Improved immobilization of Re(VII) from aqueous solutions via bimetallic Ni/Fe^0 nanoparticles: Implications towards Tc(VII) removal

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The rapid development of nuclear power technologies led to increased water contamination worldwide. Nuclear industries produce large amounts of wastewater as a byproduct of the generation of nuclear energy, containing a variety of harmful contaminants, including radionuclides, heavy metals, and other chemicals. Technetium-99 (^{99}Tc) is one of the long-lived radionuclides (half-life: 2.13×10^5 years), which represents the main fission products of uranium-238 (^{238}U) [1, 2]. ^{99}Tc commonly occurs in the heptavalent (Tc(VII)) anionic form of pertechnetate (TcO$_4^-$), which is highly mobile and soluble. Rhenium (Re) is considered the common chemical analogue for Tc owing to their similar chemical features, as they both share the same stable VII oxidation states of perrhenate (ReO$_4^-$) and pertechnetate (TcO$_4^-$), which can be reduced to IV via electron-donor materials [3]. Hence, Re(VII) can be considered the target contaminant in this work as Tc(VII) analogue.

Meanwhile, zero-valent iron nanoparticles (Fe^0) have been widely utilized as an efficient reactive material towards reducible contaminants, owing to the suitable redox (oxidation-reduction) potential (E^0: -0.44 V) [4]. In this regard, doping the surface of Fe^0 with another metal (e.g., nickel (Ni)) yields bimetallic nanoparticles with a remarkably reactive surface, higher catalytic properties, and improved removal capabilities towards reducible contaminants. Using Ni in bimetallic Fe^0 may have advantageous features, including cost-efficiency (compared to the other high-cost metals), the high catalytic activity of Ni, and the ability to act as an electron transfer medium to overcome the self-inhibition of electron transfer.

Hence, the main aim of this work is to use bimetallic nickel/iron nanoparticles (Ni/Fe^0) to enhance Re(VII) immobilization from aqueous solutions as the surrogate of Tc(VII). Different characterization techniques were used in this work to elucidate the physicochemical features of the unreacted and reacted materials, including scanning transmission electron microscopy-energy dispersive X-ray spectroscopy (STEM-EDX), X-ray diffraction (XRD), and X-ray absorption near edge spectroscopy (XANES). The influence of several reaction parameters on Re(VII) removal was investigated, including Ni/Fe^0 (wt/wt) ratio (0.05, 0.1, 0.2, and 0.4), Ni/Fe^0 dosage (0.25, 0.5, 1.0, 1.5, and 2.0 g/L), initial pH (3.0, 5.0, 7.0, 9.0 and 12.0), reaction temperature (25, 35, 45, and 55 °C), and initial Re(VII) concentration (0.25, 0.5, 1.0, 5.0, 15.0, 25.0, and 50.0 μM). Results showed a promising potential of Ni/Fe^0 in Re(VII) removal, especially at the early stage of the reaction, where Ni/Fe^0: 0.4 yielded almost full removal efficiency of initial 15.0 μM-Re(VII) within the first 10 minutes of reaction. Even at low Ni/Fe^0 dosages, such as 0.25 and 0.5 g/L, reasonable removal efficiency was achieved after 2 hours reaction time of ~73% and ~98%, respectively. The effect of initial pH on Re(VII) removal by Ni/Fe^0 was studied at acidic, neutral, and alkaline conditions. Unlike acidic/neutral pH, alkaline conditions were not favorable for Re(VII) removal by Ni/Fe^0 owing to the delayed Fe^0 oxidation, resulting in insufficient electrons available for Re(VII) reduction. As shown in Fig. 1(A), the reductive abilities were confirmed by XANES, revealing Re(VII) reduction to Re(IV)/(III) by the released electrons from Fe^0-core in both Fe^0 and Ni/Fe^0 materials. Meanwhile, a method was used to measure the electrostatic potential at the electrical double layer surrounding Ni/Fe^0 nanoparticles in solution, referred to as zeta potential. Correspondingly, the measurements depicted the point of zero charge (pH$_{PZC}$) of Fe^0 and Ni/Fe^0 to be 8.24 and 7.63, respectively, suggesting electrostatic sorption of ReO$_4^-$ on the positively charged surface of Ni/Fe^0. Theoretical reaction kinetic models (i.e., Pseudo-first- and second-order models) were suitable to describe Re(VII) removal by Ni/Fe^0, implying the involvement of chemical (i.e., reduction of Re(VII) to Re(IV)/Re(III)) and physical (i.e., electrostatic sorption) removal mechanisms. The presence of Ni^0/NiO on the Fe^0-surface resulted in providing an efficient electron-transfer medium that facilitated Re(VII) reduction (Fig. 1(B)). The aforementioned contribution of Ni/Fe^0 to the removal mechanism led to higher kinetic rates of Re(VII) reduction Fe^0. Overall, this study provides valuable insights into using Ni/Fe^0 for Re(VII) removal from water and offers guidance for future research toward the pilot-scale applications of Tc(VII) removal from nuclear wastewater.
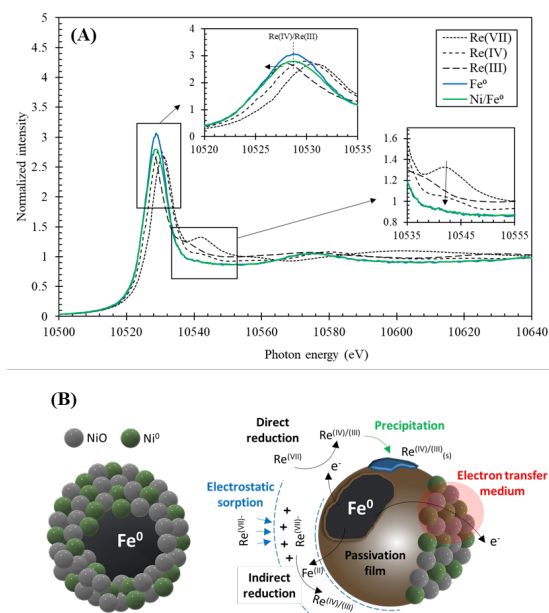

Fig. 1. Re L$_{III}$-edge (corresponding to the excitation of electrons: principal quantum number n=2) XANES spectra of spent Fe^0 and Ni/Fe^0 (A), and removal pathways of Re(VII) removal by Ni/Fe^0 (B).

References
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