Research Article

Sorption Mechanisms and Enhancement of Selected Organochlorine Pollutants in Water on Zeolites

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This study investigates the adsorption capacities of selected organochlorines on zeolites, focusing on hexachlorobenzene (HCB), hexachlorotetradecane (HCTD), hexachlorodecane (HCD), hexachlorocyclohexane (HCH), heptachlorodecane (HPCD), octachlorodecane (OCD), dichlorodiphenyltrichloroethane (DDT), and octachlorotetradecane (OCTD). The structures of the organochlorines were optimized and their Frontier molecular orbitals were calculated. The analysis of HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) energies provided insights into the molecules' electron-donating and -accepting capabilities. The present research identified the universal force field as suitable for the investigation and used it to evaluate the adsorption capacities of the pollutants on various zeolites. It was found that CLO (a cubic microporous gallophosphate) demonstrated the highest adsorption capacity for HCB among 245 zeolites, with a loading capacity of 65.84 wt%. In terms of molecules adsorbed per cell, CLO remained the highest with 120 molecules per cell for HCB, 113 molecules per cell for HCH, 43 molecules per cell for DDT, 21 molecules per cell for HCTD, 19 molecules per cell for OCTD, 47 molecules per cell for HCD, 30 molecules per cell for HPCD, and 22 molecules per cell for OCD. The analysis revealed correlations between the structural parameters of zeolites (mass, density, HVF, APV, VSA, GSA, DPS, and Di) and their adsorption capacities. The investigation delved into cluster models to understand the interaction of organochlorines with the zeolite framework. The study explored the impact of doping CLO zeolite with different atoms (Al, Si, and Na) on adsorption capacity. The results showed that doping with aluminum improved both loading capacity and adsorption energy and dissociate the chlorinated compounds during adsorption. Quantum chemical calculations show that hydrogen-based bonding of the organochlorides on the CLO is thermodynamically favorable compared to dissociative adsorption. In addition, oxygen atoms in the zeolites provide active adsorption sites. In the present work, laboratory adsorption experiments were performed, treating zeolites with heat at 400°C. Surprisingly, untreated zeolites outperformed treated ones, adsorbing up to 91% of HCB, while treated zeolites reached saturation after the third run. The study attributed the better performance of untreated zeolites to the presence of interstitial water and hydrogen atoms, which are critical for electrostatic interactions with organic compounds. In general, this research provides a comprehensive analysis of the adsorption capacities of organochlorines on zeolites, combining computational simulations and laboratory experiments.

This work's distinctive quality is its methodology that combines molecular simulations, experimental verification, doping, and interstitial water effects. The findings emphasize the importance of zeolite (a high-porosity nanostructured material) structure, composition, and treatment methods in determining their effectiveness as adsorbents for environmental pollutants.

1. Introduction

Several studies have shown that zeolites are good adsorbents of various contaminants [1]. These crystalline solids are ecologically friendly, but their framework composition has a great effect on the quantity of their micropores and other physicochemical characteristics [2, 3]. By adjusting the SiO_2/Al_2O_3 ratio (SAR), these materials' hydrophilic/hydrophobic properties can be adjusted [4, 5], while high porosity and vast surface areas are imparted to them by their 3D framework, which creates nanometer-sized channels and cages [6-7]. On the other hand, the adsorption selectivity towards host molecules is significantly influenced by the interior pore structure's shape. These factors have led to the usage of zeolites as adsorbent media for particular chemical classes, including hydrocarbons [8, 9, 10], halocarbons [11, 12], and pharmaceuticals [13, 14, 15].

The selection of zeolites as the primary focus in this study stems from their exceptional attributes that make them highly suitable for the investigation of organochlorine compounds. Zeolites possess a remarkable adsorption capacity owing to their extensive surface area and porous structure, providing an ideal environment for capturing and retaining pollutants [16]. The diverse structural frameworks among zeolite types offer a nuanced exploration into how these variations influence the adsorption performance of organochlorines. Moreover, the distinctive surface chemistries of zeolites, characterized by specific functional groups and charge distribution, play a pivotal role in understanding the nuanced interactions with targeted pollutants. The molecular sieving effect, facilitated by the porous nature of zeolites, ensures selective adsorption based on the size and shape of molecules. In addition, the cation exchange capacity intrinsic to zeolites is a crucial aspect that enhances their effectiveness in capturing and immobilizing pollutants. By delving into the impact of surface area, pore size distribution, and thermal stability—properties inherent to zeolites—the study aims to provide a comprehensive understanding of the adsorption mechanisms involved. Furthermore, the exploration of modified zeolites introduces a dimension of tailoring adsorption properties, demonstrating the versatility of zeolites as adaptable materials for addressing specific environmental challenges [17]. The present study aims at investigating the sorption mechanisms of selected organochloride pollutants on different types of zeolites (245 types), determining the influence of zeolite properties (e.g., framework structure, composition, surface chemistry) on the sorption of organochloride pollutants, and exploring the potential of modifying zeolite surfaces through functionalization or incorporation of additional materials to enhance the adsorption capacity and selectivity for organochloride pollutants. The selection of organochlorides in this study is driven by their widespread environmental presence and persistence, posing risks to ecosystems and human health. Organochlorides, found in various industrial and agricultural activities, are challenging to remediate due to their stability. The study addresses this environmental concern by investigating their adsorption on zeolite surfaces, aiming to contribute valuable insights for effective pollutant removal strategies. The choice is pragmatic, aligning with the study's goal of addressing real-world challenges and offering practical solutions.

The historical background of the study on zeolite adsorption of organochloride pollutants traces back to the 18th century, where the unique properties of zeolites first captivated scientists. Throughout the mid-20th century, systematic research into zeolite properties, including framework composition and surface chemistry, laid the foundation for their application in adsorption processes. The development of molecular mechanical techniques and statistical physics models in the latter half of the 20th century enabled a more precise understanding of zeolite-guest interactions at the atomic level. The 21st century saw a growing environmental awareness, prompting a search for sustainable solutions to water pollution. Zeolites, with their eco-friendly nature and versatile adsorption capabilities, gained prominence for environmental remediation. Recent advancements, such as the discovery of stable H-bonded adducts during drug adsorption on zeolites, fueled further exploration of zeolite-based solutions for removing organic contaminants. The ongoing research outlined in the study represents a continuation of historical developments. It aims to deepen our understanding of zeolite-guest interactions and expand zeolite applications by exploring modifications to their surfaces through functionalization and the incorporation of additional materials. The study reflects the enduring quest for innovative and sustainable technologies to address environmental challenges.

Organic molecules adsorption on zeolites adsorbents can involve both nonspecific (ionic) and specific interactions because clearly defined local chemical bonds, either covalent or supramolecular, are formed [18]. For a particular adsorbent material, the various interactions will depend on factors such as the compounds' solubility, the quantity of H-donor groups, and the acid-base properties [19]. Recent research showed that drugs adsorbed from aqueous solutions on zeolites had stable H-bonded adducts [13].

Adsorption and degradation are two key processes in the removal of organic pollutants from the environment using various materials [20]. Adsorption involves the physical or chemical adherence of pollutants to the surface of a solid material, increasing its concentration on the material's surface. This is particularly relevant in high-porosity materials like zeolites, which offer a large surface area for effective adsorption. On the other hand, degradation refers to the transformation of pollutants into less harmful substances through chemical reactions, often facilitated by catalysts or reactive materials. Both

processes play crucial roles in environmental remediation, with adsorption providing immediate pollutant removal and degradation offering a long-term solution by breaking down pollutants into less toxic forms. The choice of materials, their properties, and the specific pollutants targeted are critical factors influencing the success of these processes.

The strength and stability of the adsorption are determined by the zeolite-guest interaction energy, which is a critical factor in the adsorption process (Table 1). A stronger affinity between the zeolite and the organic pollutant is indicated by a higher interaction energy, which leads to a more efficient adsorption process. The zeolite's chemical makeup, the framework's structure, the size and shape of the organic pollutant molecule, and the type of chemical bonds that connect the zeolite and the pollutant can all have an impact on the interaction energy. Designing effective adsorbents for the removal of organic contaminants and optimizing adsorption procedures depend on an understanding of the zeolite-guest interaction energy [21]. Researchers can increase the adsorption capacity and selectivity of zeolites by adjusting the zeolite characteristics and managing the interaction energy, leading to more effective methods for water purification and environmental remediation.

