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 homogenously distributed, fine-grained crystals within volcaniclastic 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
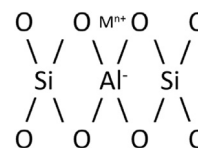

Fig. 1. The basic zeolite structure, where M represents the extra-framework cation and n is the valence of the cation.

above). Zeolites within the intermediate range tend to be the most stable species, having more heterogeneous hydrophilic surfaces within their porous crystal structure (Ramesh et al., 2011). As the ratio of Si:Al increases, so too does the hydrothermal stability and hydrophobicity of the zeolite framework (Colella and Mumpton, 2000; Inglezakis and Zorpas, 2012).

Porosity is an important factor for differentiating between zeolite species. A zeolite's porosity is determined by its crystalline structure (Colella and Mumpton, 2000). Pore sizes vary between 0.3 and 1 nm, resulting in porosities between 0.1 and 0.35 cm^3/g, respectively (Colella and Mumpton, 2000; Inglezakis and Zorpas, 2012). Owing to this microporous structure, internal surface areas tend to be very high, ranging from 300-700 m^2/g (Colella and Mumpton, 2000).

Being of a microporous structure, zeolites also exhibit molecular sieving properties under appropriate conditions. The small pore sizes of zeolite can physically exclude larger ions; meaning smaller ions are selectively exchanged (Inglezakis and Zorpas, 2012). As pore size and crystal structure vary between each zeolite species, so too does that species' potential to act as a molecular sieve. Further, zeolites only tend to work well as molecular sieves after they have been fully dehydrated (Inglezakis and Zorpas, 2012).

Cation exchange capacity (CEC) indicates the number of exchangeable cations a substance is able to hold. This is generally expressed as milliequivalents per unit mass. Zeolites of higher Si:Al ratios have the highest CECs owing to their relatively high charge deficiencies (Inglezakis and Zorpas, 2012). Occasionally, the external cation exchange capacity (ECEC) of a zeolite is reported. This distinction can be important: Owing to this material's microporous structure, a large proportion of exchange sites are located internally, out of reach to larger ions and molecules (Ming and Dixon, 1987). Thus, the ECEC refers only to the exchange sites on the external surface of the material, available to all ions and molecules (Ming and Dixon, 1987). Ming and Dixon (1987) outline a widely used method for differentiating between CEC and ECEC. Natural zeolites have CECs reported in the range of 600—4000 meq/ kg (Inglezakis and Zorpas, 2012; Ming and Dixon, 1987; Wang and Peng, 2010). Mumpton (1999) notes that the CEC values for natural zeolites are about twice the CEC for bentonite clays. For comparison, Misaelides et al. (1998) reported the following typical CECs (meq/kg) for clay minerals: mica 10, illite 50, kaolinite 100 and montmorillonite 1000.

One of the most common naturally occurring zeolite species is clinoptilolite, belonging to the family heulandite (Inglezakis and Zorpas, 2012; Kowalczyk et al., 2006). This zeolite is the most commonly used species in water and wastewater remediation applications (Apreutesei et al., 2008). It is found in extensive deposits in the United States, Bulgaria, Hungary, Japan, Iran and Australia (Mumpton, 1999). Clinoptilolite is well suited to ion exchange applications such as water filtration and gas exchange. This is because of its high pore volume, in the order of 0.34 cm^3/g, resistance to high temperatures and chemically neutral basic structure (Inglezakis and Zorpas, 2012; Mumpton, 1999). Clinoptilolite has a Si:Al ratio of between 4 and 6 and CECs in the range of 2200—2600 meq/kg (Inglezakis and Zorpas, 2012; Kowalczyk et al., 2006; Misaelides et al., 1998).

2.2. Applications for water remediation

Natural zeolite has found multiple uses in water remediation applications, particularly for the removal of cationic pollutants. This section will briefly outline the major fields to which natural zeolites may be applied for water remediation.

One of the primary uses of natural zeolites is for the removal of ammonium, NH_4^+. Ammonium is a common pollutant in

wastewater streams, be they agricultural, municipal or industrial. When released into the environment, ammonium can lead to eutrophication, dissolved oxygen depletion and fish kills (Turan, 2016). A number of studies have shown zeolite to be effective at removing ammonium (Johnson and Sieburth, 1974; Karadag et al., 2006; Turan, 2016; Wang and Peng, 2010) achieving removal rates of 2.7—30.6 mg/g (Wang and Peng, 2010). Further, it has been shown that most natural zeolites have a selectivity towards ammonium over other cations (Inglezakis and Zorpas, 2012; Wang and Peng, 2010). Natural zeolite has been shown to act as an ideal growth media for nitrifying bacteria, which go on to oxidise ammonium to nitrate (Hrenovic et al., 2003).

