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Introductory Chapter: Adsorption and Ion Exchange Properties of Zeolites for Treatment of Polluted Water

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Additional information is available at the end of the chapter

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1. Introduction

1.1. Water pollution

Over the last few decades, the world has become increasingly sensitive toward the protection of the ecosystem and its environment. As a result of the rapid increase in population and economic development; large quantities of waste were generated lead to severe environmental degradation and thereby resulting in pollution. One of the major environmental pollutions is water pollution. Waste water as one of the most reasons for water pollution may come from the domestic, agricultural, and industries.

Adsorption and ion exchange techniques for wastewater treatment have become more popular in recent years owing to their efficiency in the removal of pollutants. The most common adsorbent materials are alumina, calais, silica, zeolites, metal hydroxides, and activated carbon.

1.2. Zeolite minerals

Zeolites form a unique class of oxides, consisting of microporous, crystalline aluminosilicates that can be found in nature, or synthesized artificially. The zeolite framework is very open and contains channels and cages, where cations, water, and adsorbed molecules may reside and react. The specific adsorption and ion exchange properties of zeolites are used in industries, color removal, detergents, toothpaste, and desiccants, whereas their acidity makes them attractive catalysts [1].

Zeolites are classified into two classes, one is natural zeolites, and the other is synthetic zeolites. Natural zeolites are hydrated aluminosilicates compounds with a characteristic three-dimensional structure of tetrahedrons as TO_4 ($\text{T} = \text{Si, Al, B, Ge, Fe, P, and Co}$) joined by oxygen atoms, with large pore apertures and pore system that allow the relatively easy exchange of cations between aqueous solutions and intracrystalline sites [2, 3]. Zeolites have in its internal structure cavities and channels interconnected of molecular dimensions, where compensation cations allowing the ion exchange [4, 5]. New functional groups may introduce to zeolites through several processes of modification that improve its activity and selectivity on the removal several substances [6–8]. Several authors studied the use of modified natural zeolite on environmental applications, mainly anions uptake from effluents by adsorption processes [9–11]. Due to the excellent ion exchange ability and high surface area, natural zeolites [12, 13], and synthetic zeolites [14–16].

Nearly 600 known zeolites were discovered. International Union of Pure and Applied Chemistry (IUPAC) endorsed a general classification of zeolites structures, that is, FAU for faujasites, mordenite framework inverted (MFI) for ZSM-5, and mordenite zeolite (MOR) for mordenite.

2. Adsorption and ion exchange phenomena

Adsorption and ion exchange, take advantage of many common features in regard to application in batch and fixed-bed processes for a unified treatment. These processes involve the transfer and distribution of solutes between a fluid phase and particles.

Adsorbents are natural or synthetic materials of the amorphous or microcrystalline structure. Those used on a large scale are activated carbon, molecular sieves, silica gel, and activated alumina.

Ion exchange occurs throughout a polymeric solid, which dissolves some fluid-phase solvent. In ion exchange, ions of positive charge in some cases (cations) and negative charge in others (anions) from the fluid, replace dissimilar ions of the same charge initially in the solid. The ion exchanger exhibits permanently bound functional groups of different charge. In ion exchanger, cation exchange resins generally contain bound sulfonic acid groups; less commonly, these groups are carboxylic, phosphonic, phosphinic, and so on. Anionic resins involve quaternary ammonium groups (strongly basic) or other amino groups (weakly basic) [17].

2.1. Adsorption phenomena in zeolites

Adsorption involves, in general, the accumulation (or depletion) of solute molecules at an interface (including gas–liquid interfaces, as in foam fractionation, and liquid–liquid interfaces, as in detergency).

