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Review Article

Zeolite Application in Wastewater Treatment

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As a scarce natural resource, the preservation of water quality is of fundamental importance to guarantee its availability for future generations. Due to the increasing industrial activity, effluents are generated with a series of chemical compounds, such as nitrogenous, phosphoric, and organic compounds, heavy metals, and dyes which, if improperly disposed of, contribute to contamination, followed by significant environmental impacts, in addition to the damage to human health. The adsorption technique is an effective approach for removing contaminants from effluents, showing high versatility, due to the use of various materials as adsorbents. Belonging to a wide variety of materials, zeolites reveal to be a promising adsorbent. Zeolites are minerals found in nature or which can be synthesized from industrial residues, standing out in the treatment of contaminated effluents. Zeolite removal efficiency depends on the contaminant to be removed and can reach up to 96% for heavy metals, 90% for phosphoric compounds, 96% for dyes, 80% for nitrogen compounds, and 89% for organics. Aiming at the identification of the more relevant findings and research gaps to advance the use of zeolites in the large-scale treatment of industrial effluents, a review on the recent application of zeolites is needed. This paper presents a global view of zeolites, and a review is conducted on several recent studies using zeolites as adsorbents for the contaminants considered, indicating the main characteristics of the various adsorption systems, demonstrating the particularities of each process, and aiming to reveal useful information to provide future research, in addition to identifying points that need further investigation.

1. Introduction

Water is an essential element for life on Earth. Although about 70% of the planet's surface is covered with water, only a small portion of this volume can be consumed as freshwater. Still, much of the freshwater is in the form of glaciers, and therefore, it is not available for consumption [1]. In addition, freshwater is not evenly distributed across continents, with some parts of the world having large reserves, while others suffer from lack. Allied to the problem of the relative scarcity of this limited resource and its irregular distribution, the growing industrial activity has contributed significantly to the contamination of the waters through the disposal, often inadequate, of effluents generated [2].

As society's demand for consumption increases, the food, cosmetics, mining and metallurgy, chemical and pharmaceutical industries, among others, intensified their production, and consequently, greater attention has been paid to the effluents generated. The presence of several contaminating elements present in wastewater is common, such as heavy metals (e.g., lead, arsenic, chromium, and mercury) [3], compounds based on nitrogen [4] and phosphorus [5], dyes [6], and various organic compounds [7]. All these elements, if disposed of untreated, contaminate water, soil, plants, and animals and can eventually reach humans. For the organism, these compounds have high toxicity, and depending on the dosage and time of exposure, a series of disorders can occur. Studies indicate the appearance of several types of cancer, genetic abnormalities, damage to organs and systems, and psychological disorders due to exposure to heavy metals and organic compounds [8, 9]. In addition, the environment can also suffer significant damage when exposed to the inadequate disposal of effluents, especially those rich in dyes, nitrogen, and phosphorus. In the presence of abundance, these elements can cause eutrophication of water bodies, eliminating all aquatic life [10].

Several forms of wastewater treatment have been developed over the decades, to remove contaminating elements from wastewater, before their disposal. Techniques such as chemical precipitation [11], ionic flotation [12], electrodialysis [13], and biological treatment [14] are efficient in the treatment of effluents, but they have some disadvantages such as the generation of toxic waste that requires adequate storage, high demand for chemical reagents, high energy cost, and limited efficiency to remove contaminants with low concentration [15–18]. In contrast, the adsorption technique is promising and possesses several advantages over other techniques, which justifies its application in the treatment of effluents. One of the great advantages of the technique is its versatility, as it allows the use of various materials as adsorbents, from activated carbon to industrial wastes [19].

Several materials have been used as adsorbents to remove contaminants from water. Activated carbon, biochar, clay minerals, and advanced materials are among the most studied materials for wastewater decontamination. These materials possess the necessary features to be used for this purpose, e.g., high surface area, negative electric charge (clay minerals), and micro-/mesoporous (carbon-based) materials [20, 21]. However, some disadvantages limit their use on a large scale. Activated carbon and biochar are products of the calcination of organic matter, e.g., bamboo, corn straw, and rice husk, in an anaerobic atmosphere. The properties of the final product can vary in a wide range since it is a function of the precursor used. Another disadvantage is the high cost of production, whereas the calcination temperature can be as high as 900°C [20].

Clays are composed of phyllosilicate minerals. These minerals possess sheet-like structures, exhibiting a high specific area. Furthermore, their atomic structure provides a natural negative charge that is neutralized by a variety of cations. These properties make clays a material with the potential to be used as adsorbents. However, they are composed of a wide range of minerals, and their removal potential may be reduced or present great variation [22]. Their modification can be enhanced by a series of treatments, e.g., thermal, acidic, and surfactant modification, but these treatments increase the process costs [23].

A relatively new class of materials to be used in water treatment are the advanced materials and the nanomaterials, e.g., alumina, silica, titanium oxide, and zirconia. These materials possess small size, high specific energy, and high reactivity [24]. Among them, zeolite is a class of material that has attracted the attention of the scientific community and has the potential to be used as an adsorbent in the elimination of contaminating elements in effluents. These minerals, found in nature or synthesized, have a microporous crystalline structure (with pores opening smaller than 20 Å) [25], which guarantees their application for several purposes, such as gas separation [26], water softeners [27], catalyst [28], addition for Portland cement [29], and applications in health and animal food [30]. Exchangeable cations in the microporous structure and negative electrical charge are two of the properties that allow its application as an adsorbent, for the proper treatment of effluents.

This paper is aimed at identifying the more relevant findings and research gaps on the use of zeolites as adsorbent materials, as well as demonstrating the adsorption mechanisms and particularities of each process, revealing useful information for future research. Review studies, in most cases, bring information about natural or synthetic zeolites, and, in this paper, the reader will find information about both zeolites. A comparison between the two types of zeolites is made, discussing their advantages and disadvantages, their efficiency in wastewater treatment based on their different chemical and physical features, and how the modification of these characteristics can enhance their performance as adsorbents. The next section is dedicated to the discussion about zeolites and their properties, and Section 3 presents a review of several recent studies that used zeolites to remove five classes of contaminants. Finally, Section 4 presents the conclusions, challenges, and future perspectives to zeolite application in wastewater treatment.

2. Microporous Materials: Zeolites

2.1. Zeolite Definition. The term zeolite, derived from the Greek words *zein* (boil) and *lithos* (rock), was first used to name a mineral that expanded upon being heated, in 1758 by the Swedish mineralogist Alex Fredrick Cronsted [25, 31]. The reason for this peculiar behavior was only revealed in the year 1857, when it was discovered that these materials have a microporous crystalline structure, capable of storing water inside its pores and releasing it if heated, in theoretically infinite cycles of hydration and dehydration. At this time, it was also discovered the presence of compensation cations in zeolite crystalline structures and the ability they have to be removed by other ions in solution, through cation exchange [25, 32]. Although these properties were important in several industrial sectors, these minerals remained unused for more than 200 years. Its use on an industrial scale only started in 1905, when economically exploitable sedimentary deposits were discovered, which enabled its application in the detergent industry [33]. The first zeolite synthesis was reported in 1948 [25], during the attempt to recreate the hydrothermal conditions of its formation in nature, and the process has been widely studied since then. Currently, 230 species of zeolites are known, categorized into 133 different crystalline structures, according to rules defined by the International Zeolite Association (IZA) [33, 34].

Zeolites belong to the aluminosilicate group, formed by the union of TO_4-type tetrahedrons, or basic building units (BBU), where T represents silicon and/or aluminum atoms (Figure 1(a)). The difference in valence between silicon (+4) and aluminum (+3) leads to an excess of negative charge in the crystalline structure, which is neutralized by the presence of compensation cations, usually elements from alkali metal or alkaline earth metal family [32, 34–38]. The basic structure of zeolites can be described by the generic formula $M_{a/b}[(\mathrm{AlO}_2)_a(\mathrm{SiO}_2)_y] \cdot c\mathrm{H}_2\mathrm{O}$, where M represents

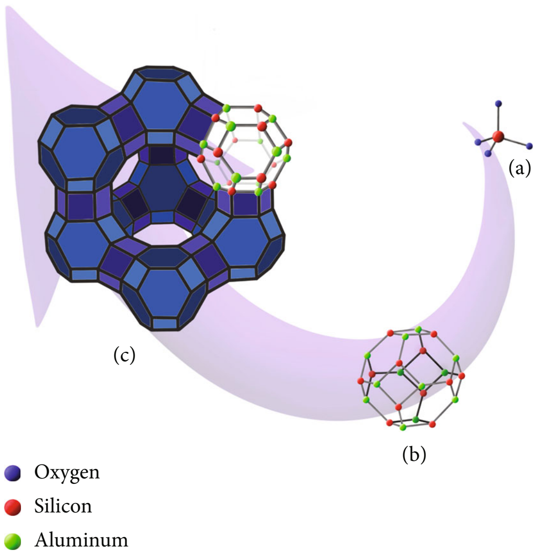

Figure 1: Basic building unit (a); composite building units (b) in the crystalline structure of FAU-zeolites (c). Oxygen atoms have been omitted for clarity.

the compensation cation ($M = Na^+$, K^+, Li^+, Ca^{2+}, Mg^{2+}, etc.) [34]. The variables a and y represent the amount of $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ tetrahedra, and c is the number of water molecules, parameters which vary between the different zeolite crystalline structures. The water molecules and the compensation cation are not part of the chemical composition of zeolites, and these species are free to enter and exit the crystalline structure without causing structural damage to the crystalline structure [35, 39, 40].

The union of $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ leads to the formation of more complex structures, known as composite building units (CBU), being represented by rings and cages. The rings are named according to the number of oxygen atoms, and rings between 4 and 12 atoms are more common. In the peripheries of the crystal lattice, the rings are called windows and define the effective diameter of the zeolite pores, which limit the entry of certain chemical species into the crystalline structure. This property gives zeolites the ability to be used as molecular sieves and catalysts, in gas separation and the petrochemical industry, respectively. Based on pore diameter, with openings smaller than 20 Å, zeolites are classified as microporous materials [25, 38, 41–43]. The union of different types of rings leads to the formation of even more complex structures called cages (Figure 1(b)). The union of the different types of cages leads to the formation of the various zeolite structures [44]. As an example, Figure 1(c) shows the unit cell of a FAU-type zeolite.