Natural zeolite filters are used for the removal of ammonia from drinking water. For example, a filtration plant at Buki Island, Hungary, reduces ammonia levels from 15-22 ppm to less than 2 ppm (Mumpton, 1999). Johnson and Sieburth (1974) suggest clinoptilolite to be an effective alternative to traditional nitrification systems. Clinoptilolite was found to be capable of removing ammonium in closed system aquaculture, achieving a 95% removal at up to 260 bed volumes.

Hrenovic et al. (2003) reported that the performance of an anaerobic/aerobic activated sludge wastewater treatment plant was enhanced by the addition of natural zeolite; phosphorus, chemical oxygen demand and nitrate levels were reduced. It was shown that natural zeolite particles acted as an effective support media for the phosphorus accumulating bacteria Acinetobacter calcoaceticus. These bacteria adsorbed to the zeolite surface, resulting in increased biological activity for the system. Natural zeolite has also been shown to be effective at removing arsenic from water and wastewater (Mohan and Pittman, 2007).

Natural zeolites have also been extensively researched and used for the removal of heavy metals from acid mine drainage, and as permeable reactive barriers to deal with groundwater contamination emanating from municipal and industrial waste disposal sites. For a comprehensive review on these topics and on further water and wastewater applications of natural zeolites, the reader's attention is drawn to a recent review by Misaelides (2011).

3. Surfactant modified natural zeolites

A surfactant, sometimes referred to as a surface active agent, can be broadly described as a substance which alters energy relationships at interfaces; specifically, they lower surface or interfacial tension (Glassman, 1948). Surfactants have a number of industrial applications, such as wetting agents, emulsifying agents and detergents (Glassman, 1948). Surfactants displaying a surface activity are characterised by a structural balance between one or more hydrophilic (water attracting) and one or more hydrophobic (water repelling) compounds (Glassman, 1948). Surfactants are classified as anionic, cationic, non-ionic or amphoteric. These classifications are based on the charge of the hydrophilic part of the surfactant molecule. An anionic surfactant is characterised by a structural balance between a hydrophobic residue and a negatively charged hydrophilic group. Conversely, a cationic surfactant balances the same hydrophobic residues with a positively charged hydrophilic group (Fig. 2) (Glassman, 1948). Non-ionic surfactants possess no ionised groups while amphoteric surfactants are of a mixed anionic-cationic structure (Glassman, 1948).

As outlined in Section 2.1, natural zeolites possess a net negative charge, owing to the substitution of aluminium within its silica framework structure. This means natural zeolites have an affinity for cations, such as ammonium. There are numerous pollutants, however, that possess an anionic charge, including many viruses and bacteria, metal anions such as chromate, nitrate, arsenate and phosphorus. Generally, these cannot be effectively treated with
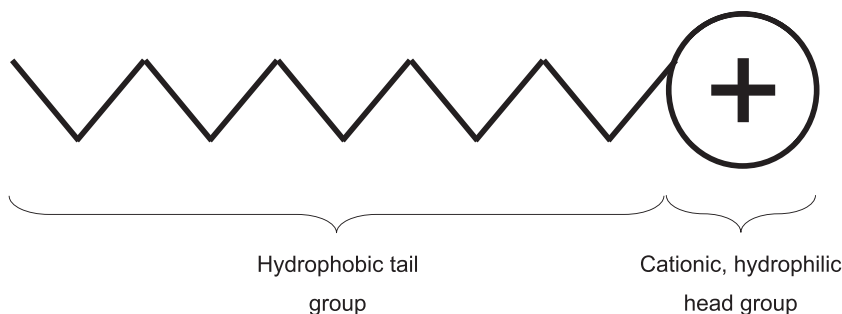
Fig. 2. Basic schematic of a cationic surfactant molecule.

natural zeolite. To overcome this issue, it is possible to modify the surface properties of zeolite, making the zeolite suitable for broader applications. A common method to achieve this is to apply a cationic surfactant to the natural zeolite surface.

Cationic surfactants selectively exchange with native inorganic cations contained within natural zeolites, forming a relatively stable organic coating on the zeolite surface (Apreutesei et al., 2008; Sullivan et al., 1998a). This modification drastically alters the surface chemistry of zeolite, facilitating adsorption of anions and cations and removal of organic nonpolar solutes through partitioning into the hydrophobic surfactant tail group (Apreutesei et al., 2008; Bowman, 2003; Inglezakis and Zorpas, 2012).

3.1. Quaternary ammonium compounds

In cationic surfactants, hydrophobic residues are balanced by positively charged hydrophilic head groups (Fig. 2), such as quaternary ammonium, sulphonium, arsonium, phosphonium or idonium (Glassman, 1948). Of these groups, quaternary ammonium compounds (QAC) are the most common type of cationic surfactant and have found the widest application for zeolite surface modification (Ivankovic and Hrenovic, 2010). It is for this reason that this review focuses solely on QAC surfactants.