The sorption and desorption processes are pivotal aspects of the studied zeolite-based organochlorine adsorption system. The investigation into sorption involves understanding how zeolites attract and retain organochlorine compounds, shedding light on the mechanisms governing the initial uptake. The zeolite's microporous structure and high surface area play a crucial role, providing ample sites for the adsorption of organochlorines. The simulations and experimental data collectively suggest that the adsorption process is influenced by factors such as the type of zeolite, structural modifications, and the specific characteristics of the organochlorine compounds. On the other hand, the exploration of desorption is equally significant, as it addresses the practical applicability and sustainability of zeolite-based remediation. The ability to desorb and release organochlorines from zeolites is vital for the regeneration and reusability of the adsorbent material. The study's emphasis on investigating desorption characteristics provides valuable insights into the reversibility of the adsorption process. Factors affecting desorption efficiency, such as temperature and pore structure, are crucial considerations for optimizing zeolite regeneration. The comprehensive nature of the study, incorporating both simulation and experimental results, allows for a nuanced understanding of sorption and desorption dynamics. The structural modifications, including silicon, aluminum, or sodium doping, contribute to tailoring zeolite properties for enhanced sorption and desorption capabilities. This strategic approach aligns with the goal of developing efficient and sustainable environmental remediation technologies. In essence, the discussion on sorption and desorption in this study highlights the multifaceted nature of zeolite-organochlorine interactions. It underscores the importance of not only effective adsorption but also the ability to release contaminants, providing a holistic perspective on the practical

Table 1: List of pollutants with their calculated zeolite-guest interaction energies for zeolite MOR and FAU obtained from literature.

Pollutant	MOR E_{zg} (kJ mol^{-1})	FAU E_{zg} (kJ mol^{-1})
Acetaminophen	−6	−12
Atrazine	43	2
Caffeine	12	5
Carbamazepine	40	11
DEET	97	6
Diazepam	17	5
Diclofenac	−15	−2
Dilantin	14	1
Estrone	100	35
Fluoxetine	100	98
Gemfibrozil	98	6
Hydrocodone	23	26
Ibuprofen	98	6
Meprobamate	97	7
Naproxen	82	2
Oxybenzone	99	47
Pentoxifylline	21	3
Sulfamethoxazole	13	0
TCEP	21	7
Triclosan	99	45
Trimethoprim	46	5

implementation of zeolite-based remediation strategies. Table 1 shows a summary of various organic pollutants with their associated interaction energy as reported in the literature for two zeolite types, MOR and FAU.

Molecular mechanical techniques enable atomic-level analysis of materials and determination of bulk properties using force fields [22]. The interactions in a molecular system are determined by potential functions. A specific instance of an adsorption process is represented by each model statement in statistical physics modeling. These models are developed progressively, starting with the simplest Langmuir model (one site energy, one site occupation, and one layer) and progressing to more complicated adsorption systems such as the Hill model (monolayer, monoenergy, and multioccupancy), double Hill (monolayer, different site energies, and mono-occupancy), or BET (multilayer, multisite energies, mono-, or multi-occupancy) [23, 24]. In order to choose the optimal material for adsorption of organochlorines (Figure 1) from water, this research offers a simulation-based method to forecast the loading ability of several zeolites. In order to determine the significance of the many descriptors that have an impact on the elimination of these organic pollutants from water, a data-based approach was used. Insights into the sorption mechanisms were provided by quantum chemical simulations. The impact of doping the zeolites with particular elements on the loading capacity was then thoroughly examined. Laboratory experiments were performed using adsorption columns, and the role of interstitial water was established.

This comprehensive study on the adsorption capacities of various zeolites for selected organochlorines, Figure 1, holds significant importance in the field of environmental science and material engineering. The research not only provides detailed insights into the structural characteristics
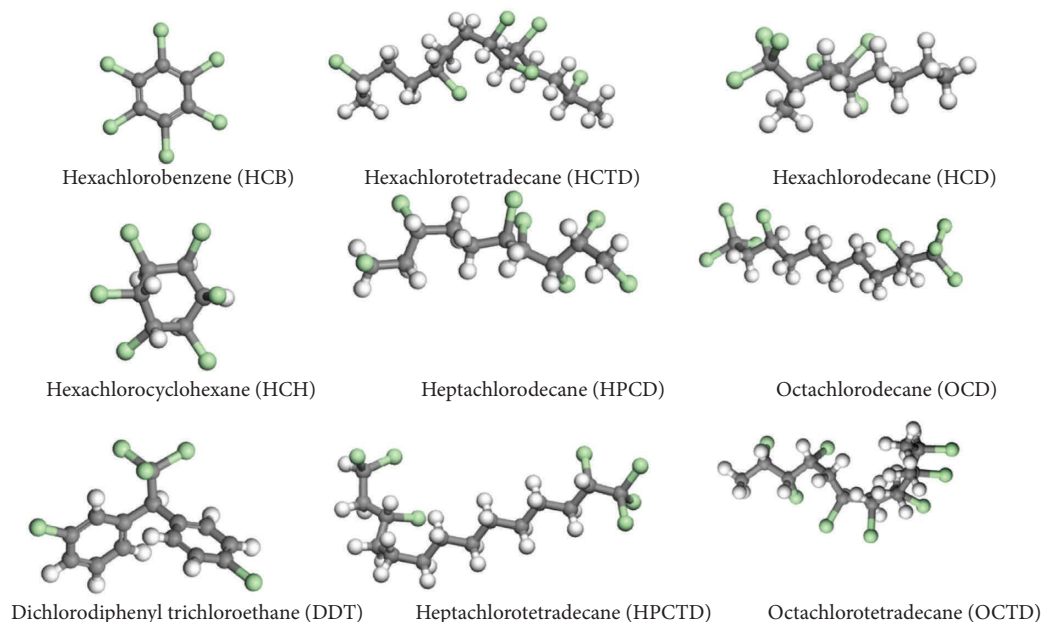
FIGURE 1: Examples of chlorinated organic pollutants that have been reported in surface and underground waters.

and performance of different zeolites but also establishes a correlation between their properties and adsorption capacities. The identification of the universal force field as the most suitable for predicting adsorption behaviors enhances the understanding of molecular interactions. Moreover, the investigation into the impact of zeolite doping on adsorption capacity, supported by thorough analysis and charge distribution studies, adds a valuable dimension to the study. The laboratory experiments, particularly the comparison between treated and untreated zeolites, reveal practical implications for zeolite application in pollutant removal. The findings emphasize the critical role of oxygen atoms in creating active adsorption sites, shedding light on a key structural feature influencing adsorption efficiency. Generally, this research contributes to the optimization of zeolite selection and treatment methods for environmental remediation, offering valuable insights for designing effective adsorbents in pollution control applications.

2. Materials and Methods

The International Zeolites Association (IZA) database provided all of the zeolites used in this simulation work [25]. The structures for the organochlorines were obtained from PubChem [26] and optimized using the Dmol3 module program [27] in material studio software [28] using the GGA/PBE functional [29] and DND basis set [30]. Grand-canonical Monte Carlo (GCMC) simulations were carried out utilizing the continuous fractional component approach (CFCMC) to explore adsorption [31]. Mostly in the grand-canonical ensemble, the chemical potential, volume, and temperature remain constant. The frugality coefficients were taken to be 1. Every location on the adsorption isotherms was created using production cycles 5×10^5. Each Monte Carlo cycle was performed using the random Monte Carlo

trials, operations of translation, rotation, regeneration, CFCMC interchange of "fractional" particles, and identities adjustments. Whole adsorption isotherms were calculated for each chlorinated compound. Material Studio software was used for all simulations [32]. The IRASPA software [33] was used to quantify the characteristic features of zeolites, including mass (M), density (D), helium void fraction (HVF), accessible pore volume (APV), gravimetric surface area (GSA), and dimensionality of the pore system (Di). To investigate the effect of silicon, aluminum, or sodium doping in the CLO zeolite, five phosphorus atoms were replaced with silicon, aluminum, or sodium. In each case, an extra framework was created in order to balance the charges. After this, new charges were assigned on all the atoms both in the zeolite structure and the extra framework created.

Clinoptilolite and faujasite zeolites were obtained commercially for experimental use. Before sorption experiments, the zeolites were activated by heating at high temperatures of 400°C under vacuum pressure for 24 hrs. The experimental setup was meticulously designed, employing columns as the primary vessels for adsorption. These columns were filled with various adsorbents, which were compacted using distilled water [34] to ensure consistency in the packing density. Two different types of zeolite adsorbent materials were used, faujasite zeolite (zeolite x) and clinoptilolite, for comparison purposes. To enhance the hydrophobic nature and Si/Al ratio of zeolite x, a mixture with silica gel in a specific ratio (5 : 3) was prepared. This careful manipulation aimed to optimize the adsorption efficiency of zeolite x when utilized in the columns. This was done for both treated and untreated zeolite. Simultaneously, clinoptilolite, known for its Si/Al ratio ranging between 4.0 and 5.3 [35], was investigated independently. Silica gel, a material with potential adsorption capabilities for organic pollutants, was also included in the experimental design for

comparison purposes. The experimental apparatus comprised five columns: one contains silica gel, another with treated zeolite x, a third with untreated zeolite x, the fourth with treated clinoptilolite, and the fifth with untreated clinoptilolite zeolite. A meticulous calibration process was implemented using various standard solutions derived from a 30 ppm stock solution of the hexachlorobenzene pollutant. Each column was filled with a predetermined amount of water to establish the initial pollutant concentration. The pollutant solution, with a known concentration of 15 ppm, was systematically passed through each column. Filtrate concentrations were confirmed through multiple iterations, providing a comprehensive dataset for determining equilibrium concentrations and evaluating the reusability of each zeolite under different conditions.

