

EVALUATION OF ACTIVATED CARBONS OBTAINED FROM COLOMBIAN MINERAL COALS FOR ADSORPTION OF CAFFEINE

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ABSTRACT

Caffeine is a natural alkaloid used as a key ingredient in craft and industrially produced beverages. The caffeine concentration in water bodies worldwide is increasing to the point of being classified as an emerging contaminant with potentially harmful effects on aquatic ecosystems. Given the importance of both, coffee and carbon production in Colombia, activated carbons prepared from local mineral coals have been considered a cost-effective alternative for the treatment of wastewater from coffee plantations. In this study, activated carbons from the Colombian regions of Cundinamarca and Santander were evaluated as matrices for caffeine adsorption in an aqueous solution. The prepared activated carbons were characterized and subjected to adsorption tests and kinetic studies. The caffeine concentration (adsorbate) and the activated carbon (adsorbent) to liquid ratio were considered as the experimental factors in the evaluation of removal capacity. The results showed that the mineral coal from the Cundinamarca region has better physicochemical (low ash and volatile matter contents and high iodine number) and better adsorption capacity, reaching specific caffeine retention of 882.1 mg/g. The adsorption process corresponds with Freundlich's adsorption model suggesting heterogeneous adsorption, while pseudo-second-order kinetics indicated the dominance of a chemical adsorption mechanism.

Keywords: Activated Carbon, Adsorption, Caffeine, Isotherm Modeling, Kinetics, Emerging Contaminant, Wastewater

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INTRODUCTION

Caffeine (CFN) is a natural alkaloid used as a key ingredient in craft and industrially produced beverages. The coffee bean is one of the main sources of CFN, covering a global market of 10.1 million metric tons and 30 billion dollars.¹ Colombia is the third-largest coffee producer worldwide with a valued coffee of the *Arabica* variety. Caffeine (CFN) is a xanthine natural alkaloid with psychostimulant activity found in several plant species and widely consumed in caffeinated as well as an additive in several pharmaceutical products. CFN is soluble in water and many organic solvents and its biodegradation and photolysis susceptibility are poor.² CFN and its main metabolite paraxanthine (1,7dimethyl xanthine) are considered anthropogenic markers and emerging contaminants. As reviewed by Korekar et al², the CFN levels reported in aquatic bodies typically range between 0.01 and 300 µg/L depending on the source and water utilization. The highest values occurred in wastewater, rivers, or lakes contaminated with urban and industrial water effluents. However, its presence is not restricted only to wastewater, it has been also found in drinking water.³ High CFN concentrations in water bodies have been reported for Latin-American coffee producers like Brazil or Costa Rica (1.10 and 0.75 mg/L, respectively)⁴, which are explained by the regular influxes of wastewater from coffee manufacturing facilities. The main harmful effects identified as a consequence of medium-high CFN concentrations in aquatic ecosystems are: (i) the increase of marine coral bleaching by exacerbating the effects of water temperature and acidification, (ii) change in skeleton formation in corals and mollusks⁵, (iii) induction of oxidative stress and mutations in clams and some species of fish^{6,7}, and (iv) increase on water nitrification by stimulating *Pseudomonas* fluorescence growth rate.⁸ The wet-

processing method is preferred for obtaining high-quality coffee since it confers better organoleptic properties to the final product. Wet coffee processing involves several steps but the de-pulping and washing stages use considerable amounts of water. The wastewater generated has high levels of turbidity, acidity, dissolved solids, chemical (COD), and biochemical (BOD) oxygen demands, beyond the recommended limits.^{9,10} In Colombia, most of the high-quality *arabica* coffee is wet-processed with a mean water usage of 50 L/kg coffee, and few studies have analyzed the physicochemical parameters of wastewater produced by coffee plantations.¹¹ Those effluents exceed by far the limits of the Colombian environmental regulations,^{11,12} and lack of the appropriate treatment, increasing the CFN levels on ground and water bodies of coffee producer areas, which cover approximately 9000 km² in the country. The lack of wastewater treatment facilities in rural areas and the low efficiency of conventional methods for the removal of emerging pollutants motivates the development of cost-effective methods for the removal and/or mineralization of CFN. The implementation of adsorption operations is a very efficient strategy for pollutants removal from wastewaters.¹³ Activated carbons (AC) prepared from different sources emerge as cheap and efficient alternatives to remove organic matter from wastewater due to their hydrophobic properties, high surface area, and affinity.^{9,14,15} AC can be obtained either from treated vegetal sources or mineral coals at a low cost, its excellent properties for wastewater remediation allow removing pollutants as persistent as the heavy metals.^{16,17} In this work, two mineral coal types from different Colombian regions (Cundinamarca and Santander) were used as CFN adsorbents, given the importance of the country as a carbon (11th World, 1st Latin-America) and coffee (3rd World, 2nd Latin-America) producer. To the best of our knowledge, this is the first report of CFN adsorption studies using AC prepared from Colombian mineral coals.

