

Comments on: **“Comparison of reductive dechlorination of p-chlorophenol using Fe⁰ and nanosized Fe⁰.”** By R. Cheng et al. J. Hazard. Mater. 144 (2007) 334.

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The article of Cheng and colleagues [1] was intrinsically interesting as its intended to compare the efficiency of conventional Fe⁰ (mm to μm size) and nanosized Fe⁰ for aqueous reductive dechlorination of p-chlorophenol. Such investigations are necessary to gain more details on the expected reactivity of nanosized Fe⁰. In fact, the introduction of nanosized Fe⁰ in groundwater remediation was not univocal [2]. Therefore, such comparative works from the same research group should be very helpful.

Unfortunately, due to the lack of a unified procedure for conducting contaminant removal experiments in investigating processes in Fe⁰-H₂O systems (here Fe⁰, 4-CP, H₂O, O₂), almost any researcher uses a different experimental procedure. This deficiency has accounted for controversial results in other branches of science [3,4]. For example, Büchler et al. [3] have found out that the strong influence of the hydrodynamic conditions due to mixing operations explains many contradictory literature results on the process of the formation, growth, and dissolution of the passive film on iron in neutral and alkaline solutions.

Despite the failure of a unified procedure, used experimental conditions should be rationalized either by the objective of the study or by field situations to be mimicked. These factors include [5,6]: elemental composition of used Fe⁰ materials, Fe⁰ pre-treatment (e.g., acid wash), Fe⁰ particle size (mm, μm, nm), buffer application, the molar ratio of Fe⁰ to contaminant (Fe⁰ mass loading and initial contaminant concentration), volume of the bottles used in the experiment, volume of model solution added, mixing operations (bubbling, shaking, stirring), geometry of the reaction vessel, experimental duration or reaction time.

The experimental conditions of Cheng et al. [1] clearly show that the set up is not appropriate to adequately achieve the goal of the study (Tab. 1). The molar ratios $\text{Fe}^0/4\text{-Chlorophenol}$ are too different for conventional Fe^0 (R_{20} and R_{40}) and synthesized nanosized Fe^0 (R_{50} and R_{100}) respectively. R-values for experiments with conventional Fe^0 clearly indicate high Fe^0 excess (750 to 3000) whereas in experiments with nanosized Fe^0 , Fe^0 excess were clearly lesser (7 to 14). This huge difference in the respective amount of conventional and nanosized Fe^0 is not justified by the authors and complicates an objective discussion of the results, since no experiment with stoichiometric Fe^0 amount was performed to serve as reference. An approach for a better interpretation of experimental results is presented below.

Another critical point of Cheng et al.^[1] work's is the used shaking intensity of 150 rpm. It is difficult to imagine which real world situation is mimicked by such a high shaking intensity. While mixing operations are generally considered as an important tool to facilitate the transport of contaminant to the Fe^0 surface, and therefore, speed up the reduction kinetics, their role in enhancing Fe^0 oxidation and hindering the formation of oxide film on Fe^0 is often ignored. Therefore mixing intensities above natural turbulences should be avoided.

In comparing the reactivity of Fe^0 materials for the removal of a given contaminant from aqueous solutions, two basic principles are available for the rationale selection of the masses to be used: (i) the reaction stoichiometry, and (ii) the Fe^0 specific surface area. Whereby, the Fe^0 specific surface area should be coupled to the reaction stoichiometry.

On the basis of the reaction stoichiometry, the used Fe^0 mass is ideally equal to the equivalent amount of contaminant to be removed. However, data from the synthetic chemistry have shown that an Fe^0 excess is always necessary. Because Fe^0 materials usually content $> 90\%$ Fe, the difference in the used masses should be minimal. This approach does not directly take into account obvious effects of particle size on the kinetics of Fe^0 oxidation (increased oxidation rate with decreasing particle size). However, by using stoichiometric amounts of Fe^0 (mm, μm and nm) the effects of particle size can be properly discussed. Cheng et al. [1]

have used various Fe⁰ excess for both material classes (Tab. 1). Because the variations for both material classes vary by two orders of magnitude (3000:15 = 200), the obtained results can not be properly discussed and have mostly a qualitative character. Clearly, if the authors have had used the same Fe⁰ excess for conventional and nanosized Fe⁰ (e.g factor 7 for conventional Fe⁰ or 100 mg in 150 mL), the reactivity comparison would have been eased.

