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USE OF MINERALS IN THE DEGRADATION OF ORGANIC POLLUTANTS FROM AQUATIC SYSTEMS

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ABSTRACT

This paper reports the potential use of mineral surfaces, particularly of iron oxides, as a starting material for the mineralization of chlorinated organic pollutants from aquatic systems. The overall mineralization rate of CCl_4 was optimal at pH 3 when goethite suspensions were utilized in the degradation process. The apparent coverage of the reactive surface sites by various contaminants has been attributed to the reduced reactivities of surface sites when pH exceeds 6.5. In order to enhance the mineralization rate of organic pollutants at environmentally significant acidity conditions, the reactive sites of goethite surfaces were first activated with a coating of Fe(II). The observed rate of mineralization of CCl_4 was increased by an order magnitude when the chemical reaction was conducted in the presence of Fe(II)-coated goethite with a pH range of 4 to 7.

1. INTRODUCTION

Chlorinated hydrocarbons, as a broad class, are at present subject to massive scrutiny by regulatory authorities throughout the world[1]. They are on the "BLACK LISTS" of all the International Conventions dealing with regulations concerning the discharge of wastes to the aquatic environment. Although there are many gaps in our current knowledge on control, fate and transport of these compounds, it is very clear that large quantities of chlorinated hydrocarbons are released to the environment, where they are rapidly dispersed into various environmental compartments. Over a period of time they could be concentrated in organisms to an extent which is hazardous.

Most of the currently available decontamination techniques such as air stripping or activated carbon adsorption, merely transfer the pollutants into another compartment without really destroying them. In contrast, bio-restoration and photo-degradation techniques have been recently introduced to destroy organic pollutants, both above ground and in-situ. However, these methods are more suitable when the organic pollutants are soluble in water and when they occur

only in minute concentrations. Research geared to developing methodologies that would help in the destruction of these toxic organic pollutants is, therefore, a pressing need in the global context.

The use of redox-sensitive mineral surfaces to degrade organic pollutants has received attention recently[2]. The rationale here is, to use redox-sensitive surface sites/ions in these minerals to trap organic pollutants thereby enhancing the transfer of electrons for mineralizing the pollutants, and changing them into relatively or totally harmless products. However, the hydrophobic nature of organic pollutants, particularly halogenated organic compounds, limits the efficient transfer of electrons into toxic molecules due to their immiscibility with water. Iron-rich mineral surfaces, particularly goethite provides an attractive alternative solution. This is largely due to the dual characteristics it exhibits in an aqueous phase: namely, hydrophobicity and hydrophilicity. Therefore, this mineral may act as a "micelle" by protruding into the hydrophobic organic pollutants in aqueous systems to facilitate the electron transfer process. It can therefore be inferred that the reaction between an organic pollutant and goethite is essentially a surface mediated process that should be addressed in detail for any systematic investigation conducted on the mineral/solution interface. In this paper, we report a methodology for the use of minerals that contain redox reaction centers for the mineralization of organic ligands in environmentally significant experimental conditions. Goethite was chosen as the mineral in this study because it was found to be a common mineral phase under iron reducing conditions. Moreover, the Fe(II)/ Fe(III) chemistry showed that this electron transfer occurs over the entire stability range of natural water[3][E = 0.5 to 1.1 V]. Hence, it is envisaged, under natural aquatic conditions, that all polyhalogenated hydrocarbons, nitroaromatic compounds and even aromatic azo compounds can in principle be reduced by a variety of Fe(II) species. However, in this investigation we have selected CCl_4 as a model organic compound. This was not only because of its significant environmental impact but also because it is a model compound for studying redox reactions potentially relevant to the environment. The ultimate aim of this project is to provide the essential first step for the development of rapid, low-cost methodologies to remediate polluted potable water resources from organic-Cl compounds.

2. MATERIALS AND METHODS

(a). Materials: Goethite was prepared in the laboratory following a slightly modified version of the procedure recommended by Atkinson et al[4]. Briefly, goethite was precipitated in alkaline conditions by mixing solutions of $FeNO_3$ and KOH. The solid was then washed repeatedly with CO_2-free double distilled water until it showed no pH change. Thereafter, the crystallographic structure of goethite was confirmed by electron micrography and X-ray diffractometry. The standard CCl_4 and butanol (internal standard) used for gas chromatographic calibrations were from M/S Sigma, USA.

