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Progress of Zeolite in Water Softening Treatment

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Abstract

In the discourse of water treatment, one naturally stumbles upon zeolite, a versatile mineral that plays a pivotal role in softening water. This indispensable process arises from the abundant presence of divalent ions, notably calcium and magnesium, which are notorious for contributing to water hardness, an issue that manifests as scale build up within crucial components like boiler and heat exchanger pipelines. The prevalence of scale not only compromises the efficiency of such systems but also incurs considerable maintenance costs. Consequently, the urgent need to combat water hardness has propelled the widespread adoption of water softening techniques, with zeolite treatment emerging as a prominent and effective approach. Over time, the evolution of zeolite treatment methods has notably enhanced the efficacy of water softening procedures. Zeolite's ion exchange capabilities enable targeted removal of divalent ions, advancing water treatment technology for efficient, sustainable solutions, combating scale build up, and ensuring water distribution system longevity. This mini review explores zeolite's role in water softening, its impact on divalent ions, and its ongoing innovation in treatment. It highlights the industry's commitment to improving water quality standards and operational reliability in various sectors.

Keywords: Calcium, hardness of water, magnesium, permanent, temporary, zeolite

INTRODUCTION

Water, covering an extensive 71% of the Earth's surface and leaving the remaining 29% to land, serves as a fundamental element that plays a vital role in supporting life on our planet. The majority of this water, approximately 97%, resides in the enormous oceans, significantly surpassing the water quantities available on the earth's surface. Despite this abundance, a major obstacle arises due to the high salt content in ocean water, making it unsuitable for direct consumption or utilization in various industrial and agricultural sectors. To overcome this challenge, societies worldwide must depend on harvested rainwater, acknowledging our complete reliance on this invaluable resource. It is crucial to emphasize the utmost importance of water quality since it has a direct impact on human health and overall well-being. When rainwater comes into contact with the earth's surface, it tends to pick up impurities, underscoring the critical necessity of maintaining water purity through appropriate treatment methods. Groundwater hydrochemistry is significantly influenced by the presence of carbonate, magnesium, and calcium ions in the earth's crust. The interaction between

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moisture, carbon dioxide, calcium, and magnesium ions leads to the creation of hard water, which is categorized into two distinct types: temporary and permanent hardness. The quality of water is a fundamental aspect that affects various industries, agriculture, and human health. Thus, it becomes imperative for communities to foster sustainable water management practices that focus on preservation and conservation efforts. The intricate balance between water sources, usage, and environmental impact underscores the importance of implementing strategies that ensure water security for current and future generations. In light of advancing technologies, innovative solutions such as desalination plants and advanced purification techniques offer promising avenues to address water scarcity challenges on a global scale. The delicate interplay between water quality, availability, and sustainability underscores the need for a comprehensive approach to water resource management that prioritizes the well-being of both ecosystems and human populations. Temporary hardness, a common issue in water treatment, is conveniently remedied through a simple boiling process, demonstrating a clear solution to this type of water quality concern. Conversely, the management of permanent water hardness necessitates the application of specific treatment methods, indicating a more complex approach required to handle this persistent issue. Interestingly, the term "zeolite" finds its etymology in the ancient Greek words "zein," meaning boiling, and "lithos," meaning stone, shedding light on the origins of this remarkable substance renowned for its efficacy in addressing water hardness challenges effectively. Characterized by a chemical formula of $Na_2O.Al_2O_3.xSiO_2.yH_2O$, zeolite, a type of hydrated sodium alumino silicate, is highly regarded for its remarkable ability to facilitate reversible ion exchanges, consequently alleviating water hardness complications with notable success. Referred to as Permutit in some contexts, zeolite operates by guiding hard water through a bed of sodium zeolite, where the ions responsible for water hardness, notably Ca^{2+} and Mg^{2+}, are captured by the zeolite while sodium ions are released in exchange. This ion exchange mechanism plays a pivotal role in eliminating hardness-causing cations from the water, simultaneously augmenting the sodium salt content, thus underlining the need for periodic regeneration of the zeolite through a straightforward regeneration procedure. Examining the chemical composition of zeolite, represented as Na_2Ze, reveals a dynamic process where for every pair of sodium ions exchanged, a single calcium or magnesium ion becomes sequestered during the intricate ion exchange process. This intricate chemical interplay showcases the efficiency of zeolite in not only mitigating water hardness issues but also in showcasing its capacity for selective ion exchange, which forms the cornerstone of its effectiveness as a reliable water treatment solution. Ultimately, the multifaceted nature of zeolite's composition and its ingenious ion exchange capabilities underscore its indispensable role in the realm of water hardness treatment and overall water quality enhancement efforts. The process of water softening utilizing zeolite typically involves a cylindrical metallic vessel with multiple zeolite beds housing ion exchange reactions as the raw water flows through them. This method offers a practical solution for dealing with water hardness issues by facilitating ion exchange reactions that effectively remove calcium and magnesium impurities from the water supply. As the raw water passes through the zeolite beds, these impurities are replaced with sodium ions, thereby softening the water and improving its quality for various domestic and industrial applications. When the zeolite reaches its limit for ion exchange, known as exhaustion, it can be rejuvenated through exposure to a 10% sodium chloride (NaCl) brine solution. This regeneration process effectively removes the accumulated calcium chloride ($CaCl_2$) and magnesium chloride ($MgCl_2$) impurities from the zeolite, thereby restoring its water softening capacity and ensuring its sustainable viability for long-term use. Upon completion of the regeneration process, the zeolite is ready to be employed again, showcasing its environmentally friendly nature in combating water hardness challenges. By utilizing zeolite for water softening, we not only address the prevalent issue of hard water but also highlight the importance of promoting water sustainability. This underscores the need for innovative strategies in managing water resources to safeguard the well-being of both society and the natural environment; emphasizing the pivotal role that zeolite plays in this critical endeavour [1].

