Removal of Humic Acid from Natural Water by ZVI/H₂O₂ Process

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Humic acid (HA), a representative fraction of the natural organic matter derived from vegetation and commonly present in natural waters, can contribute to the formation of disinfection by-products when reacting with chlorine during potable water production. These by-products may cause increased risk of cancer, especially in the bladder, and adverse reproductive outcomes [1]. Therefore, identification and removal of organic matter before the chlorination step is required to avoid or minimize the risk of formation of these by-products.

The advanced oxidation process Zero Valent Iron/Hydrogen Peroxide (ZVI/H₂O₂) has already been investigated by the present authors [2]. However, the water matrix studied was produced in the laboratory with PA reagent HA, which, according to the recent studies [3, 4] may not be a representative matrix for aquatic environments, and may not properly demonstrate the feasibility of applying in full-scale the proposed removal process. The present study has investigated the HA removal efficiency and the oxidation mechanism of the ZVI in natural water collected from Regent's Park (London, UK - 51° 31'32"N 0° 09'28"W), which contained an average dissolved organic carbon (DOC) 5.3 ± 2.2 mg.L⁻¹ and turbidity 1.2 ± 0.6 NTU. Experiments were performed with ZVI in the metallic form of iron “cuts” (small nails) (total surface area 2.56 cm²) and H₂O₂ (50% w/w) at initial pH 4.5. Humic acid degradation was evaluated in terms of DOC and absorption at UV₂₅₄. The microstructure of the oxidized ZVI was evaluated using a Zeiss Merlin field emission gun (FEG) scanning electron microscope (SEM), and a Zeiss Sigma VP FEG-SEM. Low voltage (1.5 kV) energy dispersive x-ray (EDX) spectrum image datasets were obtained using an Oxford Instruments X-Max Extreme Si Drift Detector (SDD) and AZTEC analysis system to qualitatively assess the elemental distribution in the near-surface (~20-30 nm) region of the oxidized samples.

The secondary electron (SE) SEM image in Figure 1a shows the ZVI surface in the as-received condition (before the ZVI/H₂O₂ reaction). Figure 1b shows the ZVI surface after the ZVI/H₂O₂ reaction. This SE image revealed the presence of oxides that formed on the metallic Fe surface. These oxides confirm that oxidation of ZVI by the H₂O₂ had occurred in the reaction as described by Eq. (1). As expected in this oxidative process, metallic Fe is oxidized by H₂O₂ to form ferrous iron, releasing ions into solution which subsequently react with H₂O₂ to produce a highly reactive radical (OH⁻) for the degradation of the organic matter (Eqs. (1 – 3)). Thus, a significant difference in oxidation is evident from the different oxide morphologies between Figures 1a (as-received native oxide on Fe prior to exposure) and 1b (after the ZVI/H₂O₂ process) confirming the oxidation mechanistic step of the ZVI/H₂O₂ process. Figures 2a and 2b show the formation of oxides with heterogeneous morphologies on the ZVI surface after the ZVI/H₂O₂ process. In Figure 3a the coexistence of two different morphologies can be observed in the same region. These different morphologies may be due to pH variation during the reaction, producing a variety of stable iron oxides. The LV SEM-EDX elemental maps confirming the presence of oxygen in the near-surface region of the exposed Fe specimens are presented in Figures 3b and 3c.

Fe⁰ + H₂O₂ + 2H⁺ → Fe²⁺ + 2H₂O
Fe²⁺ + H₂O₂ → Fe³⁺ + OH⁻ + OH⁻
OH⁻ + organics → oxidized products

As result of the ZVI/H₂O₂ process, treated water showed 82% HA removal at UV₂₅₄, 51% dissolved organic carbon (DOC) mineralization, and 0.82 ±0.02 mg.L⁻¹ of Fe²⁺ formation in 75 min of reaction. From these results,
it can be concluded that the Fe$^0$ “nail” samples were severely corroded by the H$_2$O$_2$ oxidizer, leading to the degradation of the undesirable organic matter through the treatment with the ZVI/H$_2$O$_2$ process [5].

References:
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Figure 1. SE images of iron cuts surface. (a) as-received condition and (b) post-ZVI/H$_2$O$_2$ in 75 minutes of reaction.

Figure 2. SE images of oxides on the Fe sample surface post-ZVI/H$_2$O$_2$ in 75 minutes of reaction.

Figure 3. (a) SE image of oxidized Fe surface post-ZVI/H$_2$O$_2$ process; (b) complementary LV EDX maps of Fe and O.