Surface Mechanism of Molecular Recognition between Aminophenols and Iron Oxide Surfaces

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Evidence is presented for the surface mechanism of molecular recognition between 2-aminophenol and hematite in a process involving aminophenol −OH and $-NH_2$ groups. The aim of the present study was to correlate the adsorption of some aminophenols on hematite with the degradation features observed in the dark or in the light. The hydroxyl group in the ortho position was observed to be a preferred position for chelation compared to the meta or para positions. Chelation was detected by diffuse reflectance Fourier transform infrared spectroscopy (DRIFT). Both the $-NH_2$ and −OH groups participate in the adsorption of aminophenol onto hematite. The bridging bidentate formation during the adsorption of 2-aminophenol is supported by the simultaneous shifts of the vibrational frequencies of C═C from 1513 to 1501 cm^{-1} and from 1403 to 1395 cm^{-1}. The matching of atomic distances between Fe−Fe bonds in the α-Fe_2O_3 crystal and the N−O bond in 2-AP allows for the formation of the bridged bidentate structure. Evidence was found that adsorption enhances degradation in dark processes. The degradation of aminophenols in the dark produced long-lived intermediates that precluded further degradation. Acceleration of the degradation was observed during a photochemically induced charge-transfer process. Highly oxidative radicals generated only under light significantly increased the degradation efficiency of 2-AP and 4-AP. The degradation of 2-aminophenol on hematite proceeded more favorably than the degradations of 3- and 4-aminophenol because of the formation of a strong surface complex between 2-aminophenol and hematite that facilitates charge transfer to the oxide surface.

Introduction

Aminophenols are residuals found in fugitive emissions from phenolic resins, azo dyes, photographic-emulsions manufacturing, and petroleum refining.[1] The slow specific removal rate makes 2-aminophenol undegradable by acclimated mixed cultures within a time period beyond the required residence wastewaters in waste treatment stations.[1] Aminophenols have been reported to cause asthma, dermatitis, and damage to the blood hemoglobin. Pioneering work has been done on aminophenol adsorption and degradation on mineral surfaces by A. T. Stone and co-workers.[2] Photochemical methods and semiconductor-mediated processes have been employed to degrade persistent organic contaminants such as chlorophenols, common industrial wastes, and textile dyes in water.[3] Photocatalytic work has been reported on aminophenol degradation on TiO_2.[4] In the present work, α-Fe_2O_3 is investigated as a photocatalyst for the degradation of aminophenol. The objective is to study in detail the adsorption and degradation of aminophenol on hematite. Iron oxides are widespread in nature and are of significance in the processes taking place in ecosystems. Hematite has been investigated in photocatalytic processes such as the water splitting reaction by Kiwi and Gratzel.[5] The poor photocatalytic activity of iron oxide was attributed to the short diffusion length of the charges generated under light. Only small-sized nanoparticles of colloidal hematite were found to be photocatalytically active. The degradation of oxalic acid on iron oxide has been reported to be a rather inefficient process.[6] However, it has been suggested that surface complex formation between hematite and electron-donating groups leads to the degradation of organic compounds.[3,4]

Materials and Methods

Solutions were prepared from high-purity (p.a.) chemicals in tri-distilled water. The aminophenols were from Fluka (99%) and were used without further purification.

Preparation of Hematite. High-surface-area α-Fe_2O_3 (150 m^2/g) was prepared according to known procedures.[7] A flask with 0.002 M HCl (2 L) was preheated to 98°C, and 16.6 g of $Fe(NO_3)_3 \cdot 6H_2O$ was added. The resultant mixture was maintained at 98°C for 7 days. The particulate was centrifuged, washed with tri-distilled water several times, and dried. Commercially available α-Fe_2O_3 (150 m^2/g) was a gift from BASF, Ludwigshaven, Germany. The surface areas of the two iron oxides were determined using N_2 adsorption by the BET method, which gave surface areas close to 150 m^2/g. The measured point of zero charge (PZC) of α-Fe_2O_3 by electrophoeretic measurements was found to be 8.4−8.5.[10]

