Removal of dyes from aqueous solutions by adsorbent prepared from coffee residues

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Abstract. This study reports the production of an adsorbent material derived from extracted coffee residues using phosphoric acid and zinc chloride as activating agents. The structural features of the materials were characterized using different analytical techniques. The BET surface areas were found between 3.81 m².g⁻¹ y 176.27 m².g⁻¹, while the FTIR analysis showed the formation of oxygenated functional groups, which are active in the adsorption process. These materials were evaluated as adsorbents for the removal of methylene blue from aqueous solution. Batch adsorption tests were performed at room temperature and the effects of contact time and, initial dye concentration was investigated. The equilibrium adsorption results were complied with Langmuir isotherm model and its maximum monolayer adsorption capacity was 15.92 mg.g⁻¹. Adsorption kinetics studies indicated that the pseudo second order model yielded the best fit for the kinetic data. This typical dependence of methylene blue uptake on kinetic studies indicated the adsorption process to be both chemisorption and diffusion controlled. The experimental data obtained in the present study indicate that coffee residues are suitable candidates for use as adsorbents in the removal of cationic dyes.

1. Introduction
Dyes are used as coloring agents in a variety of industries, and methylene blue (MB), is commonly used as the coloring agent for cotton. The discharge of wastewater from these industries to water resources causes problems due to dyes prevent light penetration and thereby reduce photosynthetic activities of water streams and disturb the aquatic equilibrium [1,2]. Therefore, the removal of dyes from wastewater with an efficient treatment needs to be developed.

Several techniques like chemical precipitation, membrane filtration, biodegradation and, ion exchange have been employed for the treatment of dye-contaminated water. However, chemical and biological methods cannot be used because of the non-biodegradable nature of the MB. Hence, the adsorption methods are easy to implement, efficient and environmentally friendly alternatives [1,2]. Among the variety of adsorbents, activated carbon is the most preferred adsorbent for the removal of dyes because of its excellent adsorption ability. However, the disadvantage of activated carbon is its high cost. Recently, many works have been studied for the development of both effective and low-cost adsorbents. Agricultural wastes are the most common raw materials being studied for this purpose since they are renewable, available in large amounts and potentially less expensive than other materials to produce adsorbents [3,4].

Coffee is one of the most important agro-industrial products. Currently, it is cultivated in more than 80 countries. In Colombia, the production is about 243 thousand tons/year, and 10% corresponds to
coffee waste or by-products [5,6]. These coffee residues could be used as a potentially effective sorbent for removal dyes from wastewater.

The aim of this study is to prepare adsorbents materials derived from coffee residues as an alternative adsorbent to efficiently remove cationic dyes from aqueous media. To evaluate the adsorptive properties of the prepared materials MB was selected as a model dye because of its ability to be strongly adsorbed onto solid materials. To predict the MB adsorption rate on the adsorbent materials, we studied the kinetic models of pseudo first order, pseudo second order, and intraparticle diffusion. Moreover, to describe the interaction between the adsorbents and MB, Freundlich and Langmuir adsorption isotherms were used.

2. Metodology

2.1. Material preparation and characterization

The collected coffee residues (CR) were washed with distilled deionized water and dried at 105°C for 12 hours. The dried residue (CR) was calcined at 550°C for 30 minutes and named CCR. Then, CR activation was performed using two different procedures: (i) CR was impregnated with H3PO4 for 5 hours, after that, heating up to 110°C for 12 hours. Then, it was subjected to activation at 300°C for 60 minutes. Finally, the material was washed with distilled water and the pH was stabilized between 6 and 7. (ii) CR was impregnated with ZnCl2 and let stirring at 200 rpm for 24 hours, then it had a heat treatment at 550°C for 30 minutes. The obtained material was washed with HCl and distilled water until reaching pH values between 6 and 7. Both materials were oven dried at 105°C for 12 hours. Prior to their use as adsorbents, they were sieved, and then only particles < 0.15 mm were used. The adsorbent materials were named as ACRH and ACRZ, for those activated with H3PO4 and ZnCl2, respectively. The characterization of adsorbent materials (CR, CCR, ACRH and ACRZ) was carried out with Scanning Electron Microscope (SEM) micrographs (Oxford Instruments), thermogravimetric analysis (TGA) (TGA Q500, TA Instruments), elemental analysis (CHNSO TrueSpec® Micro, LECO), Brunauer, Emmett and Teller (BET) analysis for surface area, the point of zero charge (pHpzc), and Fourier transform infrared spectroscopy (FT-IR) between 4000 cm−1 and 450 cm−1 (Spectrum two-PerkinElmer with UATR).