Another characteristic of zeolitic materials is the low framework density, which measures the number of T atoms (Si and/or Al) per 1000 Å^3. Typically, zeolites have a framework density ranging from 5 to 20, due to the presence of channels and cages in their structure, whereas nonzeolitic materials show values between 20 and 21 [45]. Adsorption is a physical or chemical phenomenon in which molecules accumulate at an interface. This accumulation of molecules is small about the area, and most of the materials used for this purpose are those with a high surface area. Due to their microporous structure, zeolites present a high surface area per volume, being one of the most used materials for the adsorption of liquid and gaseous substances, achieving complete removal of contaminants in effluents, even at low concentrations [46]. Table 1 summarizes natural and synthetic zeolites' main physicochemical and structural characteristics. In general, synthetic zeolites have a lower framework density, due to their higher degree of crystalline ordering, compared to natural zeolites. Consequently, synthetic zeolites have a greater specific surface area, which increases their efficiency as an adsorbent. Ion exchange occurs in zeolites due to the presence of exchangeable cations inside the crystalline structure. Upon contact with an electrolyte solution, the zeolitic cations are removed from the structure and replaced by the solution cations. The amount of exchangeable cations is called cation exchange capacity (CEC), measured in milliequivalents/g, and is dependent on the chemical and physical properties of the material [47].

2.2. Natural Zeolites. Zeolites occur in nature typically filling fractures and pores of volcanic rocks, which limits the formation of large deposits. So, this type of mineral deposit is relatively scarce. Volcanic rocks are the main precursor materials in the formation of zeolites, although other minerals such as feldspars, kaolinite, smectite, volcanic glass, or even other zeolites can fulfill this role, depending on the conditions of pressure, temperature, and presence of mineralizing fluids, in a dissolution-precipitation system [48]. Only a few countries in the world have exploitable zeolite reserves, exploited exclusively using open-pit methods. The processing of zeolitic ore is relatively simple, involving only comminution steps and grading by particle size ranges [49]. Among the 60 varieties of natural zeolites, only clinoptilolite, analcime, heulandite, laumonite, phillipsite, mordenite, chabazite, erionite, and ferrierite have large known sedimentary reserves, located mainly in China [32, 48, 49]. Zeolitic ore reserves have not been estimated as most producing countries do not disclose this information and only their estimated production is available. In terms of production, the leading countries in 2019 were China (320.000 t), Korea (150.000 t), Slovakia (120.000 t), New Zealand (100.000 t), and the United States (98.000 t) [50]. Natural zeolites, unlike synthetic ones, exhibit a wide range of mineralogical and chemical composition, crystal structure, and pore sizes, which restrain their application if more homogeneous properties are required to guarantee high efficiency. Nevertheless, natural zeolites present a lower cost than synthetic zeolites, ensuring their application in animal feed production, water treatment, odor control, gas adsorption, and pozzolanic addition to Portland cement [51].

2.3. Synthetic Zeolites. Crystalline solids can be synthesized using two approaches, whose chemical reactions occur in the solid state or the liquid state. The first class of reactions occurs slowly at relatively high temperatures, above 300°C. In the liquid state, chemical species have greater freedom of movement, and the reaction occurs faster and at lower temperatures [35, 38, 52]. Zeolite synthesis occurs in a liquid

TABLE 1: Structural and physicochemical characteristics of most important natural and synthetic zeolites used in effluent treatment.

Zeolite	Chemical formula	Framework structure	Channel dimensions (Å)	Cation exchange capacity (CEC) (meq·g^{-1})	Crystalline system	Space group	Framework density (T/1000 Å^3)	References
Natural								
Clinoptilolite	$(K_2,Na_2,Ca)_3Al_6Si_{30}O_{72}\cdot 21H_2O$	HEU	3.1 × 7.5 + 3.6 × 4.6 [001]; 2.8 × 5.7 [100]	2.2	Monoclinic	*C2/m*	17.5	[76, 116, 117]
Mordenite	$Na_8Al_8Si_{40}O_{96}\cdot 24H_20$	MOR	6.5 × 7.0 + 2.6 × 5.7 [001]	2.3	Orthorhombic	*Cmcm*	17.2	[76, 116, 117]
Chabazite	$Ca_6Al_{12}Si_{24}O_{72}\cdot 40H_2O$	CHA	3.8 × 3.8	3.8	Rhombohedral	*R3m*	14.5	[76, 116, 117]
Phillipsite	$K_2,(Ca,Na_2)_2Al_6Si_{10}O_{32}\cdot 12H_2O$	PHI	3.8 × 3.8 [100]; 3.0 × 4.3 [010]; 3.2 × 3.2 [001]	3.3	Monoclinic	*P2$_1$/m*	15.8	[76, 116, 117]
Analcime	$Na_{16}Al_{16}Si_{32}O_{96}\cdot 16H_2O$	ANA	1.6 × 4.6	4.5	Cubic	*Ia3d*	18.5	[76, 116, 117]
Erionite	$(Ca,Na_2)_{3.5}K_2Al_9Si_{27}O_{72}\cdot 27H_2O$	ERI	3.6 × 5.1	3.1	Hexagonal	P6$_3$/*mmc*	15.7	[76, 116, 117]
Scolecite	$Ca_4Al_8Si_{12}O_{40}\cdot 12H_2O$	NAT	2.6 × 3.9 [100]; 2.5 × 4.1 [001]	5.2	Monoclinic	*Cc*	16.2	[48, 73, 76]
Thomsonite	$Na_4Ca_8Al_{20}Si_{20}O_{80}\cdot 24H_2O$	THO	2.3 × 3.9 [100]; 2.2 × 4.0 [010]; 2.2 × 3.0 [001]	—	Orthorhombic	*Pncn*	17.7	[116]
Sodalite	$Na_8Cl_2Al_6Si_6O_{24}$	SOD	2.8 × 2.8	—	Cubic	*P43n*	17.2	[116]
Synthetic								
X	$Na_{58}Al_{58}Si_{134}O_{384}\cdot 240H_2O$	FAU	7.4 × 7.4	6.0	Cubic	*Fd-3*	13.3	[116, 118, 119]
Y	$Na_{58}Al_{58}Si_{134}O_{384}\cdot 240H_2O$	FAU	7.4 × 7.4	3.9	Cubic	*Fd-3m*	13.3	[116, 118]
A	$Na_{96}Al_{96}Si_{96}O_{384}\cdot 216H_2O$	LTA	4.1 × 4.5	5.3	Cubic	*Fm3c*	12.9	[116, 120, 121]
ZSM-5	$Na_nAl_nSi_{96-n}O_{192}\cdot 16H_2O, n < 27$	MFI	5.3 × 5.6	2.1	Orthorhombic	*Pnma*	17.9	[116, 122]
ZSM-11	$Na_nAl_nSi_{96-n}O_{192}\cdot 16H_2O, n < 16$	MEL	5.3 × 5.4	—	Tetragonal	*I4m2*	17.6	[116]
H-USY	—	FAU	5.5 × 5.1	3.6	Cubic	*Fd-3 m*	13.3	[116, 123]
Beta	$Na_7A_{17}Si_{57}O_{128}$	*BEA	6.6 × 6.7	1.8	Tetragonal	*P4$_1$22*	15.1	[116, 123]
ZK-5	$Na_{30}Al_{30}Si_{66}O_{192}\cdot_{98}H_2O$	KFI	3.9 × 3.9	—	Cubic	*Im3m*	14.6	[116]

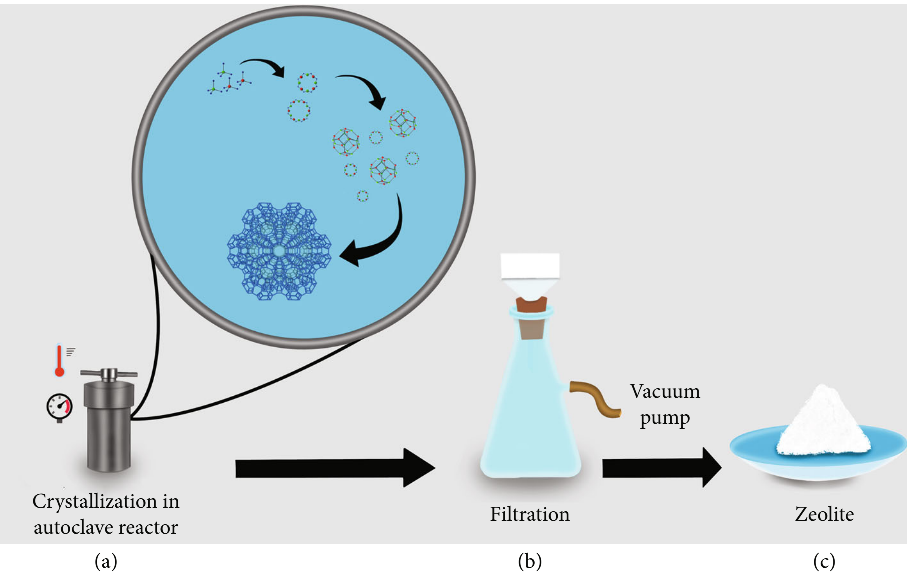

Figure 2: Hydrothermal synthesis process. The crystallization occurs in an autoclave (a). Then, the product is filtered and oven dried (b). The remaining solid is the zeolite (c).

state, and several methods can be applied, the main one being the hydrothermal method, considered one of the least costly methods. In the process, water is used as a solvent, along with the sources of silicon and aluminum. Other reagents involved in the process are the mineralizing agent (OH^-, F^-), metal cations, and structure-directing agent (usually an organic surfactant) [53]. Figure 2 illustrates the hydrothermal synthesis process. The reaction takes place in an autoclave reactor under high temperature and autogenous pressure (often up to 15 bar). The reaction product is then washed several times, filtered, and oven dried. The solid obtained is the zeolite, which can be used for a variety of applications. The temperature and time for crystallization are critical parameters for synthesis and are dependent on the zeolite to be synthesized [52]. However, the method has some disadvantages, which may limit its application. The water consumption is high, which at the end of the process generates alkaline wastewater, which is difficult to manage. Besides, the processes may require long reaction times. With advances in zeolite synthesis studies, several other methods were developed, such as nonaqueous methods (solvothermal and ionothermal synthesis, whose solvent is replacing alcohol or hydrocarbons and ionic solutions, respectively), microwave radiation methods, sol-gel methods, and ultrasound energy method. Each process has its advantages and disadvantages, and specific types of zeolite crystalline structures can only be synthesized by a certain method, which becomes a limiting factor [35, 38, 53, 54].

The synthesis of zeolites using SiO_2 and Al_2O_3 from chemical reagents is an expensive process due to the cost of manufacturing and purchasing. For this reason, the number of researches focused on locating alternative sources of silica and alumina from cheaper and abundant sources increased in the last decades [35]. Several materials, including those considered waste, have already been successfully used for this purpose. To be used as a precursor, the residue must be cheap, readily available, generated in large quantities, and rich in silica and/or alumina, with low content of contaminating elements [55]. Table 2 shows a few of the most common waste materials used in zeolite synthesis. On the other hand, the quality of these materials is very unstable, which can compromise the quality of the synthesis, requiring a process optimization step [56]. Despite their higher cost, synthetic zeolites have the advantage of presenting uniform properties, which can guarantee their application in processes that require materials with high purity. Among the properties of synthetic zeolites, the pore size distribution is an important feature to characterize this material. As shown in Table 1, natural zeolites generally present pores with smaller diameters, in addition to varying opening dimensions, depending on the crystallographic direction. On the other hand, a major characteristic of synthetic zeolites is their larger pore diameter and their uniformity, regardless of the crystallographic direction, which consequently increases their efficiency in certain applications.