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Adsorption Isotherms. Hematite (1 g/L) was suspended in different concentrations of aminophenol, and the mixture was stirred in the dark at pH 6.5−7.0 at room temperature until equilibrium was attained. The initial pH was adjusted using HCl and NaOH. A large fraction of (more than 90%) of the aminophenol adsorbed instantly on the hematite surface. For this reason, during the thermal degradation measurements, 10 min was taken as the equilibrium time**.** The aminophenol concentration was varied from 1×10^{-5} to 1×10^{-3} M during most of the experimental runs reported in this study. The samples were centrifuged in a thermostatted centrifuge (Sorvall-RMC-20) at 25 °C. The concentration in the supernatant was measured by HPLC and subtracted from the initial concentration to determine the adsorbed amount of aminophenol. FTIR analysis of samples of the aminophenol equilibrated for 10 min and for 1−2 min on the hematite surface showed almost the same adsorption. This provides evidence that the thermally degraded aminophenol can be neglected when the amounts of aminophenol adsorbed are compared. Commercially available hematite samples and samples prepared in our laboratory (see above) were used for the present study.

High-pressure liquid chromatography (HPLC) measurements were performed with a Varian 5500 unit using a gradient eluent consisting of ammonium acetate buffer (100 mM/L) and methanol in percentages of 100:1 at 0 min, 30:70 at 17 min, 70:30 at 23 min, and 100:0 at 30 min. This gradient was used in conjunction with a reverse-phase column (Spherisorb 5 ODS-2). The signals were observed at $\lambda = 281$ nm. The flow rate was 1.0 mL/min.

The CO_2 analysis was carried out in a reaction vessel provided with an inert septum. Photogenerated CO_2 in the reaction flask was monitored by a gas chromatograph (Shimadzu) provided with a Poropaq Q column and using Ar as the carrier gas. The total organic carbon (TOC) was monitored via a Shimadzu 500 instrument equipped with an ASI-502 automatic injector.

FTIR Analysis. Diffuse reflectance infrared Fourier transform (DRIFT) measurements were recorded on a Bruker IFS 55 FTIR spectrophotometer equipped with a MCT detector and a reflection attachment. The iron oxide samples after adsorption of aminophenol were filtered, dried in air, and ground with analytical-grade KBr in a ratio of 1:5. The spectra were averaged over the same number of scans (200 scans). The reflection accessory used was from Harrick Scientific Co. The quantitative aspects of spectral evaluation rely on the assumption that the aminophenol concentration on the iron oxide surface is directly proportional to the normalized Kubelka−Munk function.

Irradiation Procedures. Iron oxide (60 mg) was suspended in a 40 mL solution of aminophenol in a 60-mL Pyrex reactor. The irradiations were performed using a Suntest Solar Simulator (Hanau Suntest lamp) with a lamp intensity of 90 mW/cm^2 under atmospheric conditions. Control experiments for the degradation of aminophenol on iron oxides were also conducted in the absence of light.

Toxicology. The toxicity of the solution during degradation was followed using the standard Microtox technique. The decrease in bioluminiscence of *Photobacterium phosphoreum* in the presence of 2,4-DCP was followed as a function of irradiation time. The test employed here uses the bacteria's property of emitting light and attenuating the emission with increasing concentration of the substrate used.

