

Physicochemical Parameters of the Methylparaben Adsorption from Aqueous Solution Onto Activated Carbon and Their Relationship with the Surface Chemistry

Valentina Bernal,* Liliana Giraldo, and Juan C. Moreno-Piraján



Cite This: *ACS Omega* 2021, 6, 8797–8807



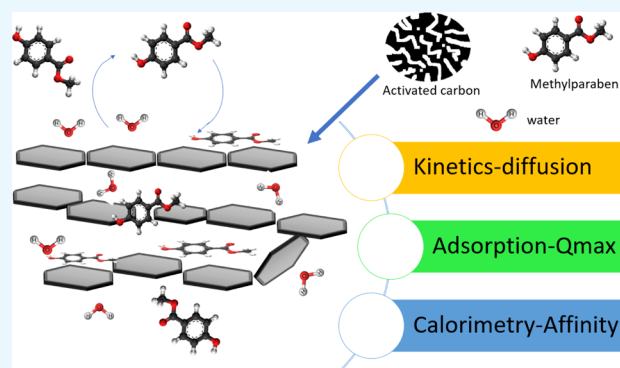
Read Online

ACCESS |

Metrics & More

Article Recommendations

ABSTRACT: The methylparaben adsorption from aqueous solution onto activated carbon is a relevant topic because of the toxicity of this compound for human and environmental health. The physicochemical parameters allow us to evaluate the performance of the adsorption and the relationship between the surface chemistry and the adsorbed amount of methylparaben. The effect of the solution chemistry on the adsorption was also evaluated. In this work, the methylparaben adsorption on three activated carbons with different physicochemical properties, specifically different contents of oxygenated groups and total basicity, is presented. Kinetic, equilibrium, and calorimetry tests were conducted. The maximum adsorbed amount of methylparaben was achieved on an activated carbon with basic characteristics, $Q_{\max} = 1.64 \text{ mmol g}^{-1}$; in the same activated carbon, the initial rate was $0.20 \text{ mmol g}^{-1} \text{ h}^{-1}$, and the value determined for the interaction enthalpy was $-12.6 \times 10^{-20} \text{ J molecules}^{-1}$, and the Gibbs energy change was close to $-14.96 \text{ kJ mol}^{-1}$.



INTRODUCTION

Methylparaben and other parabens are esters of the *para*-aminobenzoic acid; they are used in the cosmetic, alimentary, and pharmaceutical industry as antibacterial and antifungal preservatives in products with short shelf lives.¹

Methylparaben is considered an emerging pollutant by its ubiquitous presence in the water resources. In some cases, people use deep water wells for drinking water; therefore, they are exposed to the toxic effects associated with methylparaben and other pharmaceutical pollutants.^{2,3} In the literature, it was reported that the constant exposure to methylparaben generates modulation of the neutrophil function in humans and endocrine disruption associated with breast and ovary cancer.^{4,5}

It is a priority for governments to supply quality water to the population and meet the sustainable development goals proposed by the United Nations for the year 2030 and enforce the local and international technical quality standards such as the drinking water guidelines from the World Health Organization. For these reasons, water treatment plants are necessary in all countries.^{6–8}

The drinking water guidelines recommend a wide range of treatments for sanitation of raw water resources; one of them will be studied in this work because it is a tertiary wastewater treatment commonly used around the world.^{9,10} The adsorption allows the removal of inorganic and organic

pollutants depending on the adsorbent. Activated carbon is used as an adsorbent for its physicochemical properties such as the large surface area and microporosity.¹¹ For the removal of methylparaben, several adsorbents such as polymer resins, activated carbon, polymer nanoparticles, and so forth have been used. Table 1 given below summarizes some adsorbents reported in the literature and their capacity to adsorb methylparaben.

According to the data reported in Table 1, it is observed that with activated carbon, the highest adsorption capacity of methylparaben is achieved because of its large surface area and ease of preparation, but difficulties for its reuse exist.

Other techniques are used for the removal of methylparaben from the water resources; photocatalytic degradation is one of them. For this method, TiO_2 and ultraviolet light are used to convert methylparaben into CO_2 and water. However, 10 degradation compounds are produced, including dihydroxybenzene, a phenol that is also considered a pollutant. From the experimental point of view, this method is dependent on

Received: November 3, 2020

Accepted: December 2, 2020

Published: March 25, 2021



Table 1. Adsorbents and their Methylparaben Adsorption Capabilities

adsorbent	amount of methylparaben adsorbed (mmol g ⁻¹)	advantage	disadvantage	references
submicro-sized molecularly imprinted polymer	0.215	easy adsorbent preparation and high adsorption capacity	the regeneration of the adsorbent is carried out with methanol/HCl, which implies high costs	12
magnetic nanoparticles PS/Fe ₃ O ₄	0.023	easy reuse and the adsorption capacity is pH-independent	the adsorbent preparation requires several steps and the use of reagents that are toxic to the environment (2,2-azodiisobutyronitrile)	13
activated carbon-chitosan composite	0.56	used in real wastewater samples. large specific surface area easy reuse	the adsorption capacity is pH-dependent	14
lime and lemon waste (bioadsorbents)	0.11	easy adsorbent preparation and high adsorption capacity	no information is available on the reuse of the adsorbent and high variability of the starting material for the preparation of the adsorbent	15

the pH and oxygen concentration, variables that are difficult to maintain in a water treatment plant.¹⁶

The sonochemical and sonocatalytic destruction of methylparaben has also been reported in the literature. The results are similar to those obtained with photodegradation; there is the formation of a greater number of organic pollutants in the solution and the experimental conditions (200 kHz bath) are difficult to obtain in a water treatment plant.¹⁷

In conclusion, adsorption continues to be a good option to treat waters contaminated with methylparaben. In fact, when chemically modified activated carbons are used as adsorbents, an adsorption capacity of 1.45 mmol L⁻¹ is reached.¹⁸

In the heterogeneous adsorption (the adsorbent is a solid and the adsorbate is the solution), the surface energy of the adsorbent is compensated by the formation of interactions with the solvent (in greater proportion in the system) and the adsorbate; these interactions depend on the chemical groups on the activated carbon surface and the chemical structure of the adsorbate; when the adsorbent–adsorbate affinity is higher, a greater amount of adsorption will be achieved.

The adsorbate–adsorbent interactions can be formed with a specific chemical group on the activated carbon or several of them; in the first case, the process is considered homogeneous and it is described by Langmuir's model. In the second case, the process is heterogeneous by the formation of different interactions with the chemical groups on the adsorbent, and it can be described by models reported in the literature such as y/rj Freundlich model, Sips model, Toth model, and so forth.^{19,20}

For methylparaben adsorption onto activated carbon, the Langmuir model describes appropriately the equilibrium data (adsorption isotherms). In addition, Langmuir's model assumes that if the adsorbent–adsorbate interactions are one by one, a monolayer will be formed on the adsorbent surface and the energy of the process will only depend on these interactions because the interactions between the neighboring molecules adsorbed on the surface are negligible. The mathematical expression for the Langmuir model is shown in eq 1

$$Q = \frac{Q_m (\text{mmol/g}) K_L (\text{L/mmol}) C_e (\text{mmol/L})}{1 + K_L C_e} \quad (1)$$

where Q is an amount adsorbed at any concentration, Q_m is the maximum amount adsorbed, K_L is the Langmuir constant, and C_e is the equilibrium concentration.

The Langmuir constant is considered an equilibrium constant, if the adsorption process is carried out in dilute solutions where the activity coefficient is not affected. To cancel the units, K_L is multiplied by 55.5 mol L⁻¹.

