FULL PAPER

A first-principles approach for treating wastewaters

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Abstract

Numerous materials are employed for the removal of contaminants from wastewaters. However, the regeneration/reuse of these materials is still seldom practiced. Quantitative insights into intermolecular forces between the contaminants and the functional surfaces might aid the rational design of reusable materials. Here, we compare the efficacies of aliphatic (C_8H_{18}), aromatic (C_6H_6), and aromatic perfluorinated (C_6F_6) moieties at removing methylene blue (MB^+) as a surrogate cationic dye from water. We employed density functional theory with an implicit polarizable continuum model for water to accurately determine the contributions of the solvent's electrostatics in the adsorption process. Our calculations pinpointed the relative contributions of π – π stacking, van der Waals complexation, hydrogen bonding, and cation– π interactions, predicting that MB^+ would bind the strongest with C_6F_6 due to hydrogen bonding and the weakest with C_8H_{18} . Complementary laboratory experiments revealed that, despite the similar hydrophobicity of silica beads functionalized with Si– C_8H_{17} , Si– C_6H_5 , and Si– C_6F_5 groups, as characterized by their water contact angles, the relative uptake of aqueous MB^+ varied as Si– C_6F_5 (95%) > Si– C_6H_5 (35%) > Si– C_8H_{17} (3%). This first principles-led experimental approach can be easily extended to other classes of dyes, thereby advancing the rational design of adsorbents.

KEYWORDS

adsorption, binding energy, intermolecular forces, non-covalent interactions, wastewater

1 | INTRODUCTION

The worldwide consumption of water has been steadily increasing to meet the needs of humanity.^[1] Freshwater resources are being unsustainably depleted to support agricultural and industrial sectors, and the situation is exacerbated by the ongoing climate change and pervasive land and water pollution.^[2–4] In this context, wastewater treatment serves the crucial purpose of water reuse and sustainable discharge into the environment.^[5] Additionally, recovering valuable materials and resources from wastewaters is a promising approach toward circular economy.^[6–9] Treatment methods for wastewaters depend on their source and contaminants, such as the removal of oil from produced water,^[10] the remediation of municipal waste with microorganisms,^[11] or the treatment of textile effluents with macromolecular dyes.^[12] Of these, we are interested in the removal of dyes from wastewaters generated in industries, such as textile, cosmetics, pulp and paper, food and beverages, packaging, paints, and pharmaceuticals.^[12] Over 100 000 commercial dyes are known presently,^[13] with an annual consumption of $>7 \times 10^8$ kg/y.^[14] About 5% to

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10% of these dyes appear in the effluent streams of industrial wastewater and are discharged into the environment.^[12,15] Many of these dyes are potentially toxic and could lead to unintended effects.^[12,13] In response, traditional methods to remove dyes from wastewater include adsorption, ion exchange, oxidation, and coagulation/flocculation.^[16] Adsorption is the most common strategy due to its low cost, efficiency, and ease of operation.^[12] In fact, common "broad-spectrum" adsorbents for dyes include activated carbon, silica gels, fly ash, bentonite, and perlite.^[12] However, these adsorbents are not regenerated after usage and are subsequently disposed of as waste.^[13] This is because the design of adsorbents has largely been empirical and without consideration of intermolecular forces. Thus, there is a need for rationally designed reusable adsorbents for treating wastewaters.