Despite advances in the field of zeolite synthesis, the nucleation and crystallization mechanisms are still not deeply understood. A full understanding of this field can lead to the synthesis of new crystalline structures, which can further expand the field of application of these materials. Further developments in the field of synthesis methods are also needed, to reduce the cost of production and bring economic benefits to large-scale production [55].

2.4. Zeolite Modification. The effectiveness of zeolite application in certain processes depends directly on their physicochemical and structural properties. In wastewater treatment, the zeolites which present negative electrical charge and compensation cations in their crystal structure ensure the removal of cationic species but can be incompatible with the removal of anionic species and organic compounds. Thus, the modification of zeolites enables the

Table 2: Common low-cost waste materials used in zeolite synthesis.

Waste material	Oxide provided SiO_2	Oxide provided Al_2O_3	Zeolite	References
Kaolin/metakaolin	✓	✓	A, Y, 13X, ZSM-5	[31, 121, 124–131]
Glass powder	✓		A, sodalite, LOS-type zeolite, MEL-type zeolite, X, Na-P1, analcime	[132–136]
Aluminum waste		✓	13X, analcime, sodalite, A	[137, 138]
Coal fly ash	✓	✓	X, A, sodalite, 4A, Na-P1, phillipsite, thomsonite, Y	[139–145]
Fumed silica	✓		A, Na-P	[146, 147]
Red mud		✓	FAU-type zeolite, GIS-type zeolite, magnetic 4A, A, X, ZK-5	[56, 148, 149]
Oil shale ash	✓	✓	X, A	[118, 150]
Bauxite residue		✓	X, A, P	[151, 152, 172]
Electrolytic manganese residue	✓	✓	P, A, chabazite	[153]
Diatomite	✓	✓	X, Y	[85, 154, 155]
Rice husk ash	✓		A, ZSM-5, X	[15, 156–158, 173]

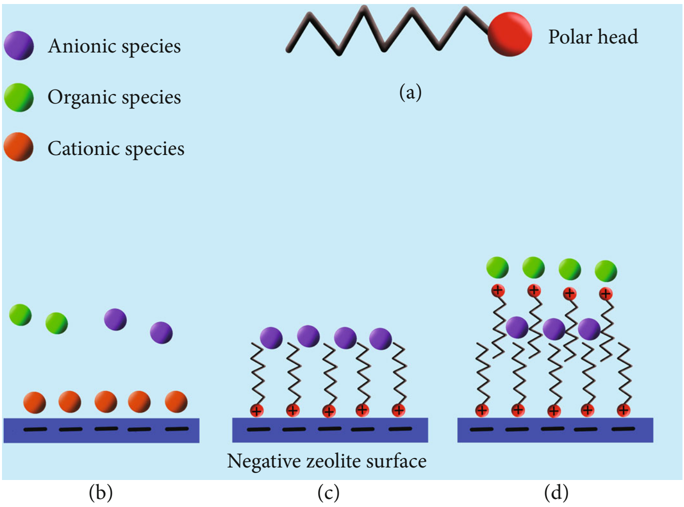

Figure 3: Zeolite can only adsorb cationic species (b). When modified by a cationic surfactant (a), zeolite can also remove anionic (c) and organic species or both (d).

removal of these compounds, in addition to increasing the removal efficiency of cationic species by natural zeolites. Due to the different geological conditions in which zeolites crystallize in nature, the presence of more than one type of compensation cation is common. Modification with a solution of inorganic salts (NaCl, CaCl, NH_4Cl, among others) contributes to uniform the compensation cations present in the crystal structure. Since each cation can be exchanged at different levels of selectivity, standardization leads to optimization of the cation exchange capacity [57].

Another type of modification that has been extensively studied recently is surfactant modification. These chemical species (Figure 3(a)) are described by having a polar head (ionic or neutral) and a nonpolar tail, composed basically of hydrocarbons. Among cationic surfactants used in the modification of zeolites to remove organic compounds, tetramethylammonium, cetyltrimethylammonium (CTMA), hexadecyltrimethylammonium (HDTMA), octadecyldimethylbenzyl ammonium (ODMBA), n-cetylpyridinium (CPD), benzyl tetradecyl ammonium (BDTDA), and stearyldimethylbenzylammonium (SDBAC) are the most commonly used [58]. As illustrated in Figure 3(b), unmodified zeolites can electrostatically attract only the cationic species in the solution. When modifying the zeolite with a cationic surfactant, below the critical micellar concentration (CMC), a surfactant monolayer is formed on the zeolite surface, in which the nonpolar tails are directed towards the bulk solution, and attracts the organic species through hydrophobic interactions (Figure 3(c)). When surpassing the CMC, a surfactant bilayer is formed, which results in the reversal of the electrical charge of the zeolite surface. Under these conditions, anions in the solution can be removed, as well as organic compounds that can still interact with the hydrophobic regions (Figure 3(d)) [59].

2.5. Zeolite Characterization for Water Treatment. The characterization of any material is of great importance for the knowledge of its physical and chemical characteristics and the prediction of its behavior during its application. In the case of zeolites for the treatment of effluents, some characterization techniques are especially relevant.

The identification of the zeolitic phases can be performed using X-ray Diffraction (XRD), which is the most used technique for this purpose. In addition to the identification of phases and the quantification by the Rietveld method (particularly in the case of natural zeolites, which present other contaminating minerals), it is also possible to determine their degree of crystallinity (in synthetic zeolites, the presence of noncrystalline material remaining after synthesis negatively affects the material's adsorption capacity) [60].

As mentioned in Section 2.1, adsorption is a phenomenon that is surface area-dependent. Furthermore, pore size also affects the efficiency and selectivity for adsorption of molecules and ions by intraparticle diffusion. Such parameters can be determined using gas adsorption-desorption techniques with the aid of the Brunauer-Emmett-Teller (BET) model, to determine the specific surface area, and Barrett-Joyner-Halenda (BJH) model, to determine the relative distribution of pore sizes. Once defined, these parameters are used to select the best zeolite to remove a particular contaminant [61].

In the case of removal of organic contaminants, the regeneration of zeolite by temperature is possible, enabling the reuse of the material, which can bring economic benefits to the process. The thermogravimetry (TG) and differential thermal analysis (DTA) techniques help detect the maximum temperature to which the zeolite can be subjected without the destruction of its crystalline structure, with a consequent reduction in its potential for removing contaminants, thus contributing to the optimization of the regeneration process [61].

Another technique that is relevant in the characterization of zeolite for effluent treatment is the determination of the material's surface electrical properties (zeta potential). Since the electrical charge of zeolites can be modified by changing the pH, the determination of the point of zero charge (pH_{PZC}) at which the reversal of electrical charge occurs contributes especially in the removal of anionic contaminants, in which it is possible to make the surface positively charged by proper pH adjustment [62].

Finally, the determination of the cation exchange capacity (CEC) must be determined, to estimate the amount of contaminant per unit of mass a given zeolite is capable of removing, which implies defining the optimal amount of zeolite for a given process [63]. Although there are other characterization techniques necessary for other applications, the abovementioned are of greater relevance in the use of zeolites for the treatment of effluents.

3. Application of Zeolites in Wastewater Treatment

The quality of industrial effluents has received increased attention due to the concern with environmental impacts in the industrial sector. In this context, an efficient collection and treatment system becomes necessary, as incorrect disposal of water has the potential to cause a series of liabilities to the environment [6, 64–71]. Besides, there is great pressure from environmental policies for the reuse of effluent, to reduce the intake of new water and preserve natural resources [72]. Due to their cationic exchange negative charge characteristics and relatively low synthesis cost, zeolites have great potential to be used in the removal of a wide variety of substances, such as heavy metals, organic compounds, dyes, and pigments, reagents, nitrogen compounds, among others [58].

3.1. Inorganic Compound Removal

3.1.1. Heavy Metals. The application of zeolites for heavy metal sequestration in effluent treatment has found the largest applicability with synthetic zeolites, followed by modified zeolites. Natural varieties, although quite attractive from an economic point of view, show the lowest metal sorption for most heavy metals, as presented in Table 3, because the mineralogical composition of natural zeolites varies greatly from one region to another and even within the same mineral deposit [49]. In addition, in many cases, more than one variety of zeolite is found in the ore, along with several other minerals which act as contaminants, since they have low metal sorption capacity. Among the contaminating minerals, quartz, albite, biotite, illite, montmorillonite, feldspar, calcite, halite, and heulandite are commonly observed [73–75]. Synthetic zeolites, constituted in most cases by a single phase, are adsorbents with high uniformity in their properties, such as pore size distribution, hydrophobicity/hydrophilicity, and the presence of a single compensation cation. The combination of these parameters guarantees their greater capacity for cation exchange compared to natural zeolites.

The modification of natural zeolites concerns a series of chemical treatments that are aimed at intensifying their properties. Chemical treatments, with acids and/or bases, lead to the removal of impurities that clog the pores, resulting in increased cation exchange capacity [58]. Another way of modifying zeolites is by using organic surfactants, which form a monolayer at the zeolite surface. Quaternary amines are the most widely used reagents for this purpose and, as cationic reagents, give the zeolites the ability to adsorb anions [76]. In Table 3, it can be observed that modified clinoptilolite demonstrated intermediate adsorption capacity between its natural and synthetic forms. The use of hexadecyl pyridinium bromide (a surfactant with the cationic site) in the modification of clinoptilolite enabled the removal of chromium, in the CrO_4^{2-} form, something that would not be possible with natural or synthetic zeolites [77]. Another heavy metal that is present in the form of anions in solution is arsenic. At pH values above 2, this element is found in the forms $HAsO_4^{2-}$, $H_2AsO_4^{-}$, and AsO_4^{3-}, and its removal is only possible with the use of modified zeolites. In a study using clinoptilolite coated with iron oxide, the removal of arsenic in the anionic solution was possible, due to its affinity for the iron oxide sites at the zeolite surface [78].

Adsorption processes that use zeolites as adsorbents are strongly affected by changes in pH, temperature, and adsorbent/solution mass ratio. When the attractive forces between

Table 3: Heavy metals removed by different zeolites, along with experimental conditions and adsorption and kinetic models.