EXPERIMENTAL

Activated Carbon Preparation and Characterization

A previous study performed a complete characterization of AC prepared with coals from seven different Colombian regions for gold adsorption in mining wastewater.¹⁸ For this study, coals from Cundinamarca (Type A) and Santander (Type B) regions were selected as promising materials for CFN adsorption. Coal samples were treated by cracking in an inert atmosphere and grinded using a disk mill (MSI industries Inc, Beaumont, TX) down to a particle size < 250 µm (60 mesh Tyler series). BET analysis (ASAP 2020, Micromeritics, Norcross, GA) was applied for microporosity, pore size, pore, volume, and surface area determinations. Proximal analysis was carried out following the ASTM standards for volatile matter (D5832), ash (D2866), and moisture (D2867) determinations. Similarly, the iodine number was determined according to the ASTM D4607 standard.

Adsorption Modeling

Synthetic solutions of CFN (20–80 mg CFN/L) were prepared by diluting CFN (98% HPLC grade, Sigma Aldrich, St. Louis, MO) in distilled water. Adsorption studies of CFN solutions at concentrations ranging from 20-80 mg/L were performed at 25°C and 170 rpm in a water bath (MRC WBT200) for 4 hours.¹⁵ The supernatants were analyzed at 273 nm wavelength in UV-Vis spectrophotometer (JASCO V-730, JASCO Inc, Easton, MD) and UHPLC-DAD (Shimadzu LC-20AT, Shimadzu Corp., Tokyo, Japan) using a Hypersil Green PAH C-18 reverse phase column (Phenomenex Inc, Torrance, CA). Acetonitrile/formic acid (10 mM, 50/50 v/v) was used as the mobile phase consisted in isocratic mode at 0.2 mL/min. For kinetic determinations, supernatant samples were taken and analyzed every 20 min. The non-linear two-parameter equilibrium models of adsorption by Langmuir, Freundlich, and Dubinin-Redushkevich were linearized (Table-1) for parameters determination at 25°C. The adjustment was assessed through the correlation coefficient (R²). All the experiments were performed in triplicate.

Table-1: Linearized Forms of the Non-Linear Equilibrium Models for Isotherm Modeling

Adsorption Model	Non-linear	Linearization
Langmuir	$q_e = \frac{q_m b C_e}{1 + b C_e}$	$\frac{1}{q_e} = \frac{1}{b q_m} \frac{1}{C_e} + \frac{1}{q_m}$
Freundlich	$q_e = K_F C_e^{1/n}$	$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$

Dubinin-Redushkevich ³	$q_e = q'_m \exp(K' \varepsilon^2)$ $\varepsilon = RT \ln(1 + \frac{1}{C_e})$	$\ln q_e = \ln q'_m - K' \varepsilon^2$
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Where, q_e is the specific adsorption (mg/g), q_m is the maximum adsorption capacity, b is the free energy of adsorption, n is the favorability of the adsorption, K_F is the adsorption capacity (mg/g) for the adsorbent, q_m' is the monolayer saturation capacity (mol/g), K' is the adsorption energy (mol²/kJ), T is the temperature (K) and R is the gas constant (kJ/mol K).

