Reactive Adsorption of Parabens on Synthesized Micro- and Mesoporous Silica from Coal Fly Ash: pH Effect on the Modification Process

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ABSTRACT: Parabens are widely used as preservatives in food, pharmaceutical, and cosmetic products. These compounds are known for their estrogen agonist activity. This research investigates the synthesis of micro- and mesoporous silica from coal fly ash at different pH values (13, 11, 9, and 7) as well as its use as an adsorbent for the removal of parabens. The materials were characterized, and X-ray fluorescence (XRF) analysis revealed that the fly ash acid treatment reduced the presence of aluminum, iron, and calcium oxides and also that silica synthesized at lower pH values (7 and 9) showed a higher SiO₂ content. X-ray diffraction (XRD) and scanning electron microscopy (SEM) analyses revealed microporous silica formation for silica synthesized at pH 13 and mesoporous silica at pH 7, 9, and 11. Adsorption tests were performed with materials, and FA-AT7 showed a higher adsorption capacity. The effect of factors (A) adsorbent mass, (B) initial paraben concentration, and (C) agitation rate on the adsorption process was studied for the FA-AT7 adsorbent using a factorial experimental design. Standardized Pareto charts revealed a negative effect of factor A, positive effect of factor B, and negative interaction effects of factors A−B for all studied parabens. Isotherms and multicomponent kinetic studies were performed. A linear type-III isotherm was obtained, and adsorption equilibrium was reached at approximately 10 min.

1. INTRODUCTION

Parabens, esters of 4-hydroxybenzoic acid, which differ only in the ester group and may be an alkyl or benzyl group, are the most popular and widely used preservatives in food, pharmaceutical, and cosmetic products due to their broad spectrum of antimicrobial activity.¹,² However, recent studies have shown that parabens possess estrogen agonist activity, being even detected in human breast tumor tissue with an average concentration of 20 ng g⁻¹ of tissue.¹⁻³ The widespread use of these compounds has led to environmental contamination.² Parabens were detected in surface waters, soils, and sediments, and indoor biota.¹,⁴ These compounds can be released into the aqueous environment mainly through wastewater treatment discharges and also as runoff from nonpoint sources and deposition of particles from the atmosphere.⁵ Most parabens are frequently found in river water at concentrations varying from nanograms per liter to micrograms per liter, and their levels depend mainly on the extent of water dilution resulting from rainfall.⁶

Paraben adsorption using absorbent materials has been studied for the removal of parabens from environmental samples.⁶,⁷ In this context, mesoporous silica from coal ash, as low-cost adsorbents, can be an effective alternative for the removal of parabens from aqueous media. In addition, this strategy can contribute to the reduction of the disposal of solid industrial waste from coal-based thermoelectric plants, such as coal ash, by transforming it into value-added products. It is estimated that around 750 million tons of coal fly ash are generated each year globally; however, the utilization rate of it is only up to 25%, especially in the production of cement and concrete, manufacture of ceramic materials, and for use as catalysts and adsorbents.⁸,⁹ Thus, it is important to study alternative uses of these wastes, as they are also a source of environmental pollution, generating large amounts of volatile organic pollutants.⁸⁻¹¹ In this context, the mesoporous silicates and aluminosilicates known as M41S,¹²,¹³ in particular their main components MCM-41 (hexagonal phase), MCM-48 (cubic phase), and MCM-50 (lamellar phase), are highlighted.¹³ These materials have regular cylindrical pores with a controllable pore diameter.
material was centrifuged and washed with deionized water until the pH was between 5.0 and 6.0. Thereafter, the solid was dried at 80 °C for 18 h. The samples were named FA and FA-AT for materials before and after acid treatment, respectively.

2.3. Micro- and Mesoporous Material Syntheses. Prior to the material synthesis, silica was extracted from fly ash. For this, in a typical procedure, 1.00 g of the acid-treated fly ash was added to 6.5 mL of NaOH (4.0 mol L⁻¹) in a reflux system, at 90 °C for 1 h. The mixture was then centrifuged at 6000 rpm for 5 min and filtered, and the supernatant was used as the silica source. The synthesis procedures were based on the works of Okada et al. and Santos et al. Herein, a reaction mixture of silicon oxide/NaOH/CTAB/H₂O with molar ratio 1.0:0.25:0.08:10.35 was used. First, 0.8917 g of CTABr was dissolved in 20 mL of deionized water, under magnetic stirring at 350 rpm, then, an aliquot of 18.5 mL of silica source was added. Finally, 2 mol L⁻¹ HCl was added slowly until a gel (at pH 7, 9, or 11) or clear (pH 13) solution was observed. The total volume of the mixture was approximately 57.0 mL. By adding the silica source and making up the volume to 57 mL, the pH of the solution was already around 13, i.e., only pH adjustment to 11, 9, and 7 was required.