2.2. Adsorption kinetics

In order to understand the kinetics behind the MB removal process, the adsorption was monitored as a function of time. Several batch adsorption experiments were carried out at 150 rpm of agitation using 0.2 g of each adsorbent material, and 50 mL of aqueous solutions of methylene blue with the concentration of 50 mg.L−1 and 100 mg.L−1 at 25°C. To determine the optimal contact time, the experimental solutions were shaken by a shaker HD-3000 (Actum) from 5 to 480 minutes and, then 5 mL solutions were taken from flasks at known time intervals. The final concentration of MB was determined using VIS-DR 3900 spectrophotometer (Hach) at a wavelength of 665 nm [7,8]. The amount of MB at time t, q, (mg.g−1) was calculated by using Equation (1).

\[ q_t = \frac{(C_0 - C_t)}{w} \times V \]  

(1)

Where q, is the adsorption capacity at time (mg.g−1), C0 is the initial MB concentration in liquid phase (mg.L−1), C, 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.

The kinetic data were analyzed in the light of pseudo first order (Equation 2), pseudo second order (Equation 3), and intraparticle diffusion (Equation 4) models.

\[ \log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} \times t \]  

(2)

\[ \frac{t}{q_t} = \frac{1}{k_2 q_e} + \frac{t}{q_e} \]  

(3)
\[ q_t = K_{di} \sqrt{t} + C_i \]  \hspace{1cm} (4)

Where, \( q_e \) is the amount of MB adsorbed equilibrium time (mg·g\(^{-1}\)), \( k_1 \) is the pseudo first order adsorption rate constant (min\(^{-1}\)), \( k_2 \) is the pseudo second order rate constant (g·mg\(^{-1}\)·min\(^{-1}\)), \( k_{di} \) (g·mg\(^{-1}\)·min\(^{1/2}\)) is the intraparticle diffusion rate constant and \( C_i \) is a dimensionless constant. The linear forms of the kinetic models are given in Equation (2-4), their plots should give a linear relationship, from which all the kinetic parameters can be determined from the intercept and slope values.

2.3. Adsorption isotherms

The adsorption experiments were carried out by taking 50 mL of MB solutions with a fix initial concentration of 50 and 100 mg·L\(^{-1}\) in different flasks of glass. The variable amount, from 0.04 to 0.24 g of each adsorbent material (CCR, ACRH, and ACRZ) was added to each flask kept on shaking of 150 rpm and equilibrated for the optimal contact time determined in 2.2 section. All experiments were done in duplicate. Langmuir and Freundlich models were tested for equilibrium description at room temperature according to Equation (5) and Equation (6), respectively [9].

\[ \frac{C_e}{q_e} = \frac{1}{Q_mK_L} + \frac{C_e}{Q_m} \]  \hspace{1cm} (5)

\[ Logq_e = LogK_e + \frac{1}{n} LogC_e \]  \hspace{1cm} (6)

Where \( C_e \) (mg·L\(^{-1}\)) correspond to the MB concentration in the aqueous solution, after equilibrium was reached. \( Q_m \) (mg·g\(^{-1}\)) and \( K_L \) (L·g\(^{-1}\)) are constants related to the maximum adsorption capacity and the adsorption energy, respectively. \( K_F \) (mg·g\(^{-1}\)) is the relative adsorption capacity and 1/n is related to the intensity of adsorption, with values of 1/n > 1 indicating favorable adsorption.

