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A Study on the Synthesis of Natural Zeolite

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Abstract – Natural zeolites are environmentally and economically acceptable hydrated aluminosilicate materials with exceptional ion-exchange and sorption properties. Their effectiveness in different technological processes depends on their physical-chemical properties that are tightly connected to their geological deposits.

The unique tree-dimensional porous structure gives natural zeolites various application possibilities. Because of the excess of the negative charge on the surface of zeolite, which results from isomorphic replacement of silicon by aluminum in the primary structural units, natural zeolites belong to the group of cationic exchangers. Numerous studies so far have confirmed their excellent performance on the removal of metal cations from wastewaters.

However, zeolites can be chemically modified by inorganic salts or organic surfactants, which are adsorbed on the surface and lead to the generation of positively charged oxi-hydroxides or surfactant micelles, and which enables the zeolite to bind also anions, like arsenates or chromates, in stable or less stable complexes.

Keywords: Zeolite, Complex, Stable

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INTRODUCTION

Natural zeolites have advantages over other cation exchange materials such as commonly used organic resins, because they are cheap, they exhibit excellent selectivity for different cations at low temperatures, which is accompanied with a release of non-toxic exchangeable cations (K^+, Na^+, Ca^{2+} and Mg^{2+}) to the environment, they are compact in size and they allow simple and cheap maintenance in the full-scale applications.

The efficiency of water treatment by using natural and modified zeolites depends on the type and quantity of the used zeolite, the size distribution of zeolite particles, the initial concentration of contaminants (cation/anion), pH value of solution, ionic strength of solution, temperature, pressure, contact time of system zeolite/solution and the presence of other organic compounds and anions. For water treatment with natural zeolites, standard procedures are used, usually a procedure in column or batch process.

Ion exchange and adsorption properties of natural zeolites in comparison with other chemical and biological processes have the advantage of removing impurities also at relatively low concentrations and allows conservation of water chemistry, if the treatment is carried out in the column process.

Subject of further academic and industrial research should be to improve the chemical and physical stability of modified zeolites and to explore their catalytic properties, which would allow their use in catalytic degradation of organic pollutants.

More careful consideration of their superb metal removal properties and awareness of possible regeneration or further use of contaminant/metal-loaded forms can considerably increase their environmental application possibilities, with a focus the reduction of high concentrations of cations and anions in drinking water and wastewater, for surface, underground and public municipal water treatment independently or in combination with others physical - chemical methods.

Natural zeolites have been used in a wide variety of applications over the world. Among these, its utilization for carrying energy in energy conversation and heat exchanging systems is noteworthy. The main objective of the present study is to investigate potential and utilization opportunities of natural zeolites in energy-related applications.

In this regard, the reserve potential of natural zeolites in Turkey is presented, while their worldwide application areas, current, and other utilization opportunities are given. High water adsorption capability and energy storage properties of natural zeolites are studied.

SYNTHESIS OF NATURAL ZEOLITE

Synthesis of zeolites was investigated in more detail to ascertain the variables important during the zeolite modification process. Application of non-hydrothermal conditions was found to be inefficient at producing a shell comprising of zeolite N and/or W. Instead, hydrothermal reactions at 175 o C were recommended. The zeolite synthesis process was shown to result in a shell of nano-crystalline zeolites. The success in creating the latter material depended upon the scale of the synthesis reaction and reaction conditions such as agitation method.

Zeolites have been successfully used as sorbents, ion exchangers, and catalysts for many decades since their discovery in the mid 1700's. These materials are crystalline, highly porous, aluminosilicates with remarkable ion exchange and sorption capacities. The various crystalline combinations of the zeolite's building units generate a great number of distinct framework types. Reversible ion exchange and dehydration are the main mechanisms behind the applications of these materials. In addition, natural zeolites are inexpensive and readily available, as zeolite-rich rock deposits are widespread throughout the globe. The properties and characteristics of zeolitic tuffs vary with their origin, including structure type and zeolite content in the mineral.

In the case of landfill leachate, the challenge is the removal of ammonia from this wastewater to the extent required by discharge limits imposed to the landfill. This leachate originates from liquids that permeate the waste in a landfill, carrying along suspended and dissolved contaminants and becoming more concentrated as it flows through the layers of waste. At the bottom of the landfill, a collection system directs the leachate to treatment, which usually consists of a combination of techniques (or a treatment train). Even with systems using reverse osmosis, the ammoniacal nitrogen content is still an issue with this effluent, especially considering that the discharge limits for this contaminant are relatively low.

Zeolite materials are normally used in filter columns when purifying water and wastewater. One of the most important parameters influencing the filter design is the hydraulic conductivity of the filter media. The hydraulic conductivity parameter relates to the rate at which water will flow through the media and it is influenced by a range of parameters such as type of media and particle size.

Applications such as filters for stormwater run-off require a precise knowledge of the hydraulic conductivity value for the materials used in the filter. Surprisingly, current standards for measuring the hydraulic conductivity of materials relate mainly to soil science and not to natural zeolites.