Metal ion	Zeolite	T (°C)	Contact time (h)	Metal concentration ($mg \cdot L^{-1}$)	S/L ratio ($g \cdot L^{-1}$)	pH	Metal sorption ($mg \cdot g^{-1}$)	Isotherm model	Kinetic model	References
Pb^{2+}	A	25	5	50-800	1	4	100.0	Langmuir	Pseudo-second-order	[148]
	A	25	0.5	100-400	—	7.5	182.0	Langmuir	—	[83]
	X	25	0.5	100-400	—	7.5	213.0			[83]
	Clinoptilolite	70	24	200-2000	10	4.5	78.7	—	—	[75]
	Na-clinoptilolite	70	24	200-2000	10	4.5	91.2	—	—	[75]
	Faujasite	25	1	70-400	2.5	4.5	25.9	Langmuir	Pseudo-second-order	[159]
	Y	26	1	100	1	6	454.5	Langmuir	Pseudo-second-order	[84]
	Clinoptilolite	20	6	103.8	100	3	51.6	Langmuir	—	[81]
	HDTMA-Y	25	24	1000.0	4	5	76.0	Langmuir	Pseudo-second-order	[160]
Cd^{2+}	A	25	5	50-800	1	4	56.5	Langmuir	Pseudo-second-order	[148]
	NaP1	22	6	10-200	2.5	6	50.8	Langmuir	—	[74]
	A	25	0.5	100-400	—	7.5	71.0	Langmuir	—	[83]
	X	25	0.5	100-400	—	7.5	92.0			[83]
	Clinoptilolite	22	6	10-200	10	6	4.6	Langmuir	—	[74]
	Clinoptilolite	70	24	110-1100	10	4.5	13.5	—	—	[75]
	Scolecite	55	24	10-5000	16	6	100.0	Freundlich	Pseudo-second-order	[73]
	Na-clinoptilolite	70	24	110-1100	10	4.5	23.6	—	—	[75]
	Clinoptilolite	20	6	81.5	100	3	7.3	Langmuir	—	[81]
	A	30	—	50-1000	3	8	736.4	Langmuir	Pseudo-second-order	[66]
	X	30	—	50-1000	3	8	684.4			
	X	30	2.5	10-160	1	7	38.3	Langmuir	Pseudo-second-order	[115]
Cr^{3+}	NaP1	22	6	10-200	2.5	4	43.6	Langmuir	—	[74]
	A+X	25	24	500	5	—	71.1	—	—	[161]
	A	25	4	50-300	1	4	41.6	Langmuir	Pseudo-second-order	[82]
	Clinoptilolite	22	6	10-200	10	4	4.1	Langmuir	—	[74]
	Mordenite	25	24	500	5	—	3.6	—	—	[161]
	Scolecite	55	24	10-5000	16	6	106.4	Freundlich	Pseudo-second-order	[73]
	X	30	2	10-160	1	7	62.1	Langmuir	Pseudo-second-order	[115]
Ni^{2+}	A	25	5	50-800	1	4	41.2	Langmuir	Pseudo-second-order	[148]
	A	25	4	50-300	1	4	9.0	Langmuir	Pseudo-second-order	[82]
	NaP1	22	6	10-200	2.5	6	20.1	Langmuir	—	[74]
	A	25	1	100-400	—	7.5	24.7	Langmuir	—	[83]
	X	25	1	100-400	—	7.5	24.9			[83]

Table 3: Continued.

Metal ion	Zeolite	T (°C)	Contact time (h)	Metal concentration (mg·L^{-1})	S/L ratio (g·L^{-1})	pH	Metal sorption (mg·g^{-1})	Isotherm model	Kinetic model	References
	Clinoptilolite	22	6	10-200	10	6	2.0	Langmuir	—	[74]
	Scolecite	55	24	10-5000	16	6	122.0	Freundlich	Pseudo-second-order	[73]
	13X	40	3	0-100	5	6	6.2	Langmuir	Pseudo-second-order	[114]
	HDTMA-Y	25	24	1000	4	5	20.0	—	Pseudo-second-order	[160]
Zn^{2+}	A	25	5	50-800	1	4	45.5	Langmuir	Pseudo-second-order	[148]
	A	25	4	50-300	1	4	30.8	Langmuir	Pseudo-second-order	[82]
	NaP1	22	6	10-200	2.5	6	32.6	Langmuir	—	[74]
	A	25	0.5	100-400	—	7.5	28.6	Langmuir	—	[83]
	X	25	0.5	100-400	—	7.5	41.0			[83]
	Clinoptilolite	22	6	10-200	10	6	3.5	Langmuir	—	[74]
	Clinoptilolite	20	6	98.6	100	3	5.1	Langmuir	—	[81]
	HDTMA-Y	25	24	1000	4	5	26.0	—	Pseudo-second-order	[160]
	X	30	2.5	10-160	1	7	45.1	Langmuir	Pseudo-second-order	[115]
Cu^{2+}	A	25	5	50-800	1	4	35.6	Langmuir	Pseudo-second-order	[148]
	A	25	4	50-300	1	4	50.5	Langmuir	Pseudo-second-order	[82]
	NaP1	22	6	10-200	2.5	5	50.5	Langmuir	—	[74]
	A	25	0.5	100-400	—	7.5	41.6	Langmuir	—	[83]
	X	25	0.5	100-400	—	7.5	48.8			[83]
	Clinoptilolite	22	6	10-200	10	5	5.9	Langmuir	—	[74]
	Clinoptilolite	20	6	97.9	100	3	4.8	Langmuir	—	[81]
	HDTMA-Y	25	24	1000	4	5	36.0	—	Pseudo-second-order	[160]
	X	30	2	10-160	1	7	64.6	Langmuir	Pseudo-second-order	[115]
Mn^{2+}	Clinoptilolite+mordenite	25	2	5-600	2.5	6	7.1	Langmuir	Pseudo-second-order	[162]
	NaOH-activated clinoptilolite+mordenite	25	2	5-600	2.5	6	20.9	Langmuir	Pseudo-second-order	[162]
	NH_4Cl-activated clinoptilolite+mordenite	25	2	5-600	2.5	6	18.5	Langmuir	Pseudo-second-order	[162]
	NaCl-activated clinoptilolite+mordenite	25	2	5-600	2.5	6	21.3	Langmuir	Pseudo-second-order	[162]
	Na_2CO_3-activated clinoptilolite+mordenite	25	2	5-600	2.5	6	19.7	Langmuir	Pseudo-second-order	[162]
	Manganese oxide-coated clinoptilolite +mordenite	25	2 h	25-600	2.5	6	30.8	Langmuir/ Freundlich	Pseudo-second-order	[163]
	Scolecite	55	24	10-5000	16	6	109.9	Freundlich	Pseudo-second-order	[73]

Table 3: Continued.

Metal ion	Zeolite	T (°C)	Contact time (h)	Metal concentration (mg·L^{-1})	S/L ratio (g·L^{-1})	pH	Metal sorption (mg·g^{-1})	Isotherm model	Kinetic model	References
As^{5+}	Iron-coated clinoptilolite	25	—	2	100	4	0.7	Langmuir	—	[78]
	Clinoptilolite	20	24	30-350	25	5	0.9	Langmuir	Pseudo-second-order	[77]
	HDPB-clinoptilolite	20	24	30-350	25	5	2.8	Freundlich	Pseudo-second-order	[77]
Cr^{6+}	Chabazite	20	24	30-350	25	5	1.5	Langmuir	Pseudo-second-order	[77]
	HDPB-chabazite	20	24	30-350	25	5	14.3	Freundlich	Pseudo-second-order	[77]
	13X	40	3	0-100	5	6	3.9	Langmuir	Pseudo-second-order	[114]

the surface and the adsorbate overcome the attraction between the adsorbate and the solvent, the ions start to concentrate on the zeolite surface. As a rule, the zeolite metal adsorption process occurs in an endothermic and spontaneous process, presenting higher rates of adsorption with increased temperature [79]. This fact was proved by Dal Bosco et al. [73], who carried out adsorption tests with Cr^{2+}, Ni^{2+}, Cd^{2+}, and Mn^{2+} in zeolite scolecite, at temperatures of 25, 40, and 60°C. The authors reported greater adsorption of all metals in tests performed at 60°C, followed by those performed at 40 and 25°C. In similar experiments, Ćurković et al. [75] analyzed the use of natural clinoptilolite to remove Pb^{2+} and Cd^{2+} at different temperatures (20-70°C). The results also indicated that the increase in temperature favors the adsorption rate in all analyzed scenarios.

The variation in pH also strongly affects the metal adsorption capacity of zeolites. In highly alkaline environments, it can be observed that the formation of metal oxides and hydroxides as a precipitated form reduces the availability of ions to be adsorbed, thus reducing the adsorption rate. In highly acidic environments, the presence of an abundant amount of H^+ in the solution impairs the adsorption due to competition between this chemical species and the metal to be adsorbed, which also reduces the adsorption rate, as verified by Zanin et al. [80]. The authors evaluated the removal of Cr^{3+}, Cu^{2+}, and Fe^{3+} using clinoptilolite, in solutions with pH 3, 4, and 5. For chromium, the removal rate was greater at pH 5, with the lowest value observed at pH 3. As for copper and iron, adsorption reached its maximum at pH 4, being slightly lower at pH 5. In solutions with pH 3, 4, and 5, Dal Bosco et al. [73] demonstrated that the adsorption density of Cd^{2+}, Mn^{2+}, and Cr^{3+} in zeolite scolecite increased progressively with the increase in pH, whereas for Ni^{2+}, the adsorption rate increased rapidly from pH 3 to 4 but showed a significant increase in the transition to pH 5. In a similar study, Alvarez-Ayuso et al. [74] varied the pH to values of 3, 4, 5, and 6, in the analysis with Zn^{2+}, Cd^{2+}, Cu^{2+}, Ni^{2+}, and Cr^{3+} using NaP1 zeolite. The Zn^{2+} adsorption values increased with increasing pH, whereas Cd^{2+}, Cu^{2+}, and Ni^{2+} showed a slight increase in the transition from pH 3 to 4, stabilizing above that value. As for Cr^{3+}, the adsorption increased significantly from pH 3 to 4, again sharply reducing from pH 5 to 6. It is evident the fundamental role of pH in the adsorption of metals in zeolites, as this governs the metal speciation in solution. Preliminary studies of the effect on the solution's pH are needed to evaluate the removal efficiency, especially when the system is multielement, as each metal has specific pH values at which certain compounds form and precipitate [81]. The pH conditions most used in the application of zeolite in heavy metal removal are close to neutrality or slightly acidic, as can be seen in Table 3.

