The band of 1600 cm$^{-1}$ to 1750 cm$^{-1}$ relates to carbonyl group (C=O) and the stretching (C=C) of alkenes. The signal at 1300 cm$^{-1}$ and 1500 cm$^{-1}$ indicates the presence of aromatic rings with C-H stretches at various locations in the ring. Another
oxygenated group such as ethers (C-O-C) shows signal at 1000 to 1100 cm$^{-1}$ and finally the signal at 2922 cm$^{-1}$ is attributed to amines (N-H). All these functional groups are important during the dye adsorption process because they act as active sites capable of interacting with dye molecules [4,5].

It has been shown that contaminant interactions with surface functional groups of the different adsorbent materials are hydrophobic interactions mainly due to the low energy of Van der Waals, donor-acceptor electron interactions between the aromatic rings of the materials and the -OH group of the dyes and hydrogen bonds between the -OH groups of materials and dyes [7].

**Figure 1.** SEM micrographs of biomass and adsorbent material. F: fiber; AF: activated fiber.

**Figure 2.** FT-IR spectra of AF before the adsorption process.

3.2. **Kinetics parameters of adsorption**

The kinetic parameters for the pseudo-first order, pseudo-second order and intraparticle diffusion models are shown in Table 3. For all conditions, typical kinetic curves were obtained, where, a fast step occurred at the beginning, and after, the adsorption rate was decreased, and finally, the curves tended to the equilibrium at 4 and 7 hours for MB concentration of 50 mg L$^{-1}$ and 100 mg L$^{-1}$, respectively. The results showed that the correlation coefficients, $R^2$, obtained for the pseudo-second order kinetic model were $\geq 0.99$, which makes it a better model to simulate the adsorption of MB onto AF. Thus, it can be inferred that the rate limiting step may be chemisorption promoted by sharing or exchange of electrons.
between the positively charged MB ions and functional groups of the adsorbent involved or covalent forces, through the exchange of electrons between the parties involved. These results are in agreement with that reported in the literature for the adsorption of MB onto different adsorbent materials obtained from agro industrial wastes [13-16].

### Table 3. Parameters of pseudo-first order, pseudo-second order and intraparticle diffusion models for the adsorption of MB on AF.

|                  | C<sub>0</sub> (mg L<sup>-1</sup>) | q<sub>e exp.</sub> (mg g<sup>-1</sup>) |
|------------------|-------------------------------|-----------------------------|
|                  | 50                           | 21.89                       |
|                  | 100                          | 25.02                       |

|                        | C<sub>0</sub> (mg L<sup>-1</sup>) | q<sub>e</sub> (mg g<sup>-1</sup>) | k<sub>i</sub> (min<sup>-1</sup>) x 10<sup>-2</sup> | R<sup>2</sup> |
|------------------------|-------------------------------|-----------------------------|---------------------------------|----------------|
| Pseudo-first order     |                               |                             | 1.36                           | 0.76           |
|                        |                               |                             | 0.67                           | 0.98           |
|                        |                               |                             | 16.65                          | 19.52          |
|                        |                               |                             | 0.98                           | 0.97           |
|                        |                               |                             | 24.21                          | 27.32          |
|                        |                               |                             | 1.00                           | 0.99           |

|                        | C<sub>1</sub> (mg g<sup>-1</sup>) | C<sub>2</sub> (mg g<sup>-1</sup>) | k<sub>d1</sub> (g mg<sup>-1</sup> min<sup>1/2</sup>) | R<sup>2</sup> |
|------------------------|-------------------------------|-------------------------------|---------------------------------|----------------|
|                        | 1.26                          | 2.76                          | 1.26                            | 0.99           |
|                        | 1.47                          | 9.13                          | 1.47                            | 0.98           |

|                        | C<sub>i</sub>: initial concentration of MB (mg L<sup>-1</sup>); ; q<sub>e</sub>: capability of adsorption at equilibrium (mg g<sup>-1</sup>); k<sub>i</sub>: adsorption rate constant; R<sup>2</sup>: correlation coefficients; k<sub>d1</sub>: Intraparticle diffusion rate constant; C<sub>n</sub>: constant |

To evaluate a possible adsorption mechanism of MB on AF, the intra-particle diffusion model was used and a good adjustment of the experimental data was observed. It was seen a general features: an initial small curved portion followed by a linear portion and then a plateau [11]. The initial curved portion is attributed to bulk diffusion and the linear portion to the intraparticle diffusion. The linear portion of the curve corresponds to the period in which intraparticle diffusion controls the adsorption process. The corresponding values of the diffusion coefficient are displayed in Table 3. For the concentration of 50 mg L<sup>-1</sup> results show that the value of k<sub>d1</sub> is lower than the value of k<sub>d2</sub>, indicating that adsorption inside of the pores is faster than surface adsorption, while for the concentration of 100 mg L<sup>-1</sup>, the opposite happens, the value of k<sub>d1</sub> is greater than the value of k<sub>d2</sub>. This may be related to the high amount of colorant available at 100 mg L<sup>-1</sup> and therefore the greater ease of diffusion on the material surface.

