On the Validity of Specific Rate Constants ($k_{SA}$) in Fe$^0$/H$_2$O Systems

Noubactep C.

Angewandte Geologie, Universität Göttingen, Goldschmidtstraße 3, D - 37077 Göttingen, Germany.
e-mail: cnoubac@gwdg.de; Tel. +49 551 39 3191, Fax: +49 551 399379

Abstract

The validity of the specific reaction rate constants ($k_{SA}$) in modelling contaminant removal in Fe$^0$/H$_2$O systems is questioned. It is shown that the current $k_{SA}$-model does not consider the large reactive surface area provided by the in-situ formed oxide film, and thus the adsorptive interactions between contaminants and film materials. Furthermore, neither the dynamic nature of film formation nor the fact that Fe$^0$ surface is shielded by the film is considered. Suggestions are made how the $k_{SA}$-model could be further developed to possibly meet its original goal.

Keywords: Adsorption; Co-precipitation, Rate constants; Reduction; Zerovalent iron.

Introduction

Johnson et al. [1] performed an analysis of factors effecting the degradation rates of halogenated hydrocarbons by elemental iron (e.g. in Fe$^0$/H$_2$O systems) with the aim to enable direct comparisons between data from independent sources. Their results showed that first-order rate constants ($k_{obs}$) from both batch and column studies vary widely and without meaningful correlation. However, normalization of $k_{obs}$ to iron surface area concentration yields a specific rate constant ($k_{SA}$) that varies by only one order of magnitude for individual contaminants. Since then, $k_{SA}$ has been considered a practical descriptor of contaminant removal kinetics in Fe$^0$/H$_2$O systems [2-4]. The validity of the $k_{SA}$-model was not established as suggested by the repeatedly reported non-linear relationship between $k_{SA}$ and the Fe$^0$ loading [2,5]. This note discusses the validity of the $k_{SA}$-model on the light of recent reports on the mechanism of contaminant removal in Fe$^0$/H$_2$O systems [6,7].
The $k_{SA}$ model: Surface area-normalized kinetics

For the sake of clarity the $k_{SA}$ model proposed by Johnson et al. [1] is given. In removal experiments by Fe$^0$, the contaminant disappearance from the aqueous phase proceeds by kinetics that are first-order with respect to contaminant concentration. Therefore, first-order rate constants ($k_{obs}$) should be characteristic of a particular contaminant and set of conditions irrespective of contaminant concentration. Half-lives ($t_{1/2}$) derived from $k_{obs}$ values should offer similar advantages of generality. Thus, $k_{obs}$ and $t_{1/2}$ are used to characterise the kinetics of contaminant removal in Fe$^0$/H$_2$O systems. Unfortunately, $k_{obs}$ (or $t_{1/2}$) could not enable satisfactorily comparison of available data. Because the rate of contaminant reduction by Fe$^0$ appeared also to be first order with respect to the available reaction sites on Fe$^0$ (available surface area), Johnson et al. [1] introduced $k_{SA}$ as a more general descriptor of Fe$^0$ reactivity. Therefore, $k_{SA}$ has been reported to be more appropriate for remediation design calculations and other intersystem comparisons than $k_{obs}$ (or $t_{1/2}$). The relation between $k_{obs}$ and $k_{SA}$ is given as:

$$k_{obs} = k_{SA} \cdot \rho_a \text{ and } \rho_a = a_s \cdot \rho_m$$  

(1)

where $k_{SA}$ is the specific reaction rate constant (Lh$^{-1}$m$^{-2}$), $a_s$ is the specific surface area of Fe$^0$ (m$^2$g$^{-1}$), $\rho_m$ is the Fe$^0$ mass loading (gL$^{-1}$), $\rho_a$ is the surface area concentration of Fe$^0$ (m$^2$L$^{-1}$).

The $k_{SA}$-model intrinsically suggests that straight-line plots should be obtained from $k_{obs}$ versus $\rho_a$, $a_s$, or $\rho_m$ (Eq. 1). However, linear relationships of this sort have not been observed as a rule [1, 2, 5, 8], suggesting that the validity of the model should be closely discussed.