The solid-liquid ratio is also an important experimental variable when investigating metal adsorption in zeolites. The changes in this parameter can directly or indirectly affect other variables, such as the pH and the solution chemical composition [79]. The increased number of particles raises the specific surface area available for adsorption to occur. In addition, the friction between the particles is more intense than in systems with lower solid percentages. As the particles break down, further increasing the available surface area, greater metal removal can be achieved [79]. It is expected that the adsorption rate will increase with dosage; however, this is not always observed. The high zeolite dosage also increases the amount of the compensation cations in the solution, which can compete with the heavy metal to be removed, leading to a reduction in the adsorption rate [79].

In heavy metal adsorption systems, it is important to consider the presence of more than one species in the solution. In a mixture of heavy metal ions, the increase in the initial concentration leads to a reduction in the adsorption of certain species, due to the greater selectivity presented by some species. Table 4 presents sequences of selectivity for the adsorption of metals in different zeolites, synthetic and natural. Several factors govern the selectivity for metal ions, which must be considered in each system investigated. Among them, it can be cited the microporous structure and the properties of the element to be removed, such as the ionic radii, hydrated ionic radii, and free hydration energy [82]. As an example, it is noticed the greater ease that lead presents of being adsorbed by zeolites. Among the metals investigated, lead presents the lowest atomic radius when surrounded by water molecules and the lowest hydration energy, which expresses the difficulty to lose the water molecules that surround the ion [82]. Therefore, the metal shows great facility to become a dehydrated ion. Although its dehydrated atomic radius is larger, the other ions tend to remain in hydrated form, which makes the penetration of dehydrated lead ions into the zeolite structure more likely, explaining that the greater selectivity in the removal of this metal is present [81].

The adsorption is strongly dependent on factors such as solution pH, temperature, adsorbent dosage, and solution initial concentration. Since these factors varied in the studies analyzed (Table 3), it is difficult to compare the performance of different zeolites. However, in a study verifying the adsorption of a mixture of heavy metals using zeolites A and X, in the same experimental conditions, Ibrahim et al. [83] observed greater efficiency in removal using phase X, since this crystalline structure has larger pores (7.4 Å), compared to phase A (4.5 Å). In a similar study, Shariatinia and Bagherpour [84] also noticed a higher affinity of lead for zeolite NaY (7.4 Å) compared to zeolite NaP1 (which has different windows depending on the crystallographic directions: 3.1 × 4.5 Å [85], 2.8 × 4.8 Å [010]). Smaller pores, of dimensions close to those of hydrated ions, limit their entry and impair the diffusion process within the crystalline structure, which compromises the performance of a particular zeolitic phase as an adsorbent.

3.1.2. Nitrogen Compounds.

As seen in Table 5, zeolites show great potential for application in ammonia removal from effluents. The synthetic versions, due to their larger pore sizes, have a greater affinity for the ammonia molecules (mean diameter of 0.283 nm), which facilitates their entry into the zeolite crystalline structure [86]. Temperature also plays an important role in the removal of ammonia by zeolite, with a reduction in the amount of ammonia removed as

Table 4: Selectivity in competitive adsorption of heavy metals by different zeolites.

Adsorption selectivity			Ionic properties				
Zeolite	Selectivity	References	Heavy metal	Hydrated radius (Å)	Unhydrated radius (Å)	Free energy of hydration (kJ·mol^{-1})	References
FAU-type	$Pb^{2+}>Cu^{2+}>Cd^{2+}>Zn^{2+}>Co^{2+}$	[164]	Pb	4.01	1.32	-1425	[165, 166]
A	$Cu^{2+}>Cr^{3+}>Zn^{2+}>Co^{2+}>Ni^{2+}$	[82]	Cu	4.19	0.72	-2010	
A	$Pb^{2+}>Cd^{2+}>Cu^{2+}>Zn^{2+}>Ni^{2+}$	[83]	Cd	4.26	0.97	-1755	
A	$Pb^{2+}>Cd^{2+}>Zn^{2+}>Ni^{2+}>Cu^{2+}$	[148]	Zn	4.30	0.74	-1955	
NaP1	$Cr^{3+}>Cu^{2+}>Zn^{2+}>Cd^{2+}>Ni^{2+}$	[74]	Co	4.23	0.72	-1915	
X	$Pb^{2+}>Cd^{2+}>Cu^{2+}>Zn^{2+}>Ni^{2+}$	[83]	Cr	4.61	0.64	-4010	
X	$Cr^{3+}>Cu^{2+}>Cd^{2+}>Zn^{2+}$	[115]	Ni	4.04	0.70	-1980	
Scolecite	$Cr^{3+}>Mn^{2+}>Cd^{2+}>Ni^{2+}$	[73]	Mn	4.38	0.80	-1760	
Clinoptilolite	$Pb^{2+}>Zn^{2+}>Cu^{2+}>Cd^{2+}$	[81]					
Clinoptilolite	$Cu^{2+}>Cr^{3+}>Zn^{2+}>Cd^{2+}>Ni^{2+}$	[74]					

Table 5: Zeolites used in ammonium removal, along with experimental conditions and adsorption and kinetic models.

Zeolite	*T* (°C)	Contact time (h)	Concentration (mg·L^{-1})	S/L ratio (g·L^{-1})	pH	NH_4^+ sorption capacity (mg·L^{-1})	Isotherm model	Kinetic model	References
Clinoptilolite	25	12	1-20	0-0.6	—	4.3	Langmuir	Pseudo-first-order	[89]
$NaNO_3$-modified clinoptilolite	25	12	1-20	0-0.6	—	8.1	Freundlich	Pseudo-first-order	
Zeolite P+analcime	25	1	5-500	5	6	17.5	Koble-Corrigan	Pseudo-second-order	[90]
Zeolite X	25	8	100-400	2	7	89.1	Freundlich	Pseudo-second-order	[86]
Zeolite A						59.3			
Chabazite	25	5	130-2080	75	7	39.3	Langmuir	Pseudo-second-order	[91]
Zeolite NaY	25	2	40-615	6.3	—	26.5	Langmuir	Pseudo-second-order	[4]
Modified Na-clinoptilolite	25	24	0-83	—	7.2	14.5	Langmuir	—	[167]
Clinoptilolite +mordenite	25	8	5-120	10	6	6.3	Freundlich	Pseudo-second-order	[88]
Zeolite NaA	25	0-2	—	—	7.9	10.5	Freundlich	Pseudo-second-order	[87]
Magnetic zeolite NaA						10.4			

the temperature increases, due to the desorption of ammonia from the surface [87]. In contrast, Widiastuti et al. [88] demonstrate in their studies that the increase in temperature increases the amount of ammonia adsorbed. These results indicate that the influence of temperature on ammonia adsorption onto zeolites is yet not well understood. Despite the importance of temperature in adsorption processes, this variable has not been thoroughly investigated, and further studies are needed to conclude its influence on the ammonia-zeolite adsorption system.

Solution pH strongly affects the adsorption process as well. At very low pH values, competition between H^+ ions makes it difficult to adsorb ammonia molecules, reducing the sorption capacity. In alkaline solutions, NH_4^+ converts to NH_3, which also reduces the adsorption rate, due to the elimination of electrostatic attraction forces between adsorbate and adsorbent. In a study analyzing ammonia adsorption in pH between 4 and 10, Fu et al. [89] observed that the greatest removal of NH_4^+ with a natural clinoptilolite occurs at pH 5-8. In adsorption tests carried out in the pH range between 2 and 11, Zhao et al. [90] verified that maximum removal of ammonia by a mixture of zeolite P and analcime, synthesized from red mud, occurs at pH 6. In a study analyzing the removal of ammonia by synthetic zeolites, A and X in the pH range between 2 and 10, Moussavi et al. [86] demonstrated that the optimum value for the removal of ammonia occurs at pH 7. These results indicate the importance that this variable presents in the removal of ammonia using zeolite as adsorbents and that the best results can be obtained at pH close to neutrality.

Another factor to be considered in ammonia removal using zeolites is the competition with other ions in the solution. The ionic species readily penetrate the zeolite pores, being easily adsorbed in comparison with molecules. Fu et al. [89] analyzed the removal of ammonia using clinoptilolite and clinoptilolite modified with $NaNO_3$ and found that the presence of Na^+, K^+, Mg^{2+}, NO_3^-, SO_4^{2-}, and Cl^- negatively affected the NH_4^+ adsorption rate. Zhao et al. [90] verified that the removal of NH_4^+ undergoes a significant reduction in the presence of cations such as Na^+, K^+, Ca^{2+}, and Mg^{2+}, due to the zeolite preference to adsorb ions. The order of selectivity in this system was defined as $Na^+ > K^+ > Ca^{2+} > Mg^{2+} > NH_4^+$. Lin et al. [91] evaluated the use of chabazite natural zeolite to remove ammonia from swine manure. The chabazite used in the tests had high calcium content, and according to the authors, the exchange rate between calcium and ammonia occurs more slowly than that for sodium, due to the higher resistance to the diffusion of Ca^{2+}, something that contributes to the reduction of the adsorption rate. In a study conducted by Haji et al. [4], on the removal of NH_4^+ using zeolite Y with different compensation cations, Na^+ proved to have the highest ammonia removal potential (91.8%), followed by Cs^+ (24.8%), K^+ (24.3%), Mg^{2+} (18.5%), and Ca^{2+} (18.5%). The authors also made a comparison with the performance of zeolite X in the removal of ammonia (both with Na^+ cation), which presented an 83.8% removal. The authors stated that, although zeolite X has a lower Si/Al ratio (which consequently results in a higher CEC), zeolite Y has a greater surface area ($980\,m^2 \cdot g^{-1}$ vs. $527\,m^2 \cdot g^{-1}$), which increases its performance as an adsorbent.

Table 5 summarizes several studies utilizing zeolites as adsorbents to remove ammonia. A direct comparison of the efficiency of different zeolite types in the removal of ammonia is difficult, due to the variability of the experimental conditions. Zeolite dosage, ammonia concentration, and contact time are factors that strongly influence adsorption, and as seen in Table 5, these variables were investigated over a wide range. Ideally, it would be necessary to develop standardized tests, under the same conditions, to identify the best zeolite to be used for ammonia removal. However, synthetic zeolites with larger pore openings showed the highest removal capacity, as in the case of zeolites X and A.