The pH effect over the syntheses was evaluated at pH values of 13, 11, 9, and 7, covering the basic to neutral pH range. In all of the procedures, the reaction mixtures were aged under magnetic stirring (350 rpm) for 24 h and then without stirring for 24 h more. After that, the reaction mixture was subjected to stirring for 30 min, and then transferred to a Teflon-lined stainless steel autoclave, and heated under autogenous pressure and static conditions at 110 °C for 24 h.

The resulting materials were washed three times with deionized water, dried at 110 °C for 12 h, and calcined at 560 °C for 6 h, with a heating rate of 1 °C min⁻¹. After cooling, the samples were further ground and sieved through 200 mesh sieves. The materials obtained from this process were named FA-AT13, FA-AT11, FA-AT9, and FA-AT7, for the samples synthesized at pH values 13, 11, 9, and 7, respectively.

2.4. Material Characterization. The chemical composition of the materials before and after the acid treatment, as well as the synthesized solids at different pH values, was determined by X-ray fluorescence (XRF) using a Rigaku spectrometer, model ZSX Mini II, operating with a tube of Pd (40 kV, 1.2 mA). Powder X-ray diffraction (PXRD) measurements were performed in Panalytical model X-Pert PRO equipment with Cu Kα (λ = 0.154056 nm) radiation for the crystalline phase with a routine power of 1600 W (40 kV, 40 mA). The high-angle diffractograms were obtained in the 2θ range from 5 to 50°, while at a low angle, the range was from 1.5 to 10° with a counting time of 762 s. The identification of crystalline phases in the samples was performed using X-Pert HighScore software (Panalytical).

Fourier transform infrared (FTIR) measurements were performed using a PerkinElmer FTIR spectrum spectrometer, with a nominal resolution of 2 cm⁻¹, in the region of 4000–400 cm⁻¹. Samples were prepared in KBr pellets (3% mass).

Scanning electron microscopy (SEM) was carried out in Quanta 450 FEG. The samples were prepared on double-sided carbon tape on an aluminum support and coated with a thin layer of gold.

Transmission electron microscopy (TEM) images were acquired with a TEM-FEG (JEM 2100F) field-emission gun transmission electron microscope (acceleration voltage 200 kV, spot size 1, alpha selector 3). The samples were prepared by

Table 1. Structures and Physical–Chemical Properties of the Parabens

| Compound | Chemical structure | CAS number | Molar Weight (g mol⁻¹) | Solubility (g L⁻¹ at 25 °C) | Log Kₐw | pKₐ₁ | pKₐ₂ |
|----------|-------------------|------------|-----------------------|-----------------------------|---------|------|------|
| MP       | ![Chemical Structure](image1) | 99-76-3    | 152.15                | 2.5                         | 1.33    | 8.17 |
| EP       | ![Chemical Structure](image2) | 120-47-8   | 166.17                | 1.7                         | 1.81    | 8.22 |
| PP       | ![Chemical Structure](image3) | 94-15-3    | 180.30                | 0.5                         | 2.34    | 8.35 |
| BP       | ![Chemical Structure](image4) | 94-26-8    | 194.23                | 0.2                         | 2.86    | 8.37 |

*Ref 19. bRef 20. cRef 21.*

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(2–30 nm), high surface area, high chemical and thermal stability, and easy silica functionalization. These properties show that these materials present a high potential for applications in the areas of adsorption, catalysis, chemical separations, and biotechnology devices. The main principle of mesoporous silica synthesis is the use of surfactants or other species as templates through a sol–gel process. MCM-41 synthesis is generally carried out in a basic or neutral medium using a silicon source and a quaternary ammonium surfactant. A gel is formed and subjected to a hydrothermal treatment, followed by the removal of the template via either calcination or solvent extraction.