Discussion

While using the $k_{SA}$ model, researchers have faced several difficulties demonstrating that $k_{SA}$ might be a “strong but incomplete predictor of the reaction rate constants” [5]. The major reason for this situation has been identified as the interplay of different processes (e.g., adsorption, electron transfer from an Fe$^0$ surface, Fe$^0$ surface passivation). Although adsorption was enumerated among the reasons of failure of the $k_{SA}$ model, little was done to
correlate the relative affinities of individual contaminants to the iron corrosion products (oxide-film). The current discussion is based on the premise that contaminants are mostly reductively transformed by electrons from Fe$^0$ (direct reduction). However, the validity of this concept has been questioned [6,7]. The concept has been revisited and completed to a more accurate one (the adsorption/co-precipitation concept). The new concept stipulates that the fundamental contaminant removal mechanisms in Fe$^0$/H$_2$O systems are adsorption onto corrosion products and co-precipitation with corrosion products [6]. The major feature of the new concept relevant for the discussion in this note is that the Fe$^0$ is permanently covered by an oxide film. Therefore, for a contaminant molecule to reach the assumed reacting surface (e.g. Fe$^0$), it must migrate across a porous film of oxides. Moreover, contaminant can be retained in the film without reduction and redox reaction within the oxide film are partly stronger than those expected at the Fe$^0$ surface [6,7]. In other words a contaminant that has disappeared from the aqueous phase might be adsorbed onto or have co-precipitated within the oxide film on Fe$^0$. Additionally, contaminant might be reduced by H/H$_2$ or Fe$^{II}$ within the oxide film, more or less far from the Fe$^0$ surface. Irrespective from the nature of the oxide-film (porosity, thickness, electronic and ionic conductivity) the abundance of iron oxides as generated by mixing operations (i) diminishes the accessibility of the Fe$^0$ surface and (ii) competes with the Fe$^0$ surface for contaminant removal as will be illustrated below. The first operation to lower these interactions is two minimize the abundance of iron oxides by avoiding (i) too large Fe$^0$ mass loadings, and (ii) too large mixing intensities.

**Importance of iron corrosion products in Fe$^0$/H$_2$O systems**

In discussing the removal process of redox-sensitive contaminants by Fe$^0$, iron corrosion products have been considered as surface coatings on Fe$^0$, mostly influencing the transfer of electrons from the underlying reductant [9]. In some cases iron corrosion was successfully used as generator of iron oxides for contaminant removal [10-12]. Nevertheless, the concept
of contaminant reduction by Fe\(^0\) (direct reduction) persists in current literature. The importance of corrosion products in term of available surface area is illustrated here.

Let’s consider a removal experiment occurring in 20 mL of a model solution with 0.1 g of a Fe\(^0\) material (mass loading: 5 gL\(^{-1}\) – iron content: 92 %) having a specific surface area of 0.5 m\(^2\)g\(^{-1}\) (surface loading: 2.5 m\(^2\)L\(^{-1}\)). The average particle size of the Fe\(^0\) is 1.5 mm. The progression of the reaction can be recorded as the fraction of reacted Fe\(^0\). For example, when 50 % of the initial Fe\(^0\) has reacted, the average particle size of the Fe\(^0\) is 0.75 mm (one half of 1.5 mm). The surface of Fe\(^0\) at that time can be deduced using equation 3 derived from equation 2 [13]:

\[
S = \frac{6}{(\rho \times d)} \quad (2)
\]

\[
S_2/S_1 = d_1/d_2 \quad (3)
\]

Where \(\rho\) is the Fe\(^0\) density (7,800 kg/m\(^3\)) [13].

On the other hand while supposing for simplification that Fe\(_3\)O\(_4\) is the sole generated iron oxide, the evolution of the relative surface area of Fe\(^0\) and Fe\(_3\)O\(_4\) are compared in figure 1. For comparison the evolution of the surface area of an inert material (granular activated carbon - GAC) is presented.