The rational design of a reusable adsorbent requires a quantitative understanding of the intermolecular and surface forces between the target contaminants and the adsorbents, such as ion- π interactions,^[17] π - π stacking,^[18] hydrogen bonding,^[19] and van der Waals interactions,^[20,21] among others.^[19] In fact, reusable adsorbents should bind contaminants with energies in the range of 5 to 10 k_bT /mol (3-6 kcal mol⁻¹), which is not only strong enough to facilitate wastewater treatment, but also weak enough to facilitate adsorbent regeneration.^[21-24] We chose methylene blue (MB⁺) as our model system, because it is a common cationic dye that is employed in the paper and pulp industry (Figure 1A).^[25] As an adsorbate, MB⁺ is quite "versatile": it can form hydrogen bonds (H-bond) with electronegative atoms such as O, N, and F; it can accept electrons in π - π stacks; it can participate in cation- π interactions^[17,26] due to its cationic nature (Figure 1B); and it can also interact through van der Waals interactions.^[27] It has been produced on a mass scale since the late 19th century, and it also serves as a starting material for numerous azine dyes.^[25] Its molecular versatility is further evidenced by its medical use to treat depression,^[28] breast cancer,^[29] malaria,^[30] Alzheimer's,^[31] and aging of the skin.^[32] Yet, quantitative insights into the factors and mechanisms governing the adsorption of MB⁺ even onto simple surfaces remain unclear. For example, it has been suggested that dispersion interactions and hydrophobic interactions are important in the adsorption of MB⁺ onto metals^[27,33] and silver iodide (AgI) suspensions,^[33] respectively, but a direct comparison of those interactions remains unavailable. Here, we utilize quantum mechanical calculations to predict binding energies of a hydrated MB⁺ cation with a broad range of aliphatic, aromatic, and perfluorinated aromatics as surrogates for adsorbents (Figure 2). Subsequently, we test these predictions through laboratory experiments using silica microspheres terminated with the same aliphatic, aromatic, and perfluorinated aromatic groups.

2 | MATERIALS AND METHODS

2.1 | Quantum mechanical calculations

Density functional theory (DFT) is a first-principles approach for predicting the electron density of molecular/ionic systems, which employs a self-consistent field approach (SCF) for solving the Schrödinger equation.^[34,35] It has been used extensively for electronic structure calculations in solid-state physics and materials science.^[24,36-39] The accuracy of DFT in studying the electronic and physical properties of materials is largely dependent on the choice of the exchange-correlation function. For example, the local density approximation (LDA) and the generalized gradient approximation (GGA) exchange-correlation functionals overestimate the dissociation energies and the hydrogen bonds, respectively,^[38] and they require a dispersion energy correction when modeling van der Waals interactions or studying water clusters.^[39] Hybrid functionals such as B3LYP^[40] provide a good example of hydrogen bonding,^[41,42] the structure of water clusters,^[43,44] chemistries at the air-water interface,^[45-49] graphene-based systems,^[50] guest-host binding of p-xylylenediamine to CB7,^[51] vibrational spectra of hexafluorobenzene,^[52] and π - π interactions in dimers of benzene and naphthalene.^[18] It should be noted that the accuracy of a DFT method crucially depends on the specific details of the molecular system.^[53,54] Here, we applied the B3LYP-level DFT to investigate the molecular interactions of MB⁺ with hexafluorobenzene (C₆F₆), benzene (C₆H₆), and n-octane (C₈H₁₈) groups (Figure 2). We accounted for the aqueous environment utilizing the Polarizable Continuum Model (PCM).^[55] We chose these groups as surrogates for functional surfaces to gain insights into the vast array of molecular interactions of MB⁺

FIGURE 1 A, A two-dimensional diagram of a methylene blue molecule. Color scheme: sulfur in yellow, nitrogen in dark blue, hydrogen in white, and carbon in gray. B, The Lewis structure of an MB⁺ cation with the positive charge on the quaternary ammonium

in an aqueous environment. We optimized numerous dimer conformations using DFT implemented in the Gaussian software^[56] at the B3LYP/6-311+G* level.^[40] For the most difficult convergence cases, as a result of encountering a shallow minima around the stationary point, we employed the option *MaxStep* = 1 that led to full convergence. We subsequently confirmed the stability of the optimized structures through frequency calculations at each stationary point.

