Letter to the Editor

Reply to comments on "Comparison of reductive dechlorination of *p*-chlorophenol using Fe^0 and nanosized Fe^0", by C. Noubactep

We published a paper about the comparison of reductive dechlorination of *p*-chlorophenol using Fe^0 and nanosized Fe^0 [1]. The comments by Dr. Noubactep considered that the set up of the experimental conditions is not appropriate to adequately achieve the goal of the study [2]. We have read the comments and considered that the comments are very useful and constructive for the further study in this field. We agreed with Dr. Noubactep's viewpoints. However, there are two issues should be discussed here in more detail. One is the molar ratios Fe^0/4-chlorophenol (4-CP), and the other is the shaking intensity used in the study. On the first issue, however, there was some misunderstanding regarding the *R*-values for the experiments. On the second issue, we did not fully agree with it.

The purpose of our experiments was to investigate and compare the dechlorination of 4-CP with conventional Fe^0 particles and nanosized Fe^0. To avoid the influence caused by the dosage of Fe^0, usually, high Fe^0 excess was applied in experimental study [3–5]. And we confirmed that the influence due to the dosage of Fe^0 was neglectable if only Fe^0 was excess. Dr. Noubactep proposed that *R*-values for the rationale selection of the masses should be used [2]. We agreed that *R*-values would be helpful for the systems with clear reaction stoichiometry. However, we think this was impractical for our experimental system because the reaction stoichiometry for our system was not clear yet. Researches on the degradation of organic contaminants by Fe^0 or nanosized Fe^0 have attracted broad attentions, the indubitable mechanism for pollutants degradation has not obtained. And the present presumption for mechanism referred to surface-mediated redox reactions between Fe^0 and chlorinated compounds, H_2 and chlorinated compounds, ferrous iron and chlorinated compounds and so on, which was really rather complicated [4–7]. Consequently, we cannot acquire an exact reaction stoichiometry for the system, so it is impossible to calculate the *R*-values.

When there are more than one chlorine atoms in the target compound, the reaction could be much more complex. Fig. 1 gives the hypothesized reaction pathways for the chlorinated ethylenes during reduction by Fe^0 [8]. It was more difficult for us to determine the reaction stoichiometry in this case. Therefore it was difficult to use *R*-values for computing the masses of iron.

As an alternative method, the same masses of Fe^0 were used in practical researches [9,10].

In addition, we should point out that there were some misunderstandings when Dr. Noubactep calculated the *R*-values for our experiments. As for conventional Fe^0, "The initial concentration of 4-CP was 20 and 40 mg/L, respectively. Metal to solution ratio was 2 and 4 g/150 mL, accordingly."[1], which indicated that we used 2 g of Fe^0 for solutions with the initial concentration of 20 mg/L, and 4 g for 40 mg/L solutions. So the *R*-values for experiments with conventional Fe^0 particles were 1500 consis-
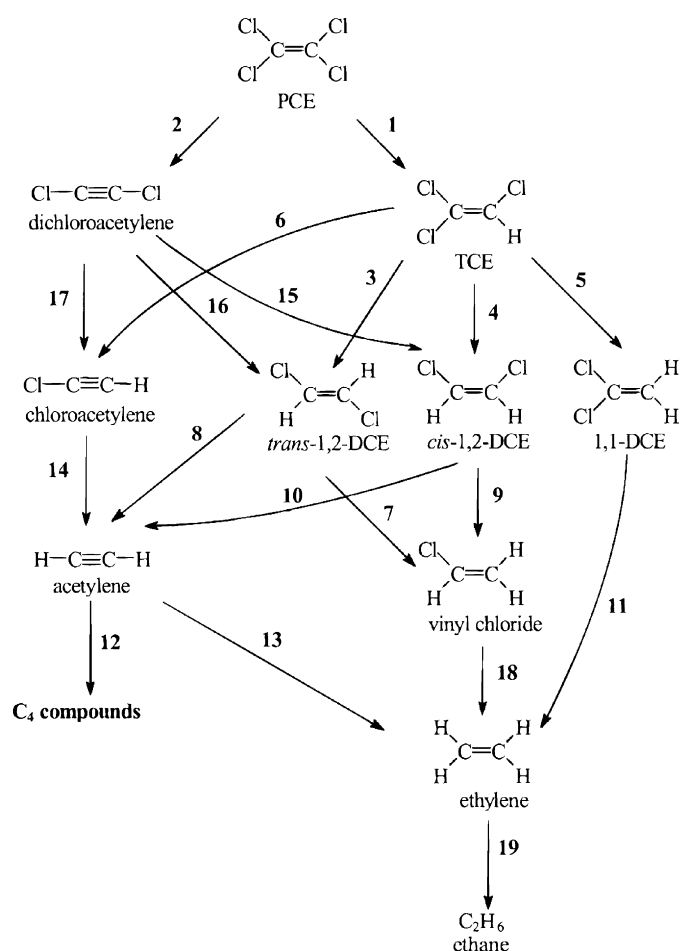