Results and Discussions

A. Adsorption of Aminophenol on Hematite. The adsorption of aminophenols as a function of solution pH is shown in Figure 1. An aminophenol concentration of 5×10^{-3} M was used for each pH selected during this study. The aminophenol adsorbed was found from the difference between the initial aminophenol concentration and the concentration found in the solution after equilibrium. When the pH was increased toward more basic values, the adsorption of aminophenol was observed to reach a maximum at pH 6−7. With further increases in pH, the adsorbed amount decreased. The absorption results show

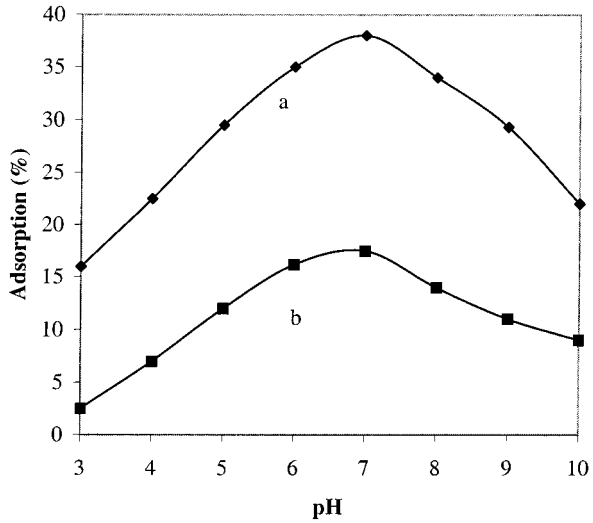

Figure 1. Variation of adsorption of (a) 2-AP and (b) 4-AP (5.0×10^{-3} M) on α-Fe_2O_3 (2 g/L) as a function of pH.

that, at very high and low pH values, only a small amount of aminophenol was adsorbed on the iron oxide surface. To understand the interaction of aminophenol on hematite, the possible reactions between the available chemical species involved in the adsorption are shown in eqs 1−7.

$$H_2L^+ + {>}FeOH \rightarrow {>}FeL + H_2O + H^+ \quad (1)$$

$$H_2L^+ + {>}FeO^- \rightarrow {>}FeL + H_2O \quad (2)$$

$$HL + {>}FeOH_2^+ \rightarrow {>}FeL + H_2O + H^+ \quad (3)$$

$$HL + {>}FeOH \rightarrow {>}FeL + H_2O \quad (4)$$

$$HL + {>}FeO^- \rightarrow {>}FeL + HO^- \quad (5)$$

$$L^- + {>}FeOH_2^+ \rightarrow {>}FeL + H_2O \quad (6)$$

$$L^- + {>}FeOH \rightarrow {>}FeL + HO^- \quad (7)$$

The chemical speciation of each 2-aminophenol (2-AP from now on) in solution and hematite was calculated as a function of pH. These results are presented in Figure 2a,b. The pK_{a1} and pK_{a2} values of 2-aminophenol are 4.7 and 9.9, respectively,[8] whereas the pK_1 and pK_2 values of hematite are 6.7 and 10.4, respectively.[9,10] From Figure 2a and b, it is seen that cationic 2-AP (H_2L^+), neutral 2-AP (HL), and anionic 2-AP (L^-) exist in solution, but there is no pH at which the three species coexist in reasonable amounts. Positively charged (>$FeOH_2^+$), neutral (>FeOH), and negatively charged (>FeO^-) surface species are present on the hematite surface. Figure 1 shows that 2-aminophenol adsorption is highest at a pH of ~7.0. The amounts of negatively charged anion (L^-) and positively charged cation (H_2L^+) are negligible at pH 7.0, as seen in Figure 2. Therefore, reactions 1, 2, 6, and 7 can be neglected because the chemical species participating in these reactions are available only at high or low pH values. By analyzing the species distributions of 2-aminophenol (Figure 2a) and iron oxide (Figure 2b) at pH 7.0, where the adsorption of 2-aminophenol is at a maximum, the amounts of neutral 2-AP (HL) and hematite surface species (>FeOH) are also found to have maximum values. From the species distributions in Figure 2, HL and >FeOH decrease or increase with decreasing or increasing pH, respectively. This coincides with the adsorption behavior