Langmuir's constant represents the affinity constant because the adsorption depends on the number of active sites available to interact with the adsorbate; therefore, at low adsorbate concentrations, the adsorbent surface is not saturated and the filling of the active sites is fast; then, as the active sites decrease, the filling rate decreases until the monolayer formation. In aqueous solutions, unlike the gas-phase adsorption, three processes are carried out at the same time: the water adsorption and its subsequent desorption induced by the formation of the adsorbate–adsorbent interactions (adsorption). Therefore, according to Langmuir's model, when the constant is increasing, the amount adsorbed

increases; then, the adsorbent affinity by the adsorbate is higher than that of water.²¹

Although Langmuir's model explains how the adsorbate molecules interact with the adsorbent, it cannot be used to explain the kinetics of the process. Therefore, it is necessary to use other models to calculate the adsorption rate. The models that consider the adsorption rate only from physical aspects are the intraparticle diffusion and pseudo-first-order or Lagergren's model. In the intraparticle diffusion model, the kinetics is divided into three zones: (i) adsorption on the external surface, (ii) intraparticle diffusion into the carbonaceous matrix, and (iii) equilibrium. In this model, the kinetics depends on the amount adsorbed at the different times and the value of the external liquid film layer.²² In the pseudo-first-order model, the adsorption rate depends on the amount adsorbed at equilibrium time, the amount adsorbed at any time, and the kinetic constant.²³

Other models contemplate the chemical aspects involved in the kinetic adsorption, two of them are the pseudo-second-order model and Elovich's model; the first model is used to calculate the initial rate of adsorption and it is proportional to the square of active sites available to interact with the methylparaben. From Elovich's model, the desorption rate can be calculated; in this model, the amount of the adsorbate adsorbed at any time is related with the inverse of the desorption. The rate decreases exponentially as the amount adsorbed increases. In addition, Elovich's model describes the adsorption rate in heterogeneous materials as activated carbon.²⁴

The kinetic and thermodynamic parameters are related with the chemical properties in the system: chemical surface groups on the activated carbon, substituents on the chemical structure of the adsorbate, and pH or ionic strength of the solution.²⁵

The adsorbent–adsorbate affinity and its effects on the amount adsorbed can be evaluated through the calorimetry tests. Immersion calorimetry is the tool used in this work to measure the energy exchanged when the activated carbon is immersed in a pure liquid solution. In this work, the calorimetry tests are carried out in water and methylparaben solutions to determine the affinity between the different components of the system (activated carbon–water and activated carbon–methylparaben) from the energy released during the immersion of the adsorbent in the liquid. This parameter is important assuming that if the adsorbate–adsorbent affinity is higher, the amount of methylparaben adsorbed will increase until reaching the amount adsorbed on the monolayer.

The immersion of the activated carbon in water allows us to determine the energy released when the water molecules bind to surface groups on the adsorbent; then, the process is exothermic and ΔH is negative. Therefore, the lower value is associated with the greater affinity for the water.

When the immersion liquid is not water or any solvent but a solution, the enthalpy is associated with the surface affinity of the adsorbate and the water and other interactions in the system.

One of the limitations of the calorimetry is the impossibility to determine the enthalpy of adsorbate–adsorbate and adsorbate–solvent interactions. However, the adsorbate–adsorbate interactions are negligible in diluted solutions, and we assume that the adsorbate is adsorbed in its hydrated form.

The immersion enthalpy depends on the following:²⁶

- 1) The extension of the surface area on the activated carbon.
- 2) The chemical nature of the adsorbent and adsorbate (affinity, polarity, and pH in solution).
- 3) The porosity of the activated carbon.

This paper presents the adsorption, kinetic, and thermodynamic data of the methylparaben adsorption onto activated carbons with different physicochemical properties (mainly contents of oxygenated groups); their effect on the uptake was also evaluated. The kinetic (initial adsorption and desorption rate) and thermodynamic parameters (Gibbs energy and enthalpy change at different concentrations of the adsorbate) were determined for the process at 293 K.

RESULTS AND DISCUSSION

The adsorption performance is highly dependent on the physicochemical characteristics of activated carbon and the adsorbate; however the surface area, porosity, and content of surface groups on the activated carbon are the most relevant characteristics of the adsorption of organic compounds from aqueous solutions. Figure 1A shows the nitrogen adsorption/

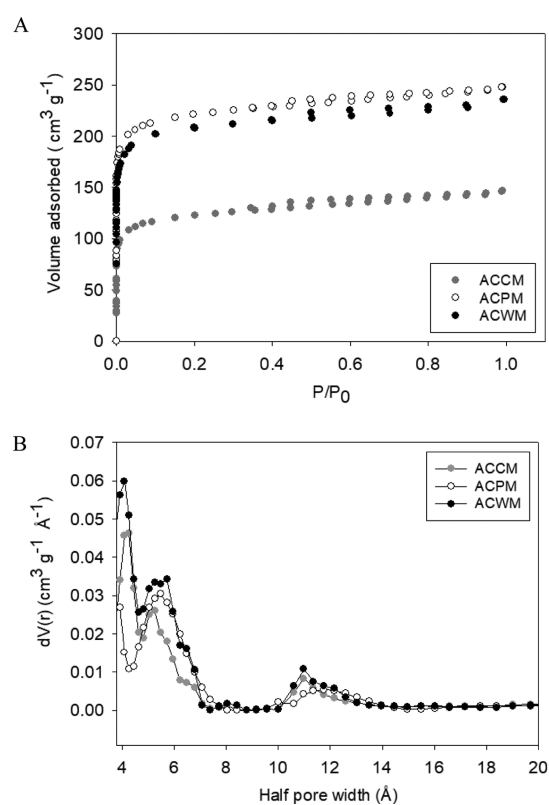


Figure 1. (A) Nitrogen adsorption/desorption isotherms (B) Pore size distribution for activated carbons (QSDFT-slit/cylindr.pores) ACWM, ACCM, and ACPM.

desorption isotherms, and Figure 1B shows the pore size distribution, while Table 2 summarizes the physical parameters obtained from the nitrogen adsorption isotherms, and Table 3 presents the chemical characteristics of the activated carbons ACWM, ACCM, and ACPM.

The nitrogen adsorption isotherms (Figure 1A) can be classified as type I (a) typical of activated carbons and other microporous adsorbents. In this type of isotherms, the uptake depends on the accessibility to the micropores and not to the

Table 2. Physical Properties of Activated Carbons ACCM, ACPM, and ACWM

	ACCM	ACWM	ACPM
surface area ($\text{m}^2 \text{g}^{-1}$)-BET	469	864	814
C	115	173	113
micropore volume ($\text{cm}^3 \text{g}^{-1}$)-DA	0.18	0.34	0.29
N	2.10	1.8	2.30
total pore volume ($\text{cm}^3 \text{g}^{-1}$)	0.21	0.35	0.34
% micropores	85.7	97.1	85.3

Table 3. Chemical Properties of Activated Carbons ACCM, ACPM, and ACWM

	ACCM	ACWM	ACPM
phenols content (molecules g^{-1}) $\times 10^{31}$	3.25	2.81	2.23
lactones content (molecules g^{-1}) $\times 10^{31}$	29.5	1.31	1.43
carboxylic acid (molecules g^{-1}) $\times 10^{31}$	6.38	1.34	3.95
total acidity (molecules g^{-1}) $\times 10^{31}$	39.5	5.45	5.60
total basicity (molecules g^{-1}) $\times 10^{31}$	44.3	44.7	123
amphoteric factor	0.89	0.12	0.05
pH_{pzc}	3.40	5.40	8.90

internal surface area of the adsorbent. The Brunauer–Emmett–Teller (BET) model was applied to the isotherms and the apparent surface area and the results show that this parameter decreases with the chemical and physical treatments carried out on the activated carbons. The modified activated carbon with nitric acid has a smaller apparent surface area than the activated carbon subjected to thermal treatment. The same trend is found for the micropore volume, where the sample without modification not only had the largest surface area but also a greater number of micropores. Indeed, the percentage of micropores with regard to the total porosity is higher than 85% in all samples, but in the activated carbon ACWM, it increases 10% more. Thus, by decreasing the amount of micropores in the activated carbons, the amount of nitrogen adsorbed decreases and subsequently the apparent surface area decreases.