3. Results and Discussion

3.1. Simulations of Organochlorine Adsorption Mechanisms to Zeolites. The structures of selected organochlorines (Figure 1) were optimized and their Frontier molecular orbitals were calculated (Figure 2). The global hardness, calculated using the HOMO energy of the orbital (E_{HOMO}), is frequently connected with a molecule's capability of donating electrons, while the LUMO energy of the orbital (E_{LUMO}), depends on the molecule's capability to accept electrons. The difference in energy between HOMO and LUMO also contributes to the explanation of the electrical and chemical properties of the particles. Hexachlorodecane possesses the smallest HOMO energy (−0.2558 eV), but dichlorodiphenyltrichloroethane has a considerably greater HOMO energy (−0.1832 eV), as determined by analyses of the electron orbitals energy levels. The HOMO-LUMO energy gaps are 0.1456, 0.1952, 0.1841, 0.1777, 0.1912, 0.1761, 0.1406, 0.1696, and 0.1977 eV for hexachlorobenzene, hexachlorotetradecane, hexachlorodecane hexachloro cyclohexane, heptachlorodecane, octachlorodecane, dichlorodiphenyltrichloroethane, heptachlorotetradecane, and octachlorotetradecane, respectively. Therefore, octachlorotetradecane has a higher stability. It has relatively a higher chemical hardness of 0.1977 eV, while dichlorodiphenyltrichloroethane is less stable and has a relatively low chemical harness of 0.1406 eV.

Considering the structure of HCB (a phenyl ring with six chlorine atoms attached on each of the carbon atoms), we first evaluated its adsorption capacities on the zeolites. Materials Studio software has a variety of inbuilt force fields which are designed for the adsorption of different categories of compounds. Thus, we first compared the outcomes of several force fields (Figure 3), in order to choose a force field that is appropriate for our systems.

In contrast to compass [36], valency-consistent force field, CVFF [37], and polymer-consistent force field, PCFF [38], we discovered that the universal force field [39] was best for organic compounds used in this investigation. Since the geometries and conformational energy differences of organic molecules, main-group inorganics, and metal complexes have been found to be predicted with moderate accuracy by the universal force field, it is suggested for

organometallic systems and other systems for which other force fields do not have parameters [40]. As a result, we concentrated on the universal force field in the primary text.

Table S1 (supporting information) displays the structural characteristics of 245 different types of zeolites along with the loading of HCB, including mass (M), density (D), helium void fraction (HVF), accessible pore volume (APV), gravimetric surface area (GSA), and dimensionality of the pore system (Di). Out of the 245 zeolites that were studied, 71 zeolites demonstrated the ability to adsorb hexachlorobenzene with CLO, a cubic microporous gallophosphate with three-dimensional channels surrounded by 20-membered rings in the shape of a four-leaf clover, having the highest capacity of 65.84 wt%. CLO showed a stepwise multilayer adsorption isotherm that only occurs when the sample surface has various adsorption site types with energetically diverse properties (Figure 4).

Conversely, the loading of all the other zeolites was relatively low with nearly a horizontal plateau isotherm. This is attributed to the limited active sites for HCB adsorption. CLO has a mass of 17728 g/mol, density of 1129 kg/m³, helium void fraction of 0.55, a dimensionality of the pore system of 3, a largest overall cavity diameter of 15.33, and a larger volumetric surface area of 1070 m²/cm³. On the other hand, RWY has a lower mass and density (2884 g/mol and 1129 kg/m³, respectively) and a higher helium void fraction, accessible pore volume, and gravimetric surface area (0.66 and 0.77 cm³/g, respectively) compared to CLO. It has a comparable volumetric surface area with respect to CLO. It has 54.23 wt% of hexachlorobenzene and is ranked the second after CLO in terms of wt%. ITV is ranked the third after RWY. Despite ITV having a larger mass, density and VSA than RWY, it possesses a lower HVF, APV, GSA, and Di compared to RWY. These differences may be used to explain why it has 33.65 wt% compared to 54.23 wt% of RWY. ITV is followed closely by IFU which has adsorption capacity of 32.41% wt. IFU has a small mass, HVF, APV, VSA, and GSA compared to ITV. This may be the reason why it has a lower capacity than ITV. However, IFU has a larger Di than ITV and this explains why it ranked after ITV. LTA has almost similar loading capacity as IFU (32.31 wt% vs. 32.41 wt%, respectively). This closeness may be attributed the closeness in VSA and Di between the two zeolites. However, LTA has a lower mass than HVF, APV, and GSA and this explains why it has a lower capacity for HCB than IFU. On the other hand, zeolite LTA has a higher density than IFU and this may be an attribute as to why it ranked fifth after IFU. Zeolite IRR has a higher mass than HVF, APV, GSA, and Di. It is expected that it has a higher capacity than LTA. However, this is not the case; instead, it has a lower wt% capacity than LTA. It has 31.31 wt% compared to 32.31 wt% of LTA. This scenario might have occurred due to the fact that zeolite IRR has a lower density and VSA compared to LTA. Zeolites FAU, SBT, and VFI are among those with similar HCB adsorption capacity, with 28.32 wt%, and it may be attributed to their negligible differences in HVF, APV, and Di. In addition, they have almost equal densities and VSA. On the other hand, zeolite TSC has the largest mass, density, and Di and yet it has a lower wt%

HOMO −0.2294

ΔE = 0.1456 ev

−0.0838

LUMO

(a)

−0.2341

ΔE = 0.1952 ev

−0.0389

(b)

−0.2558

ΔE = 0.1841 ev

−0.0717

(c)

HOMO

−0.2553

ΔE = 0.1777 ev

−0.0776

LUMO

(d)

−0.2427

ΔE = 0.1912 ev

−0.0515

(e)

−0.2495

ΔE = 0.1761 ev

−0.0734

(f)

HOMO

−0. 1832

ΔE = 0.1406 ev

−0.0777

LUMO

(g)

−0.2388

ΔE = 0.1696 ev

−0.0692

(h)

