



## Natural and synthetic zeolites in adsorption/oxidation processes to remove surfactant molecules from water



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### ABSTRACT

Iron-containing zeolites were studied as adsorbents and heterogeneous Fenton-like catalysts for the removal of the non-ionic surfactant Triton<sup>®</sup> X-100 (TX-100) from water. Adsorption tests included a variety of zeolites with different structure types (ZSM5, Beta and Y) and SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratios. Zeolites with 12-membered-ring channels and high molar ratio of SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>, indicating higher surface hydrophobicity, proved to be the most suitable adsorbents for TX-100. For preparation of iron-loaded zeolites, a Beta zeolite with a molar ratio of SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> of 200 was selected, based on its excellent adsorption properties, and compared with a natural zeolite of clinoptilolite type. Batch experiments indicated that both Fe-zeolites are active in the heterogeneous Fenton-like oxidation of TX-100 at neutral pH. However, the synthetic Fe-Beta zeolite was preferable compared to the Fe-loaded natural zeolite with respect to catalytic activity and H<sub>2</sub>O<sub>2</sub> utilization efficiency, which was interpreted in terms of differences in iron speciation and adsorption properties towards TX-100. Fe-Beta (200) was successfully applied in two cycles of adsorption/oxidation steps in a column experiment. This study shows that Fe-loaded Beta zeolites with high hydrophobicity can be suitable materials for a combined approach of adsorption/wet peroxide oxidation of chemicals with relatively high molecular weight and chain-like molecule structure, such as the non-ionic surfactant TX-100.

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### 1. Introduction

The increasing worldwide demand for clean water together with the increasing presence of hardly biodegradable pollutants in industrial effluents have initiated a growing number of studies on advanced oxidation processes (AOPs) during the last decade [1–3]. The efficiency and simplicity of AOPs is based on the generation of very reactive species (mainly hydroxyl radicals [4,5]), which are able to oxidize a broad range of recalcitrant organic pollutants to stable inorganic (H<sub>2</sub>O and CO<sub>2</sub>) or at least more biodegradable and less harmful compounds. H<sub>2</sub>O<sub>2</sub> is one of the most widely-used oxidants to generate hydroxyl radicals in water. The formation of hydroxyl radicals from H<sub>2</sub>O<sub>2</sub> can generally be triggered by ultraviolet radiation, ultrasound, or appropriate catalysts

[1]. Among the H<sub>2</sub>O<sub>2</sub>-based AOPs, treatment with Fenton's reagent (dissolved Fe<sup>2+</sup> + H<sub>2</sub>O<sub>2</sub>) is a well-known, effective, and inexpensive way to degrade organic compounds in wastewater [6]. With respect to simplicity of catalyst removal and recovery, heterogeneous catalysts are more desirable than homogeneous ones. Beside the use of solid iron-oxide minerals or zero-valent iron [7–9], several solid supports such as zeolites [10,11], activated carbon [12], clays [13], resins or mesoporous materials [14] have been studied for immobilization of iron species in heterogeneous Fenton-like catalysts. The use of these catalysts is considered an effective way to oxidize organic contaminants in water because it combines high catalytic activity, minimization of secondary waste (such as iron-hydroxide sludge from homogeneous Fenton process), good recyclability and, in many cases, a wider working pH range than the homogeneous Fenton reaction, which is restricted to acidic conditions (pH ≈ 3) [15,16].

Among the above-mentioned solid supports, zeolites have been extensively studied as Fenton-like catalyst supports for oxidation of relatively small molecules such as phenol or MTBE [1,17–22].

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Zeolites are receiving increasing attention as alternative adsorbents for removal of organic compounds from water [10,18,23,24]. Unlike carbon-based adsorbents (such as activated carbon), they are resistant to hydroxyl radical oxidation. Thus, they are suitable for the combination of adsorption and advanced oxidation of organic contaminants, such as in the heterogeneous Fenton-like reaction using Fe-loaded zeolites. Activation of hydrogen peroxide by Fe-loaded zeolites is ascribed to isolated mono- and binuclear iron species on ion-exchange positions in the zeolite pore network, leading to formation of hydroxyl radicals and possibly another strong oxidant such as the ferryl species [18,25].

To the best of our knowledge, only a limited number of studies have been carried out on the application of zeolite-supported catalysts for the oxidation of large organic molecules, focusing mainly on dyes and lignin [1,26]. However, target molecules should be able to enter zeolite pores; a certain upper size limit for a molecule to be efficiently degraded by Fe-zeolite catalyzed oxidation is expected. This is due to the fact that the reactive species formed from H<sub>2</sub>O<sub>2</sub> at the iron sites in the inner pore volume of Fe-zeolites are either immobile (ferryl species) or too short-lived (hydroxyl radicals) to be able to diffuse within or even out of the zeolite pore network into the bulk phase. For molecules which are unable to enter the inner pore volume of the Fe-zeolite catalyst, only the low proportion of iron centers at the external surface of the zeolite particles would be accessible. In their review, Hartmann et al. [1] came to the conclusion that in the studies on dye degradation by zeolite-supported catalysts, the general question of whether the large dye molecules are entering the zeolite micropores is typically not addressed. Therefore, they assumed that the observed activity might be due to iron leaching into solution or to iron species located at the external surface of the microporous crystals.