3. Results

3.1. Characterization of the materials

The results of proximate and elemental analysis of coffee residue and coffee activated materials are show in Table 1. The raw coffee residue consisted high in volatile matter content (79.7%) and low in fixed carbon (17.8%) and ash content (2.4%). After activation, the percent fixed carbon of coffee activated carbon increased and percent volatile matter decreased. These results are in agreement with those reported for biomass, which comprises a large percentage of volatile matter [10,11]. The ultimate analyses revealed the high contents of carbon and oxygen, indicating the lignocellulosic structure of this agricultural residue.

| Materials | Moisture (%) | Proximate analysis (Wt %)* | Elemental analysis (Wt %)* |
|-----------|--------------|----------------------------|----------------------------|
|           | VM | FC | Ash | N  | C   | H   | O   |
| CR        | 6.65 | 79.72 | 17.85 | 2.43 | 3.1 | 46.8 | 5.9 | 44.2 |
| ACRH      | 5.40 | 32.76 | 59.27 | 9.40 | 2.6 | 59.5 | 3.1 | 34.8 |
| ACRZ      | 8.31 | 27.72 | 69.72 | 1.24 | 2.6 | 74.0 | 3.0 | 20.4 |
|           |     |     |     |     |     |     |     |     |
|            | BET surface area (m\(^2\)·g\(^{-1}\)) | d_p (nm) | Pore volumen (cm\(^3\)·g\(^{-1}\)) | pH\(_{PZC}\) |
| CR        | 0.45 | - | - | - | - |
| CCR       | 3.81 | - | - | 0.002 | 5.9 |
| ACRH      | 176.27 | 2.45 | 0.108 | 6.4 |
| ACRZ      | 63.22 | 2.30 | 0.036 | 5.6 |

CR: coffee residues; CCR: calcinated coffee residues; ACRH: activated coffee residues with H\(_2\)PO\(_4\); ACRZ: activated coffee residues with ZnCl\(_2\); VM: volatile matter; CF: fixed carbon; N: nitrogen; C: carbon; H: hydrogen; O: oxygen; PZC: point zero charge; d_p: pore size,* dry basis,* by difference (O% = 100% - C% - N% - H%).
The SEM micrographs for coffee residues before and after activation treatment are presented in Figure 1. They are very similar to some reported studies [12-14]. It can be seen that the surfaces of the untreated CR, the calcinated CCR and the activated ACRH are irregular and contains pores of different sizes and shapes. For the ACRZ material, it was no observed porosity.

![SEM micrographs of CR, CCR, ACRH, and ACRZ](image1.png)

**Figure 1.** SEM micrographs of CR: coffee residues; CCR: calcinated coffee residues; ACRH: activated coffee residues with H₃PO₄; ACRZ: activated coffee residues with ZnCl₂.

![FT-IR spectra of ACRH and ACRZ](image2.png)

**Figure 2.** FT-IR spectra of ACRH and ACRZ before the adsorption process. ACRH: activated coffee residues with H₃PO₄; ACRZ: activated coffee residues with ZnCl₂.

FT-IR spectroscopy was used to determine the presence of different functional groups on the surface of activated materials (ACRH and ACRZ). It can be observed in the Figure 2 a large variety of
oxygenated functional groups and that there is no effect on the position and shape of the bands for the two adsorbent materials produced by chemical activation with H₃PO₄ and ZnCl₂. The band at 3812 cm⁻¹ might be due to O–H stretching of carboxylic group or adsorbed water. The band at 2851 cm⁻¹ is due to the C–H stretching vibration and, the broad band between 1585 and 1219 cm⁻¹ typically associated with C–O vibrations from groups such as lactones, esters, carboxylic acids, ethers, alcohols, and phenols. All these functional groups are important during the dye adsorption process [12-15]. Adsorption capacity may be attributed due to the competition between the weakened electrostatic interaction adsorbent-adsorbate and π–π interactions between the adsorbent material and the MB molecules.