$$Na_2Ze + Ca^{2+} \rightarrow CaZe + 2Na^+$$
$$Na_2Ze + CaCl_2/CaSO_4/\ Ca(HCO_3) \rightarrow CaZe + 2NaCl/Na_2SO_4/2NaHCO_3$$
$$(Ca^{2+}/Mg^{2+})\ Ze + 2NaCl \rightarrow Na_2Ze + CaCl_2\ \text{(or)}\ MgCl_2$$

PROGRESS IN THE ZEOLITE METHOD FOR THE WATER SOFTENING

This research delves into the application of activated Na-zeolite A as a water softening agent, emphasizing its effectiveness in removing Ca^{2+} and Mg^{2+} ions from water. Furthermore, a novel experimental approach employing easily accessible raw materials like kaolinite is shown by the synthesis of zeolite 4A from high-silica raw kaolinite for the treatment of water hardness. New technologies that have the potential to cleanse wastewater and produce green fuel, especially hydrogen, are explored. Examples of these technologies include microbial electrolysis cells (MEC) and microbial fuel cells (MFC). In addition, the development and evaluation of composite membranes for water softening applications, as shown by the research on natural clinoptilolite composite membranes, present viable approaches for the treatment of industrial wastewater. By eliminating ions that cause hardness, such calcium and magnesium, water softening technology significantly enhances the quality of the water. With an emphasis on cutting-edge technologies and materials for treating hard water, this research paper offers a thorough summary of the most recent developments in water softening technology. Additionally, the research explores the sustainable alternatives to water treatment by turning waste resources such waste glass and alum sludge into zeolite LTA for water softening. Moreover, the application of biomass-based zeolite-based geopolymers as adsorbents for water softening highlights the significance of environmentally friendly solutions in water treatment procedures. The many techniques and materials available for water softening applications are well understood thanks to numerous research on ion exchange properties, zeolites in food processing industries, and the use of carbonaceous zeolites in water softening. The application of natural zeolite in ion exchange processes and the relevance of SMZ in the treatment of water and wastewater are also thoroughly examined. In this mini review, we explore the notable advancements achieved in the realm of zeolite treatment specifically designed for water softening purposes. Throughout recent years, the predominant technique employed for water softening has been the tried-and-true zeolite method. However, with the march of technological progress, the zeolite treatment methodology has been undergoing a continual evolution incorporating a diverse range of enhancements geared towards enhancing the overall efficiency of water softening processes. The ongoing innovations in this particular field of study are making a tangible impact on the landscape of water treatment solutions, effectively opening up pathways for the emergence of more sophisticated, sustainable, and reliable techniques for softening water. This dynamic progression promises a future where water softening solutions are not only more effective but also aligned with sustainable practices (Figure 1).

