

Comments on “Sorption of triazoles to soil and iron minerals” by Y. Jia et al. [Chemosphere 67 (2007) 250–258]

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Abstract

This letter suggests possible improvements on the discussion of the adsorptive removal of triazoles by iron minerals which are possible corrosion products of elemental iron materials (Fe^0) in a recent article by Jia et al. [Jia, Y., Aagaard, P., Breedveld, G.D., 2007. Sorption of triazoles to soil and iron materials. *Chemosphere* 67, 250–258]. Also recalled is the importance of the adsorption of organics by iron corrosion products which is not properly addressed in the iron technology literature when the contaminants are redox-sensitive.

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1. Introduction

In a recent article entitled “Sorption of triazoles to soil and iron minerals” Jia et al. (2007) discussed the adsorption of triazoles to soil, iron minerals and elemental iron (Fe^0 or zerovalent iron) in order to better understand the fate and transport of these highly mobile and recalcitrant compounds in the subsurface. For this purpose benzotriazole (BTA) and methylbenzotriazole (MeBTA) were used as model contaminants. Among other results, Jia et al. (2007) found out: (i) negligible MeBTA adsorption onto Fe_2O_3 ; (ii) considerable MeBTA adsorption onto ferrihydrites; (iii) strong BTA and MeBTA adsorption onto elemental iron (Fe^0). It was concluded that using elemental iron permeable reactive barriers can be an effective technology to mitigate the migration of highly mobile triazoles in the subsurface.

The present communication aims at (i) optimising the discussion of the mechanism of triazoles removal by elemental iron materials based on the chemistry of iron

corrosion and (ii) discussing the consequence of the results of Jia et al. (2007) for the reactive wall technology.

2. Concerning the mechanism of triazoles removal by elemental iron

Jia et al. (2007) mostly considered elemental iron (Fe^0) in their discussion as pure adsorbent although they observed Fe^0 oxidation for experimental duration >48 h. This basic assumption led to the conclusion that adsorption to Fe^0 seems to be controlled by multi-layer coverage. The time dependence of contaminant removal is not shown. It could have been interesting to discuss whether there is a relation between iron oxidation ($t > 48$ h) and increased contaminant removal. Although triazoles are iron corrosion inhibitors (Yao et al., 2003), 100% corrosion inhibition will not occur. Jia et al. (2007) implicitly recognized that triazoles will not stop iron corrosion in suggesting Fe^0 materials as reactive media for the remediation of sites contaminated with triazoles. However, the dynamic nature of the process of iron corrosion is not properly addressed. The removal process for BTA in the presence of Fe^0 , via multi-layer Fe^0 surface coverage, proposed by Jia et al. (2007) is not consistent with the mechanism of Fe^0 oxidation.

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A general overview of the reaction mechanisms pertinent to the process of contaminant removal in the presence of ferrihydrite ($\text{Fe}_5\text{O}_3(\text{OH})_9$), hematite (Fe_2O_3), magnetite (Fe_3O_4), and Fe^0 are provided in Table 1. For the purpose of discussion, redox processes (here reduction) should be ignored because the triazoles as investigated by Jia et al. (2007) are not considered redox sensitive. From Table 1 it can be seen that beside ferrihydrite, hematite and magnetite several other adsorbents may exist in the Fe^0 - H_2O system (Roh et al., 2000; Schmuki, 2002). Iron oxyhydroxides are progressively generated in Fe^0 - H_2O system. In all other systems on the contrary, the total amount of adsorbent is present at the start of the experiment. Assuming for simplicity that no mineral dissolution occurs, the Fe^0 - H_2O system is the single system with varying adsorbent amounts. The in-situ generation of adsorbents alone is a strong argument for strong triazoles adsorption in the Fe^0 - H_2O system. The adsorptive characteristics of the individual iron oxides depends mostly on three factors (Anderson and Benjamin, 1985; Coughlin and Stone, 1995; Axe and Trivedi, 2002; Cornell and Schwertmann, 2003; Martin, 2005): (i) specific surface area (abundance of binding sites), (ii) porosity and pore size distribution (accessibility of binding sites), and (iii) crystallinity (reactivity of binding sites). As metastable minerals amorphous iron oxides are transformed to more stable crystalline forms upon ageing. The ageing process is known to be retarded by adsorption of inorganic and organic species (Axe and Trivedi, 2002 and references therein). As a result, hydrous amorphous iron oxides are persistent in Fe^0 - H_2O systems. Consequently, the reactivity of the Fe^0 - H_2O system is variable and depends on the relative abundance of amorphous iron oxides. The ageing process for highly porous amorphous oxyhydroxides is usually accompanied by dehydration and conversion to a less porous structure. For example, Anderson and Benjamin (1985) reported a typical specific surface area of $500 \text{ m}^2/\text{g}$ for fresh generated ferrihydrites and only $30\text{--}50 \text{ m}^2/\text{g}$ for goethite. It can be anticipated that in the initial stage of Fe^0 corrosion pertinent to the experimental conditions of Jia et al. (2007), large amounts of highly porous amorphous iron oxides (e.g. ferrihydrites) are generated and was responsible for the observed removal efficiency of Fe^0 materials.