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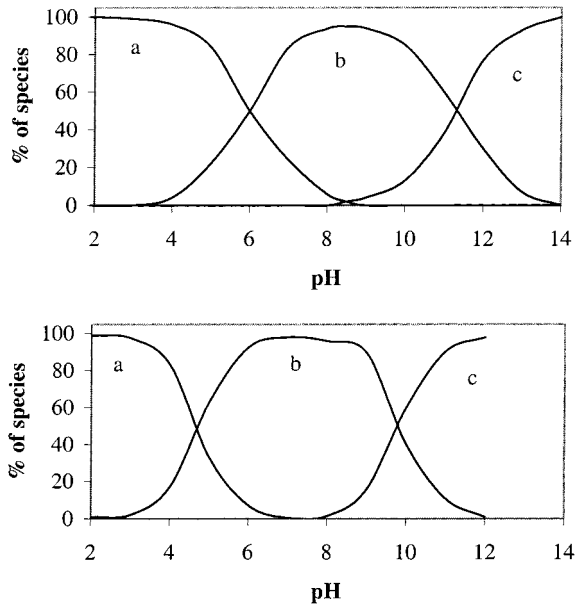

Figure 2. (a) Distribution of the surface species for α-Fe_2O_3 as a function of solution pH: (a) $>FeOH^+_2$, (b) $>FeOH$, (c) $>FeO^-$. (b) Distribution of the 2-AP species in solution as a function of pH: (a) H_2L, (b) HL, (c) L^-.

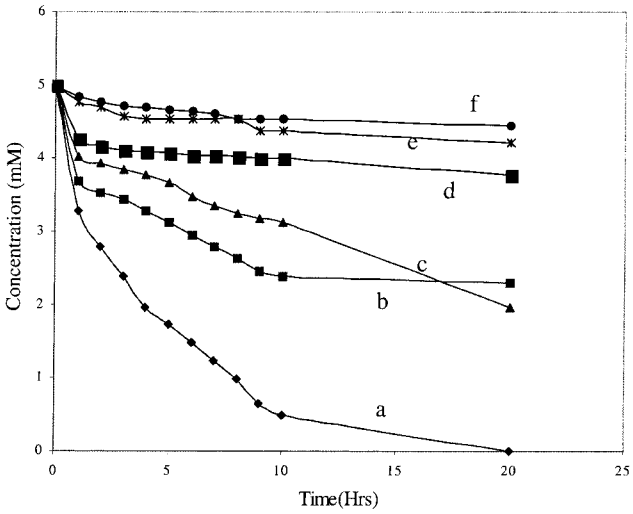

Figure 3. Aminophenol disappearance under light and dark conditions in the presence of α-Fe_2O_3: (a) 2-AP/light, (b) 2-AP/dark, (c) 4-AP/light, (d) 4-AP/dark, (e)3-AP/light, (f) 3-AP/dark.

of 2-AP on the iron oxide surface. Therefore, from reactions 3−5, it is reasonable to assume that reaction 4 leads to hematite−aminophenol surface complex formation via ligand exchange. If reaction 4 leads to the formation of the complex involved in adsorption, then the pH of the solution should not vary during the adsorption process, as there should be no H^+ concentration changes. The measurement of changes in the pH values was attempted without success, which could be due to the side reactions of aminophenol. The adsorption behavior of 4-aminophenol (4-AP) was found to be similar to that of 2-AP, but the amount adsorbed in the first case was quite low. 3-AP does not adsorb on the iron oxide surface. The −OH groups in 2-AP and 4-AP are possibly stabilized to a greater extent because of the ortho and para NH_2 groups, respectively, as compared to the NH_2 group in the meta position in 3-AP. This latter species is known to have a less-electrophilic character.

Figure 3 shows the dark- and light-induced degradations of 2-, 3-, and 4-AP on hematite. This figure indicates that aminophenols degrade in both the dark and the light when adsorbed on hematite. Adsorption experiments were carried out using 1.5 g/L iron oxide and 1×10^{-3} M aminophenol concentrations under atmospheric conditions. Two hematite samples of different origins were used (see materials and Methods), and the degradation results reported in Figure 3 were within experimental error. Of the three aminophenols studied, 3-AP is readily seen to degrade less efficiently in the dark or light, followed by 4-AP and 2-AP. The more inefficient degradation of 3-AP on iron oxide can be understood in terms of adsorption. 3-AP adsorbs poorly on the hematite surface, as mentioned before, and therefore, the surface reaction between iron oxide and 3-AP seems not to be favored. 2-AP degrades more efficiently on hematite than 4-AP, as seen from Figure 3.

