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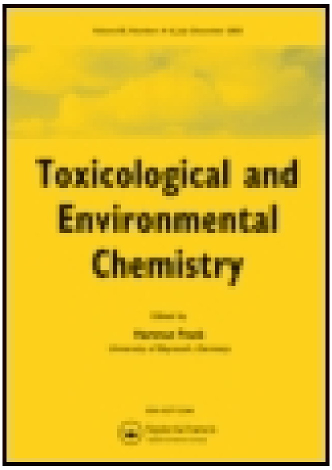

Toxicological & Environmental Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gtec20

Chemical decontamination of aniline by redox sensitive mineral surfaces part I: Kinetic Aspects

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Published online: 20 Sep 2008.

To cite this article: S. V. R. Weerasooriya, C. B. Dissanayake, K. W. V. Priyadharsanee, K. B. P. N. Jinadasa & S. S. Wickramasinghe (1993) Chemical decontamination of aniline by redox sensitive mineral surfaces part I: Kinetic Aspects, Toxicological & Environmental Chemistry, 38:1-2, 101-108, DOI: 10.1080/02772249309357880

To link to this article: http://dx.doi.org/10.1080/02772249309357880

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CHEMICAL DECONTAMINATION OF ANILINE BY REDOX SENSITIVE MINERAL SURFACES
PART I: KINETIC ASPECTS*

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(Received 10 July 1992)

Kinetic aspects of the degradation of aniline into various products has been investigated in aqueous suspensions of goethite in 0.001 M $NaNO_3$ over a range of laboratory conditions. A ligand promoted dissolution model was used to define the fate of aniline in a mineral surface mediated reaction system. At a given $[H^+]$ concentration the reaction rate was found to be dependent on both aniline and goethite concentrations.

KEY WORDS: Aniline decontamination, redox surfaces, kinetics, decontamination of chemicals

INTRODUCTION

The objective of this work was to determine the potential use of mineral surfaces in decontaminating toxic organic compounds from the aquatic environment. Several schemes are available to remediate organic compound contaminated aquifers; physical methods[1,2] such as air stripping and activated carbon adsorption have been used for above ground treatment of waste water. These methods merely transfer the contaminants from one environmental compartment to another, without destroying them. More recently biological oxidation[3] has been used to destroy organic compounds both above ground and in situ. Bio-restoration, however, is effective only when there are low concentrations of organic pollutants in the system.

Aniline and other amines may originate as environmental contaminants from the use of pesticides[4], chemical manufacturing residues[4,5], and from by-products of energy technology[4,6]. Aniline has recently been listed as a high priority compound in assessing the toxicological impacts of wastes generated by power generation plants.

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* A contribution from the IFS Environment Geochemistry Research Group.

We have, therefore, opted to use aniline as a model organic compound in obtaining background information essential for developing waste water decontamination methods.

MATERIALS AND METHODS

(a) *Materials*

The laboratory preparations of goethite were carried out as described by Atkinson *et al.*[7] previously. The specific surface area of 44.2 m^2/kg by the BET method and a pH_{zpc} of 7.00 by surface titration have also been reported.[7] The standard aniline and butanol used for gas chromatographic calibrations were from Aldrich, USA.

(b) *Methods*

All chemical reactions were conducted at 25°C at a background ionic strength level of 0.001 M $NaNO_3$ under N_2 atmosphere. The pH adjustments were done either with 0.1 M NaOH or 0.1 M HNO_3. In the time dependence study, 5 g/L goethite and 0.001 M aniline were mixed and the pH was adjusted approximately to 5.00. The reaction was well stirred throughout the experiment in a wrist action mechanical shaker. A 10.0 ml aliquot of suspension was withdrawn with an air tight syringe at predetermined time intervals. The solid particles were separated from the solution by centrifugation at 1000 rpm. A 1.00 ml filtered aliquot was used for total Fe determination by flame atomic absorption spectrophotometry (model Shimadzu GC9A). The rest of the sample was concentrated by solvent extraction to 2.5 ml of hexane. This portion was introduced into spitless type gas chromatographic analysis (model Shimadzu GC9A) for aniline and other products. Another set of experiments was conducted to determine the effect of H^+ on the reaction rate by preparing equimolar portions of aniline and goethite for a range of pH 4.00–9.50. The reaction rate dependence on either aniline or goethite concentration was determined by the method of isolation.[8]

RESULTS

Figure 1 illustrates a typical chromatogram of reaction products for reaction of goethite and aniline at pH 4.10. The peak corresponds to aniline eluted at 7.50 min retention time. We have also identified two other peaks at 10.0 min and 15.0 min. retention times respectively (see Figure 1). The mass spectroscopic structural confirmation of these products will be discussed in part two of this report.