The most adsorption processes are of gas–solid and liquid–solid interfaces, with solute distributed selectively between the fluid and solid phases. The accumulation per unit surface area is small; thus, highly porous solids with very large internal area per unit volume are preferred. Two classes of adsorption are identified, physical adsorption and chemical adsorption. Physical adsorption or physisorption involves van der Waals forces (as in vapor condensation), and retard chemical

adsorption or chemisorption, which involves chemical bonding. The former is well suited for a regenerable process, while the latter generally destroys the capacity of the adsorbent [18].

Adsorption techniques have gained favor recently due to their efficiency in the removal of pollutants. Also, adsorption process provides an attractive alternative treatment, especially if the adsorbent is inexpensive and readily available. The advantage of the adsorption process is its sludge free, clean operation, and complete removal of pollutants even from dilute solution. Therefore, adsorption considered as one of a low cost and powerful treatment processes for the removal of pollutants from waste water [19].

Zeolites are the most important inorganic cation exchangers and adsorptive materials. It shows higher cation exchange selectivities, good resistance to temperature and ionizing radiations, and excellent compatibility with the environment. Therefore, zeolites are widely used in modern technologies as selective adsorbents, molecular sieves, and particularly as catalysts. Ion exchange property is employed also as a tool for tailoring the structure in order to obtain specific performances, and so, it competes with cation exchange resins in water processing and in the purification of wastewater and sewage.

Zeolites have two main properties: adsorption and ion exchange. These two properties are due to reactive surfaces, due to the presence of Al^{3+} on adsorption sites with a Si^{4+} ion resides, and the micropores crystalline system. These properties allow the zeolite for several applications. Zeolites are essentially nontoxic and pose no environmental risk. Zeolite is also applied in toothpaste to bind calcium [20].

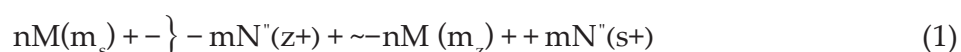
Because of their favorable ion exchange selectivity for certain cations, zeolite minerals, particular clinoptilolite, are of interest for use in the treatment of nuclear waste waters [21], municipal and industrial waste waters [22], acid mine drainage waters [23] and other construction materials.

2.2. Ion exchange phenomena in zeolites

Ion exchange is a function of solid and aqueous phase composition and aqueous solution concentration.

Ion exchange equilibria occur between two or more phases, one of which is liquid which exchanges two or more ions (cations or anions), more or less strongly bound to each phase. Ions exchangeable quantity by a solid exchanger depending on its structural features and is called the ion exchange capacity, usually expressed in meq/g. Ion transfer from one phase to the other is subject to the observance of electroneutrality and regulated by the ion concentration in both phases. This parameter is a function of both the energy of ion lattice interaction and the hydration energy (ion solution interaction).

A cation exchange reaction may be written as.



where, m and n are the valences of exchanging cations.

M and N and subscripts s and z denote solution and zeolite phase, respectively.

Ion exchange property in zeolites resulted from the presence of extra cations, located on channels and cages of it [24]. In the zeolite structures, there are various cation sites, which differ from each other in framework position and therefore, in bond energy. When the zeolite contact with an electrolytic solution, its cations escape from their sites and replaced by other cations from the solution [25]. Cation sieving may be due to the inability of the negative charge distribution on the zeolite structure to accommodate a given cation [24] (**Table 1**).

2.3. Cations and acidity in zeolites

In the tetrahedral crystal, when Al^{3+} replaces Si^{4+} ions the units have a net charge of -1 , and so the cation with a positive charges, such as Na^+ , is neutralizing the negative charge. The number of cations presents within in a zeolite structure equals the number of alumina tetrahedral. A zeolite in its sodium compensated form is presented as Na-ZSM-5, Na-X, and so if Na^+ ions are replaced by H^+ (yielding H-ZSM-5, H-X,) the zeolite becomes a gigantic poly acid. The structure of an acid site with H^+ on a Si–O–Al bridge is illustrated in **Figure 1**. As zeolite being a proton donor, the site is called a Brønsted acid, and its strength depends on the number of other aluminum ions in the environment and the local environment of the proton [20].