The thermal treatment was carried out on the activated carbon to decrease the oxygenated surface groups by their thermal instability at temperatures higher than 973 K;²⁷ however, above 1073 K, the physical structure of the activated carbon collapses and pore sizes are increased to larger than 2 nm. Then, although the activated carbons ACWM and ACPM have a similar pore volume, the number of micropores decreases in ACPM.²⁸

It is observed in the pore size distribution (Figure 1B) that the greatest number of pores is in the range between 8–16 and 20–28 Å. This implies that the methylparaben will not have restricted diffusion because its molecular size is $8.69 \times 5.02 \text{ \AA}^2$.

The oxidation with nitric acid generates a great number of oxygenated surface groups as carboxylic acids, lactones, or phenols on the activated carbon. These groups are usually formed in the edge of micropores; therefore, they generate diffusive restriction to nitrogen adsorption and the pore volume or surface area decreases.^{27,29}

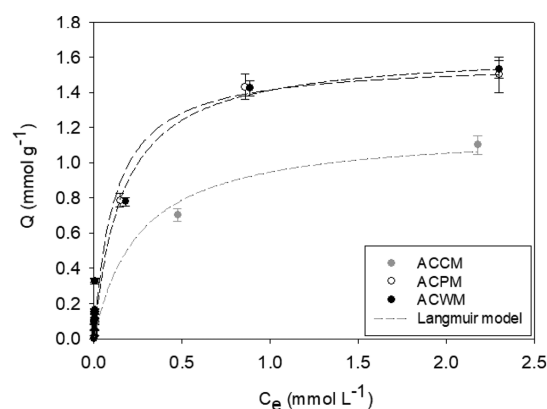
The chemical properties corroborate the effect of the treatments on the activated carbons. In ACCM, the content of phenols, lactones, and carboxylic acids increases up until 29% (lactones) compared with that in the ACWM; however, the total basicity does not change except in ACPM; this behavior can be explained by the thermal treatment and its

generation of π -electrons after the break of carbonaceous chains or aromatic rings. The π -electrons are considered Lewis bases; therefore, they are contributing to the total basicity. Moreover, the free radicals generated in the thermal process can react with the environmental oxygen creating new oxygenated surface groups.^{30,31}

The amphoteric properties of activated carbon can modify the adsorption behavior depending on the pH of solution and the ionization of the adsorbate. The amphoteric factor (AF) is defined as the ratio between the total acidity and total basicity; when the result is unity, the surface can react with acids or bases because the content of acid groups is equal to that of the basic groups. If the values are greater than 1, the surface is acidic and the adsorbent–adsorbate affinity will be toward the basic adsorbates. However, if the total basicity is highest as is the case of the activated carbons and the AF does not exceed the unity; then, the highest value corresponds to the acidic surface. On the contrary, lower values indicate higher affinity for acidic adsorbates.

The pH_{pzc} indicates the electric charge on the activated carbon surface in solution. At the pH_{pzc} , the net electric charge on the surface is zero; when the pH of solution is higher than the pH_{pzc} , the electric charge on the surface is negative. In acidic activated carbons, the pH_{pzc} is lower than in basic activated carbons because acid groups deprotonate at lowest values of solution pH. The basic activated carbons can form interactions with π -cations; then, the pH increases by adsorption of hydroniums.³²

The methylparaben adsorption isotherms on the activated carbons are shown in Figure 2. The tests were carried out at 293 K and the equilibrium data were fitted with Langmuir's model; the results of the parameters are presented in Table 4.

**Figure 2.** Methylparaben adsorption isotherms on activated carbons ACCM, ACPM, and ACWM at 293 K.

The maximum adsorption capacity was achieved on the activated carbon ACPM despite that it does not have the

Table 4. Parameters for the Langmuir Model Applied to Methylparaben Adsorption on Activated Carbons ACCM, ACPM, and ACWM

	Q_{max} (mmol g^{-1})	K_{L}	molecules of methylparaben on the monolayer $\times 10^{19}$	R^2
ACCM	1.18	217.6	7.11	0.93
ACWM	1.58	345.6	9.51	0.98
ACPM	1.64	480.6	9.88	0.97

largest surface area or the greatest number of micropores; this indicates that the methylparaben adsorption depends on the surface groups on the adsorbent and solution chemistry.

The amount adsorbed follows the trend $Q_{\max} \text{ ACPM} > Q_{\max} \text{ ACWM} > Q_{\max} \text{ ACCM}$, which is the same presented by the total basicity. In the literature, it has been reported that the main interactions on the adsorption of aromatic compounds on the activated carbons are the π -stacked interactions, which are directly related with the number of π -electrons available on the adsorbent surface; then, the methylparaben uptake is greater on the activated ACPM because it has a greater number of π -electrons available to interact with the adsorbate.

Likewise, oxidized activated carbon has a greater number of oxygenated groups; they are part of the adsorbent's structure and they can deactivate the aromatic rings of graphenic layers decreasing their reactivity.

Langmuir's model assumes that the adsorbate forms a monolayer on the adsorbent surface; therefore, if the mass of activated carbon is constant, the maximum amount adsorbed corresponds to the number of adsorbate molecules on the activated carbon surface. These data will be used to calculate the energy exchanged during the formation of adsorbate–adsorbent interactions per molecule adsorbed.

The equilibrium or affinity constant is increasing proportionally to the amount of methylparaben adsorbed, which is an expected behavior because if the adsorbate–adsorbent affinity is higher, the uptake increases, as shown in Figure 3.

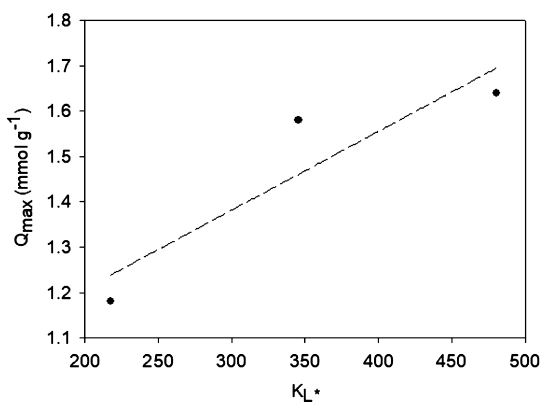


Figure 3. Relationship between the maximum adsorption capacity and the equilibrium constant.

The effect of solution chemistry was also evaluated by its importance in the adsorption of organic molecules on activated carbon and its relationship with surface chemistry. Table 5 summarizes the most relevant parameters of the chemistry solution in the methylparaben adsorption.

The pK_a value for methylparaben is 8.20 and its ionization increases with the solution pH; in water, this value is close up to 6–7, but this value changes with the presence of activated

Table 5. Equilibrium pH in the Adsorption, Percent Ionization for Methylparaben, and Charge on the Surface of the Activated Carbons ACCT, ACPM, and ACWM

	pH equilibrium	% ionization	electric charge AC
ACCM	3.07	1	+
ACWM	7.18	10	–
ACPM	7.85	33	+

carbons because they can release H^+ ions into the medium, that is, the solution pH varies depending on the number of oxygenated groups on the surface. In ACCM, the solution pH is acidic and the ionization of methylparaben can be negligible; additionally, the electric charge of the adsorbent is positive; then, the coulomb forces are not predominant in this system. On the contrary, in ACWM and ACPM, the number of ionized molecules (negatively charged) is increasing with the solution pH and it cannot be negligible; therefore, repulsive forces are present in the methylparaben–ACCM interaction and it is disfavoring the uptake. The electrostatic attractive forces between methylparaben and ACPM increase the effect of the π -stacked interactions.

In other work, the results of potentiometric titration for the samples were reported;³³ however, the pK_a distribution for the different oxygenated groups on the surface allows us to determine the number of groups that are deprotonated at a certain pH value in the solution. The adsorption data show that the affinity (represented by K_L) is proportional to the ionized molecules of the adsorbate and inversely proportional to the ionized functional groups (negative charge) on the activated carbon at equilibrium pH (Figure 4).