3.2. Adsorption kinetics
It was found dynamic adsorption of MB with initial concentrations of 50 mg.L⁻¹ and 100 mg.L⁻¹ on ACRH. With prolonged contact time, the MB adsorption capacity (qₑ) increased gradually and then reached the equilibrium, with MB removal > 90%. Our data indicate that 120 min and 60 min for the concentration of 50 mg.L⁻¹ and 100 mg.L⁻¹ of MB were sufficient to reach equilibrium. These optimal times are faster than the time for other materials using to MB removal [8,9,16,17]. In order to make the adsorption mechanism clearer, the adsorption data were fitted using the pseudo first order, the pseudo second order and the intraparticle diffusion kinetic models (Table 2). By comparing the results presented in Table 2, it can be seen that for all the experiments the calculated qₑ values were closer to the qₑ(exp) values in the pseudo second order model than those of pseudo first order model, suggesting that the pseudo second order model is more accurate to understand the kinetics for the MB adsorption process. It can be inferred that the rate-limiting step may be chemisorption promoted by either valency forces (sharing electrons), or covalent forces (exchange of electrons).

| Table 2. Parameters of pseudo first order, pseudo second order and intraparticle diffusion models. |
|-----------------------------------------------|
| Material | CCR | ACRH | ACRZ |
| C₀ (mg.L⁻¹) | qₑ(exp) (mg.g⁻¹) | 50 | 100 | 50 | 100 | 50 | 100 |
| 10.100 | 21.060 | 10.650 | 22.190 | 11.330 | 20.190 |
| Pseudo first order |
| qₑ (mg.g⁻¹) | 6.533 | 10.127 | 11.882 | 23.889 | 7.863 | 17.246 |
| K₁ (min⁻¹) | 0.097 | 0.009 | 0.040 | 0.111 | 0.043 | 0.014 |
| R² | 0.998 | 0.982 | 0.939 | 0.909 | 0.910 | 0.999 |
| Pseudo second order |
| qₑ (mg.g⁻¹) | 10.460 | 21.978 | 11.806 | 22.472 | 11.723 | 21.978 |
| K₁ (g.mg⁻¹.min⁻¹) | 0.035 | 0.002 | 0.004 | 0.017 | 0.012 | 0.001 |
| R² | 1.000 | 0.997 | 0.994 | 1.000 | 0.999 | 0.999 |
| Intraparticle diffusion |
| K₁ (g.mg⁻¹.min⁻¹) | 0.129 | 0.161 | 0.131 | 0.660 | 0.180 | 0.190 |
| C₀ (mg.L⁻¹) | 6.095 | 9.377 | 2.545 | 8.251 | 4.834 | 3.017 |
| R² | 0.932 | 0.938 | 0.861 | 0.988 | 0.976 | 0.986 |
| K₂ (g.mg⁻¹.min⁻¹) | 0.004 | 0.025 | 0.073 | 0.075 | 0.023 | 0.036 |
| C₂ (mg.L⁻¹) | 9.830 | 14.464 | 3.895 | 18.148 | 8.719 | 10.992 |
| R² | 0.992 | 0.960 | 0.991 | 0.781 | 0.803 | 0.979 |

CCR: calcinated coffee residues; ACRH: activated coffee residues with H₃PO₄; ACRZ: activated coffee residues with ZnCl₂; C₀: initial concentration of MB; qₑ: capability of adsorption at equilibrium; k₁: adsorption rate constant; R²: correlation coefficients; k₂: Intraparticle diffusion rate constant; C: constant

The intraparticle diffusion model suggests that the superficial adsorption is faster than pore diffusion for all the materials at different concentrations since the value of k₁ is greater than the value of k₂.