(b). Methods: All chemical reactions were conducted at 25°C at a background electrolyte level of 0.1M $NaClO_4$ under N_2 atmosphere. The pH adjustments were done either with 0.1N NaOH or 0.1N $HClO_4$. In the time dependence study, 5 g/L of and 100 µM of CCl_4 was mixed and the pH of the solution was adjusted approximately either to 7.07 or 3.03. A 5 ml filtered aliquot of sample was withdrawn with an air tight syringe at predetermined time intervals. After separating the solid particles by centrifugation, a portion of samples was acidified for the determination of

Fe by atomic absorption spectrophotometry. The remaining filtered portion of the sample was concentrated by solvent extraction to 1 ml of hexane. This was introduced into splitless type gas chromatographic analysis for CCl_4 and other products. Another set of experiments was conducted to determine the effect of pH on the reaction rate by preparing equimolar portions of CCl_4 and goethite for the pH range 3 to 10. Adsorption studies of Fe(II) on to goethite at varying overlying solution characteristics (pH, ionic strength, and potential determining ions etc) was carried out to determine the effect of Fe(II) coating on to mineral surface for mineralization of organic pollutants. The experimental protocols of Fe(II) adsorption on to goethite at varying pH, background ionic strength levels, and potential determining ions is straightforward and has been documented elsewhere[5]. The essential physico-chemical parameters of goethite required for this study were obtained from previously published works[5,6].

3. RESULTS AND DISCUSSION

As shown in Figure 1, the initial experimental data indicated that the destruction of CCl_4(into relatively harmless products) had not occurred to a significant extent in the reaction system containing organic ligands in aqueous solutions of Fe(II) at two different acidity levels. *[The apparent fluctuations of the CCl_4 concentration in the aqueous phase can be largely attributed to the noise inherently associated with the detection system].* This observation indicates that the electron transfer needed for mineralization of the organic pollutant is a rather slow process when the reductant is in the aqueous phase. The basic thermodynamic calculations of the goethite - CCl_4 reaction system also support this notion. For example,Gibb's free energy of reaction in the goethite - CCl_4 system, showed that electron transfer is spontaneous[7](Gibb's free energy lies between kcal/ eqv. -13.37 and -8.99). Although negative values for Gibb's free energy were obtained for Fe(II) - CCl_4 system, the hydrophobic nature of the organic ligand prevents the electron transfer step. Hence, the reaction rate of the overall process should be significantly reduced. On par with these theoretical calculations, measurements of organic ligand with reaction time are presented in Figure 2 (graph A) for a typical reaction system containing goethite and CCl_4 under inert conditions at pH 3.5. When compared with the data given in Figure 1, the overall reaction rate was enhanced significantly, thus indicating the facilitation of the essential surface mediated electron transfer step. As shown in Figure 2, the overall rate of mineralization of CCl_4 by goethite gradually decreases as reaction proceeds, giving an apparent plateau after 60 minutes. The initial rate of the overall process was calculated from the slope of this graph at t = 0 yielding a value of 1.2 E-7 /Ms. According to our data, as measured by Fe(II) in solution, the dissolution of the goethite surface is enhanced significantly when CCl_4 is present in the reaction system *(blank experiments concluded that the dissolution of goethite in the absence of organic ligand is negligible).* Interestingly, the data representing consumption of CCl_4 vs time appear to show some resemblance to data showing the presence of Fe(II) concentration with time. The similarity of rates as measured either Fe(II) or CCl_4 can be attributed to an equivalent stoichiometry in the reaction of goethite and CCl_4. The pH of the reaction system exerts a significant influence on the rate of mineralization of CCl_4. As shown in Figure 2 the initial reaction rate decreased with the increase of acidity in the solution. Several factors contribute to the observed pH dependence of the CCl_4-