Materials with different properties can be obtained by altering the synthesis conditions, such as the template/silica ratio; concentration and hydrophobicity of the template; and temperature, pH, and the nature of silica. This work investigates the synthesis of mesoporous silica from coal fly ash at different pH values (13, 11, 9, and 7) and its use as an adsorbent for the removal of parabens from aqueous solution.

2. MATERIALS AND METHODS

2.1. Reagents and Materials. Fly ash was supplied by Eneva-Energia Pecém, located at São Gonçalo do Amarante-Ceará, Brazil. The reagents HCl and NaOH and the surfactant cetyltrimethylammonium bromide (CTAB) were obtained from Vetec, Brazil. For adsorption tests, individual high-purity standards (≥99%) of methylparaben (MP), ethylparaben (EP), propylparaben (PP), and butylparaben (BP) were purchased from Sigma-Aldrich. Their physical–chemical structures and properties are summarized in Table 1. For chromatographic analysis, methanol (PanReac AppliChem ITW Reagents, high-performance liquid chromatography (HPLC) grade) was used. Acetic acid used in the mobile phase was obtained from Vetec, and NaCl, used in the determination of the point of zero charge, was obtained from Sigma-Aldrich.

2.2. Fly Ash Acid Treatment. Prior to the mesoporous material syntheses, fly ash was subjected to acid treatment so that the amount of metallic impurities present in the raw material could be reduced. This procedure consisted of mixing 8.00 g of fly ash (200 mesh) with 200 mL of HCl (2.0 mol L⁻¹) in a reflux system at 90 °C for 2 h. Then, the treated material was centrifuged and washed with deionized water.
drying a drop of the isopropl alcohol-dispersed nanoparticles for 24 h at room temperature on a carbon-coated copper grid (ultrathin carbon/holey carbon, 400 mesh copper grid, Ted Pella, Inc.). The TEM images were acquired with the sample on a single-tilt sample holder using a Gatan 831.45SMO camera, Gatan Digital Micrograph, and EMMENU programs at different resolutions.

The textural characterization of the samples was performed by gas adsorption. Nitrogen adsorption—desorption isotherms were obtained at −196 °C over a wide range of relative pressure from 0.01 to 0.995 atm with a volumetric adsorption analyzer Autosorb IQa (Quantochrome Instruments). Prior to each measurement, the samples were outgassed at 300 °C to a vacuum of 4 mmHg for 12 h. The specific surface area was calculated by the Brunauer—Emmett—Teller (BET) method. The pore size distribution (PSD) was determined using the density nonlocal density functional theory (NLDFT). The total pore volume was calculated from the adsorption isotherm at P/P0 = 0.992 for sample FA-AT13 and P/P0 = 0.985 for materials FA-AT11, FA-AT9, and FA-AT7.

### 2.5. Paraben Adsorption

#### 2.5.1. Adsorbent and pH Selection

To identify the most efficient synthesized material for further adsorption studies, initial batch adsorption tests were performed.

A total of 150 mg of adsorbents was added to 40 mL of multicomponent paraben aqueous solution at 10 mg L⁻¹ concentration, at room temperature (28 ± 2 °C), and at pH 5.0, adjusted using HCl, 1.0 mol L⁻¹, respectively; initial and equilibrium concentrations of parabens in solution, calculated by the Brunauer—Emmett—Teller (BET) method. The pore size distribution (PSD) was determined using the density nonlocal density functional theory (NLDFT). The total pore volume was calculated from the adsorption isotherm at P/P0 = 0.992 for sample FA-AT13 and P/P0 = 0.985 for materials FA-AT11, FA-AT9, and FA-AT7.

#### 2.5.2. Experimental Design and Adsorption Tests

The experimental screening design (STATGRAPHICS Centurion, StatPoint technologies, Inc., The Plains, VA) consisted of 16 + 2 (central points) experimental trials was developed. To determine the factors that influence the removal of parabens by the selected material and to investigate the interaction effects of various parameters, three factors were varied at two levels (2³) (Table 2). The variables studied were initial concentration, agitation, and adsorbent mass. The adsorption capacity was used as a response variable. For this, adsorption experiments were performed in batch using the FA-AT7 adsorbent at pH 3 for 24 h.

Based on this study and considering the concentration at which the parabens are found in the aquatic environment, the values of the parameters adsorbent mass, initial concentration of the analytes, and agitation were fixed for the kinetics and equilibrium studies.