The thermal (dark) degradation rate ($\sim 2.6 \times 10^{-4}$ mol L^{-1}/h per gram of catalyst) was found to vary linearly with the quantity of hematite in solution, and hence the surface of the hematite in suspension, which supports the idea that surface adsorption enhances the observed degradation. However, in the case of the light-induced reaction the degradation rate was observed to not vary linearly with the amount of hematite because of the inner filter effect of the hematite suspension on the incident light.

The aminophenol degradation rates were measured by monitoring the concentration changes of the aminophenols at regular intervals using liquid chromatography (HPLC) with signals monitored at $\lambda = 281$ nm. It was found that the change in concentration during the initial stages differs from that during the final reaction stages. This is not due to a different degradation mechanism. As degradation reaction progresses, the formation of intermediate products increases competition for the hematite adsorption sites with the initial aminophenol. Not all of the intermediates produced during the degradation could be identified. The aim of the present study was to correlate the adsorption of the aminophenols with the kinetics and efficiency of the ensuing degradation. HPLC determination of the 2-AP degradation intermediates mediated by hematite has previously been reported by our laboratory.[15] The final degradation rates were 4.80×10^{-4} and 1.71×10^{-4} mol L^{-1}/h for 2-AP and 4-AP, respectively. The light-induced degradation rates of both 2-AP and 4-AP were observed to be higher than the rates observed in the dark. The degradation of 2-AP under light irradiation was faster than that of 4-AP (Figure 3). The different adsorptions of 2-AP and 4-AP on the hematite surface give rise to a variation in the degradation kinetics for these two species, as will be discussed below. The initial degradation rates under illuminated conditions are 1.72×10^{-3} and 0.98×10^{-3} mol L^{-1}/h, respectively, for 2-AP and 4-AP.

Figure 4 shows that the total organic carbon (TOC) reduction is more efficient in the light than in the dark for 2-AP and 4-AP but that the initial rates of TOC decrease under light and dark conditions are small. The HPLC results shown in Figure 3 indicate a similar initial degradation pattern due to the initial aromatic ring degradation of aminophenol. These results provide evidence that the initial degradation includes both dark-induced and photochemically induced reactions. Only a fraction of the aminophenol degraded was found to undergo total mineralization during the initial stages of reaction (40−45%). The rest is possibly due to long-lived intermediates consisting of highly branched aliphatic compounds, which are not susceptible to dark degradation. The traces showing the reaction under light suggests that