In 2010, a research team led by Muhammad Adil found an interesting discovery regarding the adsorption behaviour of zeolites KP and NaP towards Ca^{2+} and Zn^{2+} ions. Their study revealed that zeolite KP exhibited a higher affinity for binding Ca^{2+} and Zn^{2+} compared to zeolite NaP. This preference was attributed to the presence of potassium ions in zeolite KP, which appeared to enhance the adsorption capabilities of the material. Interestingly, the XRD patterns and IR spectra analysis indicated that the structure of zeolite P remained consistent even after modification with potassium,

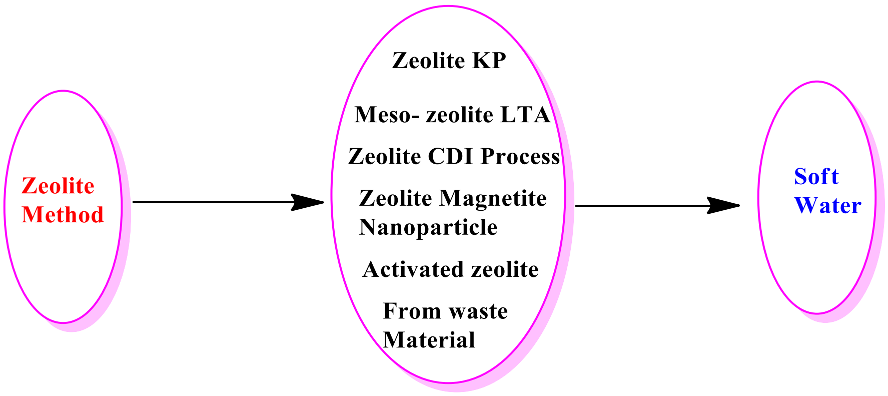

Figure 1. Development in the zeolite treatment.

