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Regular Article

Effect of surfactants on the removal of nitrobenzene by Fe-bearing montmorillonite/Fe(II)

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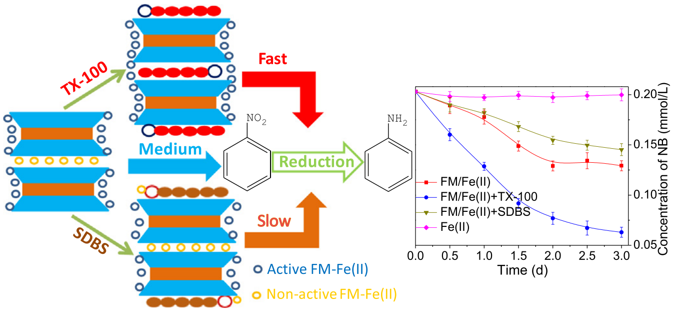
GRAPHICAL ABSTRACT



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ABSTRACT

Nonionic and anionic surfactants often occur in anaerobic environments, but their roles in the removal of organic contaminants by Fe-bearing mineral/Fe(II) have not been determined. In this study, batch experiments were performed to investigate the effects of a nonionic surfactant (TX-100) and an anionic surfactant (SDBS) on the removal of nitrobenzene (NB) by Fe-bearing montmorillonite (FM)/Fe(II). Mössbauer spectrum and XPS were applied to analyze the edge surface bound Fe(II) and secondary minerals formed on FM. The contribution of surfactant to the enrichment of NB on FM was studied. The results showed that TX-100 and SDBS had opposite effects on the removal of NB by FM/Fe(II) at neutral pH. The presence of TX-100 improved the removal efficiency of NB from 36.4% to 70.0%, and increased the initial removal rate by 1.7 times. This enhancement effect was mainly attributed to the formation of more active edge surface bound Fe(II) that can reduce more NB to aniline. Formation of more magnetite on FM and selective enrichment of NB on the reactive surface also contributed to the removal of NB. In contrast, the presence of SDBS reduced the amount of edge surface bound Fe(II) via formation of SDBS-Fe(II) complex, which decreased the removal efficiency of NB.

1. Introduction

Surfactants are a class of amphiphilic molecules simultaneously containing hydrophilic heads and hydrophobic tails. Various surfactants, particularly those that are anionic and nonionic surfactants, are generally used in household and laundry detergents, for personal care products, and as chemical additives for industrial and agricultural products. Owing to their stable structure and recalcitrance to degradation, these surfactants are widespread in soil and surface water, and subsequently accumulate in sediments, aquifers, and groundwater through leakage, rain elution, and

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surface flow over a long period [1]. Anionic and nonionic surfactants have unique solubilization to organic compounds, which enable them to be frequently used to flush organic contaminants from contaminated soils and sediments [2–5]. Therefore, anionic and nonionic surfactants accumulate to high concentrations in such anaerobic environments under surfactant treated areas, and interact with the originally widespread aqueous Fe(II), Fe-bearing minerals, and organic pollutants. Such interactions change the formation of reactive Fe(II)s and the adsorption of organic contaminants on Fe-bearing minerals, influencing the migration and transformation of organic contaminants in real anaerobic environments.

According to many previous studies, aqueous Fe(II) ions are always reductively dissolved from iron oxides in groundwater, sediments, and aquifers, and subsequently adsorb onto Fe-bearing minerals (e.g., iron oxides and Fe-bearing clay minerals) to produce mineral surface bound Fe(II) of higher reactivity than aqueous Fe (II) [6–8]. These reactive Fe-bearing minerals/Fe(II) can degrade some oxidizing pollutants including nitroaromatic and chlorinated compounds [8–10], and transform and immobilize toxic heavy metal ions on the iron minerals (e.g., U(VI), Cr(VI), and Tc) [11–13], constituting a main abiotic transformation pathway for these recalcitrant contaminants in an anaerobic environment.

Thus far, some environmentally coexisting substances such as natural organic matter [6,14–16], multi-valent metal ions [17–19], polycarboxylic acids, and anions [20–22] have been confirmed to change the reductive transformation of contaminants by Fe-bearing minerals/Fe(II) in different manners, influencing the fate and migration of these contaminants in anaerobic environments. For example, polycarboxylic acids help to form reactive Fe (II)-polycarboxylic acid complexes ($[\equiv Fe(II)L_x]^{2-nx}$), promoting the reduction of pentachlorophenol at the surface of goethite/Fe (II) [20]. Ni(II), Co(II), and Zn(II) can bound to the surface of hematite through competitive adsorption and prevent the formation of active surface bound Fe(II) [23]. In contrast, the adsorption of Cu (II) on the surface of goethite/Fe(II) accelerates the electron transfer from Fe(II) to CCl_4 and 2-nitrophenol by redox cycle of Cu(II)/Cu (I), contributing to the reduction of target pollutants by goethite/Fe (II) [18,19]. The presence of humic acids also promotes the reduction of chlorinated aliphatic pollutants by electron transfer acceleration from surface bound Fe(II) to the contaminants as a mediator [15,16]. In other research, humic acids have been found to act as a ligand to form a Fe(II)-humic acid complex with lower reactivity, inhibiting the reduction of nitroaromatic contaminants [24]. These previous studies prove that the coexisting substances play important roles in the removal and transformation of contaminants via Fe-bearing minerals/Fe(II). However, to the best of our knowledge, the effects of surfactants on the adsorption of Fe(II) and formation of reactive Fe(II)s on Fe-bearing minerals, as well as on the removal and transformation of organic pollutants in these systems, have never been studied.

