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**Synergetic combination of nano zero-valent iron, ultrasound and carboxylic acids for the removal of aqueous Cr(VI)**

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***Abstract***

Cr(VI) is a priority pollutant present in wastewater of several industrial processes such as electroplating and leather tanning; it can be also naturally present in groundwater. The usual treatment of Cr(VI) involves its reduction to Cr(III), a far less toxic and mobile species, which can be precipitated from the solution at circumneutral pH values [1]. However, conventional Cr(VI) chemical reductants, such as Fe(II) salts, require large Fe:Cr molar ratios to be efficient, generating the disposal of large amounts of dangerous sludge. Thus, more efficient Cr(VI) reduction treatments are required. In this work, the efficiency of commercial zero-valent iron nanoparticles (nZVI), ultrasound (US), and carboxylic acids (CAs) for Cr(VI) reduction was evaluated. The CAs used were citric acid (Cit) or ethylenediaminetetraacetic acid (EDTA).

The experiments were performed with 200 mL of a 0.3 mM Cr(VI) solution at pH 3 and under air bubbling (0.5 L min-1) at 30 °C for 180 min in an ultrasonic reactor (850 kHz, total power input 35 W L-1). NSTAR (Nanoiron®) was used as nZVI, with a 3:1 Fe:Cr molar ratio (the optimal ratio as determined before for N25 nZVI [2]), Cit (0 or 2 mM) or EDTA (0 or 1 mM).

In the absence of Cit or EDTA (nZVI alone or nZVI + US), or with Cit or EDTA alone (neither nZVI nor US), Cr(VI) reduction was negligible (≤ 5% of the initial [Cr(VI)]). US + Cit showed a reduction of 49% of the initial [Cr(VI)], while US + EDTA showed a 32% of reduction. On the other hand, nZVI + US + Cit yielded an 88% of Cr(VI) reduction, which was 60% with nZVI + US + EDTA. This indicates a clear synergy within the ternary system (nZVI + US + CAs). In all cases, the evolution of Cr(VI) could be fitted to a zero-order kinetic model , with *R*2 values higher than 0.94.

NSTAR nZVI particles are composed of a zerovalent Fe core surrounded by a protective shield of iron oxides that inhibits Cr(VI) reduction; thus, only the combination of US and CAs can remove this protective shield and enhance Cr(VI) reduction, being Cit more efficient than EDTA. This was reinforced by the monitoring of the evolution of the total Fe concentration in solution, with final values of 0.076, 0.26, and 0.18 mM for the systems nZVI + US, nZVI + US + Cit and nZVI + US + EDTA, respectively, indicating that Cit and EDTA promote the formation of soluble Fe complexes. Besides, in the previous experiments of US without nZVI, Cit also proved to be a better donor than EDTA, probably because it can stabilize to a higher extent intermediate peroxo-Cr(V) compounds [1].

Summarizing, there is a synergy for Cr(VI) reduction in the ternary system nZVI + US + CAs, being Cit more efficient than EDTA.

***References***

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