Measurements of organic ligand with loss of time are presented in graph A of Figure 2 for a typical reaction system containing goethite and aniline under N_2 at pH 4.20. Rates of removal of aniline by goethite gradually decreases as the reaction proceeds, giving an apparent plateau after 30 minutes. (Surface coverage experiments

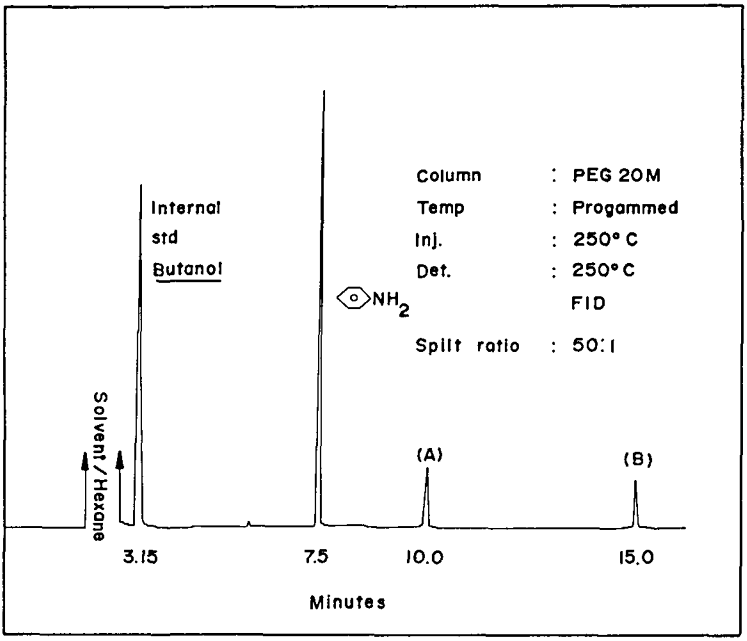

Figure 1 Chromotogram from gas chromatographic analysis of reaction products of aniline and goethite.

with aniline showed that it covers less than 8% of total available sites.) The initial rate of the reaction can be defined as the slope of the graph A at t = 0. Earlier methods of obtaining initial rates had been biased by overemphasizing the first few points[9]. We have attempted to correct this problem by selecting the individual data points so that most weight was given to the point at $t = 0$ and the least to the point at $t = 5.00$ s where reactant mixing may not be complete. The slope of the graph gave an initial rate of $1.80 \times 10^{-7}\ M^{-1}\ s^{-1}$. We have also monitored the Fe^{2+} concentration in same solutions as reaction proceeds. The graph B of figure 2 shows the variation of Fe^{2+} with time. The presence of Fe^{2+} in goethite suspension under anoxic condition signals dissolution of goethite with the consumption of aniline. (Control experiment results confirmed that the dissolution of goethite in the absence of aniline was negligible.) Graph A representing consumption of aniline vs. time appears as a mirror image of Graph B depicting the presence of Fe^{2+} concentration with time. The degree of the exactitude of these mirror images may decrease as the accuracy of the measuring instruments improve. The similarity of rates as measured either $[Fe^{2+}]$ or [aniline] has been attributed an equivalent stoichiometry in the reaction of goethite and aniline.

The pH of the medium showed a marked effect on the reaction of aniline with goethite. The initial reaction rate as obtained by increase of Fe^{2+} concentration has decreased with the increase of pH. The results of reaction rate vs pH are shown in Figure 3. Several factors[6,10] contribute to the observed pH dependence of the