#### 2.5.3. Kinetics and Equilibrium Studies

Adsorption kinetics studies were carried out in a batch system using a 40 mL multicomponent paraben solution (5 mg L⁻¹), 2 mg adsorbent mass, pH 3.0, and agitation at 300 rpm for 30 min at room temperature (28 ± 2 °C). Supernatants of the solutions were collected from the liquid phase at predetermined time intervals, and the analyte concentrations over time were verified.

The same conditions were used in equilibrium tests, where concentrations of multicomponent parabens varied from 1 to 20 mg L⁻¹, and samples were kept in contact with the adsorbent for 30 min.

Equilibrium adsorption isotherm curves, which show the relationship between the solid-phase concentration (qₑ) of the adsorbed solute (mg g⁻¹) and its concentration (Cₑ) in the liquid phase (mg L⁻¹), were built according to the Langmuir (eq 2) and Freundlich (eq 3) equations.

\[
qₑ = \frac{q_{max} K L Cₑ}{(1 + K L Cₑ)} \quad (2)
\]

\[
qₑ = K_f Cₑ^{1/n} \quad (3)
\]

where Cₑ and qₑ were previously defined; qₑ is the monolayer capacity of the adsorbent (mg g⁻¹); Kₑ is the Langmuir adsorption constant, which is related to the energy of adsorption (L mg⁻¹); K_f is (L mg⁻¹) and n are the Freundlich adsorption isotherm constants related to the saturation capacity and intensity of adsorption, respectively.

#### 2.6. HPLC/DAD Analyses

Quantitative analyses were performed using a liquid chromatograph (HPLC) (Shimadzu, 20A prominence) with a UV-DAD detector (SPD-M20A) and column-C18 (Hichrom®), with 250 × 4.6 mm² i.d, and 5 µm particle size. MeOH/acetic acid 0.1% as mobile phase was used in an isocratic gradient (70:30), respectively, for 15 min and 1.0 mL flow. The column temperature was kept at 35°C. The injection volume was 20 µL and detection, UV, at 256 nm.

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Table 2. Levels of the Studied Factors in the Experimental Design

| factors | symbols | levels |
|---------|---------|--------|
| adsorbent mass (mg) | A | -1, 0, +1 |
| initial concentration (mg L⁻¹) | B | 2, 6, 10 |
| agitation rate (rpm) | C | 5, 10, 15 |

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3. RESULTS AND DISCUSSION

3.1. Sample Characterization. 3.1.1. XRF Analysis. The chemical compositions of fly ashes without treatment (FA) and after acid treatment (FA-AT) are listed in Table 3. Fly ashes present diversified physical, chemical, and mineralogical characteristics. This variability is mainly related to the industrial process by which they were obtained.9

It can be observed in Table 3 that the FA chemical compositions are mainly due to the presence of oxides of silicon, iron, aluminum, potassium, calcium, and titanium. Different oxides, such as SrO and Y₂O₃, are also detected; however, they are found at low concentrations (below 1%). The acid treatment reduced the presence of aluminum, iron, and calcium oxides, which results in an increase in silica by 24.33%. Yilmaz and Mermer10 studied the synthesis of MCM-41 from fly ash, and according to them, a higher Si/Al ratio is related to the best ability to form mesoporous silica. In the present study, the Si/Al ratios were 1.47 and 5.59 for FA and FA-AT, respectively, suggesting that the FA-AT material presents a higher mesoporous silica formation potential.

Table 3. Content of the Oxides Based on XRF Analysis (m/m%)  

| sample     | SiO₂   | Fe₂O₃ | Al₂O₃ | K₂O  | CaO  | TiO₂ | Na₂O | other |
|------------|--------|-------|-------|------|------|------|------|-------|
| FA         | 33.07  | 33.61 | 19.81 | 4.99 | 4.46 | 1.75 | 2.31 | 45.50 |
| FA-AT      | 57.40  | 21.72 | 9.07  | 4.17 | 2.94 | 2.96 | 1.74 | 2.96  |
| FA-AT13    | 51.23  | 8.99  | 27.08 | 3.37 | 7.96 | 1.36 | 2.96 | 3.36  |
| FA-AT11    | 75.87  | 6.76  | 11.33 | 11.33| 6.76 | 4.16 | 6.76 | 0.66  |
| FA-AT9     | 94.27  | 0.90  | 3.04  | 1.13 | 0.66 | 0.66 | 1.13 | 1.13  |
| FA-AT7     | 91.76  | 1.10  | 5.67  | 1.11 | 0.66 | 0.66 | 1.11 | 0.66  |

Figure 1. High-angle X-ray diffractograms of (a) FA, (b) FA-AT13, (c) FA-AT11, (d) FA-AT9, and (e) FA-AT7.