Zeolite	Representative unit-cell formula	Void volume (%)	Channel dimensions (Å)	Thermal stability (relative)	Cation Exchange Capacity ^b (meq/100g)
Analcime	$\text{Na}_2 (\text{Al}_{16}\text{Si}_{32} \text{O}_{96}) \cdot 16\text{H}_2\text{O}$	18	2.6	High	4.54
Chabazite	$(\text{Na}_2, \text{Ca})_6 (\text{Al}_{12}\text{Si}_{24} \text{O}_{72}) \cdot 40\text{H}_2\text{O}$	47	3.7 x 4.2	High	3.84
Clinoptilolite	$(\text{Na}_3 \text{K}_3) (\text{Al}_6\text{Si}_{30} \text{O}_{72}) \cdot 24\text{H}_2\text{O}$	34	3.9 x 5.4	High	2.16
Erionite	$(\text{Na}, \text{Ca}_{0.5}\text{K}) (\text{Al}_9\text{Si}_{27} \text{O}_{72}) \cdot 27\text{H}_2\text{O}$	35	3.6 x 5.2	High	3.12
Faujasite	$\text{Na}_{58} (\text{Al}_{58}\text{Si}_{132} \text{O}_{384}) \cdot 240\text{H}_2\text{O}$	47	7.4	High	3.39
Ferrierite	$(\text{Na}_2 \text{Mg}_2) (\text{Al}_6\text{Si}_{30} \text{O}_{72}) \cdot 18\text{H}_2\text{O}$	28	4.3 x 5.5 3.4 x 4.8	High	2.33
Heulandite	$\text{Ca}_4 (\text{Al}_8\text{Si}_{28} \text{O}_{72}) \cdot 24\text{H}_2\text{O}$	39	4.0 x 5.5 4.4 x 7.2	Low	2.91
Laumontite	$\text{Ca}_4 (\text{Al}_8\text{Si}_{16} \text{O}_{48}) \cdot 16\text{H}_2\text{O}$	34	4.6 x 6.3	Low	4.25
Mordenite	$\text{Na}_8 (\text{Al}_8\text{Si}_{40} \text{O}_{96}) \cdot 24\text{H}_2\text{O}$	28	2.9 x 5.7 6.7 x 7.0	High	2.29
Phillipsite	$(\text{Na}, \text{K})_5 (\text{Al}_5\text{Si}_{11} \text{O}_{32}) \cdot 20\text{H}_2\text{O}$	31	4.2 x 4.4 2.8 x 4.8 3.3	Medium	3.31
Synthetic Zeolites					
Linde A	$\text{Na}_{12} (\text{Al}_{12}\text{Si}_{12} \text{O}_{48}) \cdot 27\text{H}_2\text{O}$	27	4.2	High	5.48
Linde X	$\text{Na}_{86} (\text{Al}_{86}\text{Si}_{106} \text{O}_{384}) \cdot 264\text{H}_2\text{O}$	50	7.4	High	4.73

^bCalculated from the unit-cell formula.

Table 1. Representative formulae, chemical composition, and selected physical properties of important zeolites [25, 26].

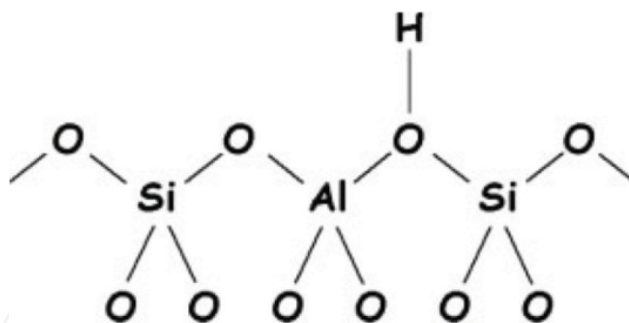


Figure 1. Example of a solid acid.

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