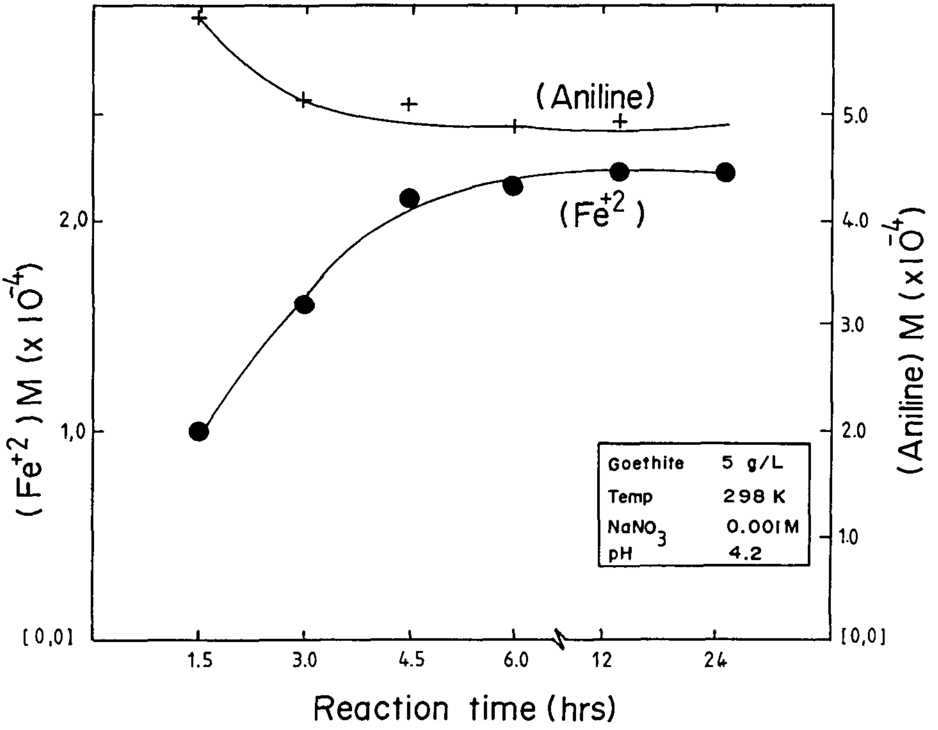

Figure 2 Concentration of soluble Fe (A) and aniline (B) as a function of time.

geothite/aniline reaction system. According to the assumptions of the triple layer surface complexation model of the solid-solution interfacial region[11], three types of surface species, namely -$FeOH_2$+, -FeOH and FeO_ have been suggested (The relative abundance of each species is dependent on bulk solution pH). When pH > pH_{zpc}, the mineral surface becomes positive increasing the relative abundance of $FeOH_2^+$ compared to FeO^-. Similarly, the mineral surface will be negatively charged when the reverse condition is true. Relative reaction rates of aniline at $FeOH_2^+$, FeOH and FeO^- surface species may differ substantially because of the charge of the leaving group. In the range of solution acidity under investigation, aniline should occur as an undissociated molecule. Thus the initial reaction rate has a high value at low pH due to the relative abundance of $FeOH_2^+$ as compared to FeO^-. The variation of reaction rate with pH is non linear. However, the reaction order with respect to surface sites and aniline concentrations in both instances showed a pseudo first order kinetics at constant pH (pH ~ 4.20). It is observed that the initial reaction rate increases with both aniline and available surface sites, and results are shown in Figure 4 only for aniline concentration at excessive goethite concentrations.

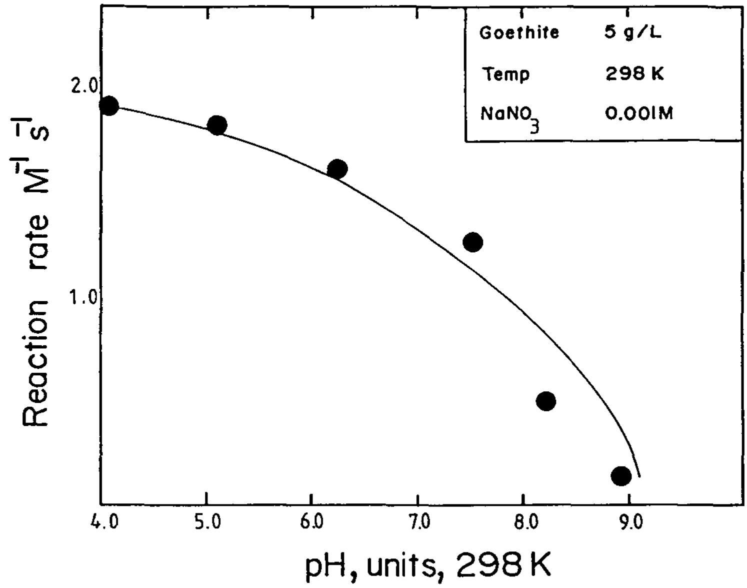

Figure 3 The variation of reaction rate as a function of pH.