Figure 2. Low-angle X-ray diffractograms of FA-AT11, FA-AT9, and FA-AT7.

Figure 3. FTIR spectra of (a) FA-AT13, (b) FA-AT11, (c) FA-AT9, and (d) FA-AT7 materials.
The disappearance of the identified crystalline phases observed in FA or even the formation of new phases in the case of zeolite synthesis suggests that the silica in its natural crystalline form in FA has reacted with NaOH during the silicon extraction step, giving rise to soluble sodium silicate and subsequent formation of new materials.31 According to Chang et al.,32 an eventual absence of formation of the MCM mesoporous material can be explained to be due to the high concentration of sodium ions. In spite of the high content of sodium ions present in the fly ash supernatant, the formation of Al-MCM-41 and MCM-41 type materials can be worked out by means of controlled pH conditions.31,33−35 Thus, mesoporous silica synthesis is highly dependent on the pH of the reaction mixture.35 In the present work, the FA-AT13 sample showed the formation of a crystalline mixture of zeolites X and Y instead of the formation of mesoporous silica. This phenomenon is possibly due to reaction conditions, such as high amounts of sodium ions, which above a key concentration may act as a structure-directing agent,33 and the high pH value of the reaction mixture.

To investigate the existence of an ordered arrangement compatible to mesoporous structures, low-angle X-ray analyses were performed for the samples of FA-AT11, FA-AT9, and FA-AT7 materials (Figure 2). An intense peak (100) was observed for all three samples, which is indicative of the presence of MCM-41 type mesoporous silica.24,35 The highest intensity peak can be observed for samples FA-AT9 and FA-AT7 and might be interpreted as an indication of the higher ordering of the mesoporous channels.34,35 However, the diffraction peaks (110) and (200), which are characteristic of the formation of the ordered hexagonal pore structure, were not observed.10,35

3.1.3. IR Analysis. The FTIR spectroscopy technique has been used extensively for the identification of the functional group of nanomaterials. The broad band at around 3500 cm⁻¹ may be attributed to surface silanol groups and physically adsorbed water molecules,23,24,35 while deformational vibrations of adsorbed water molecules caused the absorption bands at 1636 cm⁻¹.23,35 The bands between 460 and 1250 cm⁻¹ are assigned to framework vibrations of mesoporous silica. The asymmetric and symmetric stretching vibration bands of
framework Si-O-Si appearing at 1082 and 800 cm\(^{-1}\), respectively, are assigned to the porous silica material.\(^{23,36}\)

In the spectra of the FA-AT13 sample (Figure 3a), it is possible to see two signals consistent with the faujasite zeolite group, a band at 670 cm\(^{-1}\), which is related to symmetric stretching due to internal vibrations and a band at 560 cm\(^{-1}\) associated with the double-six-ring (D6R).\(^{37,38}\)

3.1.4. Scanning Electron Microscopy Analysis (SEM). SEM images of FA and the synthesized materials are shown in Figure 4. In the micrographs of the fly ash sample (Figure 4a,b), it is possible to observe that the ashes are formed in the majority by hollow spheres, namely, cenospheres. A remarkable structural change in the materials is noticed after modification (Figure 4c–f). Other researchers who studied coal fly ash found similar morphologies.\(^{9,31,34,39}\) In the FA-AT13 micrographs (Figure 4c), the formation of crystalline structures has been identified, which were previously identified by XRD analysis as a mixture of X and Y zeolite phases. In the inset (Figure 4c), the high-resolution image shows that there are structures with needle-like morphologies and others with faceted crystals that may possibly be the two phases of the zeolites identified in XRD analysis. On the other hand, FA-AT11, FA-AT9, and FA-AT7 present particles of smaller size and agglomerates typical of mesoporous silica (Figure 4d–f).\(^{10}\)