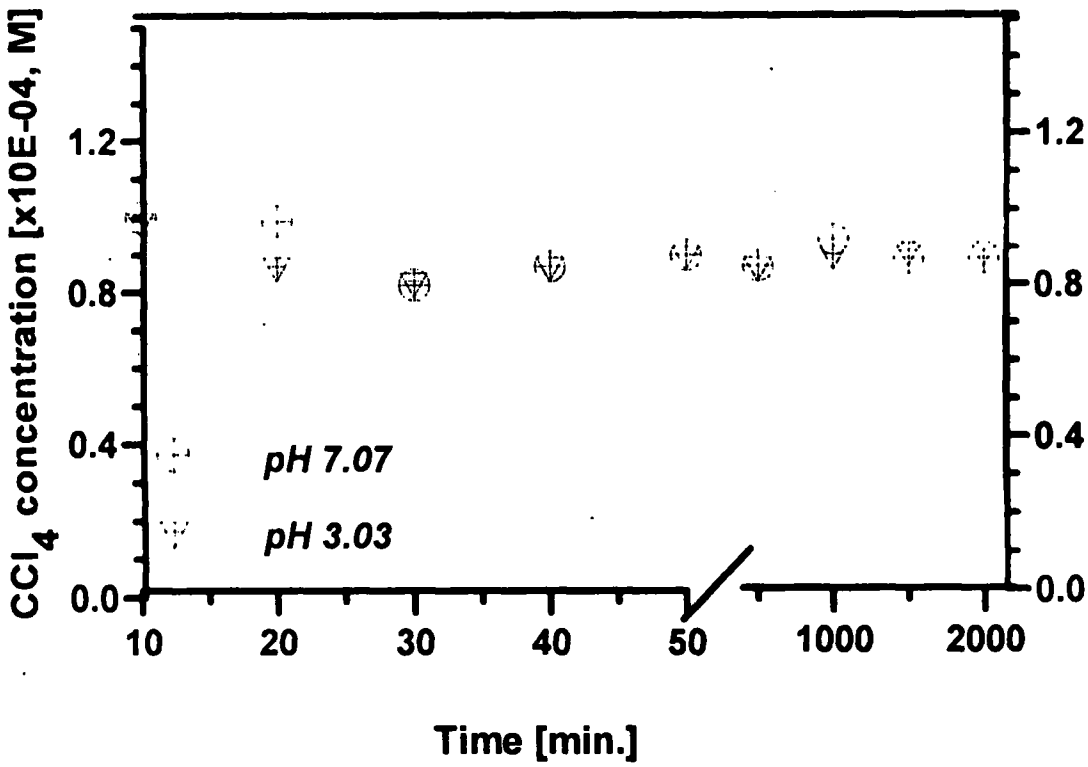

Fig. 1 Time dependent investigations of possible CCl_4 degradation by aqueous Fe[II] in 0.1M $NaClO_4$ at pH 7 and 3 respectively. The initial concentrations of Fe[II] is 100 µM. The reaction system was purged continuously with N_2 to avoid any contaminations from atmospheric gases