2.2 | Experimental: Synthesis of hollow silica microspheres

To test the quantum mechanical predictions, we performed laboratory experiments. We used commercially available hollow silica microspheres (3M Glass Bubbles)^[57] with an average diameter ranging from 16 to 65 μm (Figure S1A). We modified their surface make-up following a two-step reaction, comprising of hydroxylation and silanation (Figure S1B).^[58] To hydroxylate the microspheres, we exposed them to an aqueous solution of hydrochloric acid (pH 2) at 90°C for 1 hour (Data S1). Next, batches of microspheres were silanized using (i) triethoxy(octyl)silane, (ii) trimethoxyphenylsilane, and (iii) (pentafluorophenyl)triethoxysilane, all of which were obtained from Sigma-Aldrich (CAS: 2943-75-1, 2996-92-1, and 20 083-34-5, respectively). This protocol produced silica microspheres terminated with Si—C₈H₁₇, Si—C₆F₅, and Si—C₆H₅ groups, which we confirmed using FTIR spectroscopy (Figure S2, Data S1).^[59] Methylene blue was obtained from Sigma-Aldrich (CAS: 122965-43-9) in the quaternary ammonium salt form (C₁₆H₁₈ClN₃S·xH₂O, molecular 319.85 g/mol [anhydrous basis]). We incubated different amounts of functionalized SiO₂ microspheres (0–100 mg) in aqueous solutions containing 100 ppm MB⁺. Subsequently, the solutions were tumbled gently for 5 minutes. The separation was easy, because the hollow microspheres floated up to the air–water interface; a general scheme for adsorption is shown in Figure 3. To characterize the concentration of MB⁺ in aqueous solutions before and after adsorption, we took aliquots, diluted them with deionized water, and characterized the concentration of MB⁺ spectrophotometrically using its extinction coefficient at 663 nm (Data S2). Note: the optical attenuation of light through our solutions followed the Beer–Lambert law; the experiments were repeated at least in quadruplicates.

FIGURE 2 Ball-and-stick diagrams of: A, hexafluorobenzene; B, octane; and C, benzene. Color scheme: carbon atoms (gray), fluorine (green), and hydrogen (white)

FIGURE 3 A general scheme for the adsorption of MB⁺ onto functionalized silica microspheres. The hydrated methylene blue cation is considered with an explicit coordination water molecule. During adsorption, the adsorbent displaces this water molecule to bind with MB⁺.

3 | RESULTS AND DISCUSSION

3.1 | Methylene blue in solution

We calculated the molecular electrostatic potential (ESP) of hydrated MB^+ , which is defined as the amount of work required to bring a positive unit charge from infinity to a distance r from the molecule.^[60,61] Thus, ESP comprises the contributions of the nuclear and the electronic charges, the latter calculated by methods such as Mulliken population analysis and Löwdin population analysis.^[62] We mapped the electron density (chosen with a value of $\rho = 0.02$) onto the electrostatic potential to obtain the ESP.^[62] The electron density was obtained from a Mulliken population analysis^[60] of the optimized DFT structure of MB^+ in an aqueous environment using the GaussView software (v. 5.0)^[63] (Figure 4A). Hydrated MB^+ has a positive ESP due to the overall electron charge deficiency of the cation, with the hydrogen atoms being the most positive (blue color) due to their low electronegativity. Thus, MB^+ can potentially participate in hydrogen bonding through these H atoms by accepting electrons in π – π stacking, such as from benzene. The N and S atoms in the central ring (yellow color) behave neutrally toward electrophile/nucleophile molecules. The region between the C=C double bonds and the two tertiary nitrogen atoms also shows low electron densities (light blue color), albeit more than for the H atoms. We qualitatively infer from the ESP plot that MB^+ potentially participates in hydrogen bonding, as well as π – π stacking and cation– π interactions.