The pore size in zeolites depends on the specific framework type. The most important synthetic zeolite types with pore sizes suitable for uptake of organic molecules are ZSM5, Beta and Y zeolites (framework code: MFI, BEA and FAU, respectively [27]). The largest channels are found in zeolites with 12-membered rings such as Beta and Y zeolites with crucial diameters up to 7.7 and 7.4 Å, respectively, whereas ZSM5 zeolites have 10-membered rings and thus maximum channel diameters of 5.6 Å [27].

This study contributes to exploring the applicability of Fe-zeolites for adsorption and oxidation of relatively large target molecules. Triton® X-100 (TX-100) was selected as a representative of the class of non-ionic surfactants which are generally large and chain-like molecules, close to the size limit for access to zeolites, so that the suitability of zeolites for their adsorption cannot be easily predicted. TX-100 is a polyoxyethylene-*p*-*tert*-octylphenol (C<sub>14</sub>H<sub>22</sub>O(C<sub>2</sub>H<sub>4</sub>O)<sub>*n*</sub>) with 9–10 ethylene oxide units (Fig. 1) and a molecular weight around 625 g mol<sup>-1</sup>. Octylphenol ethoxylates are widely applied for cleaning and wetting purposes by industry as well as additives in some process chemicals [28]. Very recently it has been tested for soil washing during decontamination processes, due to its high performance in the extraction and dissolution of hydrocarbons and a variety of pesticides [29]. In order to permit such applications, it is necessary to find suitable methods for its efficient removal. On the other hand, this type of compound is of ecotoxicological relevance since its biodegradation leads to octylphenol as important metabolite – a

compound which has detrimental estrogenic effects on aquatic organisms (see [30] and papers cited therein). However, there are very few studies in the literature about the removal of TX-100 from water. Klint and Bovin reported the adsorption of TX-100 from wastewater with Y zeolite [31] and Nagarnaik et al. showed that TX-100 can be effectively degraded by the classical homogeneous Fenton reaction [32]. Recently, Arslan-Alaton et al. have also proved that Triton® X-45 can be efficiently oxidized by advanced oxidation processes [30]. Our intention was to combine the two approaches, i.e. to pre-adsorb the compound on the zeolite and then to degrade it by a heterogeneous Fenton reaction.

The first objective of this work was to select the most suitable type of zeolite adsorbent for TX-100 and to derive conclusions about the decisive zeolite properties leading to optimal adsorption. Therefore, adsorption isotherms of TX-100 on various zeolites with different hydrophobicities, pore diameters, specific surface areas, and particle sizes were determined. Subsequently, selected zeolites were loaded with iron by means of liquid ion-exchange and tested for the degradation of TX-100 in a heterogeneous Fenton-like reaction in batch experiments at neutral pH. Finally, laboratory-scale column experiments were conducted with TX-100-containing water, whereby intermittent regeneration by heterogeneous Fenton oxidation was performed. This study shows for the first time that an Fe-loaded hydrophobic Beta zeolite is suitable for a combined approach of adsorption and subsequent degradation of TX-100 by a Fenton-like process. From the mechanistic point of view the influence of iron speciation and the interplay of adsorption and oxidative degradation are discussed.

## 2. Materials and methods

### 2.1. Chemicals and reagents

TX-100 was purchased from J.T. Baker (Germany). All other chemicals and organic solvents were obtained with a purity higher than 99% and H<sub>2</sub>O<sub>2</sub> as 30 wt.% solution from Merck (Germany). All applied zeolites were provided by Süd-Chemie Zeolites (Bitterfeld, Germany), except for the natural clinoptilolite zeolite (NZ) from S&B Industrial Minerals GmbH (Oberhausen, Germany) and the Y zeolites: Y (50) from Zeochem (The Netherlands) and Y (200) from Evonic (Germany). All zeolites were obtained in powder form, except for Y (200), which is a pelletized material and was used after crushing as a sieved fraction of 63–200 μm. Properties of the zeolites are summarized in Table 1. They are denoted by their structure type with an indicator for their SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio in parentheses.

### 2.2. Preparation and characterization of iron-containing catalysts

The Fe-zeolites were prepared by means of a liquid ion-exchange method, whereby iron species were immobilized on the selected zeolites, Beta (200) and NZ (5). Briefly, 500 mL of deionized water were filled into a flask and the pH was adjusted to 3 with HCl. After bubbling with N<sub>2</sub> for 30 min (for oxygen removal), FeSO<sub>4</sub>·7H<sub>2</sub>O (0.05 M) and zeolite (5 g) were added to the solution and the suspension was stirred overnight under N<sub>2</sub>. The zeolite was then separated by centrifugation and washed twice with deionized water. Finally, the prepared catalyst was calcined at 550 °C for 5 h in a muffle furnace.

X-ray fluorescence (XRF) analysis was performed in order to quantify the elemental composition of the prepared zeolites. UV–vis spectroscopy measurements were made in diffusive reflectance mode (UV–vis/DRS, Varian Cary 3) in order to analyze the iron speciation. The procedures applied are described in more detail in a previous study [4].

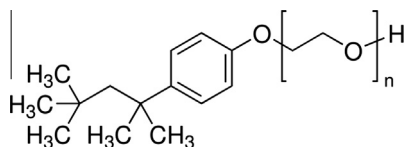


Fig. 1. The molecular structure of Triton X-100 (*n* is 9 or 10).

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