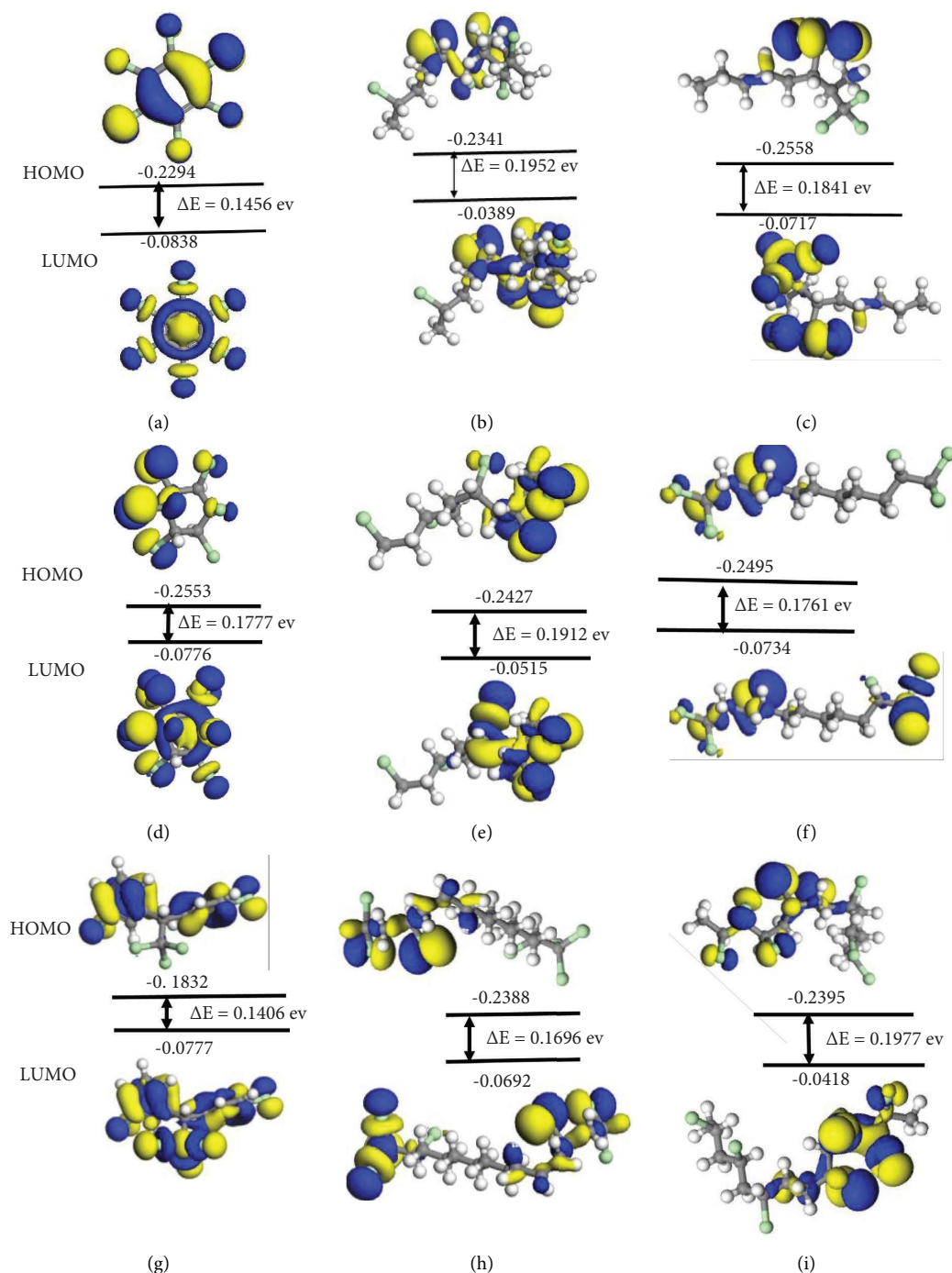−0.2395

ΔE = 0.1977 ev

−0.0418

(i)

Figure 2: Optimized structures of hexachlorobenzene (a), hexachlorotetradecane (b), hexachlorodecane (c) hexachlorocyclohexane (d), heptachlorodecane (e), octachlorodecane (f), dichlorodiphenyltrichloroethane (g), heptachlorotetradecane (h), and octa-chlorotetradecane (i), respectively. The colors gray, white, and green, respectively, represent the atoms of carbon, hydrogen, and chlorine. Positive and negative orbital values are represented by the yellow and blue sections, respectively.

HCB capacity. In comparison with CLO, TSC would be expected to have a higher percentage capacity considering mass, density, and Di. However, the opposite is seen for HCB loading. This may be attributed to low HVF, APV GSA, and VSA in TSC zeolite. Among the 71 zeolites that showed the possibility of adsorbing HCB compounds, eight of them had an adsorption capacity less than 5 wt% with two having an

adsorption capacity less than 1 wt%. All the other zeolites among the 71 had capacities above 5 wt%. A correlation analysis was done in order to get more understanding of how various structural features affect the wt% (Figure 5). The results showed that the mass of the zeolites and density were negatively correlated to adsorption capacity. This means that a heavier material would have less uptake capacity compared
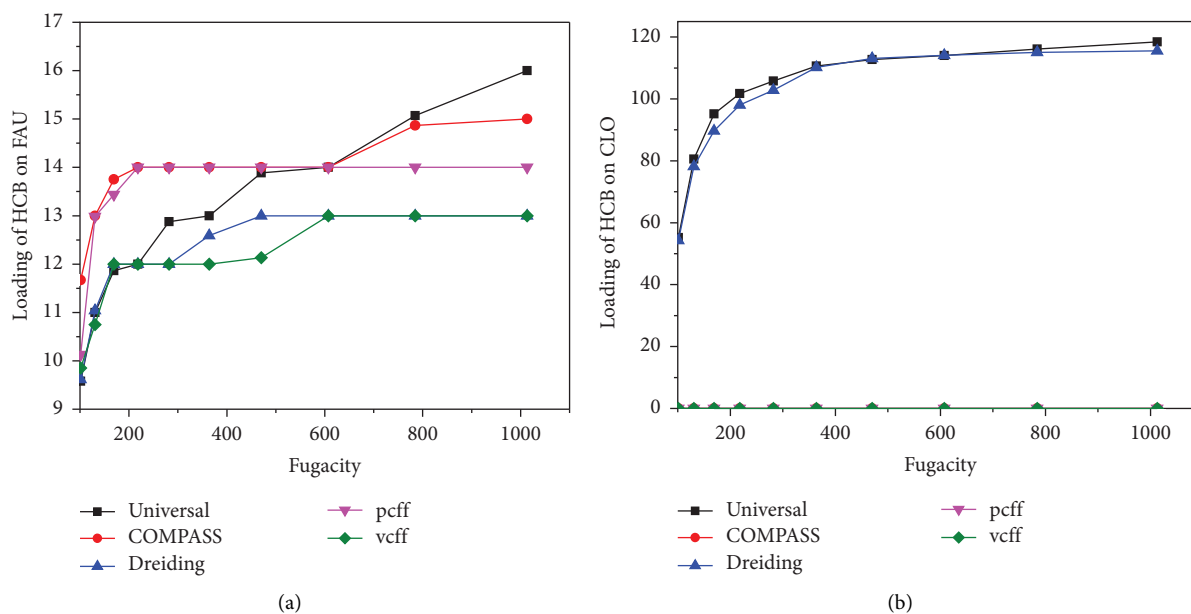
(a)

(b)

FIGURE 3: Loading of hexachlorobenzene (HCB) molecules on FAU and CLO zeolites using various force fields.
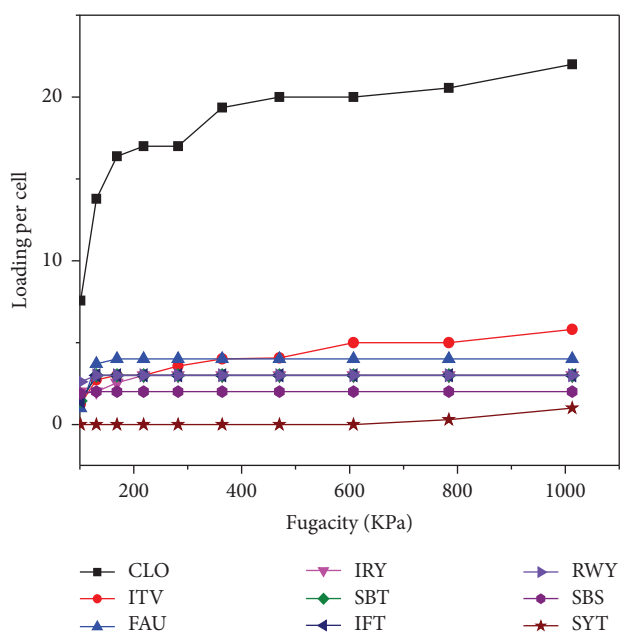

FIGURE 4: Adsorption isotherms, showing the adsorption of HCB on the selected best performing zeolites.

to a lighter material. On the other hand, HVF, APV, VSA, GSA, and Di are positively correlated to wt%. However, there is a strong positive correlation between APV and wt% compared to other parameters with a positive correlation. This implies that accessible pore volume plays a key role to the adsorption capacity of organochlorides on zeolites. This information is key to the engineering of materials to suit the applications in different fields.

Small cluster models have been applied by numerous research teams to zeolites [41-42]. In this work, the interaction of organochlorides with the zeolite framework was investigated using a cluster model (shown in Figure 6). At the level of DFT theory, the cluster was optimized. HCB was added to the system and optimized after the cluster model had been optimized. We hypothesized that HCB could adsorb on the CLO cluster dissociatively by transferring a Cl atom to the cluster, or HCB could adsorb to the cluster through hydrogen bonds. As seen in Figure 6, it is thermodynamically favorable for HCB to adsorb through hydrogen bonding as opposed to dissociative adsorption. As can be seen in Table 2, we also looked at the Mulliken charge distribution on HCB both before and after it bound to the CLO zeolite cluster. According to the findings, the chlorine atoms in the HCB structure have an electron charge of -0.06, whereas the carbon atoms have an electron charge of 0.06 each.

Thus, before adsorption, the chlorine molecule has a net zero charge. It is noteworthy to observe that upon adsorption, there was a charge transfer between CLO and HCB, giving the chlorine atoms a new charge of -0.037, -0.061, -0.057, -0.055, -0.052, and -0.056, while the carbon atoms have a charge of 0.055, 0.053, 0.054, 0.053, 0.050, and 0.054. The net charge on HCB becomes 0.001. The CLO cluster, on the other hand, has a charge of 0.002 before adsorption. It attains a charge of 0.001 after adsorption. According to the Mulliken charge values, there is a charge transfer from HCB to the CLO zeolite.

