Ionic Cross-Linking Fabrication of Chitosan-Based Beads Modified with FeO and TiO2 Nanoparticles: Adsorption Mechanism toward Naphthalene Removal in Seawater from Cartagena Bay Area

David Alfonso Patiño-Ruiz, Gesira De Ávila, Carlos Alarcón-Suesca, Ángel Dario González-Delgado, and Adriana Herrera*

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ABSTRACT: Polycyclic aromatic hydrocarbons (PAHs) are complex molecules produced by the thermal decomposition of organic matter in anthropogenic activities. Novel composites with enhanced physicochemical properties aim to overcome limitations such as adsorption capacity, affinity, and stability for PAHs adsorption. Composites based on chitosan are promising due to the good biocompatibility and adsorption properties. This study focuses on the facile preparation of chitosan beads modified with iron oxide (FeO) and titanium dioxide (TiO2) nanoparticles via ionic cross-linking (Ch-FeO/TiO2). FeO and TiO2 were synthesized performing co-precipitation and green chemistry methods, respectively. The characterization evidenced the formation of Ch-FeO/TiO2 with good crystallinity, excellent thermal stability, and superparamagnetic response, attributed to the presence of FeO and TiO2 nanoparticles. High thermal stability up to 270 °C was related to the cross-linked chitosan network. The enhanced adsorption mechanism of Ch-FeO/TiO2 was determined by removing naphthalene from water and seawater samples. The Ch-FeO/TiO2 showed a higher adsorption capacity of 33.1 mg/g compared to 29.8 mg/g of the unmodified chitosan (un-Ch) beads. This is due to the higher functional surface area of 27.13 m2/g, compared to that of 0.708 m2/g for un-Ch. We found a rapid adsorption rate of 240 min and the maximum adsorption capacity of 149.3 mg/g for Ch-FeO/TiO2. A large number of active sites allows for increasing the naphthalene molecules interaction. Adsorption in seawater samples from Cartagena Bay (Colombia) exhibits an outstanding efficiency of up to 90%. These results suggest a promising, cheap, and environmentally friendly composite for remediation of water sources contaminated with complex compounds.

1. INTRODUCTION

Cartagena de Indias is a tourist and industrial city located on the Caribbean Coast of Colombia. Cartagena has one of the most important maritime ports in the country, with a high transit of cargo ships and cruises relevant to the economy.1 However, the maritime activities, along with the industrial sector, have produced the release of a large number of pollutants into the water sources. Among these pollutants, polycyclic aromatic hydrocarbons (PAHs)2 and heavy metals3 have been extensively detected and quantified above the limit standards established by different regulations.

PAHs are complex molecules composed of two or more aromatic rings. These are widely produced from thermal decomposition of organic matter, which is generally involved in a variety of anthropogenic activities.1 Such activities may include fossil fuel uses, incineration of waste, coke and oil production, maritime transportation, construction, wastewaters from petrochemical plants, and energy generation.1 PAHs are chemically stable and resistant against biodegradation due to the hydrophobic and lipophilic nature, indicating a high persistency once in contact with the environment.6 Although over 400 PAHs have been identified, a list of 16 was recognized as the most hazardous pollutants, according to the United States Environmental Protection Agency (U.S. EPA).7 PAHs present a carcinogenic, teratogenic, and mutagenic nature and can be easily bioaccumulated in the environment, increasing their toxicity and incidence.8 PAHs have been detected in different water sources and sediments, and considering their high migration ability, can also be found in drinking water,9 and groundwater.10 Hence, several chemicals, physical, and biological techniques have been adopted for PAHs removal and degradation, such as adsorption, membrane, nanofiltration,
enzyme degradation, precipitation, sedimentation, photodegradation, and chemical oxidation.\textsuperscript{5,11,12} However, most of these methods are reported with some limitations, including high consumption of energy, low efficiency, long operational periods, high cost of equipment maintenance, and environmentally unsustainable.\textsuperscript{13}

Adsorption is being widely investigated to overcome the limitations among the current methods. This technique has proven to be simple, suitable, efficient, and environmentally friendly for the removal of PAHs, where the production of chemical or biological byproducts is minimum.\textsuperscript{14} The significant advantage comprises a possible mechanism that includes the detection and rapid removal of PAHs at low concentrations in the different water sources.\textsuperscript{15} The adsorption mechanism can be performed through different adsorbent materials, with high availability, whether synthetic or natural origin.\textsuperscript{16}

Depending on the adsorbent, the mechanism for the adsorption of PAHs in water sources is commonly based on electrostatic π−π, H-bonding, or electron donor−acceptor interactions.\textsuperscript{17} Adsorbent materials based on chitosan as bio-supports have demonstrated to be promising for adsorption of organic pollutants from water sources. Chitosan is a linear cationic polysaccharide composed mainly of a large number of protonated amine (−NH\textsubscript{3}+) and deprotonated hydroxyl (−O\textsuperscript{−}) functional groups, which provide high availability of active sites to enhance the adsorption capacity.\textsuperscript{18} Additionally, these functional groups can easily promote a chemical (grafting),\textsuperscript{19} physical (van der Waals forces),\textsuperscript{20} and electrostatic (interaction between positive and negative charges) bonds,\textsuperscript{21} leading to the formation of more complex structures.\textsuperscript{22} Although chitosan is nontoxic, biocompatible, inexpensive, reactive, and widely available in nature, it also presents some limitations, such as chemical stability, thermal resistance, mechanical strength, and low porosity.\textsuperscript{16} Also, the physicochemical properties of chitosan, including the adsorption efficiency, can be improved by the immobilization of other materials through cross-linking procedures.\textsuperscript{23}

Nanomaterials such as iron oxide (FeO) nanoparticles are widely used for the modification of biopolymers, aiming to improve the physicochemical properties.\textsuperscript{24} Two phases, Fe\textsubscript{3}O\textsubscript{4} and γ-Fe\textsubscript{2}O\textsubscript{3}, mainly compose this kind of magnetic nanoparticles.\textsuperscript{25} They have unique characteristics, including low toxicity, low cost, biocompatibility, biodegradability, large surface area, and superparamagnetism.\textsuperscript{24} Therefore, FeO nanoparticles can be extensively and easily applied for the water remediation due to the large number of active sites, which allow rapid adsorption of different pollutants, considering the facile recovery of the adsorbent and further reuse.\textsuperscript{25}