The kinetic studies considered the non-linear pseudo-first-order ($n=1$) and pseudo-second order ($n=2$) kinetic models (Eq.-1). Under the pseudo-first order assumption, the adsorption depends on the amount of available binding sites, and it is usually suitable only for the adsorption processes where equilibrium is reached after 20 or 30 minutes.¹⁵

$$\frac{dq_t}{dt} = k_n(q_e - q_t)^n \quad (1)$$

Where q_e is the equilibrium amount and q_t is the adsorbed amount at time t , and k_1 (min⁻¹) is the adsorption rate coefficient. Frequently, initial fast adsorption is followed by a slow chemisorption mechanism. Thus, an approximation for q_e must be made once the process became almost constant since the determination of the equilibrium is difficult.¹⁹ In pseudo-second order models, the adsorbate is assumed constant and the availability of binding sites depends on the adsorbate amount at equilibrium,²⁰ while the adsorption surface reaction is considered as the rate-controlling step.²¹ In such a case, the pseudo-second order rate constant k_2 (g/mg.min) is determined through linearization equation (Eq.-1).

RESULTS AND DISCUSSION

Coal Characterization and Adsorption Capacity

The coal characterization showed iodine numbers of 773.1 mg I₂/g for carbon type A and 246.4 mg I₂/g for carbon type B (Table-2). Iodine number is a common method for determination of carbon adsorption capacity and its value is directly related to the surface area since it measures the mesopores and micropores content in the AC.²² The iodine number typical range is 500–1200 mg I₂/g, which is equivalent to 900–1100 m²/g of surface area.²³ As adsorption is a surface phenomenon, the larger the specific surface area, the higher the adsorption capacity. Other additional factors may affect the adsorption capacity of AC, like the coal type and activation method, particle size, pore structure, and distribution.²³ The chemical functionality on the adsorbent surface may favor either a physical and reversible or a more stable chemical adsorption mechanism.¹⁹ In this case, the higher iodine number exhibited by type A AC suggests a higher adsorption capacity due to increased specific area and pores volume. The ash content in AC type B is almost 3-fold the present in type A. The lower ash content found in type A carbon indicates a lower mineral fraction compared to the organic fraction. Considering that the organic fraction is the activated phase in the carbonaceous matrix, also higher adsorption capacity is expected in type A AC. Nevertheless, adsorption capacity can also be increased by other factors such as the presence of catalytic minerals, oxygen chemisorption, and particular pore size distribution. Similarly, the lower volatile matter in type A AC suggests a larger active surface, which led to a higher volume of active pores in comparison with the type B carbon. The lower activation temperature of type B AC may be the cause of the difference in volatile matter levels, however, the high ash content of carbon B is more related to the regional geochemistry. The characterization results of both AC are summarized in Table-2.

Table-2: Characterization Results of ACs Prepared from Colombian Mineral Coals

AC type	Activation temperature (°C)	Iodine number (mg I ₂ /g)	Volatile matter (%)	Ash (%)	BET area (m ² /g)	Micropore area (m ² /g)	Micropore (%)	Pore size (Å)	Pore volume (cm ³ /g)
A	850	773.1	3.78	10.15	588.9	328.4	55.8	29.0	0.4265
B	700	246.4	6.68	28.35	22.6	19.4	85.8	26.5	0.0150

The maximum CFN adsorption at equilibrium was explored at adsorbent doses of 0.05 and 1.0 g/L, varying the CFN concentrations between 20 and 80 mg/L. As observed in Table-3, the increase in the CFN concentration gradient did not improve the CFN retention in type B AC at 0.05 g/L. Moreover, only a slight

increase was observed at 40 and 60 mg/L CFN concentrations at 0.1 g/L of adsorbent. This is likely due to the low specific area and the rapid saturation of available pores in type B carbon. In the case of carbon type A, the increase of the concentration gradient led to higher CFN retention. However, the adsorbent dose increase did not improve substantially the CFN adsorption, suggesting that the driving force is mainly controlled by CFN concentration when enough volume of active sites is available. The adsorption performance was assessed in terms of mass adsorbed (m_e), adsorbate retention (%), and equilibrium/initial concentration ratio (c_e/c_o). The best adsorption performance was evident for the AC obtained from coal produced in the Cundinamarca region. This AC allowed retaining CFN in a range of 55–93 % compared with a maximum of 14.5% for AC from the Santander region. Considering the low efficiency of adsorption when using the type B AC, treatment of CFN polluted wastewater with this material looks impractical. Further kinetic studies were applied for the characterization of CFN adsorption in type A carbon.