DISCUSSION

Aniline can be chemically transformed into various by-products by dissolution of geothite in anoxic conditions. In order to promote this process, the organic molecule should transfer (at least) an electron to a reaction site in the mineral surface. This electron transfer step can only be initiated by forming a goethite–aniline surface complex. However, our preliminary results indicate that aniline is weakly bonded on goethite (less than 5% max.) over a pH range of 4.00–10.00. In a recent study, MacBride[12] has noted that this weak adsorption is sufficient to initiate the electron transfer step. In developing the mechanism for the removal of aniline by goethite, the following assumptions were made after critically considering the development procedures of the dissolution model of Stone and Morgan[13] to explain the reductive dissolution of phenol by manganese oxide. (1) adsorption (even weakly) of organic compound, (2) precursor complex formation (3) electron transfer step (4) release of oxidized organic compound (5) release of reduced metal ion from a reaction site. Furthermore Zutic and Stumm[14] reported that for amorphous oxides and anions with small molecule size like F^-, both diffusion and the surface reactions have to be considered in the rate limiting step. However, if a ligand has a molecular size larger than F^-, as in this case, the detachment step is more likely to be critical. Thus we have assumed that the surface mediated step(s) is rate limiting in the overall process and a kinetic model was suggested below.

$$>\mathrm{Fe(III)} + \phi\mathrm{NH_2} = [>\mathrm{Fe(III)}.\ \phi\mathrm{NH_2}] \tag{1}$$

$$[>\mathrm{Fe(III)},\ \phi\mathrm{NH_2}] = [>\mathrm{Fe(II)},\ \phi\mathrm{NH_2}] \tag{2}$$

$$>\mathrm{Fe(II)}\phi\mathrm{NH_2} = \mathrm{Fe(II)} + \phi\mathrm{NH_2} \tag{3}$$

$$>\mathrm{Fe(II)} = \mathrm{Fe(II)_{aq}} \tag{4}$$

$$\phi\mathrm{NH_2} = \text{products (structure to be confirmed)} \tag{5}$$

Where Fe is surface site and ONH_2 is aniline molecule. The k_i is the rate constant of "*i*th" reaction. Since the intermediate surface species are so reactive, it is customary to assume that reactions (2), (3) and (4) are essentially irreversible.

The mass balance equation for total Fe [Fe(III) and Fe(II)] in the reaction system is:

$$\mathrm{Fe_{total}} = [>\mathrm{Fe(III)}] + [>\mathrm{Fe}\phi\mathrm{NH_2}] + [>\mathrm{Fe(II)}\phi\mathrm{NH_2}] + >\mathrm{Fe(II)}] + [\mathrm{Fe(II)_{aq}} \tag{6}$$

Since $\mathrm{Fe_{total}}$ is constant, without loss of generality, by taking the first derivative of equation [5] with respect to time, and invoking pseudo steady state approximation (PSSA) for highly reactive species as $[>\mathrm{Fe(III)}\phi\mathrm{NH_2}]$ $[>\mathrm{Fe(II)}\phi\mathrm{NH_2}]$ and $[\mathrm{Fe(II)_{aq}}]$;

$$\text{viz } d/dt[>\mathrm{Fe(III)}\phi\mathrm{NH_2}] = d/dt[>\mathrm{Fe(II)}\phi\mathrm{NH_2}] = d/dt[>\mathrm{Fe(II)}] = 0.$$