The immobilization of FeO nanoparticles within the chitosan structure, enhance the stability features of these nanoparticles against acidic and oxidative conditions.\textsuperscript{26}

On the other hand, titanium dioxide (TiO\textsubscript{2}) nanoparticles have been used to modify chitosan through the same cross-linking procedure, resulting in excellent adsorbent properties in the case of toluene.\textsuperscript{27} Anatase is the most stable structure of TiO\textsubscript{2} nanoparticles. This TiO\textsubscript{2} structure possesses different physicochemical advantages, such as chemical stability, non-toxicity, photocatalytic activity, antibacterial activity, high surface area, and considerable band gap energy.\textsuperscript{28,29} These properties suggest that the TiO\textsubscript{2} nanoparticles are suitable for their incorporation in other materials, allowing them to enhance the adsorption performance. Moreover, when TiO\textsubscript{2} is exposed to UV light, the surface can produce strong reactive oxygen species (ROS), such as hydroxyl radicals (·OH) and superoxide ions (O\textsubscript{2}−). These ROS provide a more reactive surface, which increases the affinity and selectivity toward the adsorption and degradation of organic molecules.\textsuperscript{30}

The cross-linking technique is usually performed to enhance the chitosan physicochemical properties, but this can decrease the number of functional groups along the biopolymer chains, reducing the number of available active sites and adsorption capacity.\textsuperscript{31} Hence, modification with nanoparticles offers additional active sites conferring a more complex chitosan structure for an enhanced adsorption process. Recent literature has reported the fabrication of composites based on chitosan as bio-supports and modified with different nanomaterials such as FeO and TiO\textsubscript{2} nanoparticles. Among the explored nanocomposites are found, cross-linked magnetic ethylenediaminetetraacetic acid (EDTA)/chitosan/TiO\textsubscript{2},\textsuperscript{32} chitosan modified with N, S-doped TiO\textsubscript{2},\textsuperscript{33} magnetic thiourea-chitosan,\textsuperscript{34} and polyaminated Fe\textsubscript{3}O\textsubscript{4}@chitosan core–shell magnetic nanoparticles.\textsuperscript{35} Adsorption experiments in aqueous solutions using chitosan composites have shown maximum adsorption capacities up to 58.6, 16.6, 6.1, 2.5, 1.2, and 0.9 mg/g for removal of benzene, toluene, naphthalene, phenanthrene, acenaphthylene, and fluorene, respectively.\textsuperscript{31,5,26} Besides, these methodologies are complex due to the use of more toxic chemicals such as hexane, methanol, and ethanol, high energy consumption due to the implementation of temperature, and longer procedures of synthesis up to 12 h.\textsuperscript{13,32} To the best of our knowledge, no studies are exploring the combination of FeO and TiO\textsubscript{2} nanoparticles (Ch-FeO/TiO\textsubscript{2}). Additionally, adsorption of naphthalene was performed for the first time using these multifunctional Ch-FeO/TiO\textsubscript{2} beads.

Hence, we hereby report an easy fabrication of beads based on chitosan as bio-supports through ionic cross-linking gelation using an injection system. The chitosan gel solution was modified with FeO and TiO\textsubscript{2} nanoparticles. The morphological features show chitosan beads with a semi-spherical shape, even when chitosan was modified with nanoparticles. X-ray diffraction (XRD) experiments show peaks corresponding to FeO (Fe\textsubscript{3}O\textsubscript{4} and γ-Fe\textsubscript{2}O\textsubscript{3}) and TiO\textsubscript{2} (anatase and rutile) phases. Magnetic characterization shows superparamagnetic behavior. The adsorption of naphthalene was carried out mainly by electrostatic interaction and chemisorption using the functional groups grafted on the bead’s structure. This statement could be corroborated through the infrared spectroscopy, which allowed us to validate the presence of protonated amine (−NH\textsubscript{3}+) and hydroxyl (−OH\textsuperscript{−}) as the typical functional groups of the chitosan structure. The presence of nanoparticles in the chitosan structure promoted enhanced adsorption due to the electrostatic interaction between the surface and the naphthalene molecule. Similar results were observed for the experimental adsorption using real seawater samples, in which naphthalene presented a high affinity toward the beads. Additionally, the naphthalene showed high stability onto the bead’s surface after being immersed in the eluent solution during the desorption tests. The as-fabricated beads were found to be very stable and suitable as adsorbent material for the treatment of water sources, indicating a potential extension of other PAHs removal.
2. RESULTS AND DISCUSSION

2.1. Characterization of Materials. Scanning electron microscopy (SEM) was used to analyze the morphology of unmodified chitosan (un-Ch) and Ch-FeO/TiO$_2$ beads. Figure 1a–d exhibits the un-Ch with a smooth and rough surface, and a semispherical shape with an average diameter size of 912 μm (see Figure S1), which is attributed to the cross-linking process using acetic acid. Despite some cavities are observed in un-Ch (see Figure 1b,c), no fissures were noted on the surface indicating compaction in the bead. In this case, the drying procedure at room temperature plays an important role, as higher temperatures promote cracking of the beads.

Figure 1e–h shows the surface of Ch-FeO/TiO$_2$ beads. Here, a rougher surface evident, in comparison to the un-Ch sample. The presence of bright particles can be assigned to FeO and TiO$_2$ nanoparticles, which are weakly attached to the composite and interact via van der Waals forces. The brighter particles correspond to FeO nanoparticles rather than TiO$_2$ due to the higher electronegativity nature of Fe ions. The TiO$_2$ structure presents less amount of oxygen, and higher electronegativity, leading to lower electronegativity. Additionally, the absence of fissures and the presence of a more compact surface can be attributed to the nanoparticles, which act as cross-linking agents, leading to the formation of a stable structure with an average diameter size of 1311 μm (see Figure S1).

Figure 1g,h reveals a microporous structure, attributed to the distribution of FeO and TiO$_2$ nanoparticles in the bead structure. A heterogeneous distribution of Fe and Ti elements is appreciated along a representative area in the energy-dispersive X-ray (EDX) mapping analysis (see Figure S2), indicating a weight percentage content of around 9 and 6 wt % for Fe and Ti, respectively. The distribution of these elements on the surface of the beads is presented as active sites, conferring a large number of points for adsorption through an enhanced coordination with the naphthalene molecules. This is supported by the electrostatic interaction between the chitosan network and the nanoparticles, and suggests that the final nanoparticles content is approximately 30% higher for FeO compared to TiO$_2$. Similar morphologic characteristics are reported by other authors using different nanomaterials, such as NaYF$_4$ Pd, and FeO nanoparticles during the preparation and modification of chitosan beads.