The discussed evolution in the reactivity of iron corrosion products with increasing stability (ferrihydrites \gg hematite) by Jia et al. (2007) is consistent with the observations from Table 1. Therefore, under the experimental conditions of Jia et al. (2007), triazoles may have been mostly removed by iron corrosion products and not by multi-layer adsorption onto the bare Fe^0 surface. While the Fe^0 specific surface area is known (or can be determined) and is certainly determinant for the materials reactivity (e.g. Johnson et al., 1996), it should not be used in discussing the results of triazoles removal. The reactive transient states (Table 1) that certainly play an important role in the process of triazoles removal are difficult to characterize (porosity, surface area, crystallinity) and their characteristics change with increasing experimental duration. These transient states also acts as adsorbents for primary corrosion products (Fe^{II} , H/H_2). The adsorption of Fe^{II} on mineral surfaces yields structural Fe^{II} ($\text{Fe}^{\text{II}}_{\text{(s)}}$, Table 1) which is a stronger reducing agent than aqueous Fe^{II} (White and Paterson, 1996).

Porous and amorphous transient state corrosion products adsorb contaminant strongly (relative high binding strength) and can entrap them in their matrix during their agglomeration (coprecipitation) or their crystallisation (Crawford et al., 1993; Füredi-Milhofer, 1981). The distinction between adsorption and coprecipitation is not always clear. Contaminant adsorption processes can occur whenever a solid substrate surface (iron corrosion products) is present. That is the solid substrate is pre-formed prior to addition of the contaminant to be removed from solution. Coprecipitation processes are subtly different to adsorption processes. In the case of coprecipitation the solid substrate is formed in the presence of the contaminant to be removed from solution (Crawford et al., 1993). In a dynamic Fe^0 - H_2O system, some contaminant molecules will be adsorbed on already available stable corrosion products (hematite or magnetite) while some others will co-precipitate with transient states (ferrihydrites, green rusts. . .).

Few studies directly compare the efficiency of adsorption and coprecipitation processes (Crawford et al., 1993 and references therein). It is believed, that coprecipitation will enhance the removal efficiency to a greater extent than that of simple adsorption. This further enhancement either

Table 1

Overview of reactants pertinent to aqueous contaminant removal in the presence of ferrihydrite ($\text{Fe}_5\text{O}_3(\text{OH})_9$), hematite (Fe_2O_3), magnetite (Fe_3O_4) and metallic iron (Fe^0)

System	Reactants	Primary mechanism	Secondary mechanism	Reactivity
$\text{Fe}_5\text{O}_3(\text{OH})_9\text{-H}_2\text{O}$	$\text{Fe}_5\text{O}_3(\text{OH})_9$	Adsorption	–	Constant
$\text{Fe}_2\text{O}_3\text{-H}_2\text{O}$	Fe_2O_3	Adsorption	–	Constant
$\text{Fe}_3\text{O}_4\text{-H}_2\text{O}$	Fe_3O_4	Adsorption	–	Constant
$\text{Fe}^0\text{-H}_2\text{O}$	Fe^0 , H/H_2 , $\text{Fe}^{\text{II}}_{\text{(aq)}}$, $\text{Fe}^{\text{II}}_{\text{(s)}}$	Reduction	–	
	$\text{Fe}(\text{OH})_2$, $\text{Fe}(\text{OH})_3$, Fe_2O_3 , Fe_3O_4	Adsorption	Coprecipitation	Variable
	FeOOH , $\text{Fe}_5\text{O}_3(\text{OH})_9$, green rusts	Adsorption	Coprecipitation	

The possible contaminant removal mechanisms are given. The generation of corrosion products is a dynamic process in the course of which contaminant can be entrapped in the mass of precipitating/ageing iron oxyhydroxides (coprecipitation). In the Fe^0 - H_2O system, Fe^0 is considered as primary reductant whereas H/H_2 , $\text{Fe}^{\text{II}}_{\text{(aq)}}$ and $\text{Fe}^{\text{II}}_{\text{(s)}}$ are secondary reductants. Therefore, secondary reductants are primary iron corrosion products (H_2 and Fe^{II}).

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