Comments on „Mechanism study of nitrate reduction by nano zero valent iron“ by Hwang et al. [J. Hazard. Mater. (2010) doi:10.1016/j.jhazmat.2010.10.078.]

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In a recent article, Hwang et al. [1] reported on the mechanism of nitrate (NO_3^-) reduction by nanoscale metallic iron (nano-Fe^0). A particular attention was paid to the fate of nitrogen species during nitrate reduction. This article with 20 peer-reviewed references is very informative. However, the objective of the study is questionable as it challenges the state-of-the-art knowledge on the mechanism of aqueous contaminant removal in the presence of Fe^0 (e.g. in Fe^0/H_2O systems) [2-4]. The view that Fe^0 is a reducing agent has been challenged three years ago [2].

Hwang et al. [1] referenced 15 peer-reviewed articles dealing with remediation with metallic iron (Fe^0 and nano-Fe^0). From these, one is a critical review published in 2008 [5], showing that the article of Hwang et al. [1] is principally well-referenced. From the remaining 14 research articles published between 1997 and 2008, only 3 did not directly deal with NO_3^-, suggesting that the authors have focused their attention on articles dealing with nitrate while preparing and presenting their work. Additionally, all 3 remaining articles not dealing with NO_3^-, used nano-Fe^0. Accordingly, Hwang et al. [1] used a commended approach to prepare and present their work. The question that arises is why the product of such an intellectual effort is not satisfying?

The problem is the origin. In fact, based on a false premise, researchers working on Fe^0 for water treatment have created a sort of *modern knowledge system* which used (or misused) scientific arguments, as will be shown below. Clearly, Fe^0 is not a reducing agent for contaminant removal including NO_3^-, and the objective of water treatment is not contaminant chemical transformation (e.g. reduction) but contaminant removal. A chemical transformation (oxidation or reduction) may render a contaminant more removable but is not a stand alone removal mechanism. In the case of NO_3^-, for example, completely reducing NO_3^- to NH_4^+ will not produce clean water, unless NH_4^+ is removed down below the MCL value (maximum concentration limit). There are five possible mechanisms for contaminant removal in Fe^0/H_2O systems: adsorption, co-precipitation, precipitation, size-exclusion and volatilization. Apart from precipitation, all other removal mechanisms are applicable to NO_3^- removal in batch systems. It is important to notice that, in a real world system, e.g. nano-Fe^0 in the subsurface reactive zone, there will be no possibility to homogenize the system by stirring the solution as Hwang et al. [1] did. Moreover, whether nitrate is reduced or not, it is progressively enmeshed by very reactive iron hydroxides and continues to be fixed while hydroxides are further transformed (crystallisation) [6]. Nitrate enmeshed in the matrix of iron corrosion products cannot be leached by water and are stable under environmental conditions. Adsorbed nitrate can be leached; it could also be reduced by adsorbed Fe^{II} and adsorbed H/H_2 from Fe^0 oxidative dissolution. The fate of reduced forms of NO_3^- is the same. The hitherto presentation has questioned the importance of quantifying the extent of NO_3^- reduction by nano-Fe^0. Furthermore, it demonstrates that mass balance without iron oxide dissolution is not possible in real systems. A better approach could be to work under relevant conditions (e.g. non-disturbed or stirred at very low speed) and evaluate the extent of desorbable N species.

In conclusion, the false premise, that contaminants are reduced in Fe^0/H_2O should be abandoned for rapid progress in the optimisation of the proven efficient technology of using Fe^0 for water treatment. Given the huge number of available publications on water treatment with Fe^0, it is obvious that individual researchers or research groups could not always be aware on the state-of-the-art knowledge. The situation is even worse for researchers from small research centres and low-income countries (mostly in the developing world). It is the responsibility of editors and other promoters of science to create the conditions to efficiently reach the large scientific community, a proven efficient tool is a special issue on recent progresses. Eleven (11) years after the special issue on the "the current state of practice and research in the area of reactive barriers" [7], a second special issue seems urgently necessary to "provide impetus to further studies in this evolving subject". [7]

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