3.1.3. Phosphoric Compounds. As zeolites have low efficiency in removing anionic species in solution, the removal of phosphoric compounds can be especially challenging, as they are present in solution in the anionic form, in a wide pH range. Below pH 2, the predominant species is H_3PO_4, while at pH between 2 and 7, between 7 and 12, and above 12, the dominant species are $H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-}, respectively, which result in electrostatic repulsion due to the negative charge. In the acidic pH range, however, sites on the zeolite surface undergo protonation, acquiring a positive electrical charge and attracting phosphate ions, which is followed by chemical interaction between the molecular species and the zeolite surface. This effect was verified by Zhang et al. [92], using granular natural zeolite to remove phosphorus from effluent. In removal tests in different pH ranges (1.8-12), it was found that the highest removal rate (close to 100%) occurred at pH 2, reaching close to 0% at pH 7 and increasing slightly in the alkaline pH range. The authors state that alkaline conditions lead to chemical precipitation, which might explain this behavior. In contrast, adsorption is favored by the expansion of the zeolite pores in acidic pH, which contributes to the increase in the surface area available for adsorption. Hamdi and Srasra [93] compared the phosphate adsorption using clay minerals (kaolinite+illite and kaolinite+smectite) and zeolite A. The pH at which the zeolite showed greater adsorption was 5.5, below the PZC of the zeolite A (PZC = 6.7) [94]. The authors explained that the adsorption of phosphate anions in zeolite occurs at positive sites that are protonated at acidic pH. The attraction of negatively charged molecules at these sites is followed by chemical interaction, leading to higher phosphate adsorption.

The modification of the surface of zeolites is a factor that contributes positively to the adsorption of phosphates since the chemical interaction between species and surfaces often exceeds the electrostatic repulsion between them. Goscianska et al. [95] evaluated the modification of synthetic zeolites NaP1 and NaA and natural clinoptilolite with lanthanum, aiming to investigate phosphate adsorption. After the modification, the specific surface area and pore volume were reduced in all varieties of zeolites. However, the amount of phosphate adsorbed by the modified zeolites was higher, especially in the case of synthetic zeolites. The authors attributed this increase in adsorption to the fact that lanthanum has a greater affinity to phosphate. X-ray diffraction tests revealed crystallized lanthanum phosphate peaks in the samples after the adsorption tests, which explains why the adsorption increased even with the reduction of the specific surface area and pore volume. Alshameri et al. [96] studied the potential of using clinoptilolite zeolite and its modified version with tetra butyl titanate to remove PO_4^{3-}. The authors state that, in this case, it is necessary to modify the surface of the zeolite using inorganic salts or organic surfactants that lead to the appearance of sites with a positive charge. As can be seen in Table 6, the adsorption capacity of natural and synthetic zeolites for phosphate is relatively low, when compared to the other contaminants evaluated in this study. However, the modification is a factor that contributes significantly to increasing the adsorption capacity.

Temperature also presents an important role in phosphate adsorption using zeolite. The increase in temperature positively affects the adsorption capacity. The phosphate molecules move more quickly in the solution, increasing their efficiency in the adsorption of the contaminant. Goscianska et al. [95] verified the increase of the adsorption capacity from 10.5 to $16.2\,mg \cdot g^{-1}$ and 57.7 to $63.9\,mg \cdot g^{-1}$, for the synthetic and modified zeolites NaP1 and LaP1, respectively, when the temperature was varied from 25 to 60°C, demonstrating the endothermic character of the process.

In the adsorption of anionic species, such as phosphoric compounds, pH control is of fundamental importance. In the case of zeolites, pH below the point of zero charges (PZC) provides the appearance of positive sites at the adsorbent surface, which makes adsorption possible.

3.2. Organic Compound Removal

3.2.1. Dyes. The removal of dyes on zeolite surfaces occurs by ion exchange properties. Table 7 shows the results of several

Table 6: Phosphate removal by different zeolites, along with experimental conditions and adsorption and kinetic models.

Zeolite	T (°C)	Contact time	Concentration ($mg \cdot L^{-1}$)	S/L ratio ($g \cdot L^{-1}$)	pH	PO_4^{3-} sorption capacity ($mg \cdot g^{-1}$)	Adsorption isotherm model	Adsorption kinetic model	References
NaP1	25-60	24 h	12.5-200	1	5.3	11.4	Langmuir	—	[95]
LaP1						58.2			
NaA						15.7			
LaA						48.9			
Clinoptilolite						20.2			
La-clinoptilolite						25.5			
Fe-heulandite	25	3 h	1-16	2.4	7	<0.2	Freundlich	—	[168]
Granular zeolite	25	20 min	20	25	1.8	3.3	Langmuir	—	[92]
Zeolite A	70	4 h	50-1000	6.6	5	52.9	Langmuir	Pseudo-second-order	[93]
Clinoptilolite	25	2 h	10-100	48	2-4	1.3	Langmuir	—	[96]
TiO_2-modified clinoptilolite				20		34.2			

studies using zeolites as adsorbents for dyes. As can be seen, synthetic zeolites have a greater adsorption capacity compared to natural ones, reflecting their greater degree of composition uniformity and physical properties (e.g., crystalline structure, pore size, and compensation cations).

Zeolites exhibit different ion adsorption selectivity and competitive adsorption in multicomponent systems. Ayar et al. [97] used natural clinoptilolite and zeolites synthesized from fly ash (analcime+sodalite) to evaluate the removal of safranine O (SO) dye in the presence of Cs^+. The authors noticed that the increase in Cs^+ concentration leads to a reduction in the removal of SO for both zeolites since the Cs^+ ions compete with the SO molecules for the active sites on the surface of the zeolite samples. Due to the difference in the pore sizes of the zeolites used, the results also indicate greater adsorption of SO by clinoptilolite (4.1 Å) in comparison with analcime and sodalite (3.2 and 2.3 Å, respectively).

In dye adsorption systems, it is important to consider the size of the molecule to be adsorbed, as this parameter strongly affects the adsorption efficiency. Wang and Zhu [98] carried out a comparative study on the removal of methylene blue and rhodamine B dyes by clinoptilolite zeolite. The larger size of the rhodamine B molecule was indicated to impair the diffusion process in the zeolite pores. The removal capacity verified for this compound, at room temperature, was 9.3 $mg \cdot g^{-1}$, 55% of the capacity verified for methylene blue (16.7 $mg \cdot g^{-1}$). In addition to the adsorption capacity, the relationship between the size of pores and pigment molecules directly affects the adsorption rate. As seen in Table 7, for natural zeolites (e.g., clinoptilolite, analcime, sodalite, and erionite), the equilibrium time is considerably longer, compared to synthetic zeolites (e.g., X and Y), which is explained by the considerably larger pores and greater adsorption capacity, even at shorter contact time [98].

The pH adjustment is also of great importance for the removal of dyes in zeolite adsorption systems. In pH in the basic range, the presence of OH^- causes a deprotonation reaction in the zeolite, inducing an increase in the negative electric charge, which intensifies the adsorption of cationic species. As verified by Oukil et al. [99], the adsorption of methylene blue (MB), a cationic dye, reaches its maximum value at pH 8. Lower adsorption was verified at pH 3, due to competition with H^+ ions, in addition to protonation reaction, which makes the zeolite surface charge positive, thus causing electrostatic repulsion between species. Badeenezhad et al. [100] found that the pH variation strongly affects the adsorption of clinoptilolite in its natural form, reaching maximum removal of MB in the pH range between 7 and 9. As for the clinoptilolite modified using iron oxide nanoparticles, the adsorption did not show much variation with the pH change, reaching removals greater than 96.4% in the pH range between 3 and 9. The authors state that an alkaline pH, the association of a small amount of available H^+, and the negative surface charge increase the electrostatic attraction of the MB molecules, favoring adsorption. In the case of modified clinoptilolite, the OH^- groups form hydroxy complexes with iron oxide present in the zeolite structure, which contributes to reducing the amount of MB adsorbed. Mittal et al. [101] used zeolite Y to remove brilliant green (BG) dye from the solution. The removal was analyzed in solutions with pH ranging from 2 to 11. In the case of removal of BG by zeolite Y, 78% of dye was removed when the pH of the solution had been adjusted to 6, with no gains in removal being observed at higher pH values, whereas a reduction in the amount of dye removed was observed below pH 6. Cationic dyes are best removed by the zeolite at pH above the point of zero charges (PZC), in which the zeolite surface presents a negative charge. Previous studies indicate that most zeolites present PZC at pH close to neutrality, as verified for zeolites A ($PZC = 6.7$) [102], Y ($PZC = 5.8$) [94], NaP1 ($PZC = 6.5$) [94], sodalite ($PZC = 6.5$) [103], and clinoptilolite ($PZC = 8$) [103]. As natural and synthetic zeolites have shown much lower adsorption of anionic dyes compared to cationic ones, due to electrostatic repulsion, pH adjustment becomes of fundamental importance in the removal of these species since zeolites can acquire positive charge in $pH < PZC$. As verified by Garg et al. [104] when

Table 7: Comparison of dye removal by different zeolites, along with experimental conditions and adsorption and kinetic models.

Dye	Dye type	Zeolite	T (°C)	Contact time	Concentration (mg·L^{-1})	S/L ratio (g·L^{-1})	pH	Sorption capacity (mg·g^{-1})	Adsorption isotherm model	Adsorption kinetic model	References
Safranine O	Cationic	Clinoptilolite Analcime+sodalite	25	1 h-40 d	1754.0	5	6.4	34.7 15.7	—	—	[97]
Methylene blue		H-USY	25	2 h	50-150	2	8	59.9	Langmuir	Pseudo-second-order	[99]
		Clinoptilolite	30-50	—	3.2-32	0.25	—	16.7-20.2	Langmuir	Pseudo-second-order	[98]
		Clinoptilolite Erionite	30	72 h	10-1300	2	5	82.0 88.0	Sips	—	[169]
		Magnetic clinoptilolite	25	45 m	25-20	—	7	52.0	Freundlich	—	[100]
Rhodamine B		Clinoptilolite	30-50	—	4.8-47.9	0.25	—	9.3-12.4	Langmuir	Pseudo-second-order	[98]
Crystal violet		Zeolite X	50	1 h	100	1	9	234.5	Langmuir	Pseudo-second-order	[105]
Brilliant green		Zeolite Y	25-55	20 min	100-800	0.4	6	409.0	Langmuir	Pseudo-second-order	[101]
Basic violet 3		Clinoptilolite Erionite	30	72 h	10-1300	2	**5**	98.0 105.0	Sips	—	[169]
Amido black 10B	Anionic	Zeolite X	25	6 h	5-50	—	4	1.4	Freundlich	Pseudo-first-order	[104]
Acid blue 25		Clinoptilolite Erionite	30	72 h	10-1300	2	5	<0.1 <0.1	Sips	—	[169]

Table 8: Zeolites used in organic compound removal, along with experimental conditions and adsorption and kinetic models.