Additionally, the surface area, volume, and pore size of all beads were determined through the Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) analysis. BET and BJH results are summarized in Table 1 for un-Ch and Ch-FeO/TiO$_2$ beads. According to the BET analysis, the surface area showed to be significantly higher for Ch-FeO/TiO$_2$ compared to un-Ch, due to the presence of nanoparticles in the chitosan structure. The nanoparticles provide a larger surface area due to the nanoscale, offering a greater surface area/volume ratio for a surface binding increment. A small pore volume and pore size were noted for un-Ch. However, these beads show a type VI isotherm (see Figure S3a), representing a typical stepwise multilayer for a uniform and nonporous surface, which is in agreement with the SEM images shown in Figure 1a–d.

In the case of Ch-FeO/TiO$_2$, the isotherm curve corresponded to type IV (see Figure S3b). The hysteresis loop and H3 steepness indicated a limitation on the adsorption through the aggregates of platelike particles forming slitlike pores. This result is consistent with those values reported for BET surface area and micropore surface area of 27.13 and 25.86 m$^2$/g, respectively, while the pore volume was found to be considerably higher than for un-Ch. The pore size distribution (see Figure S3c,d) obtained from the BJH analysis, aims to compare the number and size of pores between the beads. Here, the curve confirmed the increase in the number of pores due to the presence of nanoparticles.

Since the study is oriented to evaluate the adsorption properties of the chitosan-based beads, the discussion about the crystal structure of the synthesized materials is limited only to the phase analysis. Figure 2a shows the powder XRD patterns of the synthesized FeO and TiO$_2$ nanoparticles, as well as the un-Ch and Ch-FeO/TiO$_2$ beads. First, the TiO$_2$ pattern

![Figure 1. Scanning electron microscopy (SEM) images of (a–d) un-Ch and (e–h) Ch-FeO/TiO$_2$ beads.](https://example.com/figure1.png)

Table 1. Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) Analysis Related to the Surface Area and Porosity of the Beads

|                  | un-Ch     | Ch-FeO/TiO$_2$ |
|------------------|-----------|----------------|
| BET surface area | 0.7 m$^2$/g | 27.1 m$^2$/g |
| pore volume      | 6.8 × 10^{-4} cm$^3$/g | 4.6 × 10^{-1} cm$^3$/g |
| pore size        | 3.8 nm    | 6.8 nm        |
| micropore surface area | 0.3 m$^2$/g | 25.9 m$^2$/g |

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Figure 2. (a) X-ray diffraction (XRD) patterns of FeO and TiO2 nanoparticles, as well as un-Ch and Ch-FeO/TiO2 and (b) magnetic saturation of the FeO nanoparticles and Ch-FeO/TiO2 from the saturation magnetization vs field (M_s vs H) hysteresis loop at 300 K.

presents the reflections corresponding to the TiO_2-anatase (tetragonal crystal system, space group I₄₁/amd, no. 141). No evidence of the rutile phase was founded, and all reflections are in agreement with those registered in the JCPDS 00-002-0387 and reported in similar green chemistry synthesis. The presence of TiO_2 nanoparticles in the chitosan structures provides a larger number of active sites due to the high and reactive surface area, which is typical for the anatase structure rather than rutile. Second, the FeO nanoparticles are composed of two phases corresponding to magnetite Fe₃O₄ (cubic crystal system, Fd3m, no. 227) and maghemite Fe₂O₃ or γ-Fe₂O₃ (cubic crystal system, P4₃m, no. 213). All reflections can be indexed and agreed with those reported in the JCPDS cards 01-075-1609 and 98-015-8745, respectively. These results suggest the oxidation of Fe²⁺ to Fe³⁺ of the Fe₃O₄ phase during the synthesis, considering that γ-Fe₃O₄ is a Fe²⁺-deficient Fe₃O₄ phase. The FeO pattern confirms the coexistence of the two iron phases with high stability and magnetic response compared to the hematite phase, in which the latter only responds to magnetic fields upon heating. The average crystalline domain size was calculated using the Scherrer equation, and corresponds to 279 nm for the iron oxide nanoparticles, and 109 nm for the TiO₂ nanoparticles. Besides, the width of the peaks gives information about the nanoscale nature of the particles.

On the other hand, the XRD pattern for un-Ch beads shows a broad peak around 12°–13° related to the strong bonding between hydroxyl (–OH) and amine (–NH₂) groups after the ionic cross-linking procedure. A narrow and broad reflection appears at around 23° and determines the semicrystalline nature of the chitosan structure. These two characteristic peaks represent the (002) and (101) planes of a hydrated crystalline structure. This is due to the presence of the aforementioned hydrophilic functional groups forming intermolecular bonds within the chitosan structure. In this pattern, the peak with low intensity indicates lower crystallinity for the crystal form I, and the sharp a major crystallinity degree for crystal form II. Finally, the XRD pattern of Ch-FeO/TiO₂ shows a mixture of phases corresponding to FeO and TiO₂ nanoparticles within the chitosan structure. After the incorporation, the characteristic peaks of chitosan disappeared due to the chelation of iron and titanium ions with the hydrophilic functional groups. Hence, this type of bonding reduces the availability of –NH₂ groups for the formation of hydrogen bonds, which indicates that the chitosan structure changed to a completely amorphous structure. The low intensity for both nanoparticles peaks suggests an increase in the crystallite size, attributed mainly to the chelation with the functional groups of chitosan. However, the sharp peaks confirm that the crystalline behavior is still predominant for both nanoparticles after the cross-linking procedure. No changes in the FeO and TiO₂ phases were evidenced, indicating stability after the incorporation in the chitosan structure. Additionally, the nanoparticles provide an improvement in the physicochemical properties, such as the surface area and magnetic properties, in which this latter will be deeper discussed in the following vibrating sample magnetometer (VSM) section.