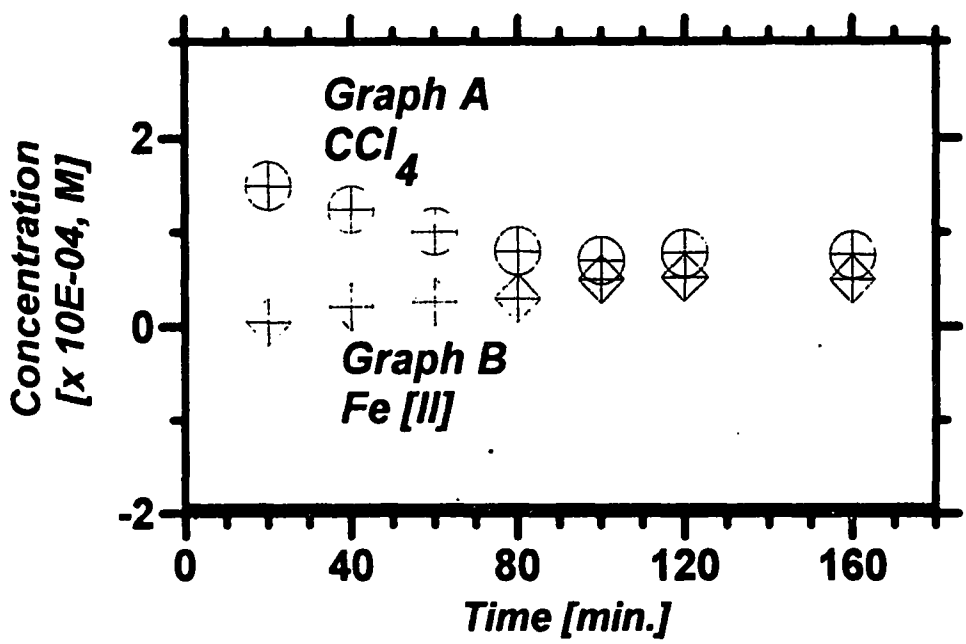

Fig. 2 Equilibrium concentrations of CCl_4 and Fe[II] of 5 g/L goethite suspensions in 0.1M $NaClO_4$. The initial solution pH was 3.3.

goethite reaction. According to the surface complexation theory[6], which assumes reactive surface sites as analogous to solution ligands. in the absence of complexations with background electrolytes, three types of surface species, namely $>FeOH_2^+$, >FeOH and $>FeO^-$ could be suggested. When the pH > pH_{zpc}, the surface sites in goethite are predominantly positive (i.e. abundant in >FeOH groups) Similarly, the reactive sites are charged negatively when solution pH < pH_{zpc}. Relative reaction rates of CCl_4 at >FeOH, $>FeO^-$ and $FeOH_2^+$ surface species may differ substantially because of the stability and positive or negative charge of leaving group. Hence, it is expected to produce an optimal reaction rate at pH < 4.50, perhaps due to the stability of H_2O as a leaving group and the reactivity of surface sites. As noted earlier[8], the contamination of surface sites by atmospheric gases is evident when pH > 5.00. For instance, the surface sites can be grossly contaminated with atmospheric CO_2 at these pH levels. As calculated by Henry's law[9], the concentration of carbonate species in solution open to atmospheric conditions is in the range of 100 - 1000 µM. It was also noted that at pH > 5.00, the concentration of carbonate species in equilibrium with the atmosphere rises by an order of magnitude for every unit of pH increase. Therefore, it is reasonable to assume that carbonate levels in waters are comparable to the concentrations of the major ions- Ca^{2+}, Na^+, Cl^-, Mg^{2+} and sulfates. Thus, most of the redox sites *[typically Fe(II)] on goethite surface may be assumed to be covered by these carbonate species [our recent X-ray photon spectroscopic (XPS) data[10] (not shown) on goethite-Cu(II) systems have shown that over 90% of surface sites are covered by carbonate species when the pH of the system is above 5].* In fact, this adventitious contamination of CO_2 was used as a reference state for the XPS investigations of non-conducting materials]. Hence, in order to increase the reactivity of surface sites, the goethite particles were coated with Fe(II) under anoxic conditions. In order to get optimal conditions for the Fe(II) coating, an adsorption experiment was conducted and the results are shown in Figure 3. As shown here, the Fe(II) adsorption on to goethite is strongly pH dependant and significant only at pH > 6.00. In other words, with increasing pH, goethite shows an increasing adsorption capacity for Fe(II), which is consistent with an adsorption mechanism involving inner-sphere complexes with deprotonated surface hydroxyls.

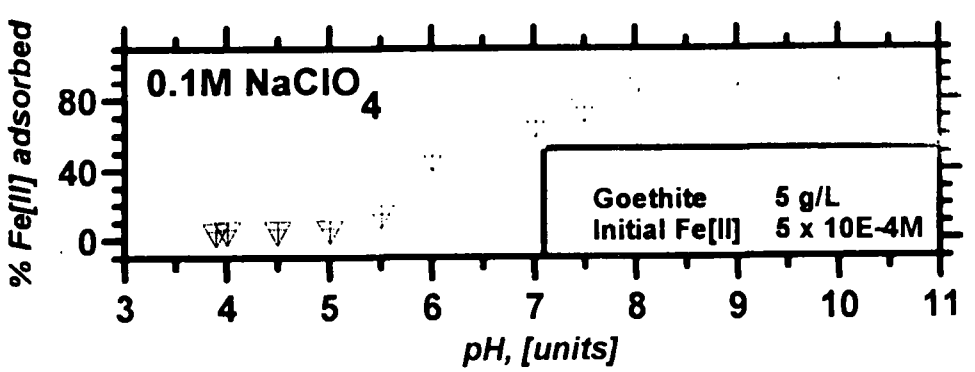

Fig. 3 Adsorption of Fe[II] on to goethite as a function of solution pH

Therefore, the Fe(II) coating on to goethite was carried out at pH > 6.5 taking special precautions to avoid atmospheric carbon dioxide contaminations. As shown in Figure 4, when the