3.3. Adsorption isotherms
Adsorption isotherms are used to calculate the maximum adsorption capacity of the materials and to study the interaction between adsorbate and adsorbent at equilibrium time. To understand the adsorption mechanism by the adsorbent materials, the experimental results were fitted using Langmuir and
Freundlich adsorption models, and the values of different isotherm constants for the adsorption of MB are listed in Table 3. The correlation coefficients obtained from Langmuir isotherm ($R^2 > 0.99$) are higher than those observed for the Freundlich model. This model predicts homogeneous adsorption occurring between the adsorbent surfaces. The $R_L$ is the separation factor that indicates the favorability of adsorption. In this work, the $R_L$ values are in the range of $0 < R_L < 1$, suggesting that there is favorable adsorption [9]. The decrease in $R_L$ when rising the MB initial concentration indicates that adsorption is more favorable at higher concentrations [8]. The material with the maximum adsorption capacity ($Q_m$) was ACRZ with a value of 54.05 mg g$^{-1}$. For this study, the Langmuir model was considered the most suitable for describing the MB adsorption mechanism by the adsorbent materials.

### Table 3. Langmuir and Freundlich isotherms parameters.

| Materials  | CCR $Q_m$ (mg g$^{-1}$) | ACRH $Q_m$ (mg g$^{-1}$) | ACRZ $Q_m$ (mg g$^{-1}$) |
|------------|--------------------------|---------------------------|--------------------------|
| C$_0$ (mg L$^{-1}$) | 50 | 100 | 50 | 100 | 50 | 100 |
| Q$_m$ (mg g$^{-1}$) | 16.34 | - | 15.92 | 27.32 | 17.60 | 54.05 |
| $K_L$ (L mg$^{-1}$) | 0.926 | - | 1.146 | 1.718 | 0.444 | 0.307 |
| $R^2$ | 0.999 | - | 0.998 | 0.998 | 0.996 | 0.990 |
| $R_L$ | 0.023 | - | 0.020 | 0.006 | 0.048 | 0.029 |
| $K_F$ (mg g$^{-1}$) | 9.421 | - | 9.808 | 19.989 | 8.300 | 18.655 |
| 1/n | 0.175 | - | 0.140 | 0.078 | 0.210 | 0.328 |
| $R^2$ | 0.928 | - | 0.922 | 0.879 | 0.953 | 0.976 |

CCR: calcinated coffee waste; ACRH: activated coffee waste with H$_3$PO$_4$; ACRZ: activated coffee waste with ZnCl$_2$; $C_0$: initial concentration of MB; $Q_m$: maximum capacity of MB; $K_L$: constant of Langmuir; $R_L$: non-dimensional separation factor; $R^2$: correlation coefficients; $K_F$: Freundlich constant; 1/n: constant.

3.4. **Comparison to other adsorbents**

Table 4 shows the maximum adsorption capacities of different materials for MB removal. It can be noted that the maximum MB uptake capacity here reported (54.05 mg g$^{-1}$) was compared with that reported for other MB adsorbents. These results make these adsorbent materials as competent for their use in the treatment of wastewater contaminated with dyes. Our approach is environmentally friendly due to the use of agro-industrial waste.

### Table 4. Maximum MB adsorption capacity (mg g$^{-1}$) of various adsorbents.

| Materials | Q$_m$ (mg g$^{-1}$) | References |
|-----------|---------------------|------------|
| CCR       | 16.34               |            |
| ACRH      | 27.32               |            |
| ACRZ      | 54.05               | This study |
| Cotton waste | 68.7                | [12]       |
| Spent coffee grounds | 18.70            | [14]       |
| Coffee ground | 36.82              | [15]       |
| Rice husk | 9.83                | [20]       |

CCR: calcinated coffee waste; ACRH: activated coffee waste with H$_3$PO$_4$; ACRZ: activated coffee waste with ZnCl$_2$.

4. **Conclusions**

In this work, coffee residues were modified by thermal and chemical treatment, using phosphoric acid and zinc chloride as activating agents to obtain adsorbent materials (CCR, ACRH, and ACRZ) for MB removal. FT-IR analysis showed oxygenated functional groups on the materials surface, which favor the MB adsorption process. Adsorption kinetics follows the pseudo second order model. Adsorption isotherm study indicated that the equilibrium data were in agreement with Langmuir isotherm model.
\(Q_m = 54.05\) mg g\(^{-1}\). The present study demonstrates a viable approach of coffee residues and their potential in removing MB from water.

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