Figure 2b shows the magnetic hysteresis loop for FeO nanoparticles and the Ch-FeO/TiO₂ beads. The magnetization curve suggests that both materials possess a superparamagnetic behavior with no remanence and coercive field at room temperature. The saturation magnetization (M_s) was 66.5 and 6.4 emu/g for FeO nanoparticles and Ch-FeO/TiO₂ beads, respectively. This superparamagnetic behavior is also given for the beads, even when the M_s value is significantly lower compared to FeO nanoparticles, which is related to the amount of magnetic material within the chitosan structure. The reduction in the M_s value is attributed to a dipolar interaction, and anisotropy degree among FeO nanoparticles contained in the chitosan structure. This is affected by the electrostatic interaction between the functional groups and the FeO nanoparticles surface, which change the magnetization dynamics of the beads. Similar magnetic chitosan modified composites exhibit analog behavior, and are suitable to be recovered using magnetic separation techniques. The magnetic properties of the Ch-FeO/TiO₂ also depend on the FeO phases, in which the presence of Fe₃O₄ and γ-Fe₂O₃ promotes enhanced spin coordination for the strong magnetic response. Accordingly, the Ch-FeO/TiO₂ are suitable for adsorption of naphthalene since they can respond to magnetic fields with no
delays, attributed to the low coercivity and remanence observed in the inset of Figure 2b.

The information of the functional groups is shown in Figure 3a. A broader band below 1000 cm$^{-1}$ for Ch-FeO/TiO$_2$, reveals the presence of two characteristic bands around 444 and 563 cm$^{-1}$ attributed to the Fe$^-$O and Ti$^-$O vibrations, respectively, confirming the FeO$^{53}$ and TiO$_2$ lattices. The bands at 1030 and 1065 cm$^{-1}$ in both beads are attributed to the C$^-$O$^-$C$^{40}$ and C$^-$OH stretching vibrations$^{55}$ respective. These bands can be associated with the carboxyl and hydroxyl groups in the chitosan structure. Moreover, the chitosan spectra exhibit the presence of amide I (CONH$_2$) and II (N$^-$H), which can be observed at 1642 and 1591 cm$^{-1}$, respectively. The appearance of amide I groups occurred mainly by the cross-linking process in the formation of linkages through ionic interaction and hydrogen bonding with the acetic acid. However, a possible protonation of N atoms due to the deacetylation degree of chitosan and the acid conditions might lead the deformation and overlap to $\text{NH}_3^+$ with the stretching vibration at around 1653 cm$^{-1}$.$^{56}$ However, the stretching vibrations at around 2867 and 2921 cm$^{-1}$ suggest some remaining C$^-$H aliphatic bonds in the chitosan structure after the deacetylation procedure. Moreover, broadband between 3132 and 3590 cm$^{-1}$ is associated with the $\text{OH}$ and N$^-$H functional groups.$^5$ The changes in the bands around 2867–2921 and 3132–3590 cm$^{-1}$ are associated with the electrostatic interaction between the different functional groups contained in the chitosan structure and the cationic surface nature of the nanoparticles.

According to the curve in Figure 3b, three weight loss stages were observed between 40 and 700 °C. A slight difference was detected between the un-Ch and Ch-FeO/TiO$_2$ beads. For the un-Ch beads, the first stage comprised mainly the elimination of 13.5% of water physically adsorbed onto the surface; then, cross-linked water molecules bonding by strong hydrogen interactions are released up to 220 °C. Further, the continuous weight loss until 270 °C, suggests the breakage of intermolecular bonds between $\text{OH}$ and $\text{NH}_2$ functional groups.$^{58}$ The higher weight loss in Ch-FeO/TiO$_2$ sample corresponds to a major amount of water adsorbed in response to the difference in the number of active sites for water adsorption. At the second stage, a notable weight loss is
attributed to the chitosan decomposition, suggesting an excellent thermal resistance up to 270 °C. After this temperature, decomposition of organic content such as carboxyl and amine groups lead to the degradation of the chitosan skeleton structure. Above 400 °C, significant oxidation and decomposition of other organic content such as methyl groups were reported.41 This leads to complete carbonization of the beads, resulting in a total weight loss of 57% for the un-Ch beads. In the case of the Ch-FeO/TiO2 sample, a last third stage appears with a total weight loss of 61.1% based on the oxidation of Fe3O4 and γ-Fe2O3 to hematite (Fe2O3).59

2.2. Adsorption and Desorption Studies. Kinetic experiments were performed to investigate the effect of contact time in the adsorption of naphthalene using the un-Ch and Ch-FeO/TiO2 beads. On the other hand, the experimental data with tolerance below 5% were fitted using the pseudo-first-order, pseudo-second-order, Elovich, and intraparticle diffusion models. Figure 4 shows the adsorption rate for both types of composites. Here, Ch-FeO/TiO2 presented faster adsorption due to the major availability of active sites on the surface. The initial stage of the curve represents the concentration gradient of the naphthalene adsorbed by the beads. The decrease of the adsorption for the pseudo-first-order curve implies a sudden shift from surface adsorption to controlled mass transfer and intraparticle diffusion on the saturated chitosan structure.

The saturation consisted of the rapid occupation of the active sites due to the high initial concentration of naphthalene, which was reached at the equilibrium times of 1440 and 240 min, with adsorption capacities of 29 and 33 mg/g for the un-Ch and Ch-FeO/TiO2, respectively. In the case of un-Ch, the high R2 value indicates that physical interaction forces with the analyte are responsible for the high but low adsorption rate. Although the adsorption rate for Ch-FeO/TiO2 was faster and higher compared to un-Ch, the R2 value slightly decreased indicating lower fitting since electrostatic interaction is the rate-limiting step rather than physical forces.

According to Figure 4 and Table 2, the nature and mechanism of adsorption can be determined using the parameters obtained from pseudo-first-order, pseudo-second-order, Elovich, and intraparticle diffusion models. The R2 values suggest a good correlation between the theoretical values for the adsorption capacities and the experimental data. However, a significant deviation is noted for the adsorption capacities calculated from the pseudo-first-order model, especially for the case of un-Ch, indicating that the equilibrium point was reached fast at high concentrations. Afterward, the adsorbate (naphthalene) moves from one position to another within the layer that was formed onto the surface.61 A better fit for the pseudo-first-order model in Ch-FeO/TiO2 due to the presence of nanoparticles was observed, offering a significantly higher number of active sites for adsorption. However, the values for the correlation coefficients (see Table 2) demonstrate that the adsorption mechanism cannot be predicted using this model since the experimental data are not fitting properly. In the case of the enhanced fitting to the pseudo-second-order model, it is suggested that the rate-limiting step is ruled by the chemical adsorption, depending on the electrostatic forces through the exchange of electrons.41

The adsorption capacities at the equilibrium point calculated for the pseudo-second order were more accurate and similar to those reported experimentally, with values of 29.67 and 36.36 mg/g for the un-Ch and Ch-FeO/TiO2 beads, respectively. From the results of the pseudo-second order, the adsorption rates depend more on the availability of active sites on the beads, rather than the concentration of naphthalene in the solution.