FIGURE 4 A, The electron density mapped with the electrostatic potential for a hydrated MB^+ cation. For the plotted density, $\rho = 0.02$, the units range from $(-0.27, 0.27)$ atomic units (a.u.). Regions with positive ESP (blue) have lower electron density than the regions with negative ESP (red). The most positive value in the ESP corresponds to the two hydrogen atoms next to the sulfur atom (yellow color). The hydrated MB^+ cation is electron deficient, with the hydrogen atoms and the aromatic rings having the lowest electron density. Snapshots from DFT calculations of a B, MB^+ -benzene dimer in π – π stacking; C, D, E, dimers between MB^+ and C_6F_6 featuring H-bonds; F, MB^+ – C_6H_{18} dimer held by van der Waals interactions. Color scheme: fluorine green, hydrogen white, carbon dark gray, sulfur yellow, and nitrogen dark blue

3.2 | Prediction of adsorption of MB⁺

Here, we detail our semiquantitative approach to predict the relative adsorption of MB⁺ by our surrogate adsorbents. In order to make our model realistic, we added a water molecule in the coordination shell of MB⁺ such that it had a binding energy of $E_{\text{MB}^+ \cdot \text{H}_2\text{O}}$. We chose that particular position of the water molecule, (Figure 3) because, therein, we obtained the strongest binding energy between the functional groups and MB⁺. We assumed that during adsorption this hydrogen bonded water molecule is displaced by the adsorbent. Figure 3 depicts this scheme with silica microspheres functionalized with C₆F₆. The released water molecule simply becomes a part of the bulk water, releasing a fixed amount of energy, $E_{\text{H}_2\text{O}}$, which is half of the energy of a water dimer. Next, we define the adsorption energy between MB⁺ and the adsorbent as,

$$E_b = E_{\text{dimer}} - (E_{\text{MB}^+} + E_{\text{adsb}}) \quad (1)$$

and

$$E_{\text{ads}} = E_b + E_{\text{H}_2\text{O}} - E_{\text{MB}^+ \cdot \text{H}_2\text{O}} \quad (2)$$

where E_b is the binding energy of MB⁺ and the adsorbent (after removing the explicit water molecule), E_{dimer} is the electronic energy of the molecular complex (MB⁺/adsorbent), E_{MB^+} is the energy of a hydrated MB⁺ cation, E_{adsb} is the energy of the adsorbent, E_{ads} is the adsorption energy that we use to calculate binding constants, and $E_{\text{MB}^+ \cdot \text{H}_2\text{O}}$ is the energy required to unbind the MB⁺·H₂O dimer. It should be noted that E_b refers to the energy holding the MB⁺-adsorbent complex together, whereas E_{ads} refers to the energy needed/released when displacing water from the MB coordination shell to form the MB⁺-adsorbent complex. We obtained a DFT binding energy for a water dimer using the PCM model at 0 K of $-5.4 \text{ kcal mol}^{-1}$, which was in good agreement with the experimental results for water dimers in vacuum ($-5.58 \text{ kcal mol}^{-1}$)^[64] and previous theoretical calculations ($-5.0 \text{ kcal mol}^{-1}$)^[65]. Thus, $E_{\text{H}_2\text{O}} = -2.7 \text{ kcal mol}^{-1}$,^[65] and using the PCM method, we obtained the binding energy for $E_{\text{MB}^+ \cdot \text{H}_2\text{O}} = -1.4 \text{ kcal mol}^{-1}$ (Figure S4, Data S3). With these predicted adsorption energies and assuming that, in our dilute solutions, only a single layer of MB⁺ adsorbs onto the functionalized surface, we used the Arrhenius equation to calculate the relative reaction rate constants (k) by taking as a reference the reaction rate constant for the C₈ aliphatic, k_{ref} . We assume that the preexponential factor, A , in the Arrhenius equation is the same in all three cases and that the transition state barrier(s) that MB⁺ has to overcome to bind to the surface are similar in magnitude in all the cases. This assumption is reasonable because the molecular interactions during the physisorption processes do not involve proton or electron transfers that would require covalent bond breaking/forming and significant electrostatic preorganization.^[66] Furthermore, we assume that thermal fluctuations ($0.6 \text{ kcal mol}^{-1}$) facilitate MB⁺, the solvent, and the surface to sample through the configurational space to find the global minima. Thus, we can estimate the relative binding rates as follows,

$$\frac{k}{k_{\text{ref}}} = e^{-(\Delta E_{\text{ads}})/k_{\text{b}} T} \quad (3)$$

where ΔE_{ads} is the adsorption energy as defined in Equation (1) and relative to the adsorption energy of the C₈ aliphatic. A simple rearrangement of Equation (3) gives us the percentages of the relative rates of adsorption as,

$$\frac{k - k_{\text{ref}}}{k_{\text{ref}}} \times 100 = \left(e^{-(\Delta E_{\text{ads}})/k_{\text{b}} T} - 1 \right) \times 100 \quad (4)$$