Table-3: Results of Adsorption Capacity for AC Prepared from Colombian Mineral Coals

AC type	AC dose (g/L)	c_o (mg/L)	c_e/c_o	Retention (%)
A	0.05	20	0.14	85.8
		40	0.31	69.3
		60	0.43	56.9
		80	0.45	55.1
	1.0	20	0.14	86.0
		40	0.07	93.5
		60	0.33	67.5
		80	0.42	58.5
B	0.05	20	0.95	5.5
		40	0.96	4.1
		60	0.98	2.4
		80	0.98	2.1
	1.0	20	0.97	3.0
		40	0.88	12.5
		60	0.86	14.5
		80	0.98	1.6

The trend of the adsorption capacity for the type A AC at increasing CFN concentrations is consistent with those results obtained by Beltrame et al.¹⁵ In that case, CFN adsorption in AC prepared from pineapple leaves but at CFN concentrations ranging between 100 and 500 mg/L, showed a q_e varying from 77.4 to 152.18 mg/g, respectively. In both cases, the effect of the initial CFN concentration is plausible given the higher driving force. Conversely, the increase of the adsorbent dose led to a decrease in the adsorption capacity, when evaluated at the same CFN concentrations. Such behavior may be caused by particle interactions like adsorption site aggregation or partial overlapping. These tend to decrease the effective area available for adsorption, even under high adsorbent concentrations. Thus, the determination of optimal operating conditions in real matrices from coffee processing wastewater must consider optimization of adsorbent dosage as a function of pollutant concentrations since the linear increase of AC dosage does not enhance the pollutant adsorption. Similar results were obtained previously by Gil et al.²⁴ when increased AC dosages from 25 to 100 mg/L, the q_e decreased by a ratio of 2.3. q_m of different adsorbents are presented in Table-4 to compare the adsorption capacity of the AC prepared with mineral coal from the Cundinamarca region. Notice that the carbon used in this work has a great removal capacity considering the data reported in other studies.

Table-4: Adsorption Capacity of AC Used for CFN Removal

Adsorbent	Adsorption capacity (mg/g)	Reference
Activated carbon from Colombian mineral coals	882.1	This work
Carbon xerogels	182.5	25
Carbon fibers from pineapple leaves	152.2	15
Oxidized carbon from <i>Luffa cylindrica</i>	59.9	26
Mg Al-LDH/biochar composite	26.2	27

Adsorption Modeling

The understanding and interpretation of adsorption isotherms are fundamental in the design and implementation of adsorption processes.²⁸ As previously described, the fit of experimental data to Langmuir, Freundlich, and Dubinin-Radushkevich adsorption models was evaluated. Additionally, the dynamic experimental data was used for the evaluation of the adjustment to the pseudo-first or pseudo-second order kinetic model. Figure-1a presents the experimental data and adsorption isotherms at 25°C for the Langmuir and Freundlich isotherm models. The plots of simulated and experimental data for CFN adsorption at 40, 60, and 80 mg/g are presented in Figure-1b, 1c, and 1d, respectively.