An investigation was done into how doping CLO zeolite affects loading capacity (Table 3). The phosphorus atoms are independently substituted with silicon, sodium, and aluminum at different locations with varied symmetrical properties in the CLO unit cell, and optimization is then performed. It is noteworthy to notice that the loading of hexachlorobenzene increases from 120 to 133, 126, and 127 molecules per cell, respectively, when CLO is doped with aluminum, sodium, and silicon, respectively. It is noted that
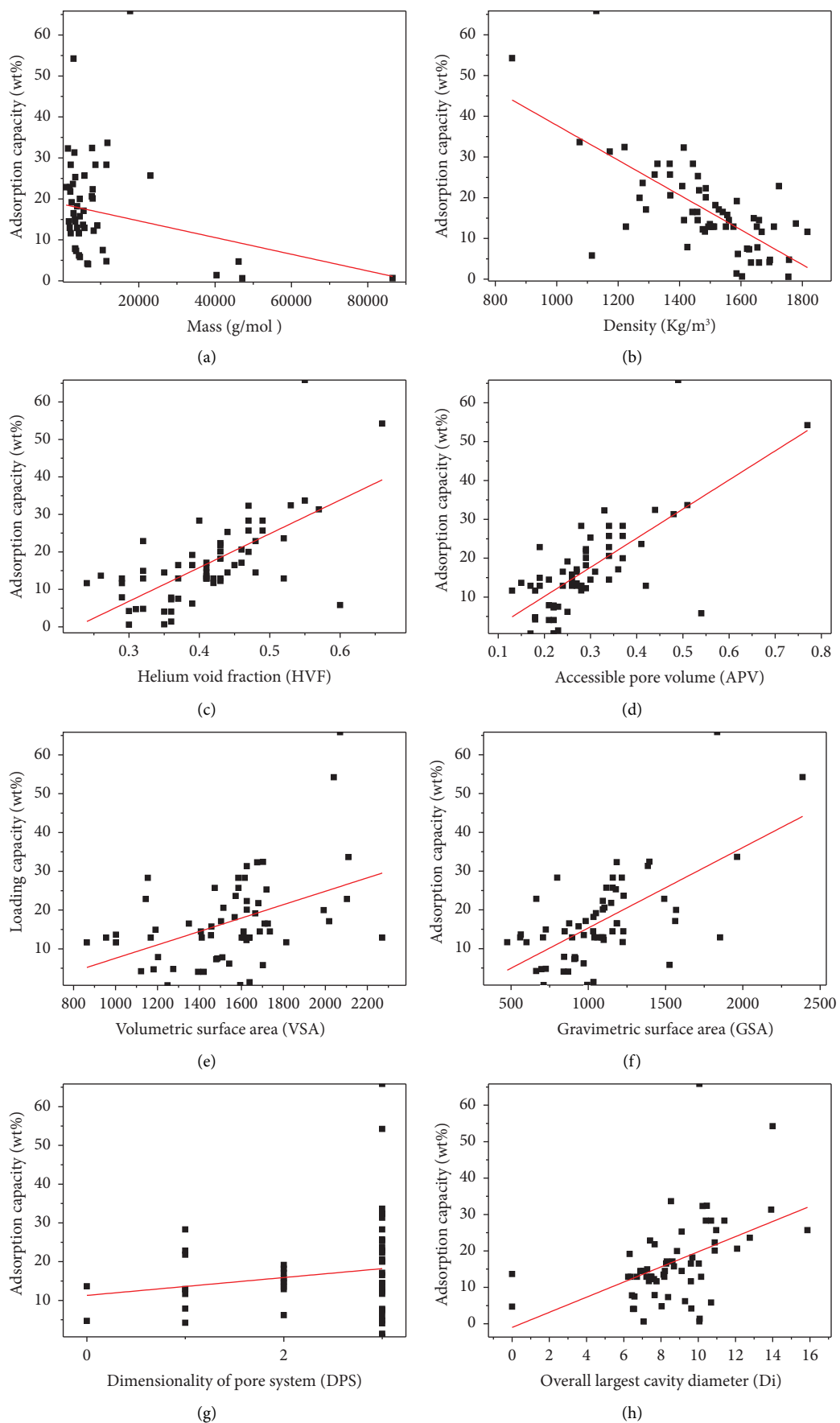
Figure 5: Correlation between zeolites structural parameters; M, D, HVF, APV, VSA, GSA DPS, Di, and adsorption capacity (wt%).
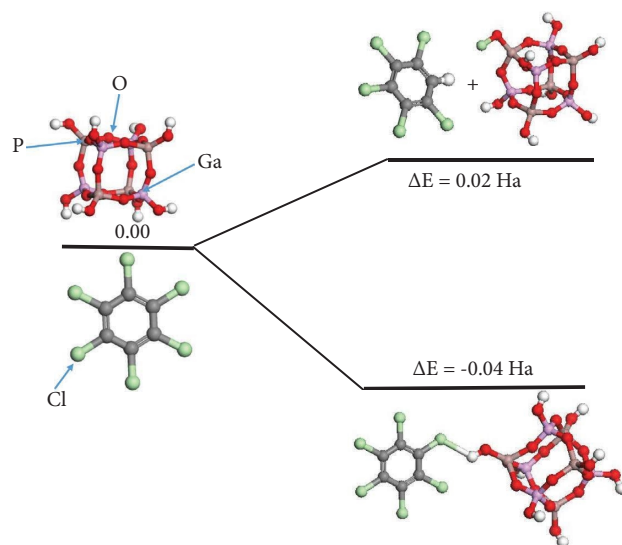
Figure 6: Structures of optimized CLO cluster and adsorbed HCB molecules on the CLO cluster.

Table 2: Mulliken charge distribution on HCB, CLO, and HCB-CLO.

HCB (before adsorption)		CLO before adsorption		HCB–CLO after adsorption	
C	0.6	Ga	1.296	Ga	1.295
C	0.6	P	1.582	P	1.579
C	0.6	O	−0.817	O	−0.816
C	0.6	O	−0.742	O	−0.757
C	0.6	O	−0.761	O	−0.742
C	0.6	O	−0.752	O	−0.754
Cl	−0.6	O	−0.74	O	−0.75
Cl	−0.6	O	−0.695	O	−0.701
Cl	−0.6	O	−0.744	O	−0.75
Cl	−0.6	Ga	1.298	Ga	1.304
Cl	−0.6	P	1.579	P	1.582
Cl	−0.6	O	−0.815	O	−0.818
		O	−0.76	O	−0.739
		O	−0.744	O	−0.741
		O	−0.754	O	−0.745
		O	−0.76	O	−0.759
		O	−0.699	O	−0.698
		O	−0.748	O	−0.757
		P	1.585	P	1.58
		P	1.578	P	1.583
		Ga	1.301	Ga	1.29
		O	−0.698	O	−0.696
		O	−0.753	O	−0.749
		O	−0.743	O	−0.755
		O	−0.697	O	−0.69
		O	−0.816	O	−0.815
		Ga	1.288	Ga	1.287
		O	−0.816	O	−0.817
				C	0.055
				C	0.053
				C	0.054
				C	0.053
				C	0.05
				C	0.054
				Cl	−0.037
				Cl	−0.061
				Cl	−0.057
				Cl	−0.055
				Cl	−0.052
				Cl	−0.056

TABLE 3: Effect of doping on adsorption capacity of CLO zeolite.

Doping atom	Loading	Wt%	Energy (kcal/mol)	Isosteric heat (kcal/mol)
Al	133	68.0	−341.178	44.892
Si	127	67.0	−360.479	127.000
Na	126	67.0	−362.833	44.992

doping CLO zeolite provides improved results in terms of both loading and wt%, whereby aluminum provided the best results (Table 3). The energy difference between the reactants adsorbed states upon doping was also investigated (Figure 7). This was done by substituting phosphorus atom with a single aluminum atom in the CLO cluster. Contrary to the undoped case, it is thermodynamically favorable for HCB to adsorb through dissociative adsorption as opposed to through hydrogen bonding. It is also worth noting that doping increases the system energy, i.e., 0.02 verses −12.25 and −0.04 verses −12.63 Ha for the undoped and doped zeolites, respectively.

The effect of Al doping on Muliken charge distribution was investigated (Table 4). The charge on each atom before and after adsorption was calculated as 0.060 on each carbon atom and −0.060 on each chlorine atom before adsorption, while −0.001, −0.001, 0.000, −0.009, −0.036, and −0.002 for carbon atoms and 0.072, 0.031, 0.033, 0.028, 0.024, and 0.028 for chlorine atoms after adsorption. While HCB has a zero charge before adsorption, after adsorption, HCB molecule inside the zeolite becomes positively charged with a net charge of 0.167. On the other hand, a doped CLO cluster is positively charged with a charge of 0.001 before adsorption. After adsorption, it acquires a −0.096 net charge, making it negatively charged. According to these Mulliken charge values, charge transfer from HCB to the CLO zeolite takes place, similar to the undoped scenario, and thus it is noted that doping does not alter the charge transfer pattern.