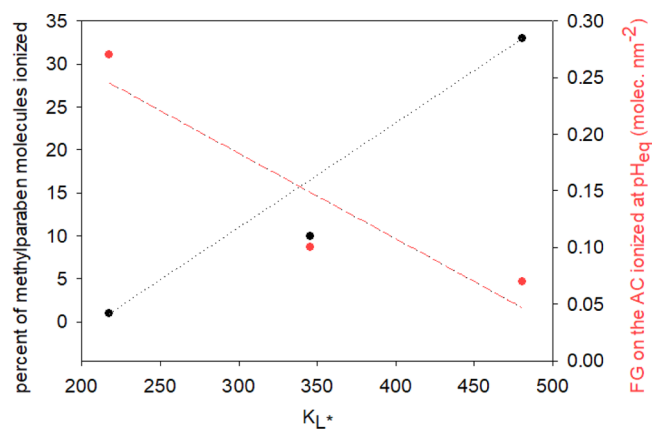


Figure 4. Relationship between the ionized molecules of methylparaben, ionized surface groups on the activated carbon, and the equilibrium constant.

The amphoteric properties of the adsorbent surface can affect the uptake; methylparaben is a weak acidic compound, so its affinity to acidic surfaces is lower; hence, the uptake increases at lowest values of the amphoteric factor, as shown in Figure 5. This trend is related with the deprotonation of acid groups and the generation of repulsive forces.

The kinetics were also determined at 293 K using a solution of methylparaben (1.31 mmol L^{-1}). The data obtained were fitted with two models where the limiting step of adsorption is the diffusion in one and the limiting step is the chemistry reactions in the other; we assume that these reactions are physical interactions between the adsorbent and adsorbate.

The kinetic data are presented in Figure 6; they were fitted with the intraparticle diffusion model and the pseudo-first-order, pseudo-second-order, and Elovich model. The parameters for each model are shown in Tables 6–9.

It was observed that the best-fitting models for the experimental kinetic data are those models used to describe chemical adsorption. For all models, the kinetic constant increases with the following trend $K_c \text{ ACPM} > K_c \text{ ACWM} > K_c \text{ ACCM}$; indeed, it is the same trend found for Q_{\max} .

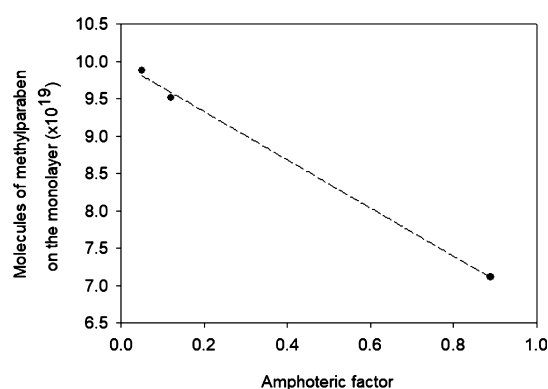


Figure 5. Relationship between the molecules of methylparaben on the monolayer and the amphoteric factor of activated carbons ACCM, ACPM, and ACWM.

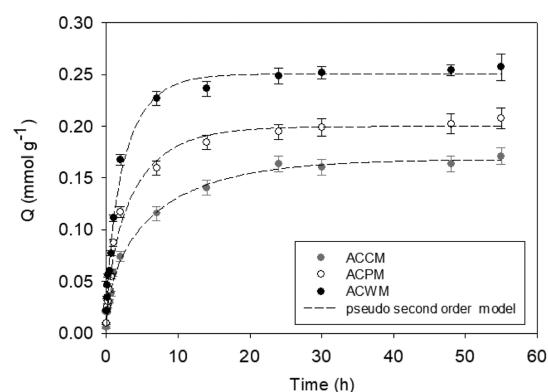


Figure 6. Adsorption kinetics for methylparaben onto activated carbons ACCM, ACPM, and ACWM.

Therefore, it corroborated the relationship between the kinetics and surface chemistry.

The intraparticle diffusion model divides the experimental data into three regions: boundary layer diffusion and intraparticle diffusion and reaction. For all samples, $K_{BL} > K_{IP} > K_R$, so the rate is higher in K_{BL} and decreases with the passage of time and the adsorbate diffusion through the carbonaceous matrix. Additionally, the external liquid film layer (C) is inversely proportional to the kinetic constant; therefore, if the external liquid film layer is formed after the diffusion stage, the active sites are microporous.

The pseudo-first-order model presents a percentage of error greater than the pseudo-second-order model. Thus, the adsorption rate of methylparaben depends on the square of the number of active sites available. The parameter V_0 represents the initial rate of the adsorption and it shows that the rate is greater in the activated carbon ACPM because of the number of π -electrons available to interact with the adsorbate.

The initial rate is also related with the adsorption of methylparaben and the solvent desorption on the adsorbent surface. If the adsorbent–solvent affinity is greater than that of adsorbent–methylparaben, more time will be required to displace the solvent on the surface and the active sites available to bind the methylparaben will be increased. Figure 7 shows the relationship between the initial adsorption rate, total basicity, and content of phenols on the activated carbon, the last correlation was made because the increases in the phenol content on the activated carbon are directly related with the affinity of the water; thus, the initial rate of methylparaben adsorption is inversely proportional to the number of phenol groups on the activated carbon surface. The total basicity represents the number of π -electrons (Lewis bases) that interact with the methylparaben (weak acid) and the relationship with the initial rate is directly proportional.

Elovich's model allows us to determine the initial rate, which follows the same trend found with the pseudo-second-order model, and the desorption rate of the adsorbate given that the adsorption is a dynamic equilibrium. It is observed that the desorption rate decreases with the adsorbent–adsorbate affinity represented as K_L and maximum adsorption capacity, Q_m . At the same time, the desorption rate increases, if the surface affinity of water is greater than that of methylparaben. For this case, the desorption rate is directly proportional to phenol content on the surface because these functional groups interact with the water and increase the solvent adsorption, as shown in Figure 8.

To determine the magnitude of the adsorbent–adsorbate and adsorbent–water interactions, we carried out calorimetric test.

In Figure 9, are presented the immersion enthalpy values of activated carbons ACCM, ACPM, and ACWM; it is observed that the immersion enthalpy increases ($\Delta H_{imm}ACCM > \Delta H_{imm}ACWM > \Delta H_{imm}ACPM$) with the phenol content on the activated carbons³⁴ and amphoteric factor. In Figure 9, it is observed that the immersion enthalpy is inversely proportional to the amphoteric factor. The water is an amphoteric molecule; thus, it can interact with acids or bases. Therefore, the increase in the enthalpy is related with the formation of hydrogen bonds between the solvent and acidic groups on the activated carbon.

The immersion and interaction enthalpy values between methylparaben and the activated carbons ACCM, ACPM, and ACWM are presented in Table 10.

The immersion enthalpies at low concentrations have values between -9.38 and -18.2 J g^{-1} ; the lowest values are achieved on the activated carbon ACCM, but this behavior is related with the solvent interaction. At medium and high concentrations, the number of methylparaben molecules can induce the displacement of the water on the surface and enthalpy

Table 6. Parameters of the Intraparticle Diffusion Model for Methylparaben Adsorption on Activated Carbons ACCM, ACPM, and ACWM.^a

compound	boundary layer diffusion (BL)			intra-particle diffusion (IP)			reaction (R)		
	K_{BL}	C_{BL}	R^2	K_{IP}	C_{IP}	R^2	K_R	C_R	R^2
ACCM	0.04	0.004	0.93	0.03	0.03	0.99	0.003	0.15	0.52
ACWM	0.06	0.002	0.97	0.04	0.05	0.97	0.006	0.17	0.94
ACPM	0.09	0.008	0.99				0.006	0.21	0.91

^aK: $\text{mmol g}^{-1}\text{h}^{-1}$ C: $\text{mmol g}^{-0.5}$

Table 7. Parameters of the Pseudo-First-Order Model for Methylparaben Adsorption on Activated Carbons ACCM, ACPM, and ACWM