Ammoniacal nitrogen removal remains a challenge for many industries, such as the example of landfill leachates. The current goal is to create effective materials which can remove and recover ammonia from solution, thus allowing for the possibility of reusing the nitrogen as a fertilizer. Therefore, media such as zeolites and resins which can exchange ammonium ions are of interest. However, we require to understand how efficient is the ion exchange treatment of for example landfill leachate, using not only natural zeolites and resins but also modified zeolites which are designed to improve performance.

Modified zeolites based on a natural zeolite core with a synthetic zeolite shell have not been tested previously for ammonium removal and recovery from solution. Natural zeolites are abundant and comparatively inexpensive. These materials exhibit some capacity for ammonium species and good selectivity. However, natural zeolites suffer from problems of very slow exchange kinetics (typically up to 72 hours to reach equilibrium) and cation capacity values.

In contrast, zeolite N has been demonstrated to possess very high capacity for ammonium ions (500 meq/100 g) and excellent selectivity in the presence of common competing cations such as calcium and magnesium. However, zeolite N is more expensive than natural zeolite and requires binding into pellets which are acceptable for practical use. Zeolite N also has an inherently high pH in solution due to the use of 1:1 Si:Al ratios in the zeolite framework.

DISCUSSION

The significance of the hydraulic conductivity parameter and its influencing factors relates to a gap in the literature regarding zeolite application. Hydraulic conductivity is a critical aspect in the design of filters and permeable barriers, and the study of this parameter has until now primarily been dedicated to soils or sand filters. This study looked at innovative stormwater runoff filters which used layers of natural zeolite and other media from Zeolite Australia, immediately before the zeolite layer. Significantly, this study intended to create new testing protocol which could be applied to determination of hydraulic conductivity of relatively coarse zeolite media.

Landfill leachate represents a significant environmental liability and as such a technical solution is of great significance. In this study, the aim was to determine if either natural zeolites or resins were applicable to landfill leachate, especially in relation to situations where a reverse osmosis system was available to remove the main contaminants apart from ammonium species. Additionally, the performance of modified zeolites of the core-shell structure for leachate treatment was examined to determine whether it had potential for use or required further development.

The issue of ammoniacal nitrogen contamination is a well-known challenge. If excessively discharged to the aquatic environment, it causes eutrophication. The degradation of nutrients is an oxygen consuming process, thus excessive nutrient loads promote enhanced oxygen consumption and proliferation of specific plant species which feed on the nutrients. Blue-green algae (or cyanobacteria) are one such species which can proliferate such that they cover the surface of the water body, thus preventing the penetration of sunlight.

A range of ion exchange media have been employed in ammonia removal, such as zeolites and resins. According to Johnson et al. in 2014, zeolites had a global market of 1.8 million tonnes per annum; the highest volume application for zeolite was use in detergents as ion exchangers to remove Ca2+ and Mg2+ from water. However, zeolites as catalysts represented the highest value application for processes such as fluid catalytic cracking (FCC). A prominent area of use is in environmental remediation, in particular, heavy metal and nutrient (nitrates and phosphates) removal due to the size of their cavities and selectivity for metals (Cd2+, Cu2+, Ni2+, Zn2+, Fe3+, Pb2+, As3+) and ammonium.

Ion exchange with zeolites is known for being environmentally friendly, cost effective (compared to other sorbents) and resilient to temperature and weather changes. The ability of zeolite processes to sustainably remove and recover ammonia in the form of a fertilizer is of particular interest.

Although ion exchange is quite effective and has many advantages, limitations have also been identified: the flow to be treated by ion exchange most of the time requires pretreatment (otherwise, efficiency may be heavily impaired and clogging problems are likely); the regeneration of the media may require high volumes of regenerant, which may incur significant cost; adequate disposal or re-purpose of the spent regenerant (brines) carrying high concentrations of nutrients is required.

Evidently, these issues may be resolved with the use of the brine (or the nutrient loaded zeolite) as a soil additive in the case of ammonia removal, however, if used for removal of heavy metals or other contaminants, other solutions need to be considered.

Lime is commonly used to reach the latter pH levels. The product of the spray tower is a contaminated gas, which then is treated with H2SO4 or with HCl; nitrogen can be recovered as ammonium sulphate. Although a popular option, air stripping has disadvantages, the most serious one is the emission of ammonia to the atmosphere, in cases where the acid absorption stage is not perfect. Because of the high volume of lime employed to raise the pH, air stripping towers often suffer from calcium carbonate scaling issues; a decrease in ammonia removal from 98 to 80 % owing to scaling of the packing material.

CONCLUSION

Overall, it is clear from this discussion that treatments for ammonia removal are varied and each shows advantages and disadvantages depending on context. Generally, nitrogen recovery, cost-effectiveness and resilience can be appointed as advantages of physical or physico-chemical processes over biological. The formation of by-products and other pollutants is of higher concern regarding AOPs and air stripping, but may be extended to ion exchange if one considers the spent regenerants management, albeit to a lesser scale.

A combination of treatments is often employed when treating landfill leachate due to its complexity; generally any single treatment will be effective for one range of contaminants but perform poorly for another. An example is the case of natural zeolite and activated carbon, the former with good efficiency for ammonia and poor for COD, and the latter with the inverse capacity and limitation.

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