Elovich model allows describing the chemical adsorption process occurring between the naphthalene and the beads. Table 2 shows that R2 values above 0.8, indicating that the adsorption increases in a short period. The Elovich model considers initial adsorption onto the beads through binding sites, which was slowly produced in this case.62 For Ch-FeO/TiO2 a large number of bonds are formed due to the electrostatic interaction with the cationic surface of nanoparticles and naphthalene takes part. The lower adsorption rate for the un-Ch indicates low stability between the chitosan network and the naphthalene molecules. Hence, the adsorption is being carried out not only by electrostatic interactions but also by van der Waals forces.

The intraparticle diffusion model proposed by Weber and Morris was performed to establish the diffusion mechanism and adsorption speed. According to Figure 5a,b, the adsorption of naphthalene is carried out from the liquid phase to the solid phase, based on a multistage behavior of film diffusion, particle diffusion, and adsorption onto the bead’s surface.63 The curve in Figure 5a can be divided into three stages. The first stage corresponds to the formation of a film onto the un-Ch, which generally occurs with fast diffusion on the surface. The second stage indicates a slow particle diffusion between the naphthalene films that were formed during the first stage. These results are in agreement with the SEM images and BJH analysis, where un-Ch showed low porosity promoting a larger second stage. The third stage indicates a decrease in the intraparticle adsorption due to the absence of available active sites. Figure 5b shows the intraparticle diffusion process of Ch-FeO/TiO2. As for un-Ch, the occurrence of three stages is noted. In the first stage, the naphthalene was adsorbed rapidly onto the surface due to the higher number of active sites. Along the second stage, particle diffusion activity among the layers of adsorbate occurs; leading a third stage, characterized by the decrease in the diffusion mechanism related to the controlled mass transfer and intraparticle diffusion among the nanoparticles. The naphthalene molecules reach the interior

| Table 2. Kinetic Model Parameters to Determine the Adsorption Mechanisms of Beads for Naphthalene Removal (Initial Concentration of 100 ppm) |
| --- |
| **kinetic model** | **parameters** | **bead type** |  |
|  |  | un-Ch | Ch-FeO/TiO2 |
| pseudo-first-order | k1 (1/min) | 0.0009 | 0.0169 |
|  | qe (mg/g) | 3.4 | 19.9 |
|  | R2 | 0.9897 | 0.8885 |
| pseudo-second-order | k2 (mg/(g min)) | 0.0017 | 0.0011 |
|  | qe (mg/g) | 29.7 | 36.4 |
|  | R2 | 0.9997 | 0.9952 |
| Elovich | β (g/mg) | 0.9 | 0.15 |
|  | α (mg/(g min)) | 6.7 × 10^−3 | 4.17 |
|  | R2 | 0.9242 | 0.8251 |
| intraparticle diffusion | Kd (mg/(g min^1/2)) | 0.09 | 1.19 |
|  | C | 25.6 | 14.8 |
|  | R2 | 0.8864 | 0.7050 |
surface of the bead leading to chemical interaction, and thus, the equilibrium. 60

Adsorption isotherms were performed to study the interaction produced between the molecules of naphthalene and the surface of the beads. Also, the Langmuir, Freundlich, and Elovich models were used to fit the experimental data (tolerance below 5%). Table 3 exhibits the high correlation coefficients of the linear fit (see Figure 6a,b). The linear fitting indicates that the adsorption process occurred mainly by the formation of multilayers on a heterogeneous surface with an exponential increase due to the uniform and high distribution of active sites. 64 This is corroborated with the EDX mapping analysis, outstanding the major contribution of FeO nanoparticles in the adsorption process attributed to the larger content in the chitosan structure. However, the heterogeneous distribution of TiO2 nanoparticles also played an important role in increasing the available active sites, allowing the high adsorption capacity. In the case of the Elovich model, the $R^2$ values for un-Ch beads were lower than those for Ch-FeO/TiO2. This might be attributed to a saturation of the bead surface when the concentration of naphthalene increases, in which after 6 mg/L, the exponential behavior decreases.

Maximum adsorption capacities ($q_m$) were calculated through the Langmuir model according to the high $R^2$ values above 0.9. The linear behavior and continuous increase of the fitting curve in both types of beads suggest the formation of one monolayer, in which naphthalene is adsorbed and remains on the surface without interacting with other molecules and migrating to other equivalent active sites. Here, the Ch-FeO/TiO2 presented higher $q_m$ values compared to the un-Ch (see Table 3), and the $K_L$ constant values indicated good adsorption performance. 65 However, the lower $K_L$ for un-Ch was attributed to the bonding interaction between the functional groups within the chitosan structure during the ionic cross-linking procedure, which reduces the available active sites, and thus, the $q_m$ value (70.9 mg/g). Meanwhile, the presence of nanoparticles in the Ch-FeO/TiO2 allowed improving the $q_m$ value to 149.3 mg/g due to the conferring of a larger surface area for more available active sites in the chitosan for adsorption of naphthalene. On the other hand, the $R^2$ values above 0.90 in the Freundlich model suggest the adsorption through monolayers, and thus, the formation of a multilayer heterogeneous surface. Moreover, $n$ values above 1.0 indicate that the adsorption process was carried out mainly by chemisorption and electrostatic interaction, rather than physical adsorption. 65 Additionally, $K_f$ constant is considerably high at 25 °C, which is generally typical for adsorption processes with endothermic nature. 66 Moreover, lower $q_m$ values are related to the high amount of water in the un-Ch, affecting the maximum quantity of naphthalene adsorbed in the available active sites. Although the literature reports of naphthalene adsorption using chitosan and related composites are scarce, our results show significantly higher adsorption capacities compared to other studies (see Table 4).