Figure 1 shows the agreement of the theory that the Fe\(^0\) surface area increases with decreasing particle size [13]. The surface area of granular activated carbon remains constant through the whole experiment and the surface area of Fe\(_3\)O\(_4\), which is zero at the start of the experiments, increases linearly through the end of the experiment. Under the experimental conditions Fe\(_3\)O\(_4\) provides more surface area to contaminants than Fe\(^0\) when Fe\(^0\) consumption is higher than 15 %. Material consumptions larger than 50 % are not likely to occur in laboratory batch experiments. When further considering the facts, that (i) Fe\(_3\)O\(_4\) is a layer on Fe\(^0\) (physical barrier), and (ii) Fe\(_3\)O\(_4\) interacts with contaminants, it is rather surprising that only the surface of Fe\(^0\) has been considered in designing the \(k_{SA}\)-model.
In the reported simulations, the value of 5.6 m$^2$g$^{-1}$ for crystalline Fe$_3$O$_4$ reported by Farrell et al. [14] is used. However, crystalline Fe$_3$O$_4$ is generated by different steps from voluminous Fe(OH)$_2$ and Fe(OH)$_3$ through amorphous Fe$_3$O$_4$. In the course of these transformations (precipitation and recrystallization), contaminants are entrapped. This discussion considers neither the nature nor the concentration of the contaminant. The $k_{SA}$-model does not account for co-precipitated contaminants nor for contaminants adsorbed within the oxide film. This fraction has certainly disappeared from the aqueous solution and is considered reduced by the $k_{SA}$-model. Therefore, it is fair to say that the validity of the $k_{SA}$-model has not been examined by any scientific method.

**Factors Effecting $k_{SA}$**

Despite surface area normalization, about one order of magnitude variability in contaminant disappearance rates was observed by Johnson et al. [1] and could not be satisfactorily explained. According to the authors, some of the variability could be due to differences in available surface area (Fe$^0$ pre-treatment, Fe$^0$ grain size distribution). A more profound source of variability in $k_{SA}$ is believed to be due to the abundance of “non reactive” fraction at total surface area as measured by the BET technique. “Reactive surface” is operationally defined as the fraction of surface area, which contributes directly to contaminant reduction.

As discussed above, the Fe$^0$ surface is not directly accessible. Therefore, the kinetics of contaminant disappearance from the aqueous solution is directly related to the abundance of corrosion products in the system. That is from the intrinsic reactivity of used Fe$^0$ and the operational conditions, mainly initial pH (and buffer application), Fe$^0$ mass loading, Fe$^0$ particle sizes, mixing intensity. Since these parameters are interdependent the validity of the $k_{SA}$ model should have been verified by performing parallel experiments (i) with different contaminants and the same Fe$^0$ materials under various conditions and (ii) with one contaminant and different Fe$^0$ samples under various conditions. On the basis of results from such experiments, an accurate discussion on the validity of the $k_{SA}$ model could be conducted.
This ambitious task requires expertise beyond one or few research groups. Such an effort may provide the environmental science community with basic information for a non-site-specific iron wall design. Alternatively or complementarily, new routes are to be explored to better characterize the reactivity of Fe\(^0\)/H\(_2\)O systems.

Concluding Remarks

The validity of the \(k_{SA}\)-model is dependent, not only on the intrinsic Fe\(^0\) reactivity and Fe\(^0\) pre-treatment, but also on the operational experimental conditions (used Fe\(^0\) mass loading, mixing intensity, Fe\(^0\) particle size, initial pH value). Currently used experimental conditions are too different from each other for a purposeful comparison by means of the \(k_{SA}\)-model. The idea behind the \(k_{SA}\)-model is that there may be common underlying mechanisms for reactions in Fe\(^0\)/H\(_2\)O systems that provide a confidence for a non-site-specific permeable reactive barrier design [4]. This logical idea may be materialized by a modified model taking into account the dynamic nature of the formation of corrosion products and their action as physical barriers on Fe\(^0\). The first step to this ambitious goal may be a standard laboratory protocol that will enable direct comparisons of generated data and ease prospective works. More research is needed, more concerted research.

Acknowledgments

English corrections on the accepted draft manuscript by Christian Schardt are gratefully acknowledged. This work was supported by the Deutsche Forschungsgemeinschaft (DFG-No 626/2-2).

References


Figure 1: Relative evolution of the surface area provided by elemental iron (Fe$^0$) and its corrosion products (e.g. Fe$_3$O$_4$) in a batch system. Granular activated carbon (GAC) is presented as an inert material whose surface area remains constant during the whole experiment. Crystalline Fe$_3$O$_4$ is taken as the model corrosion product; its specific area (5.6 m$^2$ g$^{-1}$) is taken from Farrell et al. [14]. The lines are not fitted functions, they simply connected points to facilitate visualization.