Organic compound	Zeolite	T (°C)	Contact time	Concentration	S/L ratio (g·L^{-1})	pH	Sorption capacity (mg·g^{-1})	Adsorption isotherm	Adsorption kinetics	References
Toluene Styrene Indene Hexadecane Octadecane Dioctyl phthalate	CTAB-zeolite Y	—	8 h	43 ppm	1	—	30.9	Langmuir	—	[109]
Triclosan	FAU-type	25	24 h	0.3-17.4	30	—	377.6	Langmuir	—	[107]
	BEA-type						119.0			
	MOR-type						153.2			
Phenol	HDTMA-clinoptilolite	20	4 h	10-50 ppm	20-100	—	0.8	Freundlich	—	[110]
	BDTDA-clinoptilolite						1.3			
	HDTMA-ZSM-5	—	24 h	0.0816-1.2 mmol/L	5	—	6.2	Langmuir/ Freundlich/ Redlich-Peterson	—	[112]
	CPB-ZSM-5						9.4			
	HDTMA-clinoptilolite						11.4			
	CPB-clinoptilolite						11.9			
	MCM-41						59.4			
4-Chlorophenol	HDTMA-clinoptilolite	20	4 h	10-100 ppm	20-100	—	12.7	Freundlich	—	[110]
	BDTDA-clinoptilolite	20	4 h	10-100 ppm	20-100	—	6.41			
2,4,6-Trichlorophenol	FAU-type	25	24 h	1-60 μmol/L	30	—	314.5	Langmuir		[107]
Toluene	HDTMA-Y	28	6 h	1-60 mg/L	30	—	152.4	Temkin	Pseudo-second-order	[111]
	HDTMA-ZSM-5	—	24 h	0.0816-1.2 mmol/L	5	—	9.3	Langmuir/ Freundlich/ Redlich-Peterson	—	[112]
	CPB-ZSM-5	—	24 h	0.0816-1.2 mmol/L	5	—	16.4			
	MCM-41	—	24 h	0.0816-1.2 mmol/L	5	—	145.2			
Benzene	HDTMA-Y	28	6 h	1-60 mg/L	30	—	150.4	Temkin	Pseudo-second-order	[111]
	HDTMA-ZSM-5	—	24 h	0.0816-1.2 mmol/L	5	—	7.7	Langmuir/ Freundlich/ Redlich-Peterson	—	[112]
	CPB-ZSM-5						15.0			
	HDTMA-clinoptilolite						16.6			
	CPB-clinoptilolite						23.1			
	MCM-41						112.3			
Ethylbenzene	HDTMA-Y	28	6 h	1-60 mg/L	30	—	162.2	Temkin	Pseudo-second-order	[111]
m,p-Xylene	HDTMA-Y						175.3			
o-Xylene	HDTMA-Y						164.6			

studying the adsorption of amido black 10B, an anionic dye, the highest removal rate occurred in the pH range between 2 and 5. Above this pH value, the studied zeolite (synthetic zeolite X) acquires a negative electrical charge, which leads to electrostatic repulsion and consequent reduction in the removal of the contaminant.

Temperature also plays an important role in dye adsorption using zeolites. The temperature increases the mobility of the ions and promotes the expansion of the crystalline structure of the zeolite, which causes an increase in the adsorption rate [105]. Wang and Zhu [98] analyzed the adsorption of MB and rhodamine B in natural clinoptilolite. The increase in temperature positively affected the adsorption, and for both dyes, the amount adsorbed was greater at approximately 50°C, showing the endothermic characteristic of the adsorption. On the other hand, the increase in temperature may lead to a reduction in the removal of contaminants, as verified by Garg et al. [104], who noted that raising the temperature from 293 K to 333 K resulted in a reduction in the removal of amido black 10B from 73.4% to 48.6%, due to desorption of dye molecules. Temperature becomes a factor that deserves attention, since different zeolite-dye systems can possess endothermic or exothermic behavior, leading to a positive or negative influence on the removal process. As seen in Table 7, temperature is a parameter that was not investigated in most of the studies analyzed in this review, and, as mentioned, it can affect adsorption in different ways. Further in-depth studies on the influence of temperature on dye adsorption using zeolites can provide insightful information.

3.2.2. Organic Species. The adsorption of organic compounds using zeolites is significantly dependent on the adsorbent Si/Al ratio. Low-silica zeolites present a greater amount of aluminum content in their composition, resulting in more compensation cations available, which increases their effectiveness in cation exchange. In contrast, high-silica zeolites present greater hydrophobicity and organic compound removal [106–108]. The adsorption capacity of organics on low-silica zeolites, as well as the affinity for anions, can be amplified with modifications using surfactants. This can be seen in Table 8, which shows studies on the removal of several organic compounds using surfactant-modified zeolites as adsorbents. The modification occurs due to the formation of a surfactant monolayer on the zeolite surface, with the hydrocarbon chain of the molecule facing the solution and making the zeolite hydrophobic. The surfactant concentration is of great importance because if the critical micellar concentration (CMC) is exceeded, a surfactant double layer should be formed, which returns the hydrophilic character to the zeolite [58]. Hosseini Hashemi et al. [109] evaluated the use of zeolite Y, modified with hexadecyltrimethylammonium bromide (CTAB), to remove organic pollutants from an olefin plant. Zeolite Y was modified with different concentrations of CTAB, to evaluate the influence of surfactant concentration on the removal of organic compounds. The best results were obtained with 0.025 M CTAB, whereas higher concentrations led to the formation of a double layer, increasing the hydrophilicity of the zeolitic particles and reducing the adsorption of the organic compounds. The adsorption of organic compounds in CTAB-modified zeolite Y follows the Langmuir model, whose adsorption occurs in monolayer and all sites have the same affinity for adsorbate. As all the analyzed isotherm models (Freundlich, Sips, and Dubinin-Radushkevich) presented acceptable errors, it can also be concluded that the adsorption is favorable and that it occurs basically by physical mechanisms (physisorption) [109].

Jiang et al. [107] investigated the adsorption of three organic compounds (triclosan, phenol, and 2,4,6-trichlorophenol) using four synthetic high-silica zeolites, belonging to the FAU, BEA, MFI, and MOR structures. For triclosan adsorption, FAU-type zeolite showed the highest adsorption capacity, followed by MOR and BEA-type. MFI-type zeolite was demonstrated to have a very low adsorption capacity for triclosan. In the case of trichlorophenol, the adsorption sequence was maintained, again with emphasis on the greater adsorption in the zeolite of the FAU structure. As for phenol, the amount adsorbed by all types of zeolites was lower than that for the other compounds. However, the MFI-type zeolite stood out in the removal of this chemical compound, followed by the MOR, BEA, and FAU zeolites. The authors associated the adsorption of organic compounds with the size of their hydrocarbon chains and the pore size of zeolites. In the case of FAU-type zeolite, the adsorption of trichlorophenol was greater than triclosan due to the smaller size of the first species; therefore, more molecules could pass through the pores of the FAU zeolite. The adsorption of phenol was shown to be greater in the MFI zeolite, which is the zeolite with the smallest pore size. The authors state that pores with the same order of magnitude as the molecules of organic compounds favor adsorption due to the generation of a greater attraction force between the compound and active sites in the micropores. The organic compound triclosan has been shown to adsorb following the Langmuir model, regardless of the zeolite used. Trichlorophenol followed the Langmuir model only for the FAU zeolite and adsorbed forming multilayers in the other zeolites, following the Freundlich model. Phenol was adsorbed following the Freundlich model in all the zeolites studied. According to the authors, the hydrophobicity of zeolites has secondary importance. The type and size of organic molecules (which may lead to intermolecular attraction between molecules on the adsorbent), pore size, and crystalline structure of zeolites were more relevant features in the process.

Kuleyin [110] analyzed the removal of phenol and 4-chlorophenol using natural clinoptilolite, modified with hexadecyltrimethyl ammonium (HDTMA). The authors observed that 4-chlorophenol showed the highest adsorption rate in modified clinoptilolite, since the reagent is more hydrophobic than phenol, showing a greater affinity for zeolites covered by surfactants. In terms of comparison, in the experimental conditions of $20\,\mathrm{g{\cdot}L^{-1}}$ of adsorbent, 20°C, and initial concentration of $50\,\mathrm{mg{\cdot}L^{-1}}$, natural clinoptilolite showed removal < 10% for chlorophenol and <5% for phenol, whereas modified clinoptilolite showed removals of approximately 60% for phenol and 90% for chlorophenol.

Table 9: Most used models to describe the adsorption isotherm and kinetics of zeolites in wastewater treatment systems.

Adsorption isotherm models	Model equation	Variables	References
Langmuir	(1) $q_e = q_m(K_L C_e/1 + K_L C_e)$	C_e: equilibrium concentration (mg/L)	[81]
Freundlich	(2) $q_e = K_F {C_e}^{1/n}$	q_e: equilibrium adsorption capacity (mg/g)	[82]
Sips	(3) $q_e = q_s a_s {C_e}^{n_s}/1 + a_s {C_e}^{n_s}$	K_L: Langmuir constant (L/mg) q_m: maximum adsorption capacity (mg/g)	[169]
Koble-Corrigan	(4) $q_e = a{C_e}^n/1 + b{C_e}^n$	n: empirical parameter for adsorption intensity	[90]
Dubinin-Radushkevich	(5) $q_e = q_m e^{\left(\beta\varepsilon^2\right)}$	K_F: Freundlich constant (mg/g)(mg/L)$^{(-1/n)}$	[109]
Redlich-Peterson	(6) $q_e = K_{RP} C_e/1 + B{C_e}^g$	q_s: theoretical maximum adsorption capacity (mg/g)	[112]
Temkin	(7) $q_e = (RT/b_T)\ln(A_T C_e)$	a_s, n_s: sips parameters a, b: Koble-Corrigan parameters	[170]
Adsorption kinetic models	Model equation	β: constant related to adsorption energy	
Pseudo-first-order	(8) $q_t = q_e\left(1 - e^{(-k_1 t)}\right)$	ε: Polanyi adsorption potential	[171]
Pseudo-second-order	(9) $q_t = k_2 q_e^2 t/1 + k_2 q_e t$	K_{RP}, B: equilibrium constants g: exponential constant value (0-1) A_T, b_T: equilibrium Temkin constants R: gas constant (J/mol·K) T: temperature (K)	[171]
Intraparticle diffusion	(10) $q_t = k_i t^{1/2}$	q_e, q_t: amount of adsorbed species at equilibrium at any time (mg/g) k_1: pseudo-first-order constant (h^{-1}) k_2: pseudo-second-order constant (g/mg·h) k_i: intraparticle diffusion constant (mg/g·h$^{0.5}$) t: time (h)	[113, 150]

Vidal et al. [111] performed the removal of benzene, ethylbenzene, toluene, o-xylene, and m,p-xylene Y-modified zeolite with HDTMA. The zeolites were modified in different concentrations of HDTMA, using 50, 100, and 200% of the cation exchange capacity (CEC) of the zeolite Y. It was found that the concentration of HDTMA that results in the greatest removal of the analyzed organic compounds was 100% of the CEC. Concentrations of 50 and 200% lead to an incomplete coating of the zeolite surface and the formation of a double layer of surfactant, respectively, which impairs the adsorption of the compounds. The maximum adsorption capacities obtained by the Langmuir model were 150.42, 152.41, 162.22, 175.32, and 164.58 mg·g^{-1} for benzene, toluene, ethylbenzene, m,p-xylene, and o-xylene, respectively. Ghiaci et al. [112] used natural clinoptilolite, ZSM-5, and MCM-41 to remove toluene, benzene, and phenol. The zeolites (except MCM-41) were modified with HDTMA bromide and *n*-cetyl pyridinium bromide (CPB), in different concentrations (0.5, 1.8, and 20 mmol·L^{-1}). The authors state that the pores of all the zeolites investigated are smaller than the surfactants used in the modification, which would be adsorbed only on the external surface of the particles. It was found that, in all cases, the adsorption of organic compounds on zeolites modified with CPB was greater than in those modified with HDTMA. The authors explained that this is due to the more hydrophobic nature of CPB compared to HDTMA, increasing the interaction of CPB with the organic compounds analyzed. The study revealed the greater adsorption capacity of benzene, toluene, and phenol in zeolite MCM-41, which even without previous treatment showed adsorption capacities five times greater than those of clinoptilolite and ZSM-5.