Next, we present the results of our DFT predictions for a variety of geometric confirmations between MB⁺ and C₆F₆, C₆H₆, and C₈H₁₈ groups, with the aim of identifying the relative contributions of π - π stacking, hydrogen bonding (H-bonding), cation- π interactions, and van der Waals forces to the adsorption process (Table 1).

TABLE 1 Predictions of adsorption energies, E_{ads} , for π - π stacking, H-bonding, and van der Waals interactions between MB⁺ and C₆F₆, C₆H₆, and C₈H₁₈ groups and the relative uptakes of MB⁺ with the performance of n-octane taken as the reference

(Figure) Dimer	Key molecular interactions	Adsorption energy, E_{ads} (kcal mol ⁻¹)	Predicted, relative uptake of MB ⁺ (%) using Equation (4)
(Figure 4B) MB ⁺ -C ₆ H ₆	π - π stacking	-2.9	39
(Figure 4C) MB ⁺ -C ₆ F ₆	H-bond: F-H(methyl), sided	-2.9	39
(Figure 4D) MB ⁺ -C ₆ F ₆	H-bond: F-H(methyl)	-3.0	95
C ₆ F ₆ -MB ⁺ -C ₆ F ₆	H-bond: F-H(methyl)	-3.1	95
(Figure 4F) MB ⁺ -C ₈ H ₁₈	van der Waals	-2.7	0 (reference)

3.3 | π - π stacking between MB⁺ and C₆H₆ and C₆F₆ groups

Benzene can donate electrons through its delocalized p_z orbital to MB⁺ in water. In fact, we found that the dimer MB⁺-C₆H₆ has a stable configuration in the π - π stacking conformation (Figure 4B). The optimized structure has an average intermolecular distance, $d = 4.8$ Å, between (C-C), indicating a weakly bound dimer. This result is in overall agreement with higher-level electronic structure methods such as MP2 and CCSD(T) for the π - π benzene dimer, which shows an average intermolecular distance, d , in the range 3.8-4.1 Å.^[67] We found that the adsorption energy was $E_{\text{ads}} = -2.9$ kcal mol⁻¹ (Table 1). Next, we substituted hydrogen atoms of benzene with fluorine atoms to simulate interactions of MB⁺ with C₆F₆. Fluorine has a deactivating effect on cation- π interactions^[17,68] because electrons in C-F bonds are polarized toward fluorine atoms due to the latter's higher electronegativity.^[69] Thus, C₆F₆ is unlikely to interact with MB⁺ through its π orbitals.^[26] Thus, we expected π - π stacking for the MB⁺-C₆F₆ complex to be weaker than for the MB⁺-C₆H₆ complex. Indeed, this was true—while we arranged C₆F₆ to interact with MB⁺ through π - π stacking, (Figure 4B), the C₆F₆ molecule tilted over the MB⁺ during geometry optimization and underwent a significant displacement. The final structure comprised an MB⁺-C₆F₆ complex with hydrogen bonding between a fluorine atom and a hydrogen atom of MB⁺ (Figure 4C). The shortest distance between those atoms was, $d = 3.1$ Å, and the adsorption energy was $E_{\text{ads}} = -2.9$ kcal mol⁻¹.