For comparison, we also looked into the adsorption of hexachlorocyclohexane (Table S2), dichlorodiphenyltrichloroethane (Table S3), hexachlorotetradecane (Table S4), heptachlorodecane (Table S5), octachlorodecane (Table S6), hexachlorodecane (Table S7), heptachlorodecane (Table S8), and octachlorobenzene (Table S9). It is observed that for hexachlorotetradecane, CLO zeolite was also the best with a loading capacity of 21 molecules per cell. This is equivalent to 31 wt%. This is followed by ITV, TSC, FAU, IFT, IRY, RWY, SBT, and SYT, respectively. For heptachlorotetradecane, CLO is still the best adsorbent with 22 molecules adsorbed per cell, which corresponds to 36 wt%. This is followed by ITV, FAU, IRY, SBT, IFT, RWY, SBS, and SYT. Octachlorotetradecane also exhibits CLO as the adsorbent with 17 molecules per cell. This is equivalent to 38 wt %. It is followed by TSC, ITV, FAU, RWY, IRY, IFT, SBT, DFO, and EMT, respectively. Dichlorodiphenyltrichloroethane still exhibits CLO as the best candidate for its adsorption with an uptake capacity of 43 molecules per cell. After CLO, TSC, ITV, FAU, RWY, IRY, IFT, SBT, DFO, and EMT show good adsorption capacities. On the other hand, hexachlorocyclohexane adsorbs on CLO with 113 molecules per cell which is equivalent to 54 wt%, followed by TSC, ITV, IFT, FAU, IRY, RWY, DFO, SYT, and LTA, respectively

(Table S2). The best zeolite for adsorption of hexachlorodecane is CLO which has 47 molecules per cell an equivalent of 46 wt%. This is followed by TSC, FAU, ITV, IFT, RWY, IRY, SBT, and SBS, respectively. Finally, CLO is still the best adsorbent for heptachlorodecane adsorption with 30 molecules per cell. The adsorption isotherms representing this information are shown (Figure 8). The shapes of these figures can be used to inform us that the zeolites studied have different distribution of active sites for adsorption of the selected organic compounds. However, it is evident that CLO zeolite has more active sites as seen from its adsorption isotherm. It is important to note, from these isotherms, that there are different sites on each zeolite with different energy requirement leading us to stepwise isotherm. This applies to all zeolites studied (See Figure 8). This finding led us into investigation to find out about these active sites. Adsorption locator module was thus used to identify the adsorption sites as seen in Figure 9. It is noted that the organic compounds are adsorbed through electrostatic interaction within the zeolite structure. However, in this case, oxygen atoms provide active interaction sites. It is indicated that the pores surrounded by more oxygen atoms are the most preferred. Thus, affinity for organic pollutants can be increased by increasing the number of oxygen atoms.

The performance of CLO zeolite over other zeolite materials enabled an investigation to find out possible features responsible for its best performance. Previously, it has been reported that various general structural features have an impact on sorption ability of zeolites [43-44]. However, few reports have focused on how sorption performance is influenced by the structural composition of zeolites [44]. We therefore investigated the distribution of active adsorption sites on the surfaces of the zeolites which facilitated the affinity for organic compounds. Since most of the zeolites have oxygen atoms in their framework, it was very necessary to find out the influence of these atoms to adsorption capacity. Interestingly, it was discovered that oxygen atoms played a key role in active sites provision. This implies that the more the oxygen atoms, the more the active sites on the zeolite surface, and hence more adsorption capacity. Table 5 shows a summary of the adsorption capacity versus the number of oxygen atoms.

3.2. Laboratory Adsorption Experiments of Organochlorines on Zeolites. Zeolites treatment is one of the key practices performed in order to activate them prior to any application [54]. One of the reasons why zeolites are treated is to remove interstitial water from their framework. There are several zeolites treatment methods that have been employed in previous studies [54-56]. These include heat treatment at high temperatures and acid treatment methods among
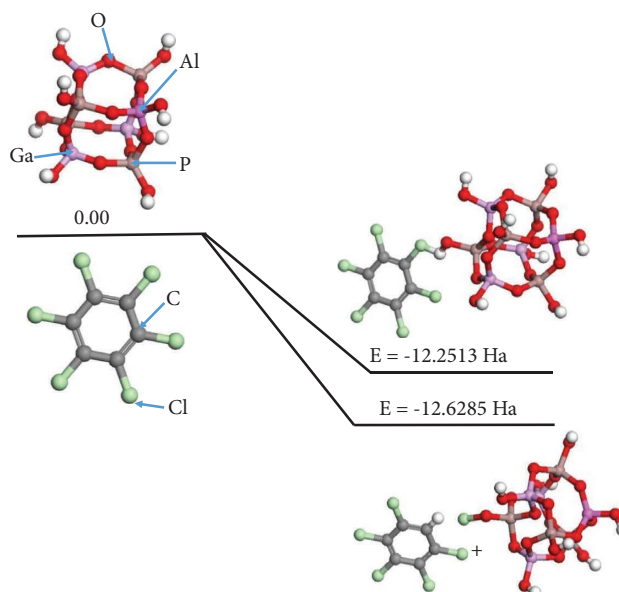
Figure 7: Optimized structures of Al-doped CLO cluster and HCB adsorbed on the doped cluster.

Table 4: Effect of Al doping on Mulliken charge distribution.

HCB (before adsorption)		Al-doped CLO cluster before adsorption		Al-doped CLO-HCB after adsorption	
C	0.6	Ga	1.281	Ga	1.19
C	0.6	Al	1.157	Al	1.229
C	0.6	O	−0.717	O	−0.633
C	0.6	O	−0.722	O	−0.613
C	0.6	O	−0.674	O	−0.644
C	0.6	O	−0.686	O	−0.6
Cl	−0.6	O	−0.673	O	−0.649
Cl	−0.6	O	−0.654	O	−0.635
Cl	−0.6	O	−0.691	O	−0.609
Cl	−0.6	Ga	1.246	Ga	1.123
Cl	−0.6	P	1.506	P	1.194
Cl	−0.6	O	−0.713	O	−0.673
		O	−0.677	O	−0.609
		O	−0.684	O	−0.607
		O	−0.733	O	−0.661
		O	−0.713	O	−0.588
		O	−0.647	O	−0.602
		O	−0.677	O	−0.645
		P	1.516	P	1.174
		P	1.511	P	1.174
		Ga	1.273	Ga	1.119
		O	−0.643	O	−0.602
		O	−0.717	O	−0.611
		O	−0.682	O	−0.6
		O	−0.651	O	−0.595
		O	−0.719	O	−0.635
		Ga	1.289	Ga	1.111
				C	−0.001
				C	0.001
				C	0.00
				C	−0.009
				C	−0.036
				C	0.002
				Cl	0.072
				Cl	0.031
				Cl	0.033
				Cl	0.028
				Cl	0.024
				Cl	0.028

(a)

