



Review

Natural and surfactant modified zeolites: A review of their applications for water remediation with a focus on surfactant desorption and toxicity towards microorganisms



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ABSTRACT

The objective of this review is to highlight the need for further investigation of microbial toxicity caused by desorption of surfactant from Surfactant Modified Zeolite (SMZ). SMZ is a low cost, versatile permeable reactive media which has the potential to treat multiple classes of contaminants. With this combination of characteristics, SMZ has significant potential to enhance water and wastewater treatment processes. Surfactant desorption has been identified as a potential issue for the ongoing usability of SMZ. Few studies have investigated the toxicity of surfactants used in zeolite modification towards microorganisms and fewer have drawn linkages between surfactant desorption and surfactant toxicity. This review provides an overview of natural zeolite chemistry, characteristics and practical applications. The chemistry of commonly used surfactants is outlined, along with the kinetics that drive their adsorption to the zeolite surface. Methodologies to characterise this surfactant loading are also described. Applications of SMZ in water remediation are highlighted, giving focus to applications which deal with biological pollutants and where microorganisms play a role in the remediation process. Studies that have identified surfactant desorption from SMZ are outlined. Finally, the toxicity of a commonly used cationic surfactant towards microorganisms is discussed. This review highlights the potential for surfactant to desorb from the zeolite surface and the need for further research into the toxicity of this desorbed surfactant towards microorganisms, including pathogens and environmental microbes.

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1. Introduction

Water that is untreated, or not treated to a sufficiently high standard, can expose its consumer to various health risks. Repercussions of exposure to such water can range from minor to life threatening (WHO, 2008). The affordability of water treatment is an important consideration; water could be treated to the highest standards, but be out of reach to certain segments of society, worsening health outcomes (WHO, 2008). Thus, any solutions that may reduce the cost of water treatment could play an important role in not only improving water quality itself, but improving access to water treatment, an appealing outcome.

Zeolites are a group of microporous aluminosilicate minerals. They occur naturally in the environment but can also be synthesised in a laboratory (Colella and Mumpton, 2000). Natural zeolites are some of the most commonly occurring sedimentary rocks (Ramesh et al., 2011). As such, they are readily available and inexpensive (Bowman, 2003). Zeolites, owing to their aluminosilicate structure, are negatively charged (Bowman, 2003; Colella and Mumpton, 2000; Inglezakis and Zorpas, 2012). When treated with a cationic surfactant, it is possible to modify the surface chemistry of the zeolite so that it may be used to treat multiple classes of contaminants: anions, cations and nonpolar organic molecules (Bowman, 2003). Zeolite, which has been treated with a cationic surfactant, is referred to as Surfactant Modified Zeolite (SMZ). The potential of SMZ as a cost effective permeable reactive barrier is significant and has indeed been extensively investigated by a number of researchers globally.

There is still work to do, however, in assessing the suitability of SMZ for water and wastewater remediation applications. Various studies have identified surfactant desorption as an issue associated with SMZ (Hrenovic et al., 2008; Li, 2006; Li et al., 1998, 2003; Misaelides, 2011; Schulze-Makuch et al., 2003). Hrenovic and Ivankovic (2007) identified that SMZs with a high surfactant loading display the greatest rates of surfactant desorption. In this case, SMZ was being investigated as a growth media for a phosphorus accumulating bacteria. Desorbed surfactant was shown to have a deleterious impact on this desired bacteria, reducing phosphate removal.

This review aims to highlight desorbed surfactant toxicity as a potentially significant factor when considering the suitability of SMZ for water and wastewater treatment. To achieve this, the composition and characteristics of natural zeolites are discussed, along with a selection of applications in which they are used. The chemistry of surfactants commonly used for zeolite modification is outlined, along with the kinetics that drive surfactant adsorption to the zeolite surface. A method to characterise how surfactant is loaded to the zeolite surface is outlined. Applications of SMZ in water remediation applications are reviewed, highlighting their use for the removal of biological pollutants, such as pathogens. Studies where surfactant desorption has been identified are outlined for comparison. The final section deals with surfactant toxicity, outlining studies that have identified this to be an issue as well as identifying areas requiring further investigation.