We see that

$$d/dt[\mathrm{Fe(II)_{aq}}] = -d/dt[>\mathrm{Fe(III)}] \tag{7}$$

Thus we can assume that the rate of goethite dissolution is equal to the rate of $[\mathrm{Fe(II)_{aq}}]$ in solution. In order to obtain an overall rate expression for the reaction system, let us consider the following rate expressions for reactions (2), (3) and (4):

$$d/dt[\mathrm{Fe(II)_{aq}}] = -k_3[\mathrm{Fe(II)}] \tag{8}$$

$$d/dt[>\mathrm{Fe(II)}] = 0 = k_2[>\mathrm{Fe(II)}\phi\mathrm{NH_2}] - k_3[>\mathrm{Fe(II)}] \tag{9}$$

$$\begin{aligned} d/dt[>\mathrm{Fe}\phi\mathrm{NH_2}] = 0 = k_1[>\mathrm{Fe(III)}[\phi\mathrm{NH_2}] \\ - k_{-1}[>\mathrm{Fe(III)}\phi\mathrm{NH_2}] - k_2[>\mathrm{Fe(II)}\phi\mathrm{NH_2}] \end{aligned} \tag{10}$$

By solving equation (9) for [Fe(II)] and substituting it in equation (10) we can get an expression for $[>\mathrm{Fe(II)}\phi\mathrm{NH_2}]$ in terms of $[>\mathrm{Fe(III)}]$, $[\phi\mathrm{NH_2}]$ and

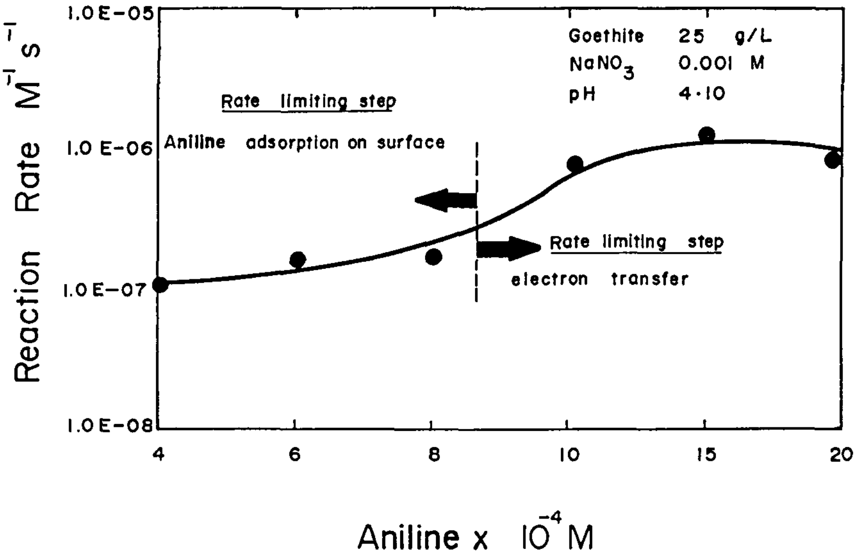

Figure 4 Variation of reaction rate as a function of aniline at pH 4.20.

$[>Fe(III)\phi NH_2]$. Again substituting in equation (8) the dissolution rate of goethite is given as in the analogous work of Stone[15]:

$$d/dt[Fe(II)_{aq}] = k_1k_2S_{total}[\phi NH_2]/\{k_1[\phi NH_2] + k_{-1} + k_2\} \qquad (11)$$

where S_{Total} is the total surface sites. At excessive concentration of geothite, the reaction rate shows a non linear relationship reaching an asymptotic approach to a maximum rate as the free aniline concentration becomes large (Figure 4). This condition can be interpreted by assuming $(k_{-1} + k_2) > k_1[\text{aniline}]$ in equation (11). In this case the adsorption of aniline on goethite is rate limiting[15]. Alternatively, if $(k_1[\text{aniline}]) > (k_2 + k_{-1})$ condition is true (at excessive concentrations of aniline), the pseudo dissolution rate is linear with respect to surface loading, yielding electron transfer step as rate limiting reaction in the overall system.

CONCLUSIONS

The chemical transformation reactions of aniline can be interpreted on the basis of the ligand promoted dissolution reaction model. The rate limiting step of the overall reaction process depends on aniline and goethite concentration at a given pH. The structural elucidation of the products for the reaction of aniline and goethite will be discussed in part II of this report.

Acknowledgements

It is our pleasure to thank Professor Cyril Ponnamperuma, the Science and Technology Advisor to HE the President of Sri Lanka for providing computational facilities, and Mr. D. G. A. Perera for going through the draft of this paper. Harshanee Aluvihare helped in drawing figures. This work was partially supported from the Third World Academy of Sciences, Italy (Grant No. RGBC 91013).

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