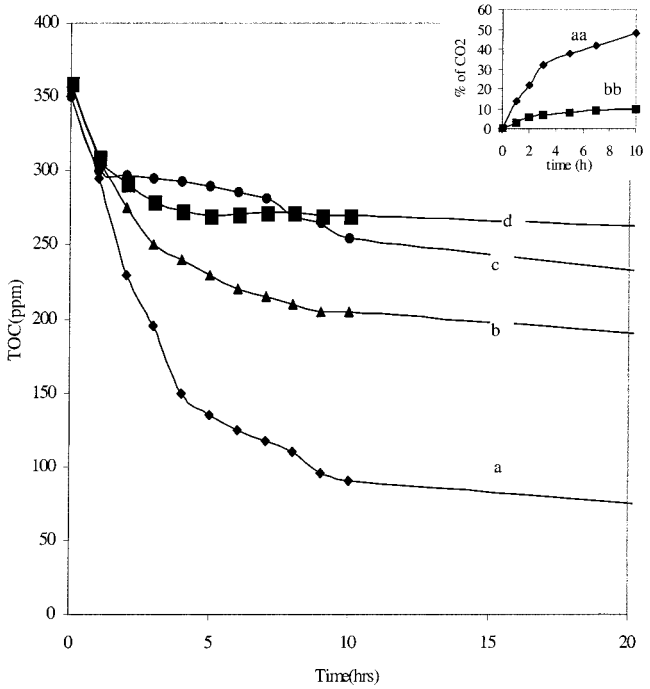

Figure 4. Total organic carbon (TOC) as a function of reaction time for aminophenol on α-Fe_2O_3: (a) 2-AP/light, (b) 2-AP/dark, (c) 4-AP/light, (d) 4-AP/dark. The inset shows the CO_2 evolution for (aa) 2-AP/light and (bb) 4-AP/light.

highly oxidative radicals generated only under light irradiation were able to contribute effectively to the degradation of 2-AP and 4-AP. In either case, it was observed that more than 75% of the initial TOC decreased in less than 5 h. The inset of Figure 4 shows the CO_2 analyses of 2-AP and 4-AP under air-saturated conditions on the iron oxide surface. Figure 4 shows that the initial CO_2 formation rates of 8.3×10^{-1} mL/h for 2-AP and 1.82×10^{-1} mL/h for 4-AP are higher than the final rates of 3.74×10^{-1} mL/h (2-AP) and 7.8×10^{-2} mL/ h (4-AP).

B. Toxicology Study during the Degradation of 2-AP and 4-AP. The toxicities of the intermediates observed during the photodegradation were analyzed by way of the Microtox test. The results are shown in Figure 5. As expected, the intermediate products are found to be less toxic than the initial compound, and the toxicity of the initial compound decreases with reaction time. These intermediates have previously been identified by HPLC methods,[15] as reported in the case of 2-AP in the Appendix of ref 1. Aminophenols are toxic even in small amounts of 5−10 ppm.[10] Figure 3 shows that, after 15 h of irradiation, a small amount of aminophenol is still present. The persistent toxicity after 15 h of pretreatment suggests the residual existence of 2-AP in solution.

C. Analysis of Adsorption and Degradation Mechanism by DRIFT Results. Figure 6 shows the diffuse reflectance infrared Fourier transmittance (DRIFT) spectra of 2-AP on the iron oxide surface at pH's of 5, 6.5, and 8.5, along with the results for unadsorbed 2-AP. The spectra were taken after adsorption of 2-AP in the dark and were refined by subtracting the untreated oxide spectrum, which eliminates the bands due to the oxide background. As shown in Figure 6, the variation in peak intensity with solution pH is minimal. This result indicates that 2-AP adsorbs on hematite over a wide pH range (5−9), as already observed in Figure 1. The spectrum of free

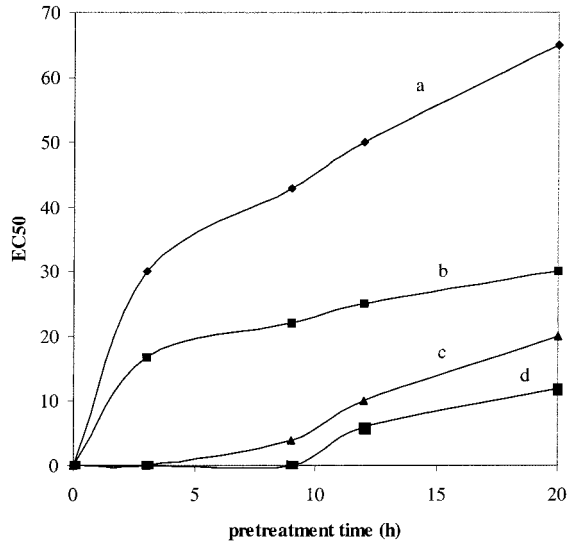

Figure 5. Toxicity variation as a function of pretreatment time for aminophenol on α-Fe_2O_3: (a) 2-AP/light, (b) 2-AP/dark, (c) 4-AP/light, (d) 4-AP/dark.