implying that the surface properties played a crucial role in determining the adsorption efficiency. Furthermore, the adsorption process of Ca^{2+} and Zn^{2+} on both zeolites was observed to follow the Freundlich isotherm model, emphasizing the heterogeneous nature of the zeolite surface. This deviation from the Langmuir isotherm model suggested that the adsorption of these cations was influenced by multiple sites on the zeolite surface rather than a monolayer formation. The potential applications of zeolites NaP and KP as effective sorbents for removing calcium and zinc cations from water sources were highlighted as a promising solution to mitigate the issues related to zinc toxicity and water hardness, thereby emphasizing the practical significance of this research finding [2]. In 2011, Thaigarajan Ramachandramoorthy and colleagues delved into the realm of water purification by examining the efficacy of utilizing natural sand materials sourced from the picturesque Rameswaram Island in South India. The research conducted involved a comprehensive assessment of water quality parameters derived from various sources including springs, tanks, and wells. Through meticulous analysis, it was revealed that the sand materials obtained from these diverse locations exhibited remarkable potential as water softening agents. A notable discovery highlighted in their study was the remarkable resemblance between the Si/Al ratio of the sand material sourced from Sethumadhava tank and that of zeolites, specifically the clinoptilolite variety. Notably, the Sethumadhava sand displayed superior characteristics such as elevated surface area, pore volume, and cation exchange capacity in comparison to the Uchipuli sand. Subsequent investigations conducted through column studies facilitated the determination of essential parameters like, column performance, and qeq. These parameters were found to be intricately linked to several critical factors including particle size, the origin of the sand material, choice of regenerant, initial Ca^{2+} concentration, and bed depth. An intriguing correlation was observed wherein the enhancement of sodium chloride concentration directly contributed to an increase in the overall efficiency of water softening processes. Through their meticulous exploration of these factors, the researchers illuminated the intricate dynamics at play in the realm of water softening utilizing natural sand materials, underscoring the potential for innovative solutions in the domain of water treatment technologies [3]. In their 2014 study, Ruifeng Li et.al. delved into the intriguing cation exchange properties of meso-zeolite LTA, focusing specifically on the exchanges involving Mg^{2+} or Ca^{2+} ions within this unique framework. Comparable to traditional zeolite LTA, meso-zeolite LTA showcases a notably high cation exchange capacity, offering promising applications in various fields. When Ca^{2+} and Mg^{2+} ions engage in exchange processes with Na+ in the zeolite structure, distinct uniform exchange sites become evident, signifying the complex nature of these interactions. The positive enthalpy values associated with the exchange of Ca^{2+} or Mg^{2+} ions suggest an endothermic characteristic, shedding light on the energy dynamics at play during these molecular exchanges. Interestingly, the acceleration of Mg^{2+} ion exchange is particularly pronounced, showcasing the preferential impact of meso-zeolite LTA in this regard. Moreover, the introduction of mesopores enhances the overall exchange kinetics, simultaneously expediting both Ca^{2+} and Mg^{2+} exchanges. This intricate interplay ultimately underscores the remarkable competitive edge of meso-zeolite LTA, especially evident in solutions containing a mix of Ca^{2+} and Mg^{2+} ions [4]. In a study conducted in 2016 by Jeyong Yoon and colleagues, a zeolite-based electrochemical softening system utilizing the Capacitive Deionization (CDI) method was discussed. This system showcased exceptional capacitance properties and effective ion exchange capabilities when employing a combination of carbon and zeolite to fabricate what is referred to as Zeolite-Modified Carbon Electrode (ZMCE). By incorporating the ZMCE into the CDI process, a significant enhancement in the softening effectiveness compared to conventional softening methods was observed. The key reason behind this improvement was attributed to the accumulation of Ca^{2+} ions from the electric field during the CDI process, leading to an increase in ion-exchange efficiency. By implementing the principle of capacitive deionization, which involves electrochemical adsorption and desorption within an electric double layer for desalination, the researchers were able to achieve a highly efficient electrochemical softening method. The development of the ZMCE involved combining carbon electrodes with zeolite particles or modified forms of zeolite along with carbon black through a slurry and pasting process. Noteworthy was the superior performance of the ZMCE in terms of removing divalent ions during the CDI process when compared to standard softening processes reliant on diffusion mechanisms. This enhanced efficiency in ion removal was primarily attributed to the migration force generated by the electrical energy utilized in CDI operations, underscoring the key role of electromigration in enhancing ion removal efficiency [5]. In their 2017 publication, Loiola et.al thoroughly examined the role of kaolin as the primary hydrothermal source of SiO_2 and Al_2O_3. This detailed investigation encompassed a comprehensive analysis of the structural, spectroscopic, and magnetic properties of zeolites A and P, as well as their corresponding composites featuring magnetite nanoparticles. The study underscored the potential of kaolin in facilitating the synthesis of zeolites A and P, with a particular emphasis on the additional silica required for the production of zeolite P. Notably, the strategic integration of magnetite nanoparticles onto the surfaces of zeolites A and P in an aqueous milieu has enabled the successful fabrication of magnetic composites. Importantly, this innovative approach did not compromise either the structural integrity of the zeolites or the magnetic properties of the nanoparticles, thus confirming the feasibility of generating high-quality zeolite composites embedded with magnetite nanoparticles. The cost-effectiveness of this synthesis route further enhances its appeal, positioning it as a viable alternative for water softening applications. The exceptional removal efficiency exhibited by the synthesized zeolites and composites highlights their potential for practical use, offering a promising solution for achieving optimal water treatment outcomes [6]. In their thorough discussion published in 2019, Anwar Usman and colleagues extensively explored the diverse properties and practical applications associated with activated zeolite-A extracted from Bangka kaolin. By implementing an adsorbent dosage of merely 1 gram, their experimental results indicated an exceptional removal efficiency of up to 95.97% for Ca^{2+} ions found in hard water, complemented by an equally impressive efficacy of 94.93% for Mg^{2+} ions present in the sample solution. These notable outcomes were achieved through experiments conducted with an initial ion concentration set at 110 parts per million (ppm) and a fixed volume of 20 millilitres. Consequently, due to the exceptional adsorption capacities of activated Na-zeolite A, it emerges as a viable solution for mitigating the effects of hard water by softening it, as well as exhibiting promise in the formulation of specialized detergents designed to combat the presence of Ca^{2+} and Mg^{2+} ions effectively within water treatment processes [7]. In their comprehensive study conducted in 2021, Graeme J. Millar and colleagues deeply explored the efficient synthesis process of zeolite LTA using unconventional waste materials. The process involved an initial step of producing zeolite LTA through alkaline fusion pre-activation of waste glass and alum sludge at a high temperature of 700 °C for a duration of two hours. This step was followed by a meticulous five-hour hydrothermal treatment at a moderate temperature of 80 °C. One of the pivotal findings highlighted in their research was the substantial increase in zeolite LTA yield, reaching an impressive 67%, specifically by optimizing the SiO_2/Al_2O_3 ratio in the feed mixture from 1 to 2.3. Furthermore, they identified the ideal composition, $9.2Na_2O:Al_2O_3:2.3SiO_2:276H_2O$, which was deemed most effective for the subsequent experimental tests. The innovative approach of recycling the mother liquor, aimed at recovering dissolved species and alkali, played a significant role in enhancing the properties of zeolite LTA. This recycling method not only led to an increase in crystallanity of zeolite LTA from 80 to 86 weight% but also boosted its calcium exchange capacity. However, an important consideration raised in the study was the energy consumption associated with the evaporation of the mother liquor and the balancing act needed to assess the potential savings from a more efficient utilization of excess alkali reagent. This financial evaluation, crucial for decision-making, determined the feasibility of implementing the recycling process. Moreover, the competitive ion-exchange phenomenon observed in the study indicated a decrease in calcium uptake on zeolite LTA when treating simulated river water, yielding a value of 65.5 mg Ca2+/g. The regeneration process, requiring a minimum of 2M NaCl solution to rejuvenate calcium-loaded zeolite LTA, displayed a decline in calcium loading capacity after multiple cycles of loading and regeneration. Despite this limitation, the technology exhibited a practical and scalable approach for converting waste materials into a valuable product suitable for local water treatment facilities as an efficient water softener. In conclusion, their findings provided valuable insights into a sustainable and innovative method for waste recycling while addressing the critical need for water treatment solutions [8]. In their 2022 publication, Abdel Nasser Kawde et.al. thoroughly discussed the intricate process involved in the exchange of calcium and magnesium ions facilitated by a specialized active layer of zeolite Na-A meticulously deposited onto a flat, porous clay support. These supports for microfiltration membranes are meticulously crafted from a combination of sintered clay and 3% w/w activated carbon through a detailed uniaxial pressing technique performed at a high temperature of 1000 °C. The hydrothermal deposition method stands out as the preferred approach for laying down the zeolite Na-A (LTA) layer on the clay support, a step crucial in enhancing the membrane's performance significantly. Upon the successful application of the zeolite Na-A onto the support structure, a series of notable transformations become evident, including a reduction in pore diameter, an augmentation in pore volume, and a notable increase in the specific surface area. Scanning electron microscopy (SEM) analyses reveal the unique characteristics of the zeolite Na-A crystals, manifesting as distinct cubic formations spanning a size range from 1.3 to 2.4 μm, further showcasing the precision and quality of the membrane fabrication process. To evaluate the efficacy of the zeolite membrane in facilitating the exchange of calcium and magnesium ions with the sodium (Na) residing within the zeolite-A cavities, filtration tests using a specially calibrated flow loop for dead-end filtration were conducted on solutions containing chloride salts of the two metals. The results obtained from these tests paint a compelling picture, indicating a remarkable 72.1% retention of Ca^{2+} ions and an impressive 93.3% retention of Mg^{2+} ions by the zeolite membrane after just 30 minutes of filtration, underscoring the membrane's efficiency and reliability. Furthermore, the complete exchange of Na^{+} ions within Zeolite-A with the calcium and magnesium ions further solidifies the membrane's suitability for water softening applications. Further investigations delved into the electrochemical behaviour of the membrane, unveiling an interesting preference for Ca^{2+} ions over Mg^{2+} ions in enhancing electron transfer as determined through electrochemical impedance spectroscopy (EIS). This intriguing finding hints at a sophisticated interplay between size exclusion mechanisms and ion exchange processes in defining the membrane's behaviour, shedding light on the complex nature of the system. In light of these meticulous analyses and promising results, it becomes evident that zeolite Na-A membranes embody several desirable characteristics, rendering them as an exceptional material choice for effectively softening hard water and offering significant potential for various water treatment applications in the future [9]. Further, Ion exchange process for the removal of hardness also discussed by so many researchers [10-11].

