# Characteristics and Mechanisms of Heavy Metal and MTBE Adsorption on Zeolites and Applications in Permeable Reactive Barriers


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**Abstract**

Groundwater contamination is a grave matter of concern due to its risks to the environment and human health caused by various inorganic and organic pollutants. A wide range of treatment technologies have been developed for groundwater remediation. Permeable reactive barriers (PRBs) filled with reactive media are one of the most promising in-situ technologies for groundwater remediation due to their low costs and suitability for the immobilization of multiple contaminants via adsorption, precipitation, degradation, etc. The reactive media are key components of PRBs and their selection needs to consider the immobilization ability as well as permeability. Zeolites have high adsorption capacity, diverse pore structure and high chemical stability, and therefore have been used as reactive materials. In addition, the application of zeolites as reactive media can reduce the fouling and clogging of PRBs compared to reductants like zero-valence iron (ZVI) because there is almost no production of secondary precipitates and/or gases. It is therefore important to investigate the potential of zeolites in PRBs for groundwater remediation of multiple contaminants, among which a few research gaps are particularly crucial. This thesis identifies these research gaps through a critical literature review and investigates them.

Zeolites are a class of crystalline aluminosilicate minerals and have three-dimensional structures constructed by $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ coordination polyhedra. The isomorphic substitution of $Si^{4+}$ by $Al^{3+}$ produces negative charges which need to be balanced by exchangeable cations in the lattice of zeolites, leading to a high CEC. Generally, as the Si/Al ratio of zeolites increases, the thermal stability, acid strength and hydrophobicity increase, whereas the ion-exchange capacity decreases. ZSM-5, a typical hydrophobic zeolite, is effective for MTBE adsorption due to its high adsorption capacity (53.55 mg/g in batch adsorption tests) and good regeneration characteristics. The adsorption reaches equilibrium within 24 hours and follows the Langmuir isotherm model and the Hill 5 kinetic model, suggesting a monolayer and homogeneous chemisorption process. The adsorption is rarely affected by the solution pH which makes it conducive to changeable environmental conditions, but the presence of

nickel ions suppresses the adsorption with Ni concentrations of 2.5–25 mg/L. The mass transfer mechanism was further explored to access the transport process of MTBE from the bulk solution to ZSM-5 pores. It was found that pore diffusion is the main rate-limiting step for the entire adsorption process.

The synchrotron-based XAFS investigation was combined with batch adsorption tests and micro-structural methods to explore the mechanisms of Pb adsorption onto clinoptilolite and ZSM-5 with or without the presence of MTBE. The batch tests show that ZSM-5 has a low adsorption capacity towards Pb, while clinoptilolite is efficient (14.39 mg/g versus 94.38 mg/g at pH 4) due to their hydrophobicity and CEC. In addition, the co-existence of MTBE can rarely affect adsorption due to different adsorption mechanisms. The synchrotron-based XAFS further suggests that Pb to Si surface site occupancy and the $PbO \cdot (H_2O)$ type of surface coating are two common adsorption mechanisms in Pb-ZSM-5, Pb-clinoptilolite and Pb-clinoptilolite-MTBE systems. The surface “embedded” Pb uptake through the Mg site on the surface described comprised the secondary mechanism in the Pb-clinoptilolite-MTBE system. The limited available number of cleaved $SiO_4$ rings on the surface possibly leads to the low adsorption capacity of ZSM-5.

Based on the clear mass transfer mechanisms and adsorption characteristics, fixed-bed column tests were carried out to simulate the PRBs and examine the column performance of zeolites. The Dose-Response model can describe the breakthrough curves of MTBE adsorption onto ZSM-5 and onto a mixed reactive medium containing clinoptilolite granules and ZSM-5 was used in fixed-bed column tests. In comparison, MTBE adsorption onto a mixed reactive medium containing clinoptilolite powders and ZSM-5 can be described by the Logit, Thomas, and Yoon-Nelson models. In addition, MTBE adsorption onto ZSM-5 at new flow rates and bed lengths can be predicted using kinetic parameters from the BDST model without further experimental run in order to facilitate the full-scale design of columns. The maximum column adsorption capacity was found to increase with the increasing bed lengths and the decreasing flow rates and MTBE concentrations. The higher minimum thickness and corresponding longevity were obtained by the replacement of granular clinoptilolite by its powder form due to the reduction of hydraulic performance of the column and the breakthrough time, and the increase in the saturation time.