QACs are derivatives of ammonium compounds of the form $(NH_4^+)Y^-$, where four hydrogen molecules bonded to a nitrogen molecule have been replaced with hydrocarbyl groups (Fig. 3) (IUPAC, 2014). This group of compounds is characterised by its property to greatly reduce the surface tension of water (Rahn and Van Eseltine, 1947). QACs may be put into the following classes of chemicals: wetting agents, detergents and emulsifiers (Rahn and Van Eseltine, 1947).

One of the most commonly used QACs for zeolite modification is hexadecyltrimethylammonium (HDTMA or $C_{19}H_{42}N^+$) (Guan et al., 2010; Ivankovic and Hrenovic, 2010). A counterion balances the charge of the molecule. Common counterions are bromide and chloride.

When a surfactant is dissolved into water, the surfactant molecules exist as monomers when at a low concentration (Ivankovic and Hrenovic, 2010). As the surfactant concentration increases,
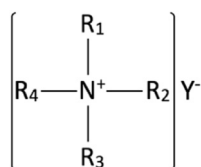
the surfactant molecules aggregate together to form micelles, reducing the energy of the system (Ivankovic and Hrenovic, 2010). The ability of surfactants to form micelles is fundamental to their detergency and solubilisation properties (Ivankovic and Hrenovic, 2010). The threshold concentration at which micelle formation commences is referred to as the critical micelle concentration (CMC) (Ivankovic and Hrenovic, 2010).

3.2. Surfactant adhesion and adsorption kinetics

Rožić et al. (2009) noted the amount of HDTMA adsorbed was proportional to the amount of clinoptilolite within the zeolite sample. Li (1999) reported that adsorption of HDTMA to the zeolite surface was a function of mixing time and initial surfactant concentration. Depending on these variables, and the CEC of the particular zeolite, HDTMA may form a monolayer or bilayer on the zeolite surface (Guan et al., 2010; Li, 1999). As outlined in Fig. 4, a monolayer is the first layer to form on the zeolite surface. Monolayer formation takes place rapidly, with HDTMA molecules and/or micelles attaching directly via cation exchange: Positively charged surfactant head groups replace extra-framework cations within the zeolite (Li, 1999). HDTMA molecules rearrange such that initially adsorbed counterions desorb. Micelles of HDTMA form on the zeolite surface when the concentration of HDTMA in solution is greater than the monolayer coverage. As HDTMA concentration increases and there is no longer space on the zeolite surface to accept further micelles, surfactant micelles rearrange so that these spaces may be filled, resulting in complete monolayer coverage. When the HDTMA concentration of the solution in which zeolite is placed is maintained above the CMC of the surfactant, a bilayer of surfactant forms (Guan et al., 2010; Li and Bowman, 1998; Rožić et al., 2009). This process is driven by hydrophobic affinity between surfactant tail groups (Guan et al., 2010; Li and Bowman, 1998; Rožić et al., 2009; Sullivan et al., 1998a). This process is outlined in detail by Li (1999).

Guan et al. (2010) utilised thermogravimetric analysis (TGA) as a means to quantify and compare the surfactant loading of four geographically diverse zeolite samples. Reeve (2016) expanded on this work to examine a clinoptilolite rich zeolite from New Zealand (NZ). Results from TGA are initially outputted as the % of the initial weight of the zeolite sample that is lost over time, via chemical or physical processes such as combustion or vaporisation, as temperature is increased at a constant rate. By taking the derivative of this mass loss curve, it is possible to identify 'peaks' in weight loss, where the sample is losing weight most rapidly.

