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Influence of manganese incorporation on structure, surface and As(III)/As(V) removal capacity of iron oxy-hydroxides

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Iron oxy-hydroxides are well defined As(V) adsorbents dominating in water treatment market. The main drawback of these adsorbents, as well as of all commercial one, is their significantly low adsorption capacity for As(III). A breakthrough for improving As(III) adsorption of iron oxy-hydroxides may come by the MnO_2incorporation. However, MnO_2 decreases the total arsenic capacity proportionally to its percentage since its efficiency for As(V) is much lower than that of an iron oxy-hydroxide. It is concluded that an ideal adsorbent capable for high and simultaneous As(III) and As(V) removal should be consisted of a binary Fe(III)-Mn(IV) oxy-hydroxide both efficient for As(III) oxidation, due to Mn(IV) presence, and capture of As(V) due to a high positively surface charge density.

This work studies the optimum parameters at the synthesis of single Fe and binary Fe/Mn oxy-hydroxides in a continuous flow kilogram-scale production reactor through the precipitation of $FeSO_4$ in the pH range 3-12, under intense oxidative conditions using $H_2O_2/KMnO_4$, that maximize arsenic adsorption. The evaluation of their efficiency was based on its As(III) and As(V) adsorption capacity (Q_{10}-index) at equilibrium concentration equal to drinking water regulation limit (C_e= 10 μg/L) in NSF challenge water. The pH of synthesis was found to decisively affect, the structure, surface configuration and Q_{10}-index. As a result, both single Fe and binary Fe/Mn oxy-hydroxides prepared at pH 4, which consist of schwertmannite and Mn(IV)-feroxyhyte respectively, were qualified according to their highest Q_{10}-index of 13±0.5 μg As(V)/ mg for a residual arsenic concentration of 10 μg/L at an equilibrium pH 7. The high surface charge and the activation of an ion-exchange mechanism between SO_4^{2-} adsorbed in the Stern layer and arsenate ions were found to significantly contribute to the increased adsorption capacity.

The Q_{10}-index for As(III) of Fe/Mn adsorbent at equilibrium pH 7 was 6.7 μg/mg, which is 3.5 times greater of that for single Fe one (1.9 μg/mg), although it is significantly lower of the respective for As(V). However, Fe/Mn oxy-hydroxide present almost equal adsorption capacity for both arsenic species in the pH range 7.5-8. The As(III) adsorption capacity of Fe/Mn oxy-hydroxides is positively affected by the Mn content and the redox potential values at equilibrium pH 6-7. The corresponding Q_{10}-index values observed in rapid scale column tests were in agreement with those of batch experiments, illustrating the improved efficiency of the qualified adsorbent compared to the common commercial arsenic adsorbents.

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