3.4 | Hydrogen bonding

As MB⁺ and C₆F₆ interacted through H-bonding instead of π - π stacking, we investigated other configurations whereby MB⁺ and C₆F₆ were oriented facing each other. The final optimized structure had two H-bonds, one between a fluorine atom and a hydrogen atom of a methyl group of MB⁺ and another between a fluorine atom and a hydrogen atom bound to an sp² carbon (Figure 4D). The shortest F-H distance was $d = 3.1$ Å with the dimer adsorption energy, $E_{\text{ads}} = -3.0$ kcal mol⁻¹. Surprisingly, although C₆F₆ can interact with MB⁺ through π - π stacking, the overall low electron density of MB⁺ and the presence of fluorine favored the formation of H-bonds. It is worth noting that the adsorption energy also varied depending on the hybridization of the carbon atom; C(sp³)-F yielded a stronger hydrogen bond than C(sp²)-F.^[70] Interestingly, even a π -electron donor like benzene yielded a lower $E_{\text{ads}} = -2.9$ kcal mol⁻¹ in comparison to the H-bonded C₆H₆-MB⁺ dimer with $E_{\text{ads}} = -3.0$ kcal mol⁻¹. To further confirm the importance of the H-bonding, we optimized two C₆F₆ molecules with one MB⁺ monomer. We found that, similar to the previous case, C₆F₆ made H-bonds with MB⁺ (Figure 4E). Fluorine atoms in the C₆F₆ groups formed H-bonds with the methyl groups in MB⁺, but the shortest H-bond distance was to the hydrogen next to the sulfur atom, $d = 2.8$ Å and $E_{\text{ads}} = -3.1$ kcal mol⁻¹ (Figure 4E). The adsorption energy was slightly greater than that of MB⁺-C₆F₆, (Figure 4D), indicating that increasing the number of C₆F₆ species near MB⁺ enhances the extent of adsorption. However, when we studied the E_{ads} of MB⁺.2(C₆H₆) in π - π stacking conformation, we did not find any increment in the adsorption energy. (Figure S5, Data S3). Thus, only in the fluorinated case did we find that the most stable configuration was that with a ratio of 2:1. The study of 3:1 or higher configurations were computationally unfeasible or unable to converge.

3.5 | Cation- π interactions

MB⁺ is a large cation that could potentially interact with a π -system. In the gas phase, fluoroaromatic compounds are known to exhibit high binding energy with cations, for example, the ab initio binding energy of fluorobenzene with a lithium ion is $E_b = -31$ kcal.mol⁻¹.^[71] However, for MB⁺ interacting with C₆F₆ in an aqueous environment, we did not find dimer configurations stabilized by cation- π interactions (Figure S6, Data S3). The final optimized structures between MB⁺ and C₆F₆ comprised H-bonds between F and H atoms similar to those seen in Figure 4B, with similar binding energy and H-bond distances. Thus, C₆F₆-MB⁺ dimers optimized from the initial configurations of π - π stacking or cation- π stacking were not stable, and the optimized structures always led to dimers interacting through H-bonding. Furthermore, C₆H₆-MB⁺ did not demonstrate configurations stabilized by cation- π interactions or hydrogen bonding (only π - π stacking).

3.6 | Van der Waals interactions

Finally, we investigated the interactions between the aliphatic chain C₈H₁₈ and MB⁺ in an aqueous solution. We found that $E_{\text{ads}} = -2.7$ kcal mol⁻¹, and the interaction was driven by van der Waals dispersion forces.^[27] The average intermolecular distance $d = 3.2$ Å (Figure 4F).

3.7 | A comparison of various intermolecular forces

Based on the predictions from quantum mechanics, we listed the E_{ads} values due to different molecular interactions in Table 1. We used Equation (4) to predict the trend in the binding constants of the three functional groups, C₆F₆ (H-bonding) > C₆H₆ (π - π stacking and

H-bonding) > C_8H_{18} (vdW dispersion). To obtain quantitative insights, we benchmarked the binding constants against the aliphatic group (C_8H_{18}) and found the relative adsorption to vary such that C_6F_6 (95%) > C_6H_6 (39%) > C_8H_{18} (0), which was an unexpected result. Next, we tested our predictions through laboratory experiments.