Figure 7 shows the adsorption of naphthalene from seawater samples. Here, Ch-FeO/TiO2 exhibits a maximum adsorption efficiency of 89.5%. The nanoparticles provided additional $\pi-\pi$ interactions, which increased the affinity with the naphthalene molecule. 68 On the other hand, un-Ch presented a similar result with an adsorption efficiency of 86.0%, indicating the important role of the functional groups in the electrostatic interaction effect during chemisorption. The presence of functional groups allowed the formation of complexes with the naphthalene molecule through intramolecular donor–

Table 3. Adsorption Model Parameters to Determine the Adsorption Performance of the Beads for Naphthalene Removal, in Which the High Maximum Adsorption Capacity Is Attributed to the Chemisorption Process and Electrostatic Interactions

| isotherm model | parameters | bead type | T (°C) | un-Ch | Ch-FeO/TiO2 |
|---------------|------------|-----------|--------|-------|-------------|
| Langmuir      | $K_L$ (L/mg) | 0.07      | 0.47   |       |             |
|               | $q_m$ (mg/g) | 70.9      | 149.3  |       |             |
|               | $R^2$       | 0.9019    | 0.9303 |       |             |
| Freundlich    | $K_f$ (mg/g)/(mg/L)$^{1/n}$ | 4.98 | 52.57 |       |             |
|               | $n$         | 1.27      | 1.12   |       |             |
|               | $R^2$       | 0.9763    | 0.9979 |       |             |
| Elovich       | $K_e$       | 0.09      | 0.53   |       |             |
|               | $q_m$ (mg/g) | 55.3      | 131.6  |       |             |
|               | $R^2$       | 0.7734    | 0.9076 |       |             |

Figure 5. Description of the adsorption mechanism using the intraparticle diffusion model for (a) un-Ch and (b) Ch-FeO/TiO2.
acceptor bonding.\textsuperscript{69} Considering the complexity of seawater samples attributed to the high concentrations of additional organic materials (89.6 mg/L), we conclude that beads possess a high affinity toward PAHs, which leads to an outstanding adsorption performance. Moreover, other physicochemical properties analyzed were the pH (8.02), conductivity (45.9 mS/cm), and salinity (89.6 mg/L),\textsuperscript{70} which might represent an effect on the nanoparticles by interfering the electrostatic interaction. Therefore, the adsorption performance of the Ch-FeO/TiO$_2$ is rather limited compared to the un-Ch, presenting a slight difference in the adsorption efficiency.

The regeneration capacity of the beads and the naphthalene stability was evaluated through desorption experiments. For this purpose, we used CH$_3$OH and CH$_2$Cl$_2$ as solvent media to increase the elution of naphthalene from the beads, since they have been widely used for the extraction and separation of this and others PAHs. According to Figure 8, the regeneration capacity was considerably low with a maximum desorption percentage of 2.9% for Ch-FeO/TiO$_2$ and 0.9% for un-Ch, using CH$_3$OH and CH$_2$Cl$_2$ solutions, respectively. The low desorption values indicate the strong affinity between the naphthalene molecule and the surface of the beads. Although the CH$_3$OH and CH$_2$Cl$_2$ concentrations are not optimized, future studies regarding the desorption process are necessary for further recycling tests. This is considering the potential use of environmentally friendlier eluent solvents, or techniques that include the photodegradation of naphthalene. This is due to the TiO$_2$ nanoparticles possessing not only a suitable surface
for adsorption but also a promising photocatalytic activity for enhanced desorption.

3. CONCLUSIONS

We report the preparation of beads using chitosan as bio-support modified with iron oxide (FeO) and titanium dioxide (TiO₂) nanoparticles. The ionic cross-linking procedure allowed us to obtain beads with semispherical shapes. Ch-FeO/TiO₂ showed the highest BET surface area and pore size. These results were attributed to the presence of nanoparticles, which promoted the formation of porosity and increased the surface area. The semicrystalline nature of chitosan changed to a completely amorphous structure due to the break of intermolecular bonding after the incorporation of nanoparticles. The presence of FeO nanoparticles conferred a superparamagnetic behavior, even when the saturation magnetization was reduced. This opens the way to a facile recovery through magnetic decantation processes. The TGA studies suggested good thermal stability of the beads, indicating an ionic strengthening of the chitosan structure.

We also performed adsorption experiments using naphthalene aiming to evaluate the stability and efficiency of the beads for environmental applications. The pseudo-second-order model properly fitted the adsorption data, indicating that chemisorption was the primary adsorption mechanism. Ch-FeO/TiO₂ presented better maximum adsorption capacity attributed to a large number of active sites on the surface. A formation of a heterogeneous layer composed of monolayers was explained by fitting the experimental data to Langmuir and Freundlich models. The absorption efficiency of beads was evaluated by performing experiments in real seawater samples. Un-Ch and Ch-FeO/TiO₂ beads showed promising adsorption results attributed to the intramolecular donor–acceptor interaction between the chitosan functional groups and naphthalene. However, Ch-FeO/TiO₂ beads presented the highest naphthalene removal, indicating that the nanoparticles conferred a high affinity toward PAHs through additional noncovalent forces. Although the desorption percentage was low, we conclude that naphthalene is highly stable on the surface of the beads. This is attributed mainly to the strong chemisorption between naphthalene and the functional groups as well as the electrostatic interaction with the nanoparticles. The Ch-FeO/TiO₂ beads represent a novel and promising platform for water remediation. However, the desorption issues need to be addressed using more efficient and environmentally friendly techniques, such as the photocatalytic properties offered by the presence of TiO₂ nanoparticles in the structure.

4. EXPERIMENTAL METHODS

4.1. Materials. Biopolymer chitosan with high molecular weight (310,000–375,000 Da), acetic acid (99%), titanium isopropoxide (97%), methanol (CH₃OH, 99.8%), and standard analytical naphthalene (99.7%) were purchased from Merck. Iron(III) chloride hexahydrate (FeCl₃·6H₂O, 98%), iron(II) chloride tetrahydrate (FeCl₂·4H₂O, 99%), dichloromethane (CH₂Cl₂, 99.8%), and absolute ethanol (99.5%) were acquired from Sigma-Aldrich. The fresh leaves were collected from the rural population of Arjona in the Department of Bolivar, Colombia. Distilled water was used in all experiments.