3.1.5. Transmission Electron Microscopy Analysis (TEM). By means of the TEM technique, it was possible to carry out larger increases for the materials FA-AT11, FA-AT9, and FA-

| Table 4. Parameters of the Porous Structure Calculated from Nitrogen Adsorption Isotherms |
|-----------------------------------------------|-----------------|-----------------|-----------------|
| material | \(S_{BET}\) (m\(^2\) g\(^{-1}\)) | total pore volume (cm\(^3\) g\(^{-1}\)) | average pore diameter (Å) |
| FA-AT13  | 186              | 0.15             | 4.2              |
| FA-AT11  | 106              | 0.29             | 52.9             |
| FA-AT9   | 109              | 0.31             | 50.9             |
| FA-AT7   | 396              | 0.62             | 50.9             |

Figure 6. \(N_2\) adsorption–desorption isotherms at 77 K and pore size distribution curves for (a, b) FA-AT13, (c, d) FA-AT11, (e, f) FA-AT9, and (g, h) FA-AT7 materials.
AT7 in more specific regions to elucidate the morphology of the materials. Figure 5 shows TEM images for FA-AT11, FA-AT9, and FA-AT7 materials. The TEM images show that all materials have numerous pores of different sizes on the surface, corroborating with the data presented in the surface area technique. Although the XRD data at a low angle indicated that all samples have some arrangement, indicated by the presence of the main diffraction peak assigned to the plane (100) of the MCM-41 structure, the TEM images indicated ordering only in samples FA-AT9 and FA-AT7, Figure 5e,f, respectively. The cause may be the treatment at alkaline pH for this class of materials, which is found to be less aggressive when compared to the one performed for samples FA-AT11 and FA-AT13 because the latter presented the formation of zeolitic structures.40 Samples FA-AT11 and FA-AT9 presented narrower pore size distributions.

The BET surface area and the pore volume of the samples ranged from 106 to 396 m² g⁻¹ and from 0.150 to 0.620 cm³ g⁻¹, respectively, as listed in Table 4. The FA-AT7 material showed the largest BET surface area (S_{BET}) (396 m² g⁻¹) and pore volume (0.62 cm³ g⁻¹). Misran et al.34 studied the nonhydrothermal synthesis of mesoporous materials at pHs 7, 10, and 13, and they found pH 7 as the optimal value for the occurrence of the condensation–polymerization process of the sodium silicate precursor.

Surface areas with higher values have been reported in the literature,23,31,33–35 which may be related to the presence of the silica. High-purity silica sources are more reactive and have higher amounts of silicate anions present in the process, which may imply condensation and hydrolysis of these anions, resulting in a larger surface area.34

3.2. Paraben Adsorption. 3.2.1. Adsorption Tests. Adsorption capacities of the synthesized materials for the homologous parabens (e.g., methylparaben, ethylparaben, propylparaben, and butylparaben) are shown in Figure 7. It can be seen that the adsorption efficiency of the materials follows the following order: butylparaben FA-AT7 > FA-AT9 > FA-AT11 > FA-AT13; propylparaben FA-AT7 > FA-AT9 ≥ FA-AT11 > FA-AT13; ethylparaben FA-AT13 > FA-AT7; methylparaben FA-AT13 > FA-AT7.

Thus, it is noted that FA-AT13 and FA-AT7 are able to remove all of the parabens studied, which differ from FA-AT11 and FA-AT9 materials that do not have the adsorptive capacity for methylparaben and ethylparaben compounds. However, this was only an initial test without adjusting the ideal conditions, so a better understanding of the process was achieved in the following stages of the experimental design.

Although FA-AT13 has a greater ability of adsorption for methylparaben and ethylparaben, however, its overall performance is surpassed by FA-AT7, which has adsorption capacities...
of 0.01, 0.07, 0.54, and 1.31 mg g\(^{-1}\) for methylparaben, ethylparaben, propylparaben, and butylparaben, respectively. It is likely that the higher adsorptive capacity of this material compared to the others can be due to its characteristics (Table 4), such as the specific surface area, pore specific volume, pore size distribution, and the adsorbate nature\(^{42,43}\). This material was therefore chosen for subsequent adsorption studies.