3.8 | Experimental adsorption of MB^+ on an organic substrate

We designed laboratory experiments to test our predictions, ie, H-bonding between MB^+ and C_6F_6 leads to a dramatically higher adsorption than that due to π - π stacking between MB^+ and C_6H_6 or van der Waals interactions between MB^+ and C_8H_{18} . To this end, we functionalized hollow silica microspheres with $-C_8H_{17}$, $-C_6H_5$, and $-C_6F_5$ moieties (Section 2.2). We employed attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy to characterize the silica microspheres before and after functionalization (Figure S2). We found the following signatures for the molecular vibrations of the functional groups: Si- C_8H_{17} : asymmetric and symmetric CH_2 vibrations around 2922 cm^{-1} and 2852 cm^{-1} respectively; Si- C_6F_5 : C=C and C-F aromatic stretching bands at 1424 cm^{-1} and 1662 cm^{-1} , respectively; and Si- C_6H_5 : C-H stretch bands at 3074 cm^{-1} and 3052 cm^{-1} and C-C stretch (in-ring) at 1624 cm^{-1} and 1434 cm^{-1} (Data S1.2). Crucially, the apparent contact angles of water droplets on glass slides silanized with $-C_6F_5$, $-C_6H_5$, and $-C_8H_{17}$ groups were similar, which led us to expect that their uptake of MB^+ might be similar in magnitude (Data S1.3, Figure S3, and Table S1). This expectation was based on the extant literature on the adsorption of simple and complex organics onto hydrophobic surfaces in water—organic fouling—a leading cause for the failure of membrane-based separation technologies.^[58,72–75] We also note that ξ -potentials of hydrocarbon and perfluorocarbon surfaces, which have been investigated extensively in the past and intensely debated on regarding their influence on interfacial charges, wetting, surface forces, and adsorption.^[44,76–78] However, it was not possible to measure ξ -potentials of our specific samples because of their buoyancy and hydrophobicity; they would not stay inside a water-filled cuvette.

To compare the uptakes of MB^+ by silica microspheres, we measured the UV-VIS absorbance spectra of 100-ppm aqueous solutions of MB^+ . The trend was as follows: Si- C_6H_5 ($95\% \pm 1.8\%$) > Si- C_6H_5 ($35\% \pm 1.9\%$) > Si- C_8H_{17} ($3\% \pm 2.5\%$) (Figure 5). The alkyl derivative Si- C_8H_{17} barely adsorbed any MB^+ , the perfluorinated benzene performed the best, and the benzene-terminated microspheres performed intermediately, according to the predictions.

We also performed the elemental analysis of the relative carbon contents of the functionalized silica beads, from the functional groups on the surfaces, and found no correlation between the amount of carbon and the extent of adsorption (see Data S1.4, Table S2). Thus, the dramatically different adsorption levels of MB^+ onto the functional groups were due to different intermolecular forces at play. After these experiments, the beads could be easily removed from the air-water interface as they floated up. We are currently developing greener methodologies for regenerating them that will be reported soon. Figure 6 summarizes this report.

The advantage of this approach relies on the calculation of relative electronic energies to study adsorption at solid-liquid interfaces. We have simplified the complex molecular representation of the functionalized (solid) surfaces by individual (functional) molecules. Of course, this approach has limitations, for instance, the use of free energies (thermal correction) instead of electronic energies at 0 K might be more accurate. However, as the adsorption energy is relatively proportional to the total electronic energy, the addition of the free energy contribution should not alter the predicted trends significantly. Furthermore, the incorporation of vibrational frequencies into our energy calculations would be misleading because the individual (functional) molecules would behave more like a liquid that, in comparison to the solid phase, possesses extra rotational degrees of