Fig. 5 presents three such derivative weight loss curves, taken from Reeve (2016), for three different samples, a SMZ made in the USA (US SMZ), which was also used in Guan et al. (2010), a NZ SMZ and the same species of unmodified NZ zeolite. It can be seen that
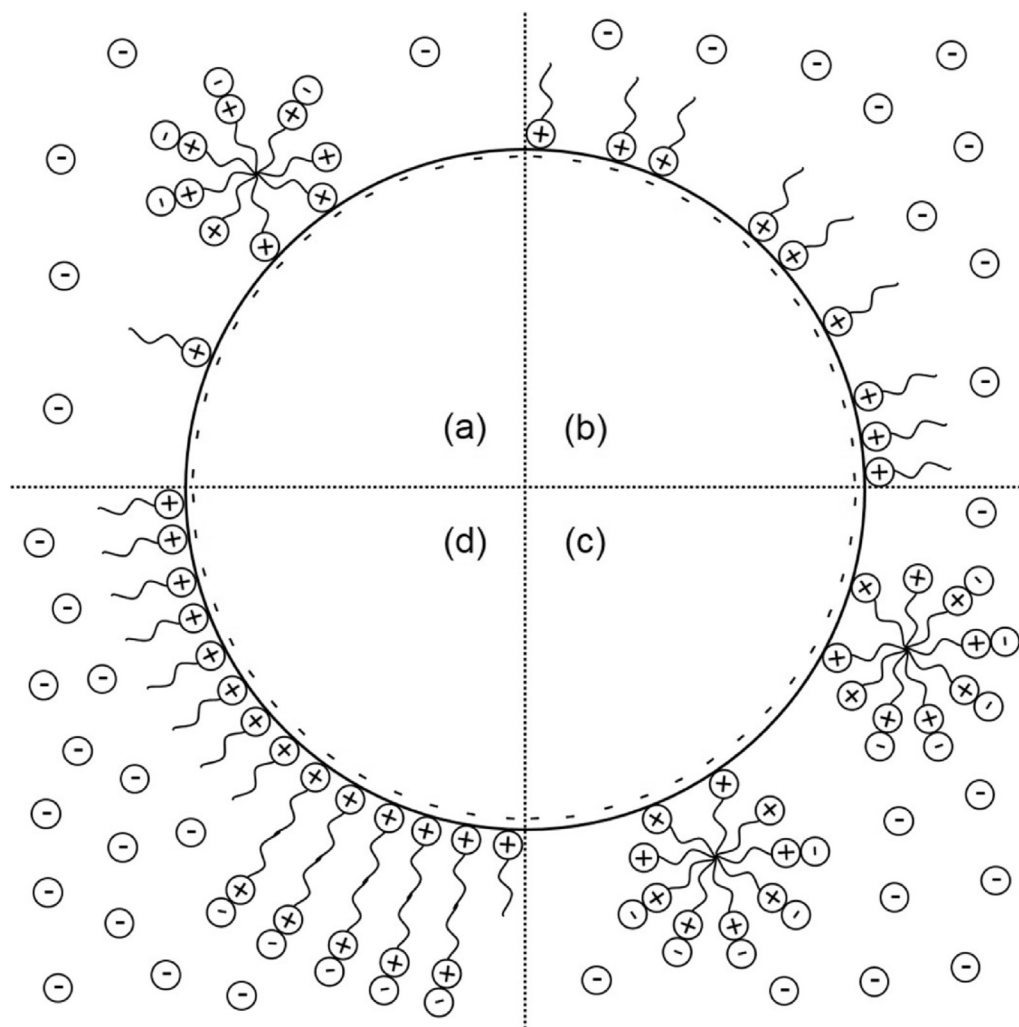

Fig. 3. The general structure of a quaternary ammonium compound, where R_1, R_2, R_3 and R_4 are hydrocarbyl groups linked to the nitrogen atom and Y^- is an anion.

Fig. 4. This figure, adapted from Li (1999), outlines the various stages of surfactant loading on the zeolite surface. Initially (a), micelles of HDTMA adsorb to the zeolite surface when HDTMA concentration in solution is below the concentration to achieve complete monolayer coverage. The rearrangement (b) of adsorbed HDTMA molecules results in desorption of initially adsorbed counterions. Micelles form (c) when the concentration of HDTMA in solution is greater than the monolayer coverage. As HDTMA concentration increases (d) and there is no longer space on the zeolite surface to accept further micelles, surfactant molecules rearrange so that these spaces may be filled, resulting in complete monolayer coverage. At this point (d), a bilayer of surfactant may begin to form through hydrophobic interactions of the surfactant tail groups.

all samples shared one mass loss peak in common which occurred at slightly above 100 °C. This peak can be attributed to the loss of unbound and physically adsorbed water within the samples (Guan et al., 2010). The US and NZ SMZ shared two further peaks (Fig. 5), the first at around 240 °C and the second at around 400 °C. These peaks correlate well with the findings of Guan et al. (2010) where four geographically diverse zeolite samples were used to manu-facture SMZ. TGA was used to assess surfactant loading. It was suggested that the first mass loss peak, which occurred between 200 and 300 °C, was attributed to the weakly bound bilayer of surfactant. The second mass loss peak, which occurred at around 395 °C, was attributed to the monolayer of surfactant. All SMZs tested by Guan et al. (2010) displayed a monolayer of surfactant, but not all displayed a bilayer. Those samples which displayed a sur-factant bilayer were found to be more efficient at nitrogen removal: Guan et al. (2010) suggests that the surfactant head groups, exposed in the surfactant bilayer (Fig. 4), facilitated the observed enhanced extraction of nitrate from solution.