4.2. Preparation of C. citratus Extract. C. citratus leaves were washed with distilled water to eliminate impurities, cut in small pieces, and dried in an oven at 60 °C overnight. The small pieces were ground to obtain a fine powder. Then, 100 g of this powder was added into a beaker with 800 mL of distilled water at 80 °C. The mixture was heated until it reduces its volume to 100 mL. Finally, the mixture was filtered to separate the C. citratus extract and stored at 5 °C.

4.3. Synthesis of Titanium Dioxide (TiO₂) Nanoparticles by Green Chemistry. TiO₂ nanoparticles were synthesized via green synthesis using the as-prepared C. citratus extract as a capping agent. Here, 50 mL of titanium isopropoxide (5 mM) was added to 15 mL of C. citratus extract under continuous stirring for 15 min. Afterward, the pH was adjusted to 8 using NaOH (1 M). A light-brown precipitate formed was collected and washed several times with distilled water and centrifuged at 5000 rpm to remove the excess of NaOH. To complete the crystallization of TiO₂, the precipitate was filtered and annealed at 700 °C for 3 h under air.

4.4. Synthesis of Iron Oxide (FeO) Nanoparticles by Co-precipitation. FeO nanoparticles were synthesized according to the traditional co-precipitation method. Here, 50 mL of FeCl₃·6H₂O (0.52 M) and 50 mL of FeCl₂·4H₂O (0.26 M) were mixed and heated up to 80 °C under continuous stirring at 120 rpm. The pH was adjusted to 10 using a NaOH solution (1 M), which was added dropwise, and then the solution was stirred for 1 h. A black precipitate formed was collected by magnetic decantation and washed several times with distilled water and once last with ethanol. Finally, the FeO nanoparticles were dried in an oven at 70 °C for 24 h.

4.5. Preparation of Chitosan Beads Modified with FeO and TiO₂ Nanoparticles. Unmodified chitosan (un-Ch) beads and chitosan beads modified with FeO and TiO₂ nanoparticles (Ch-FeO/TiO₂) were prepared through a simple ionic cross-linking procedure between opposite charges. A chitosan solution was prepared to dissolve 2 g of chitosan powder in 50 mL of acetic acid (4%). The solution was mixed for 24 h until a homogeneous gel was obtained. For the preparation of Ch-FeO/TiO₂ beads, FeO and TiO₂ nanoparticles were added into the initial chitosan gel (1:1:2 mass ratio), mixed for 1 h, and sonicated for 30 min at room temperature. Afterward, a syringe was used to add dropwise the gel solution into 500 mL of NaOH (2.5 M), with a dosing rate of 0.009 mL/s under stirring at 170 rpm, leading the formation of beads. To eliminate the excess of NaOH, un-Ch and Ch-FeO/TiO₂ beads were washed several times with distilled water and dried at room temperature. The formation of solid semispheres was observed.

4.6. Characterization. Morphological surface information was acquired using scanning electron microscopy (SEM) in a JEOL JCM 5000 NeoScope equipment. Elemental analysis was performed using an energy dispersive of X-ray (EDX, INCA Oxford) detector. Brunauer–Emmett–Teller (BET) surface area analysis and Barrett–Joyner–Halenda (BJH) pore size and volume analysis were performed using the accelerated surface area and porosimetry (ASAP) system 2020 v4.04 (Micromeritics). X-ray diffraction (XRD) patterns were acquired using a Bruker D8 Advance ECO powder diffractometer with Cu Kα radiation at room temperature in the 2θ range between 15 and 70° with a scan step size 0.02°. Physical properties measurement system (PPMS) equipped with a vibrating sample magnetometer (VSM) was used to obtain the magnetization curve of the FeO nanoparticles and...
the Ch-FeO/TiO₂ at 300 K with an applied field of 100 Oe. The functional groups were identified through Fourier transform infrared (FTIR) spectroscopy using a Nicolet Magna 760 FTIR spectrometer with a diamond crystal for the single attenuated total reflectance (ATR) mode, performing in the wavelength range of 4000−500 cm⁻¹ with a resolution of 8 cm⁻¹ and 256 scans. Thermogravimetric analysis (TGA) was performed with a temperature between 25 and 700 °C in a Mettler Toledo (STARes system model), using a nitrogen atmosphere and a temperature ramp of 10 °C/min. The naphthalene concentration was determined using an AT 6890 series plus gas chromatography equipped with an ATMSD 5973 mass spectrometer (GC-MS) and operated in a full scan radiofrequency mode. The simultaneous extraction-concentration of naphthalene was carried out in a DB-5MS column (5%-phenyl-poly(methylsiloxane), 60 m × 0.25 mm × 0.25 μm). The injection was through a split (30:1) mode using the solid-phase microextraction technique with vapor-phase monitoring, and a fused-silica fiber coated with poly( dimethylsiloxane) (PDMS)/divinylbenzene (DVB) with 65 μm of thickness. An external standardization technique was performed to obtain the calibration graph (see Figure S4) and to quantify the naphthalene in the aqueous samples. Here, the as-established response factor (RF) of the naphthalene reference standard solution at different concentrations was used.

### 4.7. Naphthalene Adsorption Studies

Adsorption experiments were performed via a batch system using a naphthalene solution. A naphthalene stock solution (100 ppm) was prepared in distilled water and CH₃OH (10% v/v) as co-solvent to improve the solubility of naphthalene. Then, un-Ch and Ch-FeO/TiO₂ were immersed in 3 mL of the naphthalene stock solution for 48 h at a constant temperature of 25 °C and covered to avoid exposure to natural light. The final concentration of beads in the naphthalene stock solution was adjusted to 3 g/L stock solution. The adsorption capacity and removal percentage were calculated as follows

\[
q_t = \frac{V(C_0 - C_t)}{m} \tag{1}
\]

\[
\mu = \frac{C_t - C_f}{C_f} \times 100 \tag{2}
\]

where \(q_t\) is the adsorption capacity (mg/g), \(\mu\) is the removal percentage, \(V\) is the solution volume (L), \(C_0\) is the initial concentration of naphthalene (mg/L), \(C_t\) is the final concentration of naphthalene (mg/L), and \(m\) is the mass of the beads (g).

