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Zeolites for nitrosamine and pharmaceutical removal from demineralised and surface water: Mechanisms and efficacy

D.J. de Ridder [a,*], J.Q.J.C. Verberk [a], S.G.J. Heijman [a], G.L. Amy [a,b], J.C. van Dijk [a]

[a] Delft University of Technology, P.O. Box 5048, 2600 GA Delft, The Netherlands
[b] King Abdullah University of Science and Technology, Thuwal, Saudi Arabia

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ABSTRACT

Zeolites with a high Si/Al ratio can be used as selective adsorbents in water treatment, targeting organic micropollutants which are removed poorly with activated carbon. Due to size exclusion, many Natural Organic Matter (NOM) components cannot access the pores, thus limiting adsorption competition between organic micropollutant and NOM. Furthermore, zeolite channel diameters are close to molecule diameters, which results in strong van der Waals interaction.

MOR200 and ZSM5, the two most hydrophobic zeolites, showed the highest removal of neutral nitrosamines in demineralised water, with higher efficacy than activated carbon. DAY and MOR30, which were relatively hydrophilic zeolites, did not show appreciable removal of any of the nitrosamines. When nitrosamines were adsorbed from surface water, there was no influence of competition with, or pore blockage by, NOM components on nitrosamine removal for ZSM5 zeolite, in contrast to activated carbon.

Repulsion of negatively charged pharmaceuticals was significant for ZSM5, which had a Si/Al ratio of 80. MOR200 had a Si/Al ratio of 200, indicating a lower Al content than ZSM5 and, as such, a lower negative surface charge. Charge effects were not observed for MOR200.

A relationship was found between the Stokes diameter of the pharmaceuticals and nitrosamines, and their removal by ZSM5 and MOR200, indicating that a "close fit" adsorption mechanism is more likely than hydrophobic interaction in these zeolites.

Due to their selective nature, adsorption on zeolites should only be considered as an additional treatment step to existing processes, dedicated for the removal of specific organic micropollutants. Less specific treatment techniques, such as activated carbon filtration, are still required to ensure a broad barrier for organic micropollutants in water treatment.

1. Introduction

Zeolites are a group of minerals which can be used in water treatment as a selective ion exchange resin for NH_4^+ removal or as a selective adsorbent [1]. This selectivity can be attributed to the small pore size and small variation in pore size distribution. Zeolites consist of a framework of SiO_4 and AlO_4 in a tetrahedral structure, which are linked together by oxygen atoms. These tetrahedral structures can be ordered in various distinct ways, such as the MFI, Mordenite (MOR) or Faujasite (FAU) frameworks (Fig. 1).

The most well known zeolites with the MFI framework are ZSM5 zeolite and silicalite. This framework consists of straight channels with dimensions 5.3 * 5.6 Å (0.53 * 0.56 nm). These channels are interconnected with slightly smaller channels, with dimensions 5.1 * 5.5 Å. The framework of Mordenite zeolite consists of straight, parallel channels of 6.5 * 7.0 Å and 2.6 * 5.7 Å. There are no interconnecting channels in the MOR framework. Y Zeolite is of the family of zeolites with the Faujasite framework type. In this framework, 3-dimensional "cages" are connected with each other, having an internal diameter of about 13 Å and four openings with a diameter of 7.4 Å.

Zeolites can be interesting to use for adsorption of organic micropollutants, as they have some distinct advantages over activated carbon:

- Most of the Natural Organic Matter (NOM) components present in water cannot enter pores <10 Å [2,3]. As such, adsorptive competition of NOM with organic micropollutants is minimal for zeolites [4–6]. Adsorption kinetics can however be slower in the presence of NOM [5].
- Zeolites are stable over a wide range of temperatures and acidic conditions. As such, in contrast to carbon, the loss of material during regeneration is not to be expected [7].

* Corresponding author. Tel.: +31 (0) 15 2786588.
E-mail address: d.j.deridder@tudelft.nl (D.J. de Ridder).