CONCLUSION

The Zeolite Method has proven to be exceptionally effective for water treatment, as evidenced by research findings highlighting its superior performance in completely removing hardness compared to other softening methods available. This method stands out for its simplicity and high efficacy in tackling hardness issues, making it a preferred choice for many applications. Exploring the evolution of the zeolite treatment method in detail within this mini review provides valuable insights for scientists and researchers looking to enhance their understanding of the advancements in water treatment technologies. By delving into the nuances of zeolite treatment processes, professionals in the field can gain a deeper appreciation for the overall improvements that have been made, leading to more informed decision-making and optimized utilization of zeolite in water treatment applications. The in-depth analysis of the zeolite treatment method presented in this mini review serves as a valuable resource for those seeking to delve deeper into the intricacies of water treatment technologies. By elucidating the key features and benefits of the Zeolite Method, this review contributes to the body of knowledge surrounding effective water treatment strategies. Researchers and practitioners alike can leverage this information to enhance their understanding of zeolite treatment and its potential for driving advancements in the field. Overall, the comprehensive examination of the zeolite treatment method offered in this review serves to illuminate the significant progress that has been achieved in water treatment technologies. By shedding light on the effectiveness and advantages of the Zeolite Method, this mini review equips scientists and industry professionals with the insights needed to make informed decisions and propel further innovation in water treatment methodologies. In summary, the research's combined results improve our understanding of water treatment practices while also highlighting the significance of ongoing investigation and refinement of novel technologies for water softening, filtration, and contamination removal. This paper is an important resource for researchers, food industry professionals, lawmakers, and environmental engineers who are interested in using zeolites and other cutting-edge materials to treat water sustainably.

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