It is concluded that, while SMZ displays great potential for water and wastewater treatment, a better understanding of surfactant toxicity is crucial when determining the suitability of SMZ for water remediation applications.

2. Natural zeolites

Zeolite as a rock was first discovered by Swedish geologist Alex Fredrik Cronstedt in 1756. Upon collecting a sample of zeolite from a copper mine, he heated the rock and observed the release of large amounts of steam, from water adsorbed within the mineral

structure (Colella and Mumpton, 2000; Inglezakis and Zorpas, 2012). From this observation the name 'zeolite' was coined, from the Greek words for boiling stone (Inglezakis and Zorpas, 2012).

Synthetic zeolites were first synthesised in laboratories in the 1930s and found significant market demand in the 1960s, when this material was utilised on a large scale by the petroleum industry for catalytic cracking purposes (Inglezakis and Zorpas, 2012). Demand for synthetic zeolites again peaked in the 1970s, when synthetic zeolites were found to be suitable replacements for phosphate compounds in laundry detergents (Inglezakis and Zorpas, 2012). These increases in demand caused zeolite research to intensify (Colella and Mumpton, 2000; Inglezakis and Zorpas, 2012). Although natural zeolite had been known of for some time, it was not until the mid-20th century that large zeolite deposits were discovered. As research into synthetic zeolites intensified, it was identified that these low-cost natural zeolites had similar properties to the higher-cost synthetic materials and, as such, natural zeolite research also intensified, along with the material's market share. There are now over 50 species of natural zeolite recorded (Kowalczyk et al., 2006; Ramesh et al., 2011). This section considers natural zeolitic composition, focusing on those with mineral compositions favourable to ion exchange. Applications of natural zeolites in water remediation applications will be briefly discussed.

2.1. Zeolitic composition and characteristics

Natural zeolites are generally described as a volcanogenic sedimentary mineral, forming in the veins, cavities and vugs of volcanic rocks (Inglezakis and Zorpas, 2012). Alternatively, they may form as homogeneously distributed, fine-grained crystals within volcanoclastic and sedimentary rocks. In any case, naturally occurring zeolites are classified as sedimentary deposits (Inglezakis and Zorpas, 2012).

The basic zeolite structure, presented two-dimensionally in Fig. 1, is composed of TO_4 tetrahedra, where T is Si, Al (Colella and Mumpton, 2000). Silica, SiO_2 , is an uncharged solid. Thus, the addition of Al^{3+} to the silica framework creates a charge imbalance which results in a net negative charge (Inglezakis and Zorpas, 2012). The framework structure of zeolite is composed of channels and cages, occupied by H_2O molecules and extra-framework cations such as K^+ , Na^+ , Ca^{2+} and Mg^{2+} which act to balance the negative charge of the zeolite (Inglezakis and Zorpas, 2012). These extra-framework cations are ion exchangeable and, as such, are required to keep the overall charge balance of the framework (Colella and Mumpton, 2000; Inglezakis and Zorpas, 2012).

Species of natural zeolite vary greatly in composition. The ratio of Si to Al within a zeolite's structure is one of the most important factors when considering the applicability of a zeolite to ion exchange applications. Natural zeolites tend to be of lower Si:Al ratios, owing to the general absence of conditions necessary to form zeolites of a high Si:Al ratio in the environment (Colella and Mumpton, 2000). Zeolite species can be classed into three groups based on their Si:Al ratio (Ramesh et al., 2011): low Si:Al ratio (1–1.5), intermediate Si:Al ratio (2–5) and high Si:Al ratio (10 and

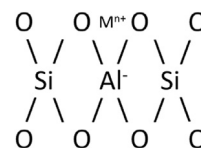


Fig. 1. The basic zeolite structure, where M represents the extra-framework cation and n is the valence of the cation.

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