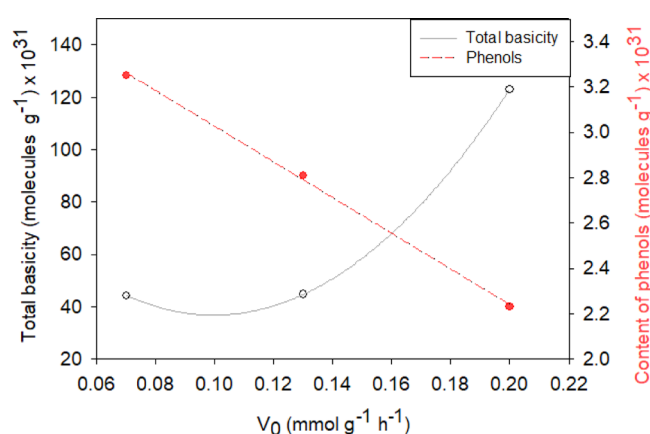
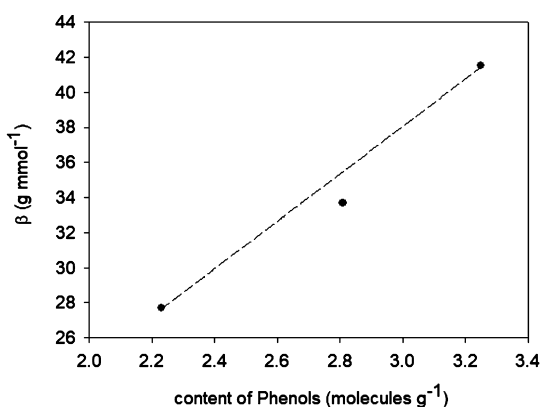
	compound	Q_{TSS} (mmol g ⁻¹)	Q_{Exp} (mmol g ⁻¹)	% error	K_{PFO} (h ⁻¹)	R^2
ACCM	methylparaben	0.16	0.17	5.3	0.34	0.98
ACWM		0.19	0.21	10	0.51	0.98
ACPM		0.25	0.26	3.9	0.61	0.98

Table 8. Parameters of the Pseudo-Second-Order Model for Methylparaben Adsorption on Activated Carbons ACCM, ACPM, and ACWM

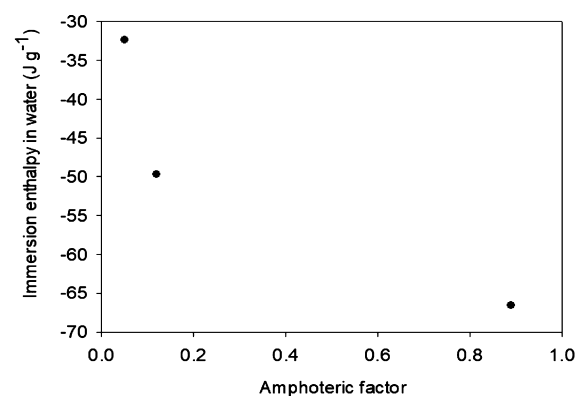
	compound	Q_{TSS} (mmol g ⁻¹)	Q_{Exp} (mmol g ⁻¹)	% error	K_{PSO} (g mmol ⁻¹ h ⁻¹)	V_0 (mmol g ⁻¹ h ⁻¹)	R^2
ACCM	methylparaben	0.17	0.17	0	2.47	0.07	0.99
ACWM		0.21	0.21	0	2.94	0.13	0.99
ACPM		0.26	0.26	0	2.99	0.20	0.99

Table 9. Parameters of the Elovich Model for Methylparaben Adsorption on Activated Carbons ACCM, ACPM, and ACWM

	compound	α (mmol g ⁻¹ h ⁻¹)	β (g mmol ⁻¹)	R^2
ACCM	methylparaben	0.43	41.5	0.94
ACWM		0.63	33.7	0.95
ACPM		1.10	27.7	0.94

**Figure 7.** Relationship between the initial rate of methylparaben adsorption on activated carbons ACCM, ACPM, and ACWM, their total basicity, and content of phenols.**Figure 8.** Relationship between the desorption rate (β) and content of phenols on the activated carbons ACCM, ACPM, and ACWM.

decreases to values lower than those determined at low concentrations of methylparaben.

**Figure 9.** Relationship between the immersion enthalpies of activated carbons on ACCM, ACPM, and ACWM in water and their amphoteric factor.**Table 10.** Enthalpy Changes for Methylparaben Adsorption on Activated Carbons ACCM, ACPM, and ACWM

	initial concentration (mmol L ⁻¹)	ACCM	ACWM	ACPM
immersion enthalpy (ΔH_{imm}) J g ⁻¹	0.33	-17.8	-15.4	-11.4
	0.66	-18.2	-10.1	-9.38
	1.32	-30.3	-39.7	-25.4
	3.29	-30.7	-54.0	-41.1
	6.58	-69.5	-59.3	-49.7
interaction enthalpy (ΔH_{AC-MET}) J g ⁻¹	0.33	48.8	41.3	21.0
	0.66	48.4	39.5	23.0
	1.32	36.0	10.0	6.99
	3.29	36.3	-4.27	-8.73
interaction enthalpy at the monolayer concentration (ΔH_{AC-MET}^M) J molecules ⁻¹ × 10 ⁻²⁰	6.58	-4.08	-10.1	-12.6

The interaction enthalpy is directly related with the adsorbent–adsorbate affinity; the positive enthalpy values (endothermic) indicate that the system requires energy from the surroundings to break the solvent–adsorbent interactions or the adsorbate–solvent interactions (hydration layer); however, it is assumed that methylparaben is adsorbed in its hydrated form. The exothermic enthalpy changes indicate the formation of new interactions.

For ACCM, the interaction enthalpies for methylparaben adsorption are positive until reaching the concentration of 3.29

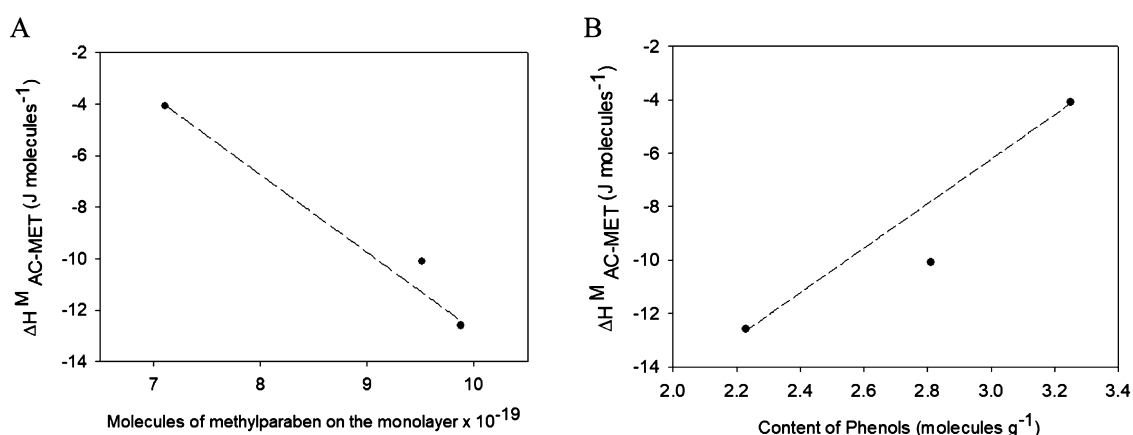


Figure 10. Relationship between the interaction enthalpy and (A) number of molecules on the monolayer or (B) content of phenols on the activated carbons.

mmol L⁻¹; this shows the highest affinity of this activated carbon to the water. At the highest working concentration, the enthalpy values are negative in all activated carbons, indicating that the active sites in the activated carbon have been occupied by the methylparaben.

Figure 10 A shows that an increase in the number of molecules on the monolayer generates a higher interaction enthalpy; as the process releases energy, it has more stability. Therefore, the stability of the systems follows the trend ACCM > ACWM > ACPM, which is contrary to that of the amphoteric factor and the high content of phenols on the activated carbons (Figure 10 B).

The contribution of the ester group was calculated using the interaction enthalpy at 6.58 mmol L⁻¹ and the interaction enthalpy was calculated for the phenol under the same conditions of concentration and temperature. Then, the Hess law was applied, and the results are shown in Figure 11.