By calculating the change in weight loss % from the outputted TGA data, it is possible to estimate the surfactant loading of the sample for the monolayer and bilayer of surfactant. These estimates, from Guan et al. (2010) and Reeve (2016) are included in Table 1.

3.3. Applications of SMZ for water remediation

SMZ has been extensively researched for the removal of various anionic, cationic and non-polar organic pollutants from water and various reviews have been compiled on this subject (Apreutesei et al., 2008; Jiménez-Castañeda and Medina, 2017; Misaelides, 2011; Mohan and Pittman, 2007; Turan, 2016; Wang and Peng, 2010). While these reviews, collectively, provide an extensive overview of the ways in which both natural and surfactant modified zeolites can be used to remediate chemical pollutants, no review, to the authors' knowledge, provides a detailed overview of the ways in which SMZ has been used to remediate waters contaminated with biological pollutants such as bacteria and viruses. This section aims to concisely outline a range of such studies to provide a wider appreciation of the types of water remediation applications in which SMZ may be applied. Table 2 provides an overview of some of the key details outlined in this section.

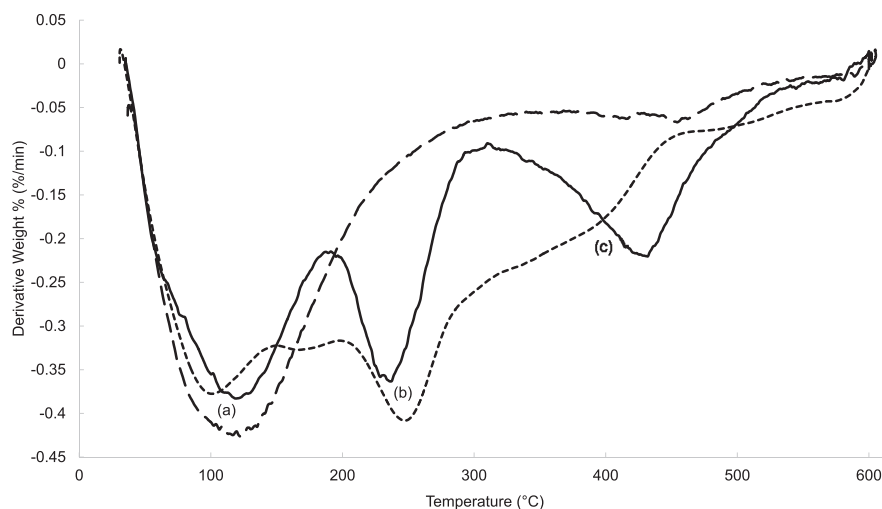Extensive research was undertaken by researchers at the New

Fig. 5. Three derivative curves plotted on one set of axes for comparison: US SMZ (Short dashed line), NZ SMZ (Solid line) and NZ natural zeolite (Long dashed line). It can be observed that all samples shared one mass loss peak at (a) slightly above 100 °C, attributed to the loss of unbound and physically adsorbed water within the samples. The US and NZ SMZ shared two further peaks, the first at (b) around 240 °C attributed to the loss of the weakly bound bilayer of surfactant and the second (c) at around 400 °C attributed to the loss of the monolayer of surfactant. Figure adapted from Reeve (2016).

Table 1
Comparison of zeolite and surfactant (HDTMA-Br) chemistry for selected zeolite species.

SMZ origin	CEC (meq/kg)	Clinoptilolite abundance	ECEC (meq/kg)	SI:Al ratio	Initial Surfactant Concentration (mM)	Total Surfactant Loading (mmol/kg)	Surfactant Loading First Layer (mmol/kg)	Surfactant Loading Second Layer (mmol/kg)	Surfactant Surface Configuration	Source
USA	900	74%	100	5.35	67	219	110	110	Bilayer	Guan et al. (2010)
Croatia	1600	60%	160	4.65	67	133	68	65	Bilayer	Guan et al. (2010)
Australia	1200	Primarily clinoptilolite	Not provided	5.97	67	75	75	n/a	Monolayer	Guan et al. (2010)
China	Not provided	Not provided	Not provided	5.56	67	137	137	0	Monolayer	Guan et al. (2010)
New Zealand	1000–1200	Not provided	Not provided	5.46	90	174.68	99.8	74.88	Bilayer	Reeve (2016)
Turkey	1347	70%	Not provided	Not provided	0.477, 1.535, 2.586, 3.665 and 5.187	Up to 204.0	Not provided	Not provided	From partial monolayer to bilayer	Hrenovic et al. (2008)

Mexico Institute for Mining Resources and Technology (NMT) to further the development of SMZ as a permeable reactive barrier for water remediation. Pathogen removal was a focus area of this research. These studies used a particular clinoptilolite rich zeolitic tuff from the St Cloud mineral deposit in New Mexico, USA. It was milled and screened to a 0.4–1.4 mm grain size. It was modified with both HDTMA-Br and HDTMA-Cl. The material used in these studies was patented as a tool for the removal of biological pathogens (Schulze-Makuch et al., 2007).