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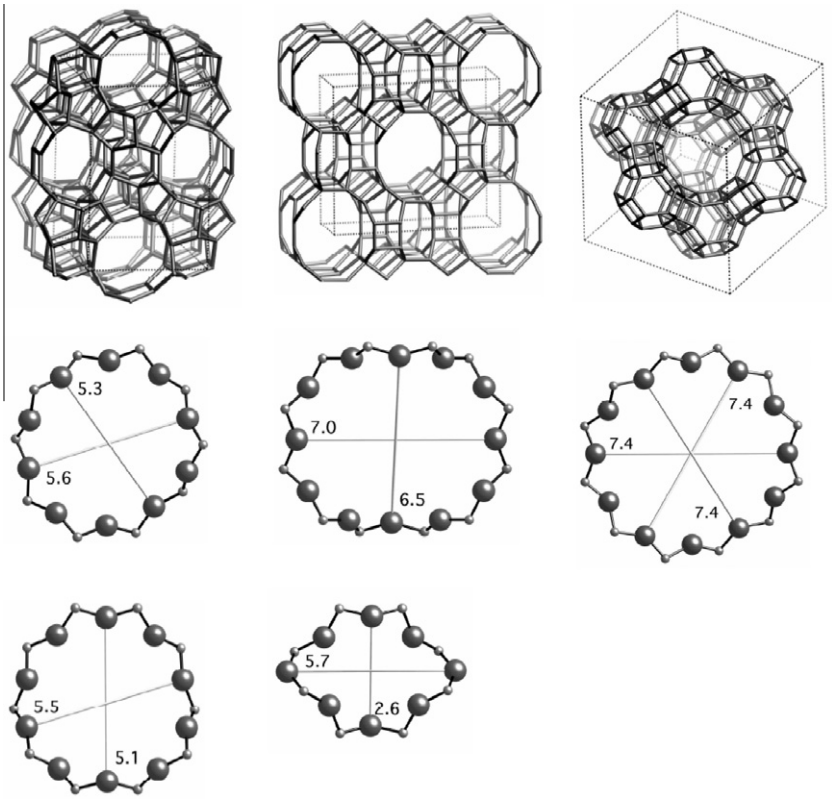

Fig. 1. Zeolite frameworks MFI (left), MOR (middle) and FAU (single cage) (right) (www.iza-structure.org/databases). Source: Baerlocher et al. (2001).

It should be stressed that activated carbon is effective for adsorption of a broad range of solutes (barrier-function), while zeolites are selective. Due to their selectivity, zeolites should not be regarded as a replacement for activated carbon, but rather as additional, dedicated adsorbent for a limited amount of target solutes. Target solutes can be solutes which require high removal due to high influent concentrations and/or strict effluent regulations, or which show poor removal with activated carbon.

Various authors have related zeolite hydrophobicity to aluminum content where a higher aluminum content indicates higher affinity for water [8–10]. Specific mechanisms for zeolite–water interaction are proposed by Bolis and Busco (2006);

- electron pair donor–acceptor interaction between aluminum and pollutant. This occurs at Lewis acid sites and has the highest bonding energy (109–160 kJ/mol),
- H bond donor–acceptor interaction. This can occur at Brønsted acid sites ($Si–OH^{+}–Al^{-}$) and silanol sites (Si–OH), with a bonding energy of 65 kJ/mol and 49 kJ/mol, respectively.

Silanol sites are created by defects in the zeolite framework and can explain that even all-silica zeolites can adsorb water.

Generally, the removal of organic micropollutants from aqueous solution is enhanced when zeolites with high Si/Al ratio (i.e. hydrophobic zeolites) are used [7,10–13]. However, it was found that above a Si/Al ratio of 90, the removal of MTBE on ZSM5 zeolite did not improve [4].

The channel dimensions of the zeolites are another important aspect affecting solute removal. Besides size exclusion effects, it was also observed that solutes, which *do* fit in the channels of ZSM5, MOR or Y zeolite, were removed more effectively when they *fit tightly*, because of larger van der Waals interactions [7,14]. An alternative or additional explanation is that in the small channels of ZSM5 zeolite (about 5.5 Å) water is unable to form a structure which is typical for its liquid form and is actually present as vapor, making it easier for solutes to transport through the channels of ZSM5. In the larger cages of Y zeolite, water is still present in its liquid form [15].

In the literature, only limited solutes were used to investigate the importance of zeolite hydrophobicity or zeolite channel diameter. As such it is difficult to separate and generalize removal mechanism in order to assess the adsorption efficacy for other solutes. A broader set of solutes was used by [16], and differences in solute adsorption were attributed mainly to the close-fit mechanism.

Nitrosamines, among which NDMA is the most well known, are potent carcinogens [17]. They can enter the environment via industrial waste disposal, or can be formed during chlorination. A wide range of pharmaceuticals have been detected in surface waters at trace levels, and mainly originate from discharges of treated municipal wastewater [18,19].

This research aims to investigate the influence of solute size and hydrophobicity on adsorption on zeolites. For this purpose, a broad set of nitrosamines and pharmaceuticals is selected that vary in these aspects. Furthermore, the influence of NOM on nitrosamine adsorption is investigated.

2. Materials and methods

A set of seven neutral nitrosamines was selected with differences in hydrophobicity and molecular size (Table 1). An additional set of 15 neutral, positively or negatively charged pharmaceuticals, varying in hydrophobicity and size, is shown in Table 2.

Solute molecular weight (M_W) and log K_{ow} values were obtained from Chem ID plus. Hydrophobicity was expressed as log D to include the influence of solute charge, according to [20]: