

## Adopting magnetite nanoparticles synthesis into drinking water treatment requirements: The case of hexavalent chromium

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Considering the high specific surface area of nanoparticles in comparison to their bulk counterparts, surface adsorption of toxic pollutants present in drinking water or wastewater is commonly proposed as an efficient way to develop their use in water treatment. However, keeping the effective adsorption surface of nanoparticles at high levels is not favorable in typical packed-bed filters, which use micron-sized granules. Such limitation promotes the application of magnetically-responsive nanoparticles such as magnetite ( $\text{Fe}_3\text{O}_4$ ) since they can easily be captured by applying an external magnetic field. The potential of nanomaterials to operate as efficient adsorbents for the removal of hexavalent chromium, a very toxic and mobile aqueous chromium contaminant in water has been widely demonstrated in recent years. The ideal adsorbents to capture Cr(VI) are those that can deliver maximum electron donor potential in order to initiate reduction to an insoluble Cr(III) state. In the case of magnetite nanoparticles, the affinity of magnetite to Cr(VI) is attributed to the incompletely oxidized  $\text{Fe}^{2+}$  ions in its structure which favor electron transfer and reduction of Cr(VI) to insoluble hydroxides

This work examines the impact of hydroxyl excess and the role of counterions during the synthesis of  $\text{Fe}_3\text{O}_4$  nanoparticles by oxidative precipitation of  $\text{FeSO}_4$  as critical parameters determining the potential for Cr(VI) uptake from polluted water. The synthesis of studied  $\text{Fe}_3\text{O}_4$  nanoparticles was typically carried out through the precipitation of  $\text{FeSO}_4$  in an alkaline environment which was accompanied by the partial oxidation of the  $\text{Fe}^{2+}$  initiated by nitrate ions when the temperature is increased. Various samples were prepared by varying the  $\text{OH}^-$  excess in the range of  $-0.10$  up to  $+0.03$  M and characterized according to their composition, morphology, and surface configuration [1]. Their efficiency for Cr(VI) removal was evaluated by batch adsorption tests, carried out under similar conditions with drinking water purification in the concentration range below 10 mg/L. Results indicate that a small increase above  $+0.02$  M features nanoparticles with an uptake capacity of 2.5 mg/g owed to the decrease in particles size and enhancement of the reducing potential. In another set of samples, the iron source ( $\text{FeCl}_2$ ,  $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$ ), the oxidizing agent ( $\text{KNO}_3$ ), the alkaline agent (KOH) and the water/ethanol ratio were varied in order to identify any positive effect of the Hofmeister effect which described the competition between the counterions and the intermediate phase of green rust for water molecules. The use of ferrous chloride was found to bring an improvement in the uptake capacity ( $\sim 3$  mg/g) due to the smaller particle size which is obtained. On the opposite, all other alternatives were caused a decrease in the obtained efficiency.

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[1] K. Kalaitzidou et al., Water 14, 1335 (2022)