Schulze-Makuch et al. (2002) and Schulze-Makuch et al. (2003) evaluated the ability of various reactive media, including SMZ modified with HDTMA-Cl, to remove bacteria and viruses from groundwater pumped from a well lined with filter packs of reactive media. Up gradient of this well was a constructed wetland through which wastewater was spiked with *E. coli* and the F-RNA bacteriophage, MS2. Wastewater was drawn through the filter packs and out of the well for analysis. It was found that the SMZ initially removed 100% of *E. coli* and more than 99% of MS2. After five months, however, while 100% removal of *E. coli* continued, there was no significant removal of MS2.

Other filter media have been evaluated using quaternary ammonium chloride to modify zeolite (Abbaszadegan et al., 2006; Fox et al., 2010). These were shown to remove *E. coli* and bacteriophages at a greater rate than a non-modified control. Batch

experiments were initially conducted prior to column studies. A 1–2 log$_{10}$ removal of bacterial pathogens and bacteriophages was identified in comparison to a non-coated control, which reported an average 0.27 ± 0.6 log$_{10}$ removal during column experiments. Fouling of the filter media was identified as a potential issue, though it was somewhat remedied by backwashing the filter packs.

Li et al. (2014) determined the removal of wild and laboratory spiked *E. coli* from stormwater sourced from metropolitan Melbourne, Australia. It was demonstrated, through gravity fed column studies, that a zeolite modified with copper Cu^{2+}, rather than a QAC, was effective at removing *E. coli* over a 24 month test period. With a 40-minute contact time, this material consistently achieved a 2-log$_{10}$ reduction in *E. coli* concentration from the natural stormwater. The mechanism of removal was considered most likely the antimicrobial effect of copper, either adsorbed or free.

Hrenovic et al. (2008) investigated the interaction between phosphate accumulating bacteria and SMZ to determine whether SMZ, modified with HDTMA-Br, could be used to enhance phosphate removal in an activated sludge wastewater treatment plant. Here, SMZs of differing grain size and surfactant coating, ranging from patchy monolayer to complete bilayer, were used. SMZ was mixed in a solution of phosphate-accumulating bacteria and synthetic wastewater. While phosphate removal was found to be enhanced, it was also identified that surfactant coverages at or

Table 2
Comparison of SMZ for the removal of various pollutants from water and wastewater.

Pollutant	Setting	Water source	Zeolite	Surface modification	Surfactant configuration	Grain size (mm)	Removal efficiency	Source
FRNA Bacteriophage MS2	Filter packs lining in water well	Constructed wetland	USA, St Cloud mine	HDTMA-Br	Bilayer	0.4–1.4	99% when fresh, negligible after five months	Schulze-Makuch et al. (2003); Schulze-Makuch et al. (2002)
E. coli	Filter packs lining in water well	Constructed wetland	USA, St Cloud mine	HDTMA-Br	Bilayer	0.4–1.4	100% over five month period	Schulze-Makuch et al. (2003); Schulze-Makuch et al. (2002)
Bacterial pathogens	Packed column	Simulated wastewater	Commercially sourced from USA	Quaternary Ammonium Chloride	n/a	Not provided	1-2 log$_{10}$	Abbaszadegan et al. (2006); Fox et al. (2010)
E. coli (both laboratory and 'wild' strains)	Packed column	Urban stormwater	Australia	Copper, Cu2+	n/a	0.3–0.6	2 log$_{10}$ after 40 min	Li et al. (2014)
Phosphorus (interaction with P-accumulating bacteria)	Batch experiments	Wastewater from activated sludge WWTP	Bigadic, Turkey	HDTMA-Br	From partial monolayer to bilayer	<0.122 and 0.25–0.5	SMZ effective for P removal with monolayer surfactant coverage. Higher surfactant coverages resulted in reduced performance owing to the biocidal effect of surfactant on P accumulating bacteria.	Hrenovic et al. (2008)

above patchy bilayer were deleterious towards the P-accumulating bacteria, owing to the bactericidal effect of desorbed surfactant. Thus, the study concluded that care had to be taken with regard to the degree of surfactant loading used, as higher surfactant loadings resulted in higher rates of surfactant desorption.