The treatment carried out with FA-AT7 provided the largest BET surface area (\(S_{BET}\)) (396 m\(^2\) g\(^{-1}\)) and pore volume (0.52 cm\(^3\) g\(^{-1}\)) and probably increased its hydrophobicity; as a result, its adsorption capacity increases as the paraben hydrophobicity increases. According to Cooney et al.\(^{42}\), the lower the solute solubility, the better the adsorption. Also, an increase in the molecular size of the substituent group usually enhances adsorption, especially for a homologous series of parabens.

There is, in fact, a generalization, known as Traube’s rule, which states that “the adsorption of organic substances from aqueous solutions increases strongly and regularly as we ascend the homologous series”.\(^{42}\) Traube’s rule in fact had originally been applied to the adsorption of solutes from a polar solvent on a relatively nonpolar solid. A similar reversal of Traube’s rule was observed in the case of adsorption from a relatively nonpolar solvent by a polar solid. Examples are the short-chain fatty acids (heptanoic acid) that adsorb on the calcite surface to a lesser extent.\(^{44}\)

### 3.2.2. Point of Zero Charge (\(pH_{pzc}\))

The solution pH may affect the degree of ionization, functional group dissociation, adsorbate structure, and adsorbent surface functionality.\(^{45}\) The \(pH_{pzc}\) determination of an adsorbent allows us to identify trends in the variations of surface charge as a function of pH.\(^{46,47}\) \(pH_{pzc}\) around 7.0 was found for FA-AT7 (Figure 8a), indicating the presence of a positive surface charge in solutions whose pH is below this value and a negative surface charge at a higher pH.\(^{48}\) Nairi et al.\(^{49}\) studied \(pH_{pzc}\) for mesoporous silicas MCM-41 and SBA-15 types and found \(pH_{pzc}\) to be around 6.0.

The adsorption performance of FA-AT7, according to the pH, is shown in Figure 8b. At pH values 3, 5, and 7, an increase in the adsorption capacity with the increase of the paraben molecular size (or hydrophobicity) can be observed. On the other hand, there are no significant variations in the paraben adsorption at pH values 3, 5, and 7, and this is due to the \(pK_a\) values of these compounds (Table 1). Since the parabens are majorly in the neutral form in the studied pH range, which means that there are no opposing charges, the electrostatic forces are not predominant in the adsorption mechanism.

Hydrophobic forces and/or hydrogen bonds might be the principal adsorption mechanisms,\(^{50,51}\) taking into consideration the paraben proprieties studied (Table 1), mainly low water solubility and \(\log K_{ow}\), since there is an increase in the adsorption capacity with the increase of the paraben carbon chain. At pH 3, the adsorption capacity was higher; thus, this
pH was chosen for the later studies. At pH values 5 and 7 (values generally found in surface water), the material presented the adsorptive capacity approximate to the results identified at pH 3, indicating no relevant interference of this parameter in the studied range, which would facilitate the application of the adsorbent for resolving practical environmental problems.

### 3.2.3. Factorial Experimental Design

The factorial design methodology, unlike experiments that vary one factor at a time, is an excellent tool for the individual study, as well as for the interaction effects of all parameters simultaneously, since the variables can influence each other and the ideal value for one of these variables may depend on the values of other variables. This interaction between variables is a recurrent phenomena.

The studied factors were as follows: (A) adsorbent mass, (B) initial paraben concentration, and (C) agitation rate. The FA-AT7 adsorption capacity was used as a response. Standardized Pareto charts are shown in Figure 9.

The factor A showed a significant negative effect. At higher mass dosage, the probability of collisions between the adsorbent particles is higher, generating aggregates, which might reduce the total surface area and cause difficulty in the diffusion of the adsorbates into the material. On the other hand, the factor B showed a positive effect for all studied parabens, which might be related to the increase in the driving force in the aqueous phase, increasing the rate of diffusion. It is worth noting that A–B interaction factors showed a negative effect, which means that although the initial concentration parameter has an individual positive effect, the increase of the two factors from the lower to the higher level reduced the adsorption capacity of the material.