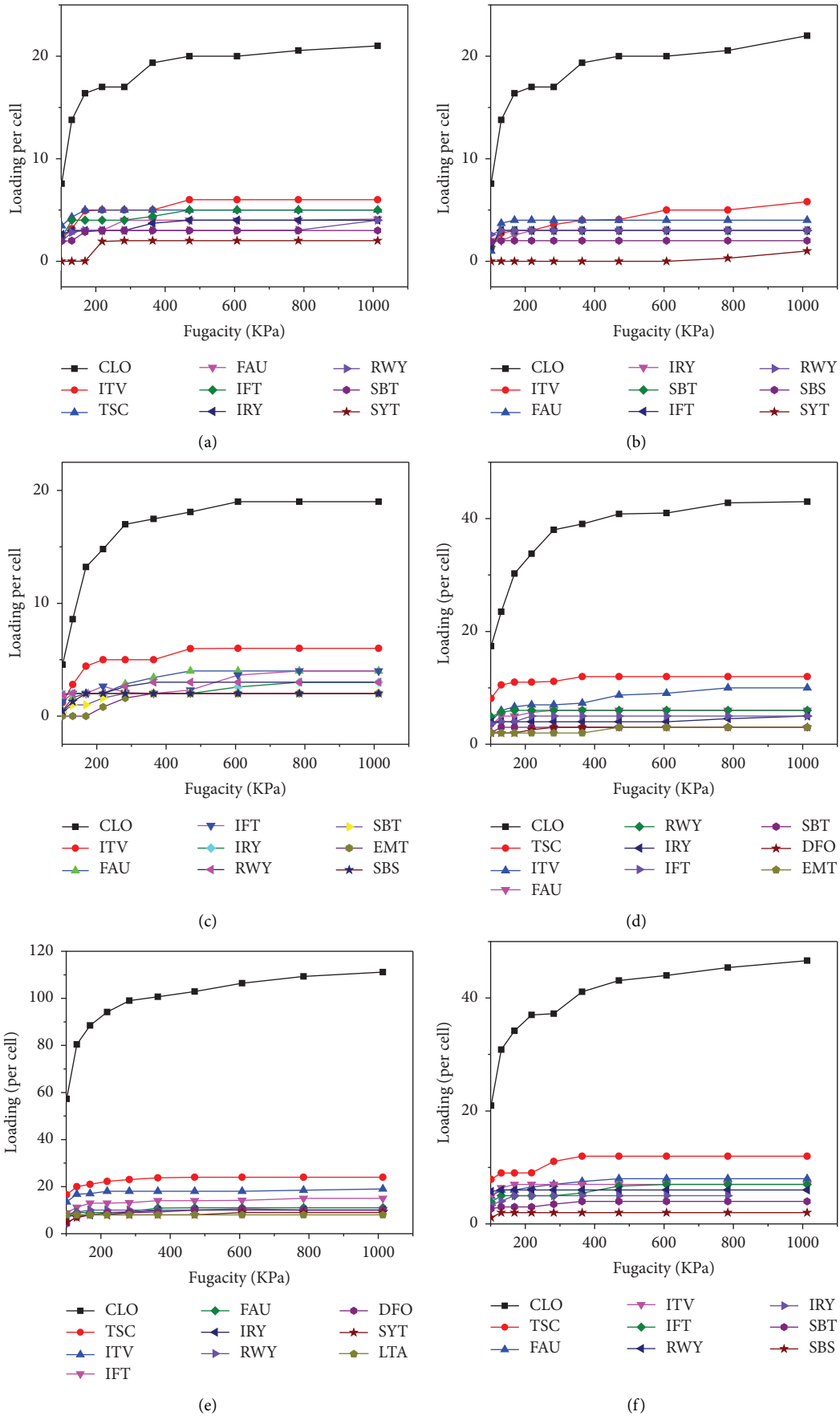

(b)

(c)

(d)
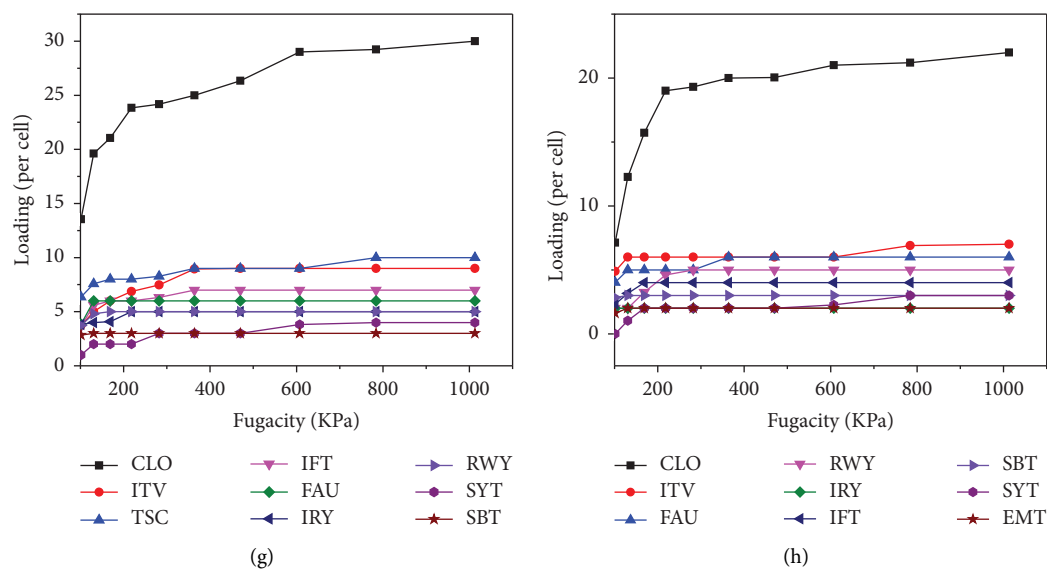

(e)

(f)

FIGURE 8: Continued.

(g)

(h)

Figure 8: Adsorption isotherms for other chlorinated pollutants.
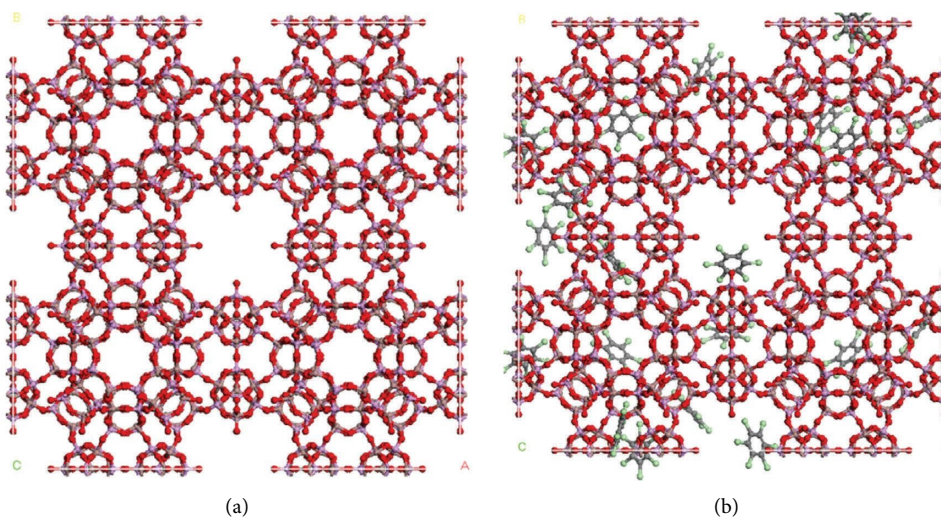

(a)

(b)

Figure 9: (a) CLO zeolite framework. (b) Adsorption sites for hexachlorobenzene within the CLO zeolite.

others. In the current study, the effect of heat treatment at 400°C to adsorption of chlorinated compounds was investigated.

Since columns were used for adsorption experiments, packing was done using distilled water by first preparing slurry to facilitate compact packing. The results showed that the selected zeolites could not make slurry since they were highly hydrophobic. This hydrophobicity is attributed to a low Si/Al ratio. Interestingly, it was discovered that the Si/Al ratio could be improved by adding silica gel powder to the zeolite in the ratio 3 : 5 (silica: zeolites). This was discovered after several trials as shown in Table 6.

The sorption results showed that clinoptilolite zeolite could not be used in columns for adsorption since it caused logging in the columns. As such no solution could be

obtained from the column for analysis. On the other hand, the sorption results for silica gel were not pronounced. This therefore showed that silica gel could not adsorb organic pollutants but increased hydrophilic nature of zeolites (Table 7). This result closely agreed with the present literature on the use of silica gel in adsorption [57].

Basing on the results obtained, it was discovered that the untreated zeolite performed better than the treated one. From Table 7 above, the treated zeolite adsorbed 3.2 ppm, 0.3 ppm, 0.1 ppm, 0 ppm, and 0.2 ppm for the five time runs, respectively. This trend indicates that the treated zeolite could reach saturation point only after the third run, after which no more pollutant could be adsorbed. This means that if one were to re-use the adsorbent, then it could be used three times before recovery is done. On the other hand,

TABLE 5: Correlation of oxygen atoms in adsorbate to high pollutant loading rate.

Pollutant	Carbon atoms	Chlorine atoms	Zeolite	No. of oxygen atoms	Reference (oxygen atoms)	Loading per cell	Average adsorption energy (kcal)
Hexachlorobenzene	6	6	CLO	5152	[45]	120	−641
			RWY	—	[46]	12	−98
			ITV	379	[47]	21	−130
			IFU	260	[48]	13	−178
			LTA	600	[49]	13	−229
Phenanthrene	14	0	CLO	5152	[45]	132	999
			TSC	897	[50]	30	3
			ITV	379	[47]	26	131
			FAU	624	[51]	16	−3
			IFT	317	[52]	16	−18
Hexachlorotetradecane	14	6	CLO	5152	[45]	21	−124
			ITV	379	[47]	6	−46
			TSC	897	[50]	5	−65
			FAU	624	[53]	5	−95
			IFT	317	[52]	5	−108
Octachlorotetradecane	14	8	CLO	5152	[45]	19	−102
			ITV	379	[47]	6	−10
			FAU	624	[51]	4	−74
			IFT	317	[52]	4	−65
			IRY	154	[46]	3	−39

TABLE 6: Determination of appropriate zeolite silica mixing ratio in order to improve Si/Al ratio in the zeolite.

Amount of zeolite (g)	Amount of silica (g)	Comment
0.5	0.0	Hydrophobic
	0.1	Hydrophobic
	0.2	Hydrophobic
	0.3	Hydrophilic
	0.4	Hydrophilic
	0.5	Hydrophilic

TABLE 7: Hexachlorobenzene removal by faujasite zeolite and silica gel for five runs into columns.

Material	Amount removed (ppm)				
	1	2	3	4	5
Treated faujasite zeolite	3.2851	0.3393	0.149	ND	0.2149
Untreated faujasite zeolite	5.3294	0.5091	0.7353	0.2262	ND
Silica gel	0.5882	ND	0.1132	ND	ND

ND = not detected.