For this purpose, we chose nitrobenzene (NB) and Fe-bearing montmorillonite (FM) as a model organic contaminant and Fe-bearing mineral, respectively, to investigate the effects of a nonionic surfactant (octylphenol polyethoxylete (TX-100)) and an anionic surfactant (sodium dodecyl benzenesulfonate (SDBS)) on the removal of NB by FM/Fe(II) via batch experiments. The removal and transformation of NB in the presence of surfactant at different concentrations and pH values were investigated. Through combined analysis of Mössbauer spectra, oxidation/reduction potential (ORP) and X-ray photoelectron spectroscopy (XPS), the contributions of surface bound Fe(II), secondary minerals, and NB adsorption on FM to the removal of NB were studied to clarify the underlying mechanism for the effects of surfactants on NB removal by FM/Fe(II).

2. Materials and methods

2.1. Materials

FM with a cation exchange capacity (CEC) of 68 mmol/100 g was obtained from Zhejiang Fenghong New Materials Company, and its chemical components are shown in Table S1. The FM particles were ground and then sieved through 100 mesh prior to use. Nitrobenzene (NB, >99.5%), aniline (>99.0%), 3-(N-morpholino) propanesulfonic acid (MOPS, >99.5%), $FeCl_2 \cdot 4H_2O$, TX-100, and SDBS were purchased from Shanghai Aladdin Chemicals. All other chemicals were of analytical grade. All solutions were prepared using 18 MΩ (Milli-Q Gradient, Millipore, USA) deionized water under ambient conditions.

2.2. Batch experiments for NB removal

The batch experiments were conducted in 25-mL serum bottles consisting of 3.0 mmol/L $FeCl_2$, 3.0 g/L FM, and 5.0 mmol/L of each surfactant (TX-100 or SDBS) in an anaerobic chamber of 99.99% N_2. The pH of the reaction solution was buffered by MOPS (20 mmol/L) at 7.0 unless otherwise indicated. After sealing with Teflon-lined butyl rubber septa and aluminum crimps, each serum bottle was transferred to an orbital shaker at 150 rpm, and incubated at 25 °C in the dark overnight, to ensure equilibrium adsorption of Fe(II) on the surface of the FM. Then, a certain amount of NB was added to each serum bottle to ensure the NB concentration was 0.203 mmol/L and the reaction volume was 20 mL. The solution was incubated under the same condition for 3 days. At different time intervals, samples were collected and separated by centrifugation at 8000 rpm, and the resultant solids were extracted using methanol solution two times. The residual NB and produced aniline concentrations (including supernatant and extract) were measured. All experiments were conducted in triplicate.

2.3. Analytical methods

Quantitative analysis of the NB and aniline were performed using a high-performance liquid chromatography (HPLC) instrument (Shimadzu Technologies, Inc.) equipped with a Shimadzu LC-20AT Binary pump, an ultraviolet/visible detector, and a C18 analytical reversed-phase column (Symmetry C18, 250 mm × 4.6 mm × 5 μm, Shimadzu, Japan). The methanol–water mixture (65:35, v/v) was used as mobile phase at a flow rate of 1.0 mL/min, and the analytical wavelength was set to 270 nm.

To determine the amount of ion exchanged Fe(II) and edge surface bound Fe(II) formed on the FM, both Fe(II) species were chemically extracted using the method described by Jaisi et al. [25]. Ion exchanged Fe(II) was collected via exchange with NH_4^+ in a NH_4Cl solution (0.2 mol/L, pH 7.0), and edge surface bound Fe(II) was collected via exchange with H^+ and Na^+ in a Na-acetate buffer (1.0 mol/L and pH 4.25). The detailed procedures were as follows: After equilibrium adsorption of Fe(II) on the FM, the resultant solid sample was collected and washed using deionized water two times. Then, the solid sample was re-suspended in 10 mL of NH_4Cl solution and agitated at 150 rpm in the dark for 2 h. As the NH_4Cl extraction ceased, the extracted ion exchanged Fe(II) in the supernatant was filtered through a 0.22-μm membrane and determined using the 1,10-phenanthroline colormetric method [8]. After this, the remaining solids were washed with deionized water two times, and re-suspended in 10 mL of Na-acetate buffer and agitated at 150 rpm in the dark for 4 h. As the acetate buffer extraction ceased, the edge surface bound Fe(II) was collected and determined using the same method.