#### 4.7.1. Naphthalene Adsorption Kinetics Determination

The adsorption kinetics determination was done using 50 mL of the previous un-Ch and Ch-FeO/TiO₂ solutions. The solutions were placed in a shaker, covered to avoid exposure to natural light, and shook at 175 rpm, under a constant temperature of 25 °C. The adsorption was performed for 48 h. All samples were immediately filtered and stored in amber vials for GC-MS analysis. The experimental data were adjusted using four different kinetics models, considering the pseudo-first-order model (eq 3), pseudo-second-order model (eq 4), Elovich model (eq 5), and Weber–Moors model (eq 6).

\[
\ln(q_e - q_t) = \ln q_e - k_1 t \tag{3}
\]

\[
q_t = \frac{1}{\beta} \ln \alpha \beta + \frac{1}{\beta} \ln t \tag{5}
\]

\[
q_t = k_2 t^{1/2} + C \tag{6}
\]

where \(q_t\) is the naphthalene adsorbed at the given time (mg/g), \(q_e\) is the naphthalene adsorbed at the equilibrium (mg/g), \(k_1\) is the pseudo-first-order constant, \(t\) is the given time (min), \(k_2\) is the pseudo-second-order constant, \(\alpha\) and \(\beta\) are the Elovich adsorption and desorption rate, respectively, \(C\) is the boundary layer effect (mg/g), and \(k_\alpha\) is the intraparticle diffusion constant.

#### 4.7.2. Naphthalene Adsorption Isotherms

Naphthalene adsorption isotherms were carried out in similar batch systems, as described in the adsorption kinetics studies. For these experiments, four naphthalene stock solutions of 20, 40, 60, and 80 ppm were prepared. Shaking time was reduced to 36 h based on the adsorption kinetic studies. Afterward, the beads were separated, and the supernatants were filtered and stored in amber vials for GC-MS analysis. Three isotherm models were used to adjust the experimental data, which allowed evaluating the adsorption distribution between liquid and solid phases in equilibrium data. Linear Langmuir’s model (eq 7) establishes that the adsorption is given by the formation of a monolayer, in which no interaction between adsorbed molecules occurs. On the other hand, the Freundlich model (eq 8) considers the formation of a heterogeneous surface through the multilayers of adsorbed molecules. Finally, the Elovich model (eq 9) consists of the exponential adsorption of molecules on the surfaces of the adsorbent.

\[
C_e = \frac{1}{q_e} \left( \frac{q_m}{K_f} \right) + \frac{C_e}{q_m} \tag{7}
\]

\[
q_e = K_f C_e^{1/n} \tag{8}
\]

\[
q_e = K_e C_e e^{-(q/q_m)} \tag{9}
\]

where \(C_e\) is the final concentration of solute (mg/L), \(q_e\) is the solute adsorbed at the equilibrium (mg/g), \(q_m\) is the maximum solute adsorbed (mg/g), \(K_f\) is the Langmuir constant, \(K_e\) and \(n\) are the Freundlich constants, and \(K_e\) is the Elovich constant.

#### 4.8. Desorption Tests

Desorption experiments were performed to determine the potential reusability of the beads. Two solutions of CH₃OH (40% in distilled water) and CH₂Cl₂ (30% in methanol) were prepared to evaluate the desorption of naphthalene from the un-Ch and Ch-FeO/TiO₂. Naphthalene can be extracted using CH₃OH as co-solvent due to the hydrogen-bonding capability in the presence of water. However, a water mixture was used to avoid co-solvent effects, but with a higher concentration compared to that used for the adsorption experiments. In the case of the second mixture, the CH₂Cl₂ is widely used for PAHs extraction in sediments. Therefore, this mixture was used as an eluent agent, considering that the beads are solid samples. The previously recovered beads were added into 100 mL of the CH₃OH and CH₂Cl₂ solutions. The solutions were placed in a shaker, covered to avoid exposure to natural light, and shook at 175 rpm, under a constant temperature of 25 °C for 24 h.
Afterward, the beads were separated, and the supernatants were filtered and stored in amber vials for GC-MS analysis.

4.9. Adsorption of Naphthalene in Seawater. To evaluate the adsorption capacity in real complex systems, tests using seawater were performed. The seawater samples were collected in the Cartagena Bay area (latitude: 10°24′5″N and longitude: 75°31′59.3″O). This area was selected based on preliminary studies of our group. The adsorption experiments were carried out using the same methodology previously described.

**ASSOCIATED CONTENT**

![Image](https://pubs.acs.org/10.1021/acsomega.0c02984)

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c02984.

Size distribution, detailed EDX analysis for elemental composition, N₂ adsorption/desorption isotherms, GC-MS calibration graph, most relevant GC-MS chromatograms, and adjustments of the experimental data to the kinetic and isotherm models (PDF)

**AUTHOR INFORMATION**

**Corresponding Author**

Adriana Herrera — Programa de Doctorado en Ingeniería, Grupo de Nanomateriales e Ingeniería de Procesos Asistida por Computador and Programa de Ingeniería Química, Grupo de Nanomateriales e Ingeniería de Procesos Asistida por Computador, Universidad de Cartagena, 130010 Cartagena, Colombia; Email: aherrera@unicartagena.edu.co

**Authors**

David Alfonso Patiño-Ruiz — Programa de Doctorado en Ingeniería, Grupo de Nanomateriales e Ingeniería de Procesos Asistida por Computador, Universidad de Cartagena, 130010 Cartagena, Colombia; orcid.org/0000-0002-6683-8557

Gesira De Avila — Programa de Ingeniería Química, Grupo de Diseño de Procesos y Aprovechamiento de Biomasa and Programa de Ingeniería Química, Grupo de Nanomateriales e Ingeniería de Procesos Asistida por Computador, Universidad de Cartagena, 130010 Cartagena, Colombia

Carlos Alarcón-Suesca — Departamento de Física, Grupo de Física de Nuevos Materiales, Universidad Nacional de Colombia, AA 5997 Bogotá D.C., Colombia; Laboratoire de Réactivité et Chimie des Solides (LRCS), Université de Picardie Jules Verne, 80039 Amiens, France

Ángel Dario González-Delgado — Programa de Ingeniería Química, Grupo de Nanomateriales e Ingeniería de Procesos Asistida por Computador, Universidad de Cartagena, 130010 Cartagena, Colombia; orcid.org/0000-0001-8100-8888

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.0c02984

**Notes**

The authors declare no competing financial interest.

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