TABLE 8: The remaining hexachlorobenzene compound concentration after adsorption.

Material	Concentration				
	1	2	3	4	5
Treated zeolite x	2.7149	2.3756	0.2262	0.2262	0.1131
Untreated zeolite x	1.4706	0.9615	0.2262	0	ND
Silica gel	4.4118	4.4118	4.2986	4.4118	4.2986

untreated zeolite adsorbed 5.3 ppm, 0.5 ppm, 0.7 ppm, and 0.2 ppm for the five run times, respectively. This trend is quite interesting in the sense that the material could not reach saturation after the five re-uses. This is due to the fact that the remaining concentrations after the third run could not be detected, implying that most the compounds had been adsorbed and the material could still adsorb more. Table 8 shows the remaining concentrations after every run through the columns. In addition, the amount of compound adsorbed after every run through the columns was much higher than that of treated zeolite. Previous researchers have explained the effect of various treatment methods to adsorption of methylene blue. Hor and co-authors [58] reported that both the physico-chemical methods of acid treatment and base treatment were able to boost the performance of natural zeolite from 41% to 98.8%, and 52.2%, respectively. However, their report showed that combining reduced performance would be observed when any of the methods were combined. This shows that different treatment methods favor different adsorbates. Our present work therefore reveals that thermal treatment as a method of zeolite treatment lowers the zeolite performance, as compared to untreated zeolites.

The percentage removal calculation reveals that untreated zeolite removes up to 91% of hexachlorobenzene. Comparing this experimental work with the simulated results, we were able to find out that for organic pollutants, untreated zeolites performs better than treated zeolite. This is based on the fact that, one, our computations of the Mulliken charge analysis performed (Table 2) revealed that there is charge transfer between the zeolite and organic pollutants during adsorption. Secondly, the interaction mechanisms between the zeolite and hexachlorobenzene involve electrostatic interaction through hydrogen bonding (Figure 6), and thirdly, the number of active sites in the zeolites for organic pollutant adsorption heavily depended on the number of oxygen atoms present in the structure (Table 5). Integrating these three simulation findings with the experimental results, we found out that, heating the zeolite, apart from removing inorganic impurities, also removes interstitial water from the zeolite framework. This interstitial water within the zeolite structure contains the hydroxyl radicals which are reactive with organic molecules. They contain a negative charge which reacts with the positive charges in the compound (ion exchange). Thus, heating the zeolite material reduces the value of negative hydroxyl ions and therefore the reaction between the zeolite and the positive organic compound reduces. This causes poor performance of the heated zeolite and the better performance of the untreated zeolite material. Secondly, since the interaction mechanism involved between the zeolite and the hexachlorobenzene is electrostatic through hydrogen bonding, heating reduces the number of hydrogen atoms in the zeolite framework which could facilitate the interaction. Hence, the untreated zeolite with more hydrogen atoms performs better. Finally, the simulation results indicated that the active adsorption sites for organic pollutants under study were provided by the oxygen atoms. Since water molecules compose of oxygen atoms, heating would mean removing more oxygen atoms from the framework. Therefore, there would be less oxygen atoms which could bond with the chlorine atoms in the organochloride compounds (Figures 6 and 7). Thus, the treated zeolite adsorbs less than the untreated one. It is worth noting that the present findings, both experimental and computational, have strongly agreed as discussed.

Comparing our study with the previous study by Kuldeyev et al. [59] on the adsorption of heavy metals on zeolites, it noted that our finding on the zeolite treatment methods contradicts what was suggested in their study. The study focused on enhancing the adsorption capabilities of natural zeolites from the Shankanay deposit in Kazakhstan for heavy metal ions in water. The researchers employed thermal methods to modify the zeolites and increase their specific surface area and porosity. Three stages of activation were conducted, involving cleaning the zeolites with water vapor, demineralization through acid treatment, and high thermal activation in an inert atmosphere. The results showed that thermal activation significantly improved the adsorption capacity of the zeolites for various heavy metals. The optimal condition was found to be a thermal treatment at 550°C for approximately 2 hours. The heat-treated zeolites demonstrated high adsorption capacities, with percentages ranging from 83% to 100% for copper, cadmium, lead, and

nickel. The adsorption process was found to be rapid, with intense adsorption occurring within the first 10 minutes. The residual concentration of heavy metals in the filtered water remained within the permissible limits for drinking purposes. The study concluded that natural zeolites from the Shankanay deposit have high potential as cost-effective sorbents for the treatment of heavy-metal-polluted water, particularly in wastewater treatment and water softening applications in the metallurgical industry. The findings also suggested that thermal treatment may be more efficient than chemical treatment in enhancing the adsorption capacity of zeolites, but further research is needed to confirm this. However, this contradiction may be as a result of different interaction mechanisms between the zeolite and the material.

3.3. Factors That Affect Adsorption of Organochlorine Pollutants on Zeolites. The outcomes of the current study may be influenced by a number of factors. The zeolite's own characteristics, such as its surface area, pore size, surface charge, and composition, are important. The adsorption behavior can be affected by changes in the solution's pH and temperature, as well as the presence of other chemicals or pollutants. The molecular size and hydrophobicity of the organochlorine compounds, as well as other physicochemical characteristics, affect their adsorption affinity. The adsorption kinetics and achievement of equilibrium are influenced by the contact time and agitation level. Important factors to take into account also include the presence of rival chemicals and the capacity to regenerate and re-use zeolite materials. For precise and dependable findings in research involving the adsorption of organochlorine chemicals utilizing zeolite materials, it is important to comprehend and regulate these aspects.

3.4. Significance of This Study. This study has significant consequences for environmental cleanup initiatives. It clarifies the adsorption mechanisms at work and shows the critical role played by electrostatic interactions, particularly hydrogen bonding. Researchers can create more effective adsorbents for removing organochlorines from contaminated settings based on this understanding. In addition, in order to help with the selection of zeolites for particular remediation projects, the study compares the adsorption capacities of various zeolite materials and identifies certain zeolites with high adsorption capacities for particular pollutants. Understanding how zeolite structural characteristics affect adsorption performance might help in the design and optimization of zeolite materials with improved qualities. The study examines the effects of doping zeolites with various elements and finds that doping, especially with aluminum doping, can increase loading capacity. Lastly, the experiments show how crucial it is to take into account how zeolite materials are treated, with untreated zeolite exhibiting greater adsorption capacity and reusability. Collectively, these effects help us better understand how organochlorine adsorption operates, direct the design and selection of zeolites, and offer helpful tips for enhancing adsorption procedures in environmental remediation. Ultimately, this

helps us create more efficient methods for removing organochlorine pollutants from contaminated sites. Despite its value, the present study has a number of shortcomings that need to be acknowledged. First off, the study was carried out in a controlled laboratory setting, which might not accurately reflect the complexity of real-world settings. In addition, the investigation of the kinetics of the process, which is essential for developing effective remediation solutions, was not done as much in the study as it was largely on equilibrium adsorption. The analysis of individual organochlorine compounds also fails to take into account the occurrence of combinations in real-world situations, where many pollutants may interact and compete for adsorption sites. The restrictions on mass transfer, reactor design, and the behavior of zeolite materials at greater scales may all provide difficulties for scaling up the findings to broader uses. In addition, not much study has been done on the long-term stability and durability of zeolite materials, which is crucial for assessing the viability and sustainability of zeolite-based remediation solutions. By addressing these restrictions, future research will improve our knowledge and speed the creation of more efficient and useful environmental cleanup technologies.

4. Conclusions

In this work, the investigation into organochlorine adsorption using zeolites, combining simulation and experimental approaches, has delivered impactful findings. Simulation work utilizing the IZA database and PubChem, along with GCMC simulations, deepened our understanding of adsorption mechanisms. Material Studio and IRASPA software facilitated quantitative zeolite analysis. Experimental validation with clinoptilolite and faujasite zeolites, subjected to strategic treatments, aligned with simulation results, emphasizing the study's robustness. Structural modifications, including silicon, aluminum, or sodium doping, and variations in the Si/Al ratio revealed their impact on adsorption efficiency. The inclusion of different zeolite types and silica gels for comparison enhanced practical relevance. Rigorous column adsorption tests and calibration curves provided quantitative insights. This study effectively bridges simulation and experimentation, highlighting zeolites' adaptability in pollutant remediation. The results affirm zeolites' potential as versatile and sustainable materials for environmental applications, advancing the understanding of their efficacy in water purification and environmental protection.

Data Availability

The research data used to support the findings of this study are included within the article and supporting information thereof attached.

Conflicts of Interest

The authors declare that they have no conflicts of interest that could have appeared to influence the work reported in this paper.

Acknowledgments

Supplementary Materials

See the supporting supplementary information for Tables S1 to S9. (*Supplementary Materials*)

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