Fig. 1. Hypothesized reaction pathways for the chlorinated ethylenes and other intermediates during reduction by Fe^0.
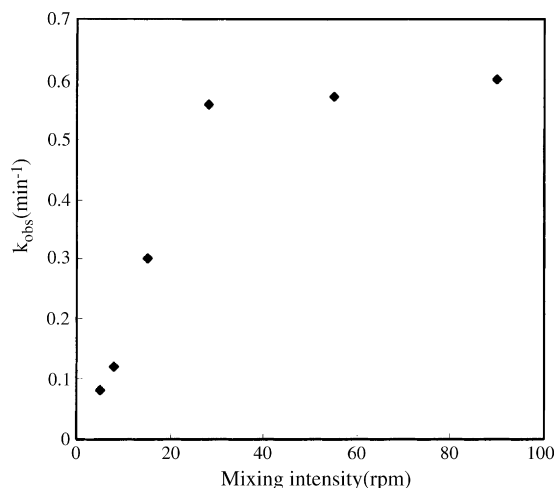
Fig. 2. The effect of mixing intensity on the observed pseudo-first-order rate constant k_{obs}.

tently. As for nanosized Fe^0, the initial concentrations of 4-CP were 20 and 50 mg/L for comparative experiments, respectively, therefore the R-values should be 14 and 35, accordingly. As for the solutions of 80 and 100 mg/L, they were set up for durability experiment but not for comparative study. So comparison of their R-values was meaningless.

The different R-values used for different materials were based upon the difference of reactivity of both materials. As Dr. Noubactep regarded, "The comparison on the basis of the available surface area (S) is based on the determination of the specific surface area (SSA in m^2/g)" [2]. The SSA of nanosized Fe^0 was about 35 m^2/g, while that of conventional Fe^0 was about 0.9 m^2/g according to the published references [10]. The difference of SSA for both material classes varied more than one order of magnitude (35/0.9). For this purpose, the variations for both material (1500/14) was reasonable.

As for the vigorous mixing operations, it was indeed impossible in real world. But we can use this high shaking intensity to avoid the influence due to mass transfer in experimental study, this is a common way when the researchers do such experiments. Moreover, Choe et al. [11] studied reductive denitrification by nanosized Fe^0, and found that the observed reaction rate constant exhibited a linear proportionality with the mixing intensity when it was lower than 40 rpm, as shown in Fig. 2.

It can be seen that the k_{obsb} remained almost constant when the mixing intensity was over 40 rpm [11]. To better achieve the purpose of study, we should avoid the influences due to var-

ious unidentified factors in experimental study. The set up of our experimental conditions could avoid the influence caused by some possible factors, and explain the experimental results reasonably.

Thanks so much for Dr. Noubactep's interest and his precious comments.

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