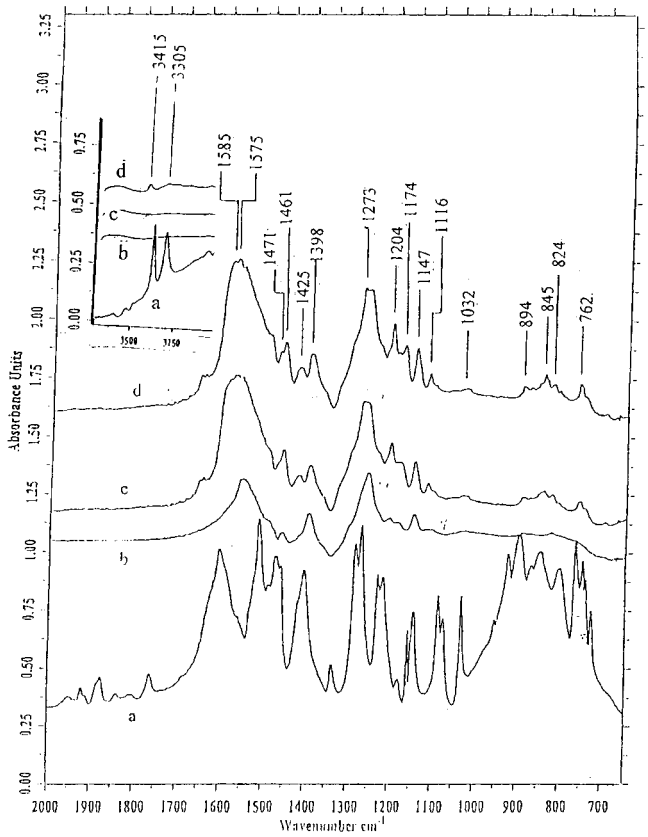

Figure 6. FTIR spectra of 2-AP adsorbed on α-Fe_2O_3 surface as a function of solution pH: (a) free 2-AP, (b) pH 5.0, (c) pH 6.5, (d) pH 8.5.

2-AP has been shown to consist of two bands[11,12] at 3587 and 3305 cm^{-1}. These bands represent the asymmetric and symmetric N−H stretching vibrations of the two hydrogen of the $-NH_2$ group of 2-AP. The N−H bending (scissoring) peak appears at 1617 cm^{-1}, and the N−H

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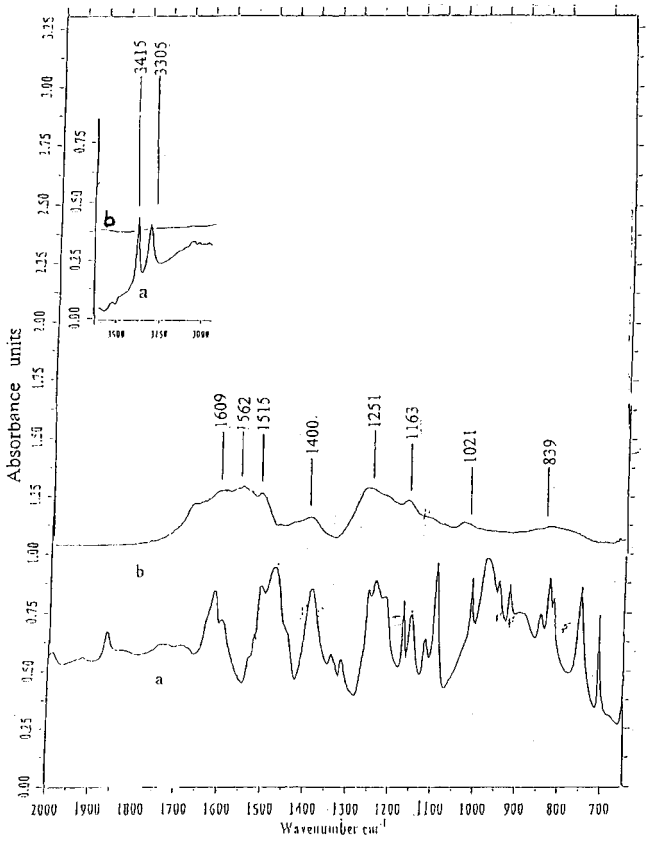

Figure 7. FTIR spectra of 4-AP adsorbed on α-Fe_2O_3 surface: (a) free 4-AP, (b) pH 8.5.