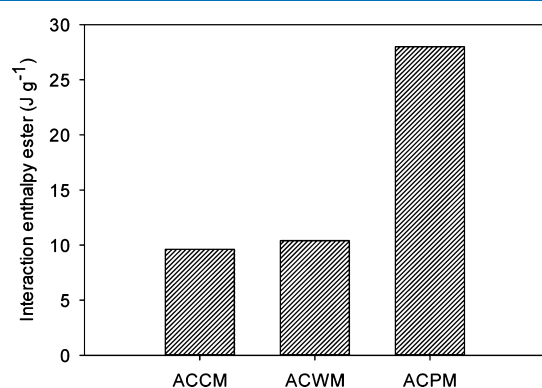


Figure 11. Contribution of the ester group to the interaction enthalpy of methylparaben adsorption on activated carbons ACCM, ACPM, and ACWM.

The contribution of the ester group to the enthalpy is endothermic; thus, the highest contribution to the adsorbate–adsorbent interaction is by the phenolic ring; it proves that the activated carbons have great affinity to molecules containing functional groups capable of forming hydrogen bonds or π -stacked interactions. The low contribution of the ester group to the adsorbate–adsorbent interactions is associated with its volume, which can generate steric hindrance. In ACPM, the enthalpy value is higher because the phenolic ring is

deprotonated and increases the electrostatic forces in the system.

Finally, the equilibrium constant was used to determine the Gibbs energy change using eq 2. The results are presented in Table 11.

$$\Delta G = -RTL \ln K_L \quad (2)$$

R is the gas constant and T is the temperature in Kelvin.

Table 11. Gibbs Energy Change for Methylparaben Adsorption on Activated Carbons ACCM, ACPM, and ACWM

	ACCM	ACWM	ACPM
ΔG (kJ mol ⁻¹)	-13.1	-14.2	-15.0

All values for Gibbs energy change are negative; therefore, the adsorption of methylparaben on activated carbons is classified as a spontaneous process.

CONCLUSIONS

The methylparaben adsorption on activated carbons depends on the chemical characteristics of the adsorbent and solution. The maximum adsorbed capacity (Q_{\max} ACPM = 1.64 mmol g⁻¹) decreases on activated carbons with a great number of acidic groups because these groups increase the affinity to the water; additionally, a highest value of the amphoteric factor is related with a decrease in the amount of methylparaben adsorbed because methylparaben is a weak acid and its affinity is to basic surfaces.

The initial rate of adsorption is inversely proportional to the content of phenol groups on the activated carbon because these groups favor the formation of adsorbent–solvent interactions and increase the desorption rate.

The immersion enthalpies have values between -9.38 and -69.5 J g⁻¹. The values are greater when the concentration of methylparaben increases, indicating the displacement of water on the adsorbent surface.

The Gibbs energy change is negative in all systems; the values are between -13 and -15 kJ mol⁻¹.

METHODOLOGY

Activated Carbons. Three activated carbons were used for this study. ACWM is an activated carbon without modification; this adsorbent was acquired commercially and made from

coconut shell and physical activation with CO₂ according to the safety datasheet attached by the manufacturer. The activated carbon was conditioned for its use by immersing it in dilute HCl solution and washing with distilled water until the wash waters had a constant pH (5–6). Some physicochemical characteristics reported by the manufacturer are shown in Table 12.

Table 12. Safety Datasheet of the Activated Carbon ACWM

trade	Carbochem LQ-900S (Carbochem Inc., U.S.A)
activation	physical, CO ₂ , 1073 K
particle size	1–1.5 mm
iodine number	850–950 mg I g ⁻¹
density	50–500 g L ⁻¹

The activated carbon ACWM was subjected to chemical and physical treatments to modify its initial properties. The chemically modified activated carbon was called ACCM. A quantity of ACWM was weighed and then, it was immersed in nitric acid solution (30 g of ACWM/600 mL of HNO₃ solution 5 M) at boiling point for 2 h; this treatment oxidized the chemical groups on the surface. Once the chemical treatment has been carried out, the adsorbent was washed with water at room temperature. The wash was repeated until the wash waters had a constant pH (3–4). Before storage, the adsorbent was put in an oven to dry the sample at 383 K. Finally, the activated carbon was stored in an amber glass container.

ACPM is the name of the activated carbon modified by thermal treatments. A quantity of ACWM was weighed and then, it was deposited in a quartz cell and put in a furnace at 1173 K for 2 h. The heating ramp was 2 K min⁻¹ in a nitrogen (inert) atmosphere. Once the procedure has finished, the activated carbon is left in the furnace with nitrogen flow until the next day. The activated carbon was stored in an amber glass container.

The physicochemical characterization of activated carbons was determined by nitrogen adsorption at 77 K, Boehm titration, and mass titration. The detailed procedure was previously published.³⁵ However, some aspects will be briefly reported. The physical properties of activated carbons were determined using the nitrogen adsorption isotherms and mathematical models such as the BET model to determine the surface area, Dubinin–Astakhov model to calculate the micropore volume, and density functional theory to calculate pore size distribution from the kernels charged in software of the sortometer (Quantachrome Instruments, Anton Paar, U.S.A).

The chemical characteristics were determined by Boehm and mass titration. Boehm titration is a back titration of basic solutions (with different strengths) that have been previously put in contact with the activated carbon until they reach a chemical equilibrium. It allows us to determine the content of carboxylic acids, lactones, and phenols on the activated carbon. In the case of the total basicity, the procedure changes and an acid is used as the immersion liquid.³⁶

Mass titration is used to determine the p*H*_{pzc}; with this value, the electric charge on the adsorbent surface in solution can be known.³⁷

Adsorption Tests. For the adsorption tests, the concentration range selected for the methylparaben solutions was between 0.07 and 6.58 mmol L⁻¹. These solutions were

prepared from a stock solution with a concentration of 13.2 mmol L⁻¹, which was made of 2 g of analytical-grade methylparaben (PanReac chemistry SLU, Castellar del Vallès, Barcelona, Spain) and then, it was added to 1 L of distilled water; the solution was stirred at 150 rpm and stored at 293 K. The working solutions were prepared with distilled water and an adequate aliquot.

A quantity of 100 mg of the activate carbons (ACWM, ACCM, and ACPM) is weighed and put in an amber glass containers and 25 mL of methylparaben solution was added and stirred at 100 rpm for 10 min. The containers were stored for 10 days at room temperature (293 ± 1 K) with sporadic agitation (100 rpm), as it was reported in previous studies.³⁸

At 10 days, an aliquot of the solution in the container is taken and the remaining concentration of methylparaben was determined by UV–vis spectroscopy at λ_{max} = 254 nm (GENESYS 10S Vis spectrophotometer, Thermo Fisher Scientific, Madison, WI, USA), and the calibration curves were previously characterized. The adsorbed amount of methylparaben for each concentration and activated carbon was calculated using the equation

$$Q = \frac{(C_0 - C_e \text{ (mmol/L)})V \text{ (L)}}{mAC \text{ (g)}} \quad (3)$$

where *Q* (mmol g⁻¹) is the amount adsorbed; *C*₀ is the initial concentration of methylparaben in solution before the adsorption; *C*_e is the adsorbate concentration at equilibrium; *V* is the volume of the solution used for adsorption tests; and *m* represents the activated carbon mass.

The experimental data were fitted with the Langmuir model using the nonlinear equation.

Kinetics. The kinetic tests were carried out following the same procedure used in the adsorption test but the concentration of the methylparaben solution was 1.31 mmol L⁻¹. The containers with the activated carbon and solution were stirred each for 15 min at 100 rpm and room temperature. An aliquot of the solution is taken from the containers each at 5 min during the first hour and then every half hour until the fifth hour and finally every hour until the methylparaben concentration remains constant. The remaining concentration in the supernatant was determined by UV–vis spectroscopy at λ_{max} = 254 nm and the mass balance was determined by eq 7. The analyses were carried out at 293 K.