3.3. Kinetic Studies. The adsorption kinetic models help to understand the mass transfer adsorption mechanisms, in addition to providing information about the adsorption rate and general performance of the adsorbent [80]. Ideally, an ideal adsorbent should possess a high adsorption capacity allied with a rapid adsorption rate. The mass transfer mechanism includes three steps. The first is the external diffusion, in which the adsorbate is transferred to the solid through a liquid film layer. The concentration of adsorbate governs the driving force, and the external diffusion occurs faster in the case of higher concentrations. The second step is the internal diffusion when the adsorbate penetrates the pores. Finally, the third step is the interaction of the adsorbate with the active sites in the adsorbent [113]. Table 9 shows the equations of the most widely used adsorption isotherm and adsorption kinetic models applicable for adsorption systems, including zeolites as adsorbents. The pseudo-second-order model best fits the experimental data in the studies analyzed in this review (as verified in Tables 3–8). This model, adequate for solutions with low concentration, indicates that the material utilized as adsorbent possesses a large number of active sites. Low silica zeolites possess a high amount of aluminum in their crystallographic structure, each one representing an active point for adsorption, which is why the second-order model is the one that best represents the phenomenon. Despite being widely applied in adsorption kinetic studies, pseudo-first- and pseudo-second-order models cannot explain the mass transfer mechanism, being considered empirical models. Thus, the mechanism is better explained by internal diffusion models such as the intraparticle diffusion model. This model assumes that the diffusion of adsorbate into the pores of the adsorbent is the slowest step in the adsorption process. Graphically, the process is represented by a straight line that may pass through the origin. In this case, intraparticle diffusion is the only mechanism that limits the process, and the adsorption on the outer layer takes place instantaneously. Otherwise, there is an indication that more than one mechanism is controlling the adsorption process [113].

In the case of heavy metal adsorption, the intraparticle diffusion model has also shown adherence in some studies, as verified by Jin et al. [114], indicating that the adsorption occurs initially on the external surface of the particles, followed by adsorption within the pores in the crystalline structure of the particles. Since metallic ions present dimensions of the same order of magnitude of the pores, the adsorption occurs quickly, regardless of the zeolite used or the heavy metal to be removed.

For ammonia, results of adsorption experiments performed by Zhao et al. [90] and Lin et al. [91] indicated that in the first 5 minutes of contact, ammonia removal reached 56.4% for analcime and P zeolites and 50% for chabazite zeolite, respectively. Although the intraparticle diffusion model did not present a good correlation with the experimental data, it is believed that the diffusion was the main adsorption mechanism acting in the first 30 minutes of contact [91].

Considering the adsorption of dyes, the data demonstrate that, for the zeolites and dyes analyzed, adsorption on the external surface occurs quickly. However, the intraparticle diffusion rate is quite reduced, reflecting the difficulty that the molecules present in entering the pores of the zeolite, due to its size. At this point, the more uniform chemical composition (greater stability of the Si/Al ratio) and pore size of synthetic zeolites show greater adsorption potential for dyes. Once again, it is important to consider the relationship between the size of the dye molecule and the pore dimensions of the zeolite to assess the time required for the adsorption to occur, this information being essential to design the processes for removing this type of contaminant.

As for kinetics of phosphoric compound adsorption, Hamdi and Srasra [93] verified that most of the phosphorus was removed within a 2 h interval, with no further removals being verified after this time. This suggests that adsorption occurs only on the surface, and the entry of molecules into the interior of the zeolite pores was impaired. However, adsorption kinetics has not been investigated in most studies. Further studies on the kinetics of phosphoric compound removal using zeolites are necessary to have a better understanding of the adsorption process, in addition to allowing the determination of the optimal contact time for the design of treatment systems for this type of effluent.

The adsorption of organic compounds onto zeolites differs from the process of removal of other contaminants because hydrophobic interactions between adsorbent/adsorbate are of greater importance. The modification of zeolites using surfactants makes this interaction possible by the appearance of a hydrophobic monolayer at the zeolite surface. However, the surfactant molecules are too compared to the pore sizes, and the coating only occurs on the surface of the particles. Studies carried out by Kuleyin [110] demonstrate that removal occurs within the first 30 minutes of contact and quickly stabilizes, indicating that the diffusion in the zeolite pores is a limiting factor for adsorption. The process did not fit well with the intraparticle diffusion model, which confirms the external character of the adsorption of organic molecules. Since adsorption occurs on the surface of the particles, it is expected that the particle size of the zeolite used may influence the efficiency of the process. Considering natural zeolites, the comminution process can be optimized with prior knowledge of this parameter. However, granulometry is not among the physical parameters of the adsorbents used in the analyzed studies. Another factor that may influence the adsorption process, which has not been investigated, is pH. The variation of this variable can affect the ionization state of the molecules, both the surfactant and the adsorbate, which can strongly influence the process.

3.4. *Adsorption Isotherms.*

The analysis of adsorption isotherms reveals important information, such as maximum adsorption capacity (mg/g) and the adsorption mechanism, which can be used in the development of adsorption systems for wastewater treatment [76]. The isotherm models are represented by curves that relate the amount of adsorbate at the adsorbent surface and the concentration of the adsorbate in the liquid phase, at a constant temperature. Table 9 shows the existing adsorption isotherm models in the literature used to characterize the adsorption on microporous materials. The models most commonly adopted to represent the adsorption isotherms are the Langmuir and Freundlich models, which assume a uniform distribution in monolayers at the adsorbent surface and the multilayer adsorption on a heterogeneous surface of the adsorbent, respectively [76]. Temkin's model assumes the existence of an adsorbate-adsorbate interaction, which confirms that the presence of hydrophobic tail group interaction is a dominant factor in the process. The Redlich-Peterson model is similar to the Langmuir and Freundlich models, but it is more suitable for wider ranges of contaminant concentration, also fitting well in processes with this characteristic [111].

According to data collected in Table 3, the Langmuir model was the one that best fitted the experimental data of the studies analyzed, indicating that the adsorption to the heavy metal system using zeolites as adsorbents occurs with the formation of a monolayer on the surface of the particles. The adsorption rate is higher in the first minutes of contact, at which more active sites are available for adsorption. As the sites on the surface are occupied, the ions migrate into the pores within the crystalline structure [114]. In addition to adsorption, ion exchange is also present as a mechanism for removing heavy metals in solution, as indicated by Bai et al. [115] and Hui et al. [82], who verified an increase in sodium concentration in solution after the equilibrium time is reached.

For ammonia adsorption, among the studies analyzed in Table 5, the Langmuir isotherm model showed the best adherence to experimental data, indicating that the adsorption of these molecules occurs with the formation of a monolayer. The Freundlich model also showed good applicability, indicating the heterogeneity of the adsorbent surface, in addition to the fact that the process occurs spontaneously [87].

Comparable to nitrogenous compounds and heavy metals, the dye adsorption process occurs mainly by cationic exchange and electrostatic interactions. The process is favored for zeolites with a lower Si/Al ratio, in which the largest amount of aluminum atoms contributes to a greater negative charge. As each negative site is capable of adsorbing only one dye molecule, a monolayer is formed. As shown in Table 7, most studies indicate that the Langmuir isotherm best represents the adsorption process, which confirms this theory.

For phosphoric compounds, the process occurs by electrostatic attraction, and, as in the previous cases, each site can adsorb only one molecule, leading to the formation of a monolayer. The Langmuir isotherm illustrates this phenomenon well, and this model best fitted the experimental data available for the investigation on the use of zeolites as adsorbents.

In the case of organic compounds, the Langmuir model fits well with the experimental data, indicating that the hydrophobic interaction process allows the formation of a monolayer of contaminant molecules over the surfactant layer, and the process occurs spontaneously, as indicated by the good fitting of the Freundlich isotherm. As seen in Table 8, there is also an indication of good adjustment by the Temkin and Redlich-Peterson isotherms, demonstrating the hydrophobic interaction between the adsorbate and the surfactant-modified zeolite.

4. Conclusions, Challenges, and Future Perspectives

Based on investigations conducted by several authors, it can be seen that synthetic zeolites have greater adsorption capacity for the various compounds analyzed, due to high degree ordering in the crystalline structure and, consequently, standardization of pore sizes and cation exchange capacity. Natural zeolites are less efficient since the presence of contaminating minerals reduces adsorption efficiency. Therefore, modification of natural zeolites is an alternative to enhancing their properties for application in wastewater treatment.

As for contaminants, heavy metals, dyes, and ammonium are readily adsorbed by zeolites, with fast kinetic rates. However, for anionic species, such as phosphoric compounds and some heavy metals (e.g., chromium and arsenic), adsorption is impaired, due to electrostatic repulsion, but possible at specific pH ranges. Organic compounds, which are predominantly hydrophobic, have been removed using zeolites by modifying them with surfactants, creating a hydrophobic layer on the surface of the zeolite, which increases its affinity for these compounds. In this case, the dosage of the surfactant becomes an important variable to be considered.

Despite a large number of bench-scale researches which show the effectiveness of zeolites as contaminant adsorbents, further studies on adsorption kinetics (phosphoric compounds), temperature (dyes), granulometry, and pH (organic compounds), desorption, and pilot-scale investigations are necessary. Furthermore, synthetic solutions are used in the research, which does not reflect the characteristics of real wastewater. The presence of other chemical species in this scenario could affect the adsorption mechanisms in different ways and is important to consider the presence of these elements to apply zeolite in large-scale industrial applications.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Authors' Contributions

Luciano Fernandes de Magalhães worked on conceptualization, investigation, data curation, writing (original draft), writing (review and editing), and visualization. Gilberto Rodrigues da Silva worked on writing (review and editing), supervision, and project administration. Antônio Eduardo Clark Peres worked on supervision.

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