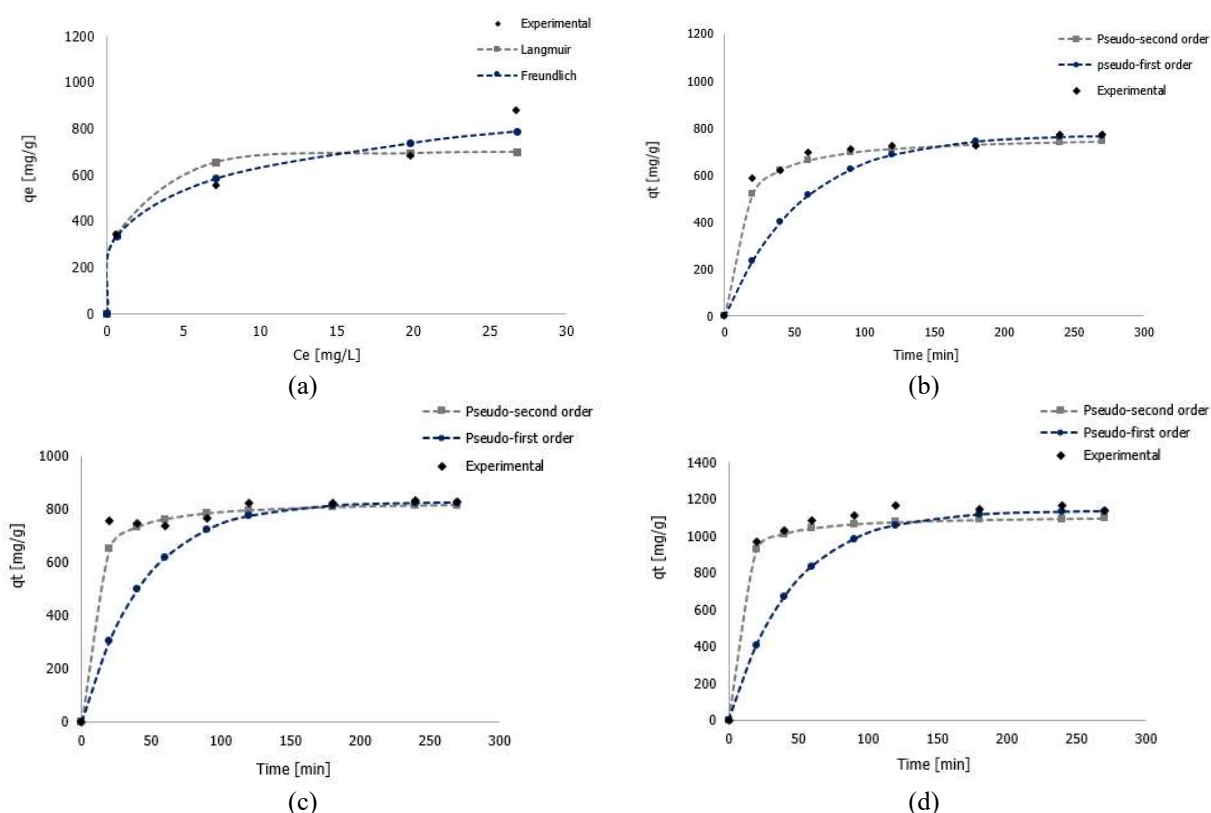


Fig.-1: CFN Adsorption Modeling with AC Prepared From Colombian Mineral Coals. (A) Langmuir and Freundlich Adsorption Isotherms, (B) CFN (40 Mg/G) Adsorption Kinetics, (C) CFN (60 Mg/G) Adsorption Kinetics, (D) CFN (80 Mg/G) Adsorption Kinetics

On the one hand, the Langmuir model depicts a monolayer sorption occurring on homogenous surfaces, and then balancing the adsorption and desorption rates.^{26,28} On the other hand, the Freundlich model describes non-ideal adsorption occurring on heterogeneous sites, assuming an exponential distribution of the active sites and their energies.^{26,28} The Dubinin-Radushkevich model assumes a multilayer pore-filling mechanism on heterogeneous surfaces with Gaussian energy distribution.²⁸ Table-5 presents the results of model fitting and their correlation coefficients (R^2). The experimental data of CFN adsorption on the type A AC fitted better to the Freundlich isotherm model, with an R^2 value of 0.96, in addition to an error of 6.7%. As observed in Figure-1a, the Freundlich isotherm fits better when considering the complete range of concentrations while the Langmuir isotherm shows a better fit at low concentrations. Usually, the CFN adsorption in AC fits well with Freundlich and Langmuir models as other authors have previously shown.^{14,15,26,29} Hamdaoui and Naffrechoux³⁰ have suggested for the Freundlich model that n values between 2 and 10 represent good adsorption, values ranging from 1–2 moderately difficult, while $n < 1$ is characteristic of poor adsorption. The fit of experimental data to the Freundlich isotherm model suggests heterogeneous adsorption and the value of the n parameter of 4.405 indicates a favorable adsorption process since the interaction between the CFN and the AC possibly follows a chemical mechanism. According to the Giles et al.³¹ classifications, the CFN adsorption isotherm corresponds to an L-type, as usually occurs

with dilute solutions. The initial trend suggests that as the available sites are occupied, it becomes more difficult for the solute to find binding sites thus, the molecule is more likely to be adsorbed flatly than vertically.