FIGURE 5 Absorbance spectra obtained after treating 20-mL MB^+ solutions (initial concentration: 100 ppm) with 100 mg of silica microspheres functionalized with: A, Si- C_8H_{17} ; B, Si- C_6H_5 ; and C, Si- C_6F_5 . MB^+ absorbance in the solution after incubation followed this trend: Si- C_6H_5 ($95\% \pm 1.8\%$) > Si- C_6H_5 ($35\% \pm 1.9\%$) > Si- C_8H_{17} ($3\% \pm 2.5\%$). In all the cases, the operational pH was 6.8; all experiments were repeated at least in quadruplicates

FIGURE 6 Summary of laboratory experiments. (Left panel) Hollow silica microspheres functionalized with $-\text{C}_6\text{F}_5$, $-\text{C}_6\text{H}_5$, and $-\text{C}_8\text{H}_{17}$ groups were added to water containing 100 ppm MB^+ . (Middle panel) Intermolecular interactions between the silanized silica surfaces and MB^+ ions in water (Right panel). The final outcome of our simulated water treatment experiments: Pentafluorobenzene performed the best, followed by benzene and the aliphatic group as follows: C_6F_5 (95% $\pm 1.8\%$) > $\text{Si}-\text{C}_6\text{H}_5$ (35% $\pm 1.9\%$) > $\text{Si}-\text{C}_8\text{H}_{17}$

freedom. Despite these limitations, the model predictions are in excellent agreement with experimental observations and should be extendible toward the development of rational treatment protocols for other wastewaters.

4 | CONCLUSION

Towards rationally designing reusable adsorbents for complex contaminants in wastewater streams, such as from textile, cosmetics, pulp and paper, food and beverages, packaging, paints, and pharmaceutical industries, we investigated molecular interactions of MB^+ with C_6F_6 , C_6H_6 , and C_8H_{18} groups as surrogate adsorbents. DFT was employed with the Polarizable Continuum Model to accurately determine the contributions of the solvent's electrostatics during adsorption. Model calculations predicted that the primary intermolecular interactions of MB^+ with these functional groups were hydrogen bonding between MB^+ and C_6F_6 ; $\pi-\pi$ stacking between C_6H_6 and MB^+ ; and van der Waals dispersion interactions between C_8H_{18} . Based on this, the relative magnitudes of the predicted binding constants for MB^+ were: C_6F_6 (95%) > C_6H_6 (39%) > C_8H_{18} (0). Thus, DFT predicted that fluorinated aromatics are more suitable for removing MB^+ from water than ordinary aromatics and hydrocarbons. Gaining these molecular insights from an exclusively experimental approach would be very difficult. For instance, one cannot predict the observed behaviors based on water contact angles, which are often used to assess surfaces' ability to aggregate organics in water by hydrophobic interactions.^[79] Indeed, our laboratory experiments with functionalized silica microspheres confirmed the predicted trends: $\text{Si}-\text{C}_6\text{F}_5$ (95% $\pm 1.8\%$) > $\text{Si}-\text{C}_6\text{H}_5$ (35% $\pm 1.9\%$) > $\text{Si}-\text{C}_8\text{H}_{17}$ (3% $\pm 2.5\%$). Thus, this report illustrates that a clear understanding of intermolecular forces is crucial in designing adsorbents for complex wastewater contaminants, such as dyes. This approach can thus be extended to anionic/zwitterionic/uncharged dyes, other wastewater contaminants, and also for finding greener and fouling-resistant materials/approaches.^[80–85] Taken together, our findings suggest that this first-principles approach, supported by laboratory experiments, for the rational design of functional materials in the treatment of wastewaters can contribute to the sustainable use of water.

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AUTHOR CONTRIBUTIONS

Adriano Santana: Conceptualization; investigation; data curation; formal analysis; writing-review and editing. **Andreia Farinha:** Conceptualization; investigation; validation; data curation; project administration; writing-review and editing. **Aniela Torano:** Investigation; Data curation; writing-review and editing. **Mahmoud Ibrahim:** Methodology; validation. **Himanshu Mishra:** Conceptualization; data curation; formal analysis; funding acquisition; investigation; methodology; project administration; resources; supervision; writing-original draft; writing-review and editing.

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