Surfactant desorption from SMZ has been identified as a potential issue in research relating to chromate removal. While SMZ was proven successful for chromate removal when SMZ was fresh, the material's performance reduced over time due to surfactant desorption (Li, 2004, 2006; Li and Bowman, 1998, 2001; Li and Hong, 2009; Sullivan et al., 1998b). A detailed discussion of surfactant desorption is provided in Section 3.4.

For a comprehensive review of zeolites (both unmodified and modified) as adsorbents for the removal of various chemical pollutants from water and wastewater, the reader's attention is drawn to Wang and Peng (2010). Here, the removal of ammonium, heavy metals, inorganic anions, dyes, humic substances and other organics is reviewed. Apreutesei et al. (2008) provides another comprehensive review on this subject, giving further detail on anionic contaminants, BTEX pollutants, other organic pollutants and cationic contaminants. More information on ammonium removal can be found in Turan (2016). Mohan and Pittman (2007) reviewed various adsorbents, including zeolite, for arsenic removal. Jiménez-Castañeda and Medina (2017) reviewed SMZ and clays for the removal of heavy metals from water.

3.4. Surfactant desorption

The long-term stability of surfactants bound to the zeolite surface has been identified as a potential issue for the ongoing use of SMZ in water remediation contexts (Hrenovic et al., 2008; Li, 2006; Li and Bowman, 2001; Li et al., 1998, 2003; Misaelides, 2011; Schulze-Makuch et al., 2003). This section outlines laboratory experiments which investigated the chemical stability of HDTMA bound to the zeolite surface and several field and laboratory studies which identified this as a potential issue. A comparison of the zeolite and surfactant chemistry for zeolite species discussed in this section is provided in Table 1.

Li et al. (1998) considered the long-term chemical and biological stability of SMZ during laboratory batch and column experiments. This study found more than 90% of HDTMA remained bound to the zeolite surface after washing with 100 pore volumes of high ionic strength solution. However, this reduced to 80% when solutions of low ionic strength were used. This report concluded SMZ was a suitable adsorbent for long-term in situ applications and as a substrate for enhanced bioremediation.

Schulze-Makuch et al. (2003), discussed in Section 3.3, identified the efficiency with which SMZ removed MS2 significantly decreased over the five-month test period, while removal of E. coli remained constant. The gradual washing off of HDTMA-Br was one of the hypothesised explanations for this observation.

A subsequent report by Li et al. (2003) further investigated HDTMA desorption from charged zeolite surfaces. This study identified surfactant desorption was a function of surfactant loading, type of mineral substrate and flow rate. It was found the HDTMA bilayer was less stable than the monolayer: Surfactant desorbed at a higher rate from the bilayer than it did from the monolayer. This study concluded cationic surfactants were subject to slow desorption from charged mineral surfaces such as that of zeolite. It was suggested that, particularly for SMZ used in low velocity applications such as in permeable reactive barriers, this desorption might not be an issue.

Hrenovic et al. (2008), discussed Section 3.3, identified that SMZs with a bilayer or patchy bilayer of surfactant coverage exhibited the greatest desorption of HDTMA and resultant bactericidal effects on the P-accumulating bacterium Acinetobacter junii. Desorption of surfactant was reduced at lower coverage levels of patchy monolayer and monolayer. Resultantly, it was recommended that lower surfactant coverages be used to minimise surfactant desorption and related bactericidal effects.

The retardation of chromate transport through SMZ packed columns has been studied (Li, 2006; Li and Hong, 2009). In Li and Hong (2009), a range of SMZ grain sizes were used, including <0.4, 1.4–2.4 and 3.6–4.8 mm. Different surfactant loadings were also used: 80, 130 and 240 mmol/kg. It was found smaller SMZ grain sizes resulted in higher retardation of chromate transport, owing to their ability to adsorb a larger amount of HDTMA-Br. Through monitoring the Br counterion concentration, it was observed that

slow but persistent desorption of the surfactant bilayer occurred throughout the experiment. This affected the SMZ's ability to remove chromate from solution and indeed led to gradual desorption of adsorbed chromate when the column was flushed with water.

Li and Bowman (2001) studied potential processes to regenerate HDTMA-Br and -Cl modified zeolite which had been saturated with chromate and perchloroethylene. For the regeneration of chromate saturated SMZ, two methods were investigated. Firstly, they flushed the saturated material with a carbonate extraction solution composed of sodium carbonate and sodium hydroxide. Secondly, chromate was reduced to Cr(III) *in situ* using sodium dithionite. It was found that both methods were able to partially regenerate the chromate-saturated SMZ. The carbonate extraction method resulted in a lowered sorption capacity of the regenerated material. The chromate reduction method resulted in a lowered chromate sorption intensity, potentially due to the increased competition with sulphate. Air sparging of perchloroethylene saturated SMZ was found to be effective to fully restore the sorption capacity of SMZ. Air sparging was also shown to be effective for zeolites saturated with other volatile organic compounds (Altare et al., 2007; Ranck et al., 2005).