The kinetic data were adjusted with the following models: intraparticle diffusion (eq 4), pseudo-first and pseudo-second-order model (eqs 5–7) and Elovich model (eq 8).

$$q_t = K_{ID} \text{ (mmol/g h)} t^{0.5} \text{ (h)} + C \text{ (mmol/}\sqrt{\text{g)}} \quad (4)$$

where *K*_{ID} is a kinetic constant, *t* is the time, and *C* represents the external liquid film layer

$$\frac{\partial q_t}{\partial t} = K_{PFO} \text{ (h}^{-1}\text{)}(q_e - q_t) \text{ (mmol/g)} \quad (5)$$

where *K*_{PFO} is a kinetic constant and *q*_e and *q*_t are the amount adsorbed at equilibrium and at each time, respectively.

$$\frac{\partial q_t}{\partial t} = K_{PSO} \text{ (g/mmol h)} (q_e - q_t)^2 \quad (6)$$

$$V_0 = K_{PSO} q_e^2 \quad (7)$$

where K_{PSO} is a kinetic constant and V_0 is the adsorption initial rate.

$$q_t = \left(\frac{1}{\beta \text{ (g/mmol)}} \text{Ln} (\alpha \text{ (mmol/g h)} \beta t) \right) \quad (8)$$

where β is the desorption rate and α is the adsorption rate.

Calorimetry Test. Immersion enthalpies were determined for activated carbons ACWM, ACCM, and ACPM in methylparaben solutions at 293 K. The concentration range of the solution was divided into three groups to determine the enthalpy changes: 0.33–0.66 mmol L⁻¹ for low concentrations, 1.32 mmol L⁻¹ for intermediate concentrations, and 3.29–6.58 mmol L⁻¹ for high concentrations.

The instrument used to carry out the tests was a heat conduction microcalorimeter type Tyan. The calorimeter is made up of a stainless-steel cell that is embedded in a metal block. The measurement system is through thermopiles that surround the cell, and they determine the energy transferred when the activated carbon is put into contact with the immersion liquid. The energy released during this process is visualized in the calorimeter as electric potentials.

A total of 10 mL of the immersion liquid was put in the cell (water or methylparaben solutions); a glass ampoule containing 100 mg of activated carbon is fitted into the lid of the calorimeter, and the calorimeter is capped and turned on. The potential recording is started until obtaining a baseline and then, the glass ampoule is broken by hitting it against the lower wall of the cell; the electric potential increases to a maximum value and begins to decrease to the baseline. The calorimeter requires electric calibration. The immersion enthalpy is represented by eq 9 and can be calculated with eq 10.

$$\begin{aligned} \Delta H_{\text{imm}} S \ln(\text{J/g}) &= \Delta H_{\text{AC-H}_2\text{O}} (\text{J/g}) + \Delta H_{\text{AC-MET}} (\text{J/g}) \\ &+ \Delta H_{\text{H}_2\text{O-H}_2\text{O}} (\text{J/mol}) \\ &+ \Delta H_{\text{H}_2\text{O-MET}} (\text{J/mol}) \\ &+ \Delta H_{\text{MET-MET}} (\text{J/mol}) \end{aligned} \quad (9)$$

$$\begin{aligned} \Delta H_{\text{imm}} \\ &= \frac{K_{\text{calorimeter}} (\text{watts/V}) * \text{AUC immersion peak (V*s)}}{\text{mass of activated carbon (g)}} \end{aligned} \quad (10)$$

where $K_{\text{calorimeter}}$ represents the calorimeter constant obtained by electric calibration. AUC is the area under the curve of the immersion peak.

The assays were made in water to determine the adsorbent–solvent affinity; the test was also carried out using the methylparaben solutions. With these values, the interaction enthalpy can be calculated using the Hess law, as shown in eq 11. The interaction enthalpy measures the adsorbate–adsorbent affinity.

$$\Delta H_{\text{AC-MET}} (\text{J/g}) = \Delta H_{\text{imm}} S \ln(\text{J/g}) - \Delta H_{\text{AC-H}_2\text{O}} (\text{J/g}) \quad (11)$$

In addition, phenol solutions (at the same concentration of methylparaben) were used to determine the contribution of the ester group to the adsorbate–adsorbent interactions because methylparaben contains the phenolic ring, as shown

in Figure 12. This test was only carried out at 6.58 mmol L⁻¹ and using water as a solvent.

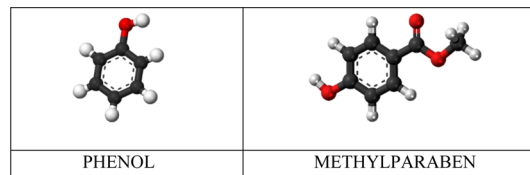


Figure 12. Chemical structures of the phenol and methylparaben.

The black spheres represent carbon atoms, the white spheres represent hydrogen atoms, and the red spheres represent oxygen atoms.

AUTHOR INFORMATION

Corresponding Author

Valentina Bernal – Departamento de Química, Universidad de los Andes, Bogotá, D. C 11711, Colombia; orcid.org/0000-0001-6901-7773; Phone: +573394949 ext. 3478; Email: v.bernal2@uniandes.edu.co

Authors

Liliana Giraldo – Departamento de Química, Universidad Nacional de Colombia, Bogotá, D. C 01, Colombia

Juan C. Moreno-Piraján – Departamento de Química, Universidad de los Andes, Bogotá, D. C 11711, Colombia

Complete contact information is available at: <https://pubs.acs.org/10.1021/acsomega.0c05368>

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

All authors acknowledge the financial support provided by the Vice Presidency for Research & Creation publication fund at the Universidad de los Andes.

REFERENCES

- (1) Li, J.; Jiang, J.; Pang, S. Y.; Sun, S.; Wang, L.; Zhou, Y.; Wang, Z.; Gao, Y. Oxidation of Methylparaben (MeP) and P-hydroxybenzoic Acid (p-HBA) by Manganese Dioxide (MnO₂) and Effects of Iodide: Efficiency, Products, and Toxicity. *Sci. Total Environ.* **2019**, *661*, 670–677.
- (2) Wang, J.; Liu, Y.; Kam, W. R.; Li, Y.; Sullivan, D. A. Toxicity of the Cosmetic Preservatives Parabens, Phenoxyethanol and Chlorphenesin on Human Meibomian Gland Epithelial Cells. *Exp. Eye Res.* **2020**, *196*, 108057.
- (3) Matwiejczuk, N.; Galicka, A.; Zaręba, I.; Brzóska, M. M. The Protective Effect of Rosmarinic Acid against Unfavorable Influence of Methylparaben and Propylparaben on Collagen in Human Skin Fibroblasts. *Nutrients* **2020**, *12*, 1282.
- (4) Nowak, K.; Jabłońska, E.; Radziwon, P.; Ratajczak-Wrona, W. Identification of a Novel Target for the Action of Endocrine Disrupting Chemicals: Inhibitory Effect of Methylparaben on Human Neutrophil Functions. *Environ. Sci. Pollut. Res.* **2020**, *27*, 6540–6548.
- (5) Kizhedath, A.; Wilkinson, S.; Glassey, J. Assessment of Hepatotoxicity and Dermal Toxicity of Butyl Paraben and Methyl Paraben Using HepG2 and HDFn in Vitro Models. *Toxicol. Vitro* **2019**, *55*, 108–115.
- (6) Griggs, D.; Stafford-Smith, M.; Gaffney, O.; Rockström, J.; Öhman, M. C.; Shyamsundar, P.; Steffen, W.; Glaser, G.; Kanie, N.;

Noble, I. Sustainable Development Goals for People and Planet. *Nature* **2013**, *495*, 305–307.

(7) Connor, R. *The United Nations World Water Development Report 2015: Water for a Sustainable World*, 1st ed.; United Nations Educational, Scientific and Cultural Organization: Paris, 2015; pp 37–41.

(8) World Health Organization *Guidelines for Drinking-Water Quality*, 3rd ed.; WHO Library Cataloguing-in-Publication Data: Geneva, 2008; pp 485–503.

(9) Tahar, A.; Choubert, J.-M.; Coquery, M. Xenobiotics Removal by Adsorption in the Context of Tertiary Treatment: A Mini Review. *Environ. Sci. Pollut. Res.* **2013**, *20*, 5085–5095.