CCl_4 mineralization experiments were repeated with Fe(II)-coated goethite the reaction rate was increased significantly. This observation indicates the availability of reaction sites with different activity in Fe(II)- coated goethite samples. *(However, it is important to note that these differences in reactivity cannot be attributed to the factors influencing the actual electron transfers).* Hence we postulated that with increasing involvement of less reactive sites, the generation of reactive sites by adsorption of Fe(II) becomes a more and more dominant factor in determining the overall mineralization rate of organic pollutants. A generalized mechanism for the mineralization of organic-Cl compounds in goethite mediated systems can be suggested as given in Figure 5.

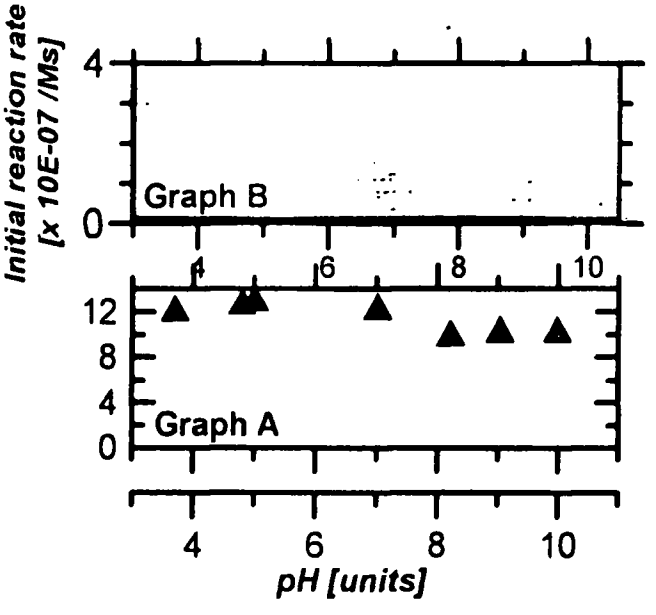

Fig. 4 Variation of initial reaction rates of CCl_4 degradation as a function of pH. Graph A: 5 g/L Fe[II] coated-goethite. Graph B: 5 g/L goethite

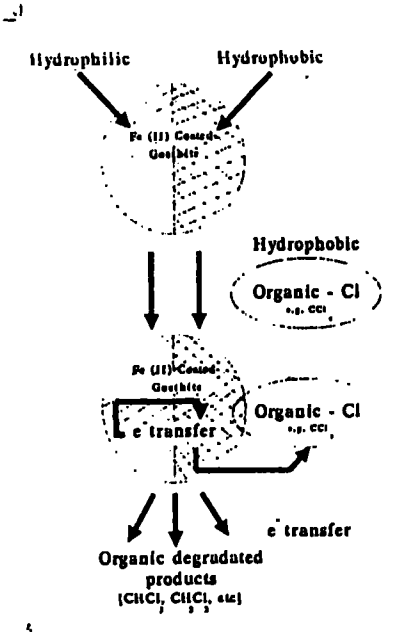

Fig.5 Postulated framework of mineral induced degradation of organic pollutants from aquatic systems

4. CONCLUSIONS

The preliminary data of this investigation clearly demonstrated that at a pH range of 5 to 7, the Fe(II)-coated goethite mineral surfaces were very reactive towards the degradation of organic-Cl pollutants. These observations will undoubtly provide the essential first step for the development of mineral-induced low cost, decontamination methodologies of polluted water laden with toxic organic compounds. This new approach towards the development of novel techniques to remediate polluted water supplies is in consonance with the recommendations for environmental conservation as made in the newly prepared National Environmental Action Plan of Sri Lanka[11].

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