On the other hand, values of C<sub>1</sub> and C<sub>2</sub> indicate the effects of the boundary layer. The larger values for C<sub>i</sub> indicate which stage contributes most to the limiting step of the reaction rate. It can be said that the adsorption of MB on AF is a process that involves multiple steps (adsorption on the external surface and diffusion within the adsorbent pores) and that its limiting stage depends on the concentration of the dye.

### 3.3. Isotherms experiments

These studies allow to describe the interaction between dye and adsorbent material, and to know the adsorption capacity of the material in the equilibrium. Table 4 shows the parameters for the analyzed models. For all cases, the shape of the curves indicate favorable adsorption. The higher correlation coefficients of R<sup>2</sup> = 0.97 suggest that the Langmuir model can be applied to fitting the experimental data, which indicates the presence of homogeneous sites that interact with the MB. Maximum MB
uptake capacities, represented by \( Q_m \) in Langmuir equation, were 29.85 mg g\(^{-1}\) and 24.10 mg g\(^{-1}\) for 50 mg L\(^{-1}\) and 100 mg L\(^{-1}\) of MB, respectively. These \( Q_m \) are comparable value to other residue-based adsorbents reported in the literature for MB adsorption at ambient temperature (Table 5) [5,13]. In the present study, the calculated \( R_L \) values for the adsorption of MB on AF were found equal to 0.15 and 0.02 (0 < \( R_L < 1 \)) at initial concentrations of 50 mg L\(^{-1}\) and 100 mg L\(^{-1}\), respectively. These \( R_L \) values confirmed that AF is favorable for adsorbing MB from water.

Freundlich isotherms indicate that, there are different types of interactions between the adsorbent and the adsorbate during the adsorption process. That is, the MB can be adsorbed on AF by diffusion through the pores and by interaction with functional groups.

### Table 4. Parameters of Langmuir and Freundlich adsorption isotherm models for MB adsorbed by AF.

| \( C_0 \) (mg L\(^{-1}\)) | 50 | 100 |
|---------------------------|----|-----|
| **Langmuir**              |    |     |
| \( Q_m \) (mg g\(^{-1}\)) | 29.85 | 24.10 |
| \( K_L \) (L mg\(^{-1}\)) | 0.12 | 0.58 |
| \( R_L \)                  | 0.15 | 0.02 |
| \( R^2 \)                  | 0.97 | 0.97 |
| **Freundlich**             |    |     |
| \( K_F \) (mg g\(^{-1}\)) | 10.21 | - |
| \( 1/n \)                  | 0.24 | - |
| \( R^2 \)                  | 0.89 | - |

\( C_0 \): initial concentration of MB; \( Q_m \): maximum capacity of MB; \( K_L \): constant of Langmuir; \( R_L \): non-dimensional separation factor of adimensional separation; \( R^2 \): correlation coefficients; \( K_F \): Freundlich constant; \( 1/n \): constant.

### 3.4. Comparison to other adsorbents

Table 5 compares the maximum adsorption capacity, \( Q_m \), of AF (this study) and different adsorbent materials obtained from agro industrial residues for MB removal. The maximum MB uptake capacities for AF is comparable with those reported by other authors. This suggests that our material has a great potential to apply it as an adsorbent of dyes from aqueous solutions.

### Table 5. Adsorption capacities (\( Q_m \) calculated from Langmuir model) of MB adsorbed by various adsorbents.

| Adsorbente     | \( Q_m \) (mg g\(^{-1}\)) | Reference |
|----------------|--------------------------|-----------|
| AF             | 29.8                     | This study|
| Shell eggs     | 2.2                      | [14]      |
| Pine wood      | 3.9                      | [15]      |
| Avocado seed   | 16.0                     | [16]      |

### 4. Conclusions

Experiments were conducted to investigate the potential of palm oil residue (fiber) as an adsorbent for the removal of methylene blue from aqueous solutions. The AF characterization shows that this material presents morphological and textural properties suitable to be used as an adsorbent. The results indicated that the pseudo-second order equation provided the better correlation of the adsorption data, and equilibrium data demonstrated favorable adsorption and were better described by Langmuir model with the maximum adsorption capacity of MB on AF of 29.85 mg g\(^{-1}\) and 24.10 mg g\(^{-1}\) for the MB concentration of 50 mg L\(^{-1}\) and 100 mg L\(^{-1}\), respectively. Our results indicate that AF can be used as an effective low-cost agricultural waste adsorbent for the removal of MB dye from aqueous solutions.

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