Table 5. Parameters of the Models for Adsorption Isotherms

|                | methylparaben | ethylparaben | propylparaben | butylparaben |
|----------------|---------------|--------------|---------------|--------------|
| **Langmuir**   |               |              |               |              |
| \(Q_{\text{max}}\) (mg g\(^{-1}\)) | 0.0034        | 0.0017       | 0.0024        | 0.0017       |
| \(K_L\) (L mg\(^{-1}\))            | 0.9926        | 0.9985       | 0.9966        | 0.9876       |
| \(R^2\)         | 1.1243        | 1.0197       | 12.6321       | 225.4440     |
| SQE             | 0.3726        | 0.1576       | 0.4509        | 6.2133       |
| HYBRID          | 0.8071        | 1.6329       | 4.0535        | 10.2246      |
| **Freundlich**  |               |              |               |              |
| \(K_F\) (mg g\(^{-1}\) (mg L\(^{-1}\))^\(-1/n\)) | 0.9653        | 1.0100       | 1.0430        | 1.1297       |
| \(1/n\)         | 0.9653        | 1.0100       | 1.0430        | 1.1297       |
| \(R^2\)         | 0.9934        | 0.9990       | 0.9986        | 0.9962       |
| SQE             | 1.0064        | 0.6613       | 5.2004        | 68.7664      |
| HYBRID          | 0.3356        | 0.1763       | 0.3001        | 1.3138       |

Figure 11. Experimental and theoretical isotherms of (a) methylparaben, (b) ethylparaben, (c) propylparaben, and (d) butylparaben onto the FA-AT7 adsorbent in the multicomponent system. Conditions: 5 mg L\(^{-1}\), pH 3.0, stirring rate: 300 rpm, mass adsorbent: 2.0 mg, and temperature (28 ± 2 °C).
speed favored the interactions between the adsorbate and adsorbent, possibly due to its contribution in the process of mass transfer. While the interaction effect of agitation with the adsorbent mass (AC) is negative, the interaction of the same variable with the initial concentration of the analytes (BC) is positive, only for methylparaben. These results can be justified by the strong effect of adsorbent mass and initial concentration factors, indicating a considerable influence on their interaction.

3.2.4. Adsorption Kinetics. Based on the factorial experimental design results, for the kinetics and equilibrium tests, the adsorbent mass and agitation conditions were set at 2 mg and 300 rpm, respectively. Regarding the parabens’ initial concentration, the value used was 5 mg L\(^{-1}\). This concentration was selected considering the levels of parabens detected in the aquatic environment\(^{1,4}\) and the HPLC system used in quantification.

The equilibrium time for multicomponent adsorption of parabens onto the FA-AT7 adsorbent is shown in Figure 10. The paraben adsorption process in the mesoporous silica investigated is fast, with an equilibrium time reached in approximately 5 to 10 min.

Barczak et al.\(^{59}\) found fast adsorption; only a few minutes were needed to approach 90% of equilibrium values for diclofenac onto mesoporous silica. These authors associated their results with the medium pore size of the materials and, consequently, facilitated the diffusion of the molecules inside them.

3.2.5. Adsorption Equilibrium. It can be seen in Figure 11 that the experimental adsorption isotherm is linear (type-III), indicating that the mass of adsorbate retained per unit adsorbent mass is proportional to the adsorbate equilibrium concentration in the fluid phase.

The adjustment using the Langmuir model is not adequate to estimate the \(Q_{\text{max}}\) which is evidenced by the high error values obtained (Table 5). The Freundlich model was better adjusted to the experimental data. \(K_f\) and 1/n values indicated the following order: methylparaben < ethylparaben < propylparaben < butylparaben, which indicates a higher material surface heterogeneity effect for methylparaben (higher “n” value), leading to a strong interaction between the adsorbate and adsorbent. 1/n values above 1 indicate cooperative adsorption, which means that interactions between species of adsorbates are present in the system.\(^{60,61}\) Other studies also found a better fit using the Freundlich model in mesoporous materials.\(^{45,62,63}\)

4. CONCLUSIONS

The pH effect played a role in the mesoporous silica synthesis process; at pH 7, a more ordered structure and a higher surface area and pore volume were found, leading to an adsorbent with good efficiency to adsorb paraben compounds, and at pH 13, the formation of microporous crystalline structures such as X- and Y-zeolites is favored. Fly ash acid treatment prior to the syntheses was important to reduce metallic impurities in fly ash. The adsorption capacity of mesoporous silica increased with the molecular mass of the parabens; thus, propyl and butyl parabens were adsorbed more than others, probably due to their higher hydrophobicity.

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Notes
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