Table-5: Results of Parameters for the Adsorption Models

Langmuir	Freundlich	Dubinin-Redushkevich
$q_m = 719.036$	$K_F = 375.289$	$q_m = 698.242$
$b = 1.501$	$n = 4.405$	$K' = 1.209 \times 10^{-7}$
$R^2 = 0.907$	$R^2 = 0.955$	$R^2 = 0.785$
$APE = 10.39\%$	$APE = 6.68\%$	$APE = 11.9\%$

Regarding the kinetics of adsorption, CFN adsorption into the type A AC proceeds rapidly, reaching a high mass of adsorbate incorporated into the AC in the whole concentration range. By increasing the contact time beyond 20 min, the adsorption rate declines, thus leading to the equilibrium at 240 min for the diluted samples and 180 min for the most concentrated samples. The initial and fast adsorption rate is explained by the high availability of active sites on the adsorbent. As the active free sites are rapidly occupied, the adsorption rate decreases, and finally, the remaining sites are not occupied as a consequence of the repulsion forces between the adsorbed and the non-absorbed molecules.²⁶ The experimental kinetic parameters are summarized in Table-6.

Table-6: Pseudo-First and Pseudo-Second Order Kinetic Parameters for CFN Adsorption in Type A AC

Concentration (mg/g)	Pseudo-first order kinetics	Pseudo-second order kinetics
40	$K_1 (\text{min}^{-1}) = 0.0183$ $R^2 = 0.7984$ error = 17.89%	$K_2 (\text{g/mg.min}) = 0.00013$ $R^2 = 0.9987$ error = 3.63%
60	$K_1 (\text{min}^{-1}) = 0.0230$ $R^2 = 0.8245$ error = 15.45%	$K_2 (\text{g/mg.min}) = 0.00020$ $R^2 = 0.9993$ error = 3.78%
80	$K_1 (\text{min}^{-1}) = 0.0222$ $R^2 = 0.7816$ error = 17.73%	$K_2 (\text{g/mg.min}) = 0.00016$ $R^2 = 0.9993$ error = 4.49%

The experimental data fitted better to the pseudo-second order model, according to the observed R^2 values of over 0.99, compared to the considerably lower values calculated for the pseudo-first order model (0.78-0.82). This is also evidenced in the plots of simulated and experimental data displayed in Figure-1a, b, and c. Also, the error was lower for the pseudo-second order model, with values of 3.63%, 3.78%, and 4.49%, for 40, 60, and 80 mg/L of CFN, respectively. Therefore, the CFN adsorption process in type A AC follows a pseudo-second order kinetics, which is consistent with the previous works of CFN adsorption on other ACs.^{14,15,26,29} The pseudo-second order kinetics is considered a special case of Langmuir kinetics, in which the adsorbed amount is constant and the availability of binding sites depends on the adsorbate concentration at equilibrium.^{15,19} This model also indicates that CFN adsorption is controlled by the chemisorption, where electrons are shared between the CFN molecules and the functional groups on the AC surface.^{15,20}

CONCLUSION

The characterization of two activated carbons prepared from Colombian mineral coals was performed to investigate the adsorption capacity as an alternative for the treatment of wastewater containing caffeine. The adsorption studies showed that mineral coal from the Cundinamarca region in the center of the country has better adsorption properties, with maximum removal of 882.1 mg CFN/g AC at a 0.05 g/L of adsorbent dose. The higher iodine number and lower ash content led to a higher caffeine adsorption capacity. The higher surface area and pore volume also led to rapid adsorption kinetics approaching the equilibrium condition at approximately 10 minutes. In the concentration range explored the removal of the pollutant was not improved when increasing the AC ratio suggesting that the activated carbon was far from saturation in all cases. Further optimization of the AC to liquid ratio may contribute to a proper dosage of AC according to the caffeine concentration on wastewater. Since the type A carbon has a high adsorption capacity, an increase in the adsorbent load only increases the treatment cost without increasing the pollutant removal rate. The caffeine adsorption process was better described by Freundlich's model with a correlation

coefficient of 0.96 and 6.7% of the average error with respect to experimental data. This suggests a multilayer caffeine adsorption over a heterogeneous surface instead of monolayer adsorption. Similarly, the kinetic studies showed that experimental data fitted to the pseudo-second order kinetic model ($R^2=0.99$) indicating that adsorption is controlled by a chemical mechanism rather than by a physical mechanism. The high adsorption capacity exhibited by the activated carbon prepared from local mineral coal, in addition to its low cost in the country, places the activation of local mineral coals as a feasible option to add value to this low-price commodity. At the same time, those activated carbons could be used as a cost-effective alternative for wastewater treatment on coffee plantations aimed to reduce the impact of this activity on the surrounding ecosystems.

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