The reactivity comparison on the basis of the available surface area (S) is based on the determination of the specific surface area (SSA in m²/g). Assuming a spherical particle, SSA can be calculated by the following equation:^[7]

$$SSA \cong S = \frac{\text{Surface Area}}{\text{Mass}} = \frac{\pi d^2}{\rho[(\pi/6)d^3]} = \frac{6}{\rho d} \quad (\text{Eq. 1})$$

Where ρ is the iron density. For two Fe⁰ materials of different particle diameter (d_1 , d_2), the surface area ratio can be deduced from Eq. 1 by the following equation:

$$\frac{S_1}{S_2} = \frac{d_2}{d_1} \quad (\text{Eq. 2})$$

Equation 2 suggests that, if the specific surface area of one material (S_1 or S_2) is known, then the used mass of the other material can be calculated from its SSA-value. The comparison on the SSA basis is the most rigorous approach as heterogeneous processes are surface controlled. However, the materials have to be hold in suspension to assure the direct availability of the total surface. For this purpose, the use of vigorous mixing operations (above natural turbulences) is operationally justified. Because Cheng et al. [1] ($d_2/d_1 \leq 2700$) have not reported any SSA-value, the appropriated amounts of individual Fe⁰ materials can not be further discussed here. Ideally, one should start with the mass of nanosized Fe⁰ yielding the monolayer Fe⁰ surface coverage. If the surface (cross section) of the contaminant molecule is not available, one should start with the mass of nanosized Fe⁰ yielding stoichiometric contaminant reduction and deduced the mass corresponding mass of

conventional Fe^0 . Then the masses can be increased in the same proportion depending on the observed removal goals.

The above remarks corroborate the necessity of a unified experimental procedure for the investigation of the processes of contaminant removal in Fe^0 - H_2O systems. A particular attention should be paid to the reaction stoichiometry (molar ratio Fe^0 /contaminant). Generally, the Fe^0 mass loading (ρ_m in g/L) is given and considered for example in the expression of k_{obs} to account for the available surface area [8]. But ρ_m alone is meaningless, even though Fe^0 is in large excess in the large majority of works [9,10].

In conclusion, when two (or more) Fe^0 materials to be employed in an investigation possess different surface areas, differences in surface area loading need to be accounted for in order to make accurate reactivity comparisons. For each Fe^0 material, the area loading (in m^2 surface/L) is found by multiplying the B.E.T. surface area (in m^2/g) times the employed mass loading (ρ_m in g/L). Clearly, comparisons have to be performed on the basis of surface area loadings as the surface area (particle size) is not the only reactivity determining factor.

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Table 1: Summary of the experimental conditions of Cheng et al. [1]. ZVI refers to the Fe⁰ material; m¹_{ZVI} is the mass of Fe⁰ material containing the equivalent amount of Fe⁰ for stoichiometric reduction of 4-Chlorophenol; m_{ZVI} is used amount of Fe⁰ material; The ratio m_{ZVI}/m¹_{ZVI} gives the excess factor (7 to 1500); ρ_m (g/L) is the Fe⁰ mass loading, R_i is the molar Fe⁰/contaminant ratio at i (mg/L) initial concentration. 4-Chlorophenol (4-CP): 128.6 g/mol.

4-Chlorophenol				Iron material (Fe ⁰)		
[4-CP] ₀	[4-CP] ₀	V	n	m ¹ _{ZVI}	m _{ZVI}	m _{ZVI} /m ¹ _{ZVI}
(mg/L)	mM	(L)	(mM)	(mg)	(mg)	(-)
20	0.156	0.15	0.0233	1.33	2000	1500
40	0.311	0.15	0.0467	2.66	2000	750
50	0.389	0.01	0.0039	0.22	3	14
80	0.622	0.01	0.0062	0.35	3	9
100	0.778	0.01	0.0078	0.44	3	7
common iron particles (conventional Fe ⁰)						
m _{ZVI}	m _{Fe0}	n _{Fe0}	ρ _m	n _{Fe0}	R ₂₀	R ₄₀
(g)	(g)	(mol)	(g/L)	(mM)		
2	1.96	0.035	13.3	35	1500	750
4	3.92	0.070	26.7	70	3001	1500
synthesized iron particles (nanosized Fe ⁰)						
m _{Fe0}	V	n _{Fe0}	ρ _m	n _{Fe0}	R ₅₀	R ₁₀₀
(g)	(L)	(mol)	(g/L)	(mM)		
0.003	0.01	0.000054	0.3	0.054	14	7