3.5. HDTMA biological toxicity

In aquatic environments, cationic surfactants are recognised as posing the greatest hazard; even low environmental concentrations could adversely impact an aquatic ecosystem (Ivankovic and Hrenovic, 2010). The primary mode of action of QACs is acute toxicity at the cell wall, with the predominant target being the cytoplasmic membrane (Block, 2001; McDonnell and Russell, 1999). This targeting of the cell wall relates to the amphiphilic nature of the surfactant molecule: The interaction between cell wall and surfactant relates directly to the partition coefficient between aqueous and membrane phases (Ahlström et al., 1997; Vieira et al., 2008). By extension, the partition coefficient is related to the CMC of the surfactant (Ahlström et al., 1997; Vieira et al., 2008).

The chemical stability of HDTMA on the zeolite surface has been identified as a potential issue for its use in water remediation contexts (Hrenovic et al., 2008; Li, 2006; Li and Bowman, 2001; Li et al., 1998, 2003; Misaelides, 2011; Schulze-Makuch et al., 2003).

Ivankovic and Hrenovic (2010) identified that the ecotoxicity profile of quaternary ammonium compounds, such as HDTMA, is incomplete. A better understanding of the toxicity of HDTMA towards bacteria and viruses is critical when considering the suitability of SMZ for water remediation. Literature relating to the biological toxicity of HDTMA is outlined in this section.

Nye et al. (1994) considered the feasibility of treating soils with HDTMA-Br to immobilise the spread of organic pollutants. Here, soil was mixed with differing concentrations of HDTMA-Br (determined as % of soil CEC). Heterotrophic bacteria were subsequently enumerated. It was found the effect of treating soil with HDTMA-Br, under the experimental conditions used, occurred in two stages. Initially HDTMA-Br was found to have an adverse impact on the aerobic heterotrophic organic pollutant degrading soil population. However, toxicity was greatly reduced when the surfactant was bound to the cation exchange sites present in soil, suggesting the soil bacteria population initially affected by the surfactant's presence may be able to re-establish.

Li et al. (1998) reported similar findings to those of Nye et al. (1994). This study investigated the long-term chemical and biological stability of SMZ. It was shown HDTMA, when bound to the zeolite surface, was resistant to microbial degradation over a 12—17 week incubation period under both anaerobic and aerobic conditions. It was shown HDTMA, when bound to the zeolite surface, was

not toxic to microorganisms: HDTMA bound to the zeolite surface did not inhibit microbial growth.

Hrenovic and Ivankovic (2007) studied the toxicity of HDTMA-Br and anionic surfactant sodium dodecyl sulphate towards a pure strain of the P-accumulating bacteria *Acinetobacter junii*. Here, *A. junii* was exposed to various concentrations of surfactant and resulting inactivation was quantified in terms of percentage inhibition of bacteria colony forming units in comparison to a control. Hrenovic et al. (2008) evaluated SMZ for the removal of P-accumulating bacteria to enhance the treatment process of an activated sludge wastewater treatment plant. It was identified that the removal of P-accumulating bacteria by these SMZs was partially attributable to the bactericidal effect of desorbed HDTMA, as discussed in Section 3.4. Thus, the study concluded SMZs prepared with a monolayer of surfactant coverage, which were less prone to desorb HDTMA, may be suitable for use in wastewater treatment.

Ivankovic and Hrenovic (2010) noted there was a lack of literature pertaining to the toxicity of HDTMA-Br in the environment. While Li et al. (1998) identified HDTMA was non-toxic to microorganisms when bound to the zeolite surface, no study, to the authors' knowledge, has quantified the toxicity of desorbed surfactant towards pathogenic bacteria and viruses or towards environmental microorganisms. As HDTMA-Br is one of the primary surfactants used in zeolite modification, further research could focus on the toxicity of this surfactant towards microorganisms, including pathogenic bacteria and viruses, as well as environmental microbes such as soil microorganisms.

4. Conclusions

SMZ displays great promise in multiple areas of water remediation and is worthy of further investigation. The 'washing off' or desorption of surfactant from SMZ has been identified as a potential issue for the use of SMZ in water remediation contexts. There are limited data regarding the toxicity of desorbed surfactant and the effects of such toxicity. Further research should focus on the toxicity of cationic surfactant HDTMA-Br, one of the primary surfactants used in zeolite modification, towards pathogenic bacteria and viruses as well as environmental microorganisms more generally. A better understanding of surfactant toxicity is crucial when determining the suitability of SMZ in water remediation applications, particularly for the removal of viruses and bacteria, and for use in conjunction with natural treatment systems.

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