(10) Marañón, E.; Castrillón, L.; Fernández-Nava, Y.; Fernández-Méndez, A.; Fernández-Sánchez, A. Tertiary Treatment of Landfill Leachates by Adsorption. *Waste Manag. Res.* **2009**, *27*, 527–533.

(11) Li, Y.; Du, Q.; Liu, T.; Peng, X.; Wang, J.; Sun, J.; Wang, Y.; Wu, S.; Wang, Z.; Xia, Y.; et al. Comparative Study of Methylene Blue Dye Adsorption onto Activated Carbon, Graphene Oxide, and Carbon Nanotubes. *Chem. Eng. Res. Des.* **2013**, *91*, 361–368.

(12) Meng, M.; Wang, Z.; Ma, L.; Zhang, M.; Wang, J.; Dai, X.; Yan, Y. Selective Adsorption of Methylparaben by Submicrosized Molecularly Imprinted Polymer: Batch and Dynamic Flow Mode Studies. *Ind. Eng. Chem. Res.* **2012**, *51*, 14915–14924.

(13) Chen, H.-W.; Chiou, C.-S.; Chang, S.-H. Comparison of Methylparaben, Ethylparaben and Propylparaben Adsorption onto Magnetic Nanoparticles with Phenyl Group. *Powder Technol.* **2017**, *311*, 426–431.

(14) Mashile, G. P.; Mpupa, A.; Nqombolo, A.; Dimpe, K. M.; Nomngongo, P. N. Recyclable Magnetic Waste Tyre Activated Carbon-Chitosan Composite as an Effective Adsorbent Rapid and Simultaneous Removal of Methylparaben and Propylparaben from Aqueous Solution and Wastewater. *J. Water Process Eng.* **2020**, *33*, 101011.

(15) Fernandez-Sanroman, A.; Acevedo-García, V.; Pazos, M.; Sanromán, M. A.; Rosales, E. Removal of Sulfamethoxazole and Methylparaben Using Hydrocolloid and Fiber Industry Wastes: Comparison with Biochar and Laccase-Biocomposite. *J. Clean. Prod.* **2020**, *271*, 122436.

(16) Lin, Y.; Ferronato, C.; Deng, N.; Wu, F.; Chovelon, J.-M. Photocatalytic Degradation of Methylparaben by TiO₂: Multivariable Experimental Design and Mechanism. *Appl. Catal., B* **2009**, *88*, 32–41.

(17) Savun-Hekimoğlu, B.; Ince, N. H. Sonochemical and Sonocatalytic Destruction of Methylparaben Using Raw, Modified and SDS-Intercalated Particles of a Natural Clay Mineral. *Ultrason. Sonochem.* **2019**, *54*, 233–240.

(18) Moreno-Marenco, A. R.; Giraldo, L.; Moreno-Piraján, J. C. Dataset of the Immersion Enthalpy of Activated Carbons Chemically Modified in Methylparaben Aqueous Solution: Relation with Adsorption. *Data Brief.* **2019**, *25*, 104100.

(19) Swenson, H.; Stadie, N. P. Langmuir's Theory of Adsorption: A Centennial Review. *Langmuir* **2019**, *35*, 5409–5426.

(20) Rodrigues, E.; Almeida, O.; Brasil, H.; Moraes, D.; dos Reis, M. A. L. Adsorption of Chromium (VI) on Hydrotalcite-Hydroxyapatite Material Doped with Carbon Nanotubes: Equilibrium, Kinetic and Thermodynamic Study. *Appl. Clay Sci.* **2019**, *172*, 57–64.

(21) Salvestrini, S. A Modification of the Langmuir Rate Equation for Diffusion-Controlled Adsorption Kinetics. *React. Kinet. Mech. Catal.* **2019**, *128*, 571–586.

(22) Abdallah, M. M.; Ahmad, M. N.; Walker, G.; Leahy, J. J.; Kwapinski, W. Batch and Continuous Systems for Zn, Cu, and Pb Metal Ions Adsorption on Spent Mushroom Compost Biochar. *Ind. Eng. Chem. Res.* **2019**, *58*, 7296–7307.

(23) Guo, X.; Wang, J. A General Kinetic Model for Adsorption: Theoretical Analysis and Modeling. *J. Mol. Liq.* **2019**, *288*, 111100.

(24) Wu, F.-C.; Tseng, R.-L.; Juang, R.-S. Characteristics of Elovich Equation Used for the Analysis of Adsorption Kinetics in Dye-Chitosan Systems. *Chem. Eng. J.* **2009**, *150*, 366–373.

(25) Jian, J.-M.; Zhang, C.; Wang, F.; Lu, X.; Wang, F.; Zeng, E. Y. Effect of Solution Chemistry and Aggregation on Adsorption of Perfluorooctanesulphonate (PFOS) to Nano-Sized Alumina. *Environ. Pollut.* **2019**, *251*, 425–433.

(26) Silvestre-Albero, J. Characterization of Microporous Solids by Immersion Calorimetry. *Colloids Surf., A* **2001**, *187–188*, 151–165.

(27) Figueiredo, J. L.; Pereira, M. F. R.; Freitas, M. M. A.; Órfão, J. J. M. Modification of the Surface Chemistry of Activated Carbons. *Carbon* **1999**, *37*, 1379–1389.

(28) Carvajal-Bernal, A. M.; Gómez-Granados, F.; Giraldo, L.; Moreno-Piraján, J. C. Influence of Stacked Structure of Carbons Modified on Its Surface on N-Pentane Adsorption. *Heliyon* **2019**, *5*, No. e01156.

(29) Gokce, Y.; Aktas, Z. Nitric Acid Modification of Activated Carbon Produced from Waste Tea and Adsorption of Methylene Blue and Phenol. *Appl. Surf. Sci.* **2014**, *313*, 352–359.

(30) Carrasco-Marín, F.; Rivera-Utrilla, J.; Joly, J.-P.; Moreno-Castilla, C. Effects of Ageing on the Oxygen Surface Complexes of an Oxidized Activated Carbon. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 2779–2782.

(31) Grajek, H.; Świątkowski, A.; Witkiewicz, Z.; Pakula, M.; Biniak, S. Changes in the Surface Chemistry and Adsorptive Properties of Active Carbon Previously Oxidised and Heat-Treated at Various Temperatures. I. Physicochemical Properties of the Modified Carbon Surface. *Adsorpt. Sci. Technol.* **2001**, *19*, 565–576.

(32) Dong, Y.; Gao, M.; Song, Z.; Qiu, W. Adsorption Mechanism of As(III) on Polytetrafluoroethylene Particles of Different Size. *Environ. Pollut.* **2019**, *254*, 112950.

(33) Rodríguez-Estupiñán, P.; Giraldo, L.; Moreno-Piraján, J. C. *Carbonaceous Porous Materials for the Adsorption of Heavy Metals: Chemical Characterization of Oxidized Activated Carbons*, 2018.

(34) Bernal, V.; Giraldo, L.; Moreno-Piraján, J. Physicochemical Properties of Activated Carbon: Their Effect on the Adsorption of Pharmaceutical Compounds and Adsorbate-Adsorbent Interactions. *C* **2018**, *4*, 62.

(35) Bernal, V.; Erto, A.; Giraldo, L.; Moreno-Piraján, J. Effect of Solution pH on the Adsorption of Paracetamol on Chemically Modified Activated Carbons. *Molecules* **2017**, *22*, 1032.

(36) Boehm, H. P. Some Aspects of the Surface Chemistry of Carbon Blacks and Other Carbons. *Carbon* **1994**, *32*, 759–769.

(37) Noh, J. S.; Schwarz, J. A. Estimation of the Point of Zero Charge of Simple Oxides by Mass Titration. *J. Colloid Interface Sci.* **1989**, *130*, 157–164.

(38) Bernal, V.; Giraldo, L.; Moreno-Piraján, J. C. Adsorption of Pharmaceutical Aromatic Pollutants on Heat-Treated Activated Carbons: Effect of Carbonaceous Structure and the Adsorbent-Adsorbate Interactions. *ACS Omega* **2020**, *5*, 15247–15256.