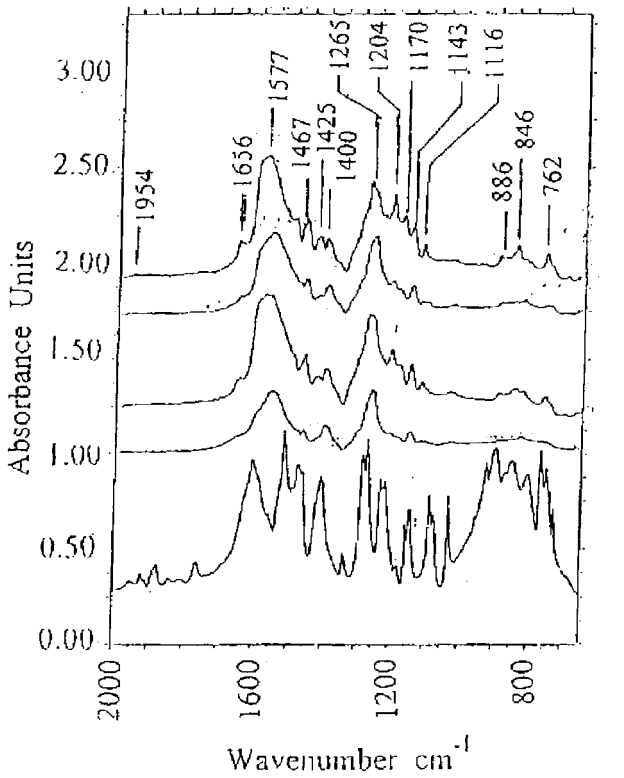

Figure 8. FTIR spectra of adsorbed 2-AP on α-Fe_2O_3 as a function irradiation time (a) free 2-AP, (b) 1 h, (c) 4 h, (d) 8 h, (e) 20 h.

bending peaks appears in the region 650−900 cm^{-1}. The band at 1290 cm^{-1} is due to the aromatic C−N stretching vibration, while the band at 1345 cm^{-1} involves −OH bending. The relatively broad band at 1273 cm^{-1} is due to the C−O stretching vibration. The bands at 1513 and 1403 cm^{-1} are assigned to the aromatic ring C═C stretching vibrations.

The adsorbed spectra of 2-AP at pH 5, 6.5, and 8.5 are given in Figure 6b−d, respectively. The analyses of these spectra indicate that the adsorption mechanism of 2-AP does not vary in the pH 5−9 region. The following peaks were missing after adsorption of 2-AP on iron oxide surface: the N−H asymmetric band at 3587 cm^{-1}, the N−H symmetric band at 3305 cm^{-1}, and the O−H bending peak at 1345 cm^{-1}. The lack of these bands indicates that both the NH_2 and OH groups of 2-AP participate in the adsorption of aminophenol on hematite. The formation of inner-sphere bonding at the initial adsorption stage was further substantiated by the shift in the IR band positions of 2-AP. The shifts in the C═C vibrational frequencies from 1513 and 1403 cm^{-1} to 1501 and 1395 cm^{-1}, respectively, are attributed to the change in the electron distribution and symmetry of the ring during the formation of a complex between 2-AP and the hematite surface. Both the nitrogen and oxygen groups of aminophenol have been reported to be able to participate in bridged bidentate or chelate bidentate complexation with hematite.[11,12] Considering the atomic distances in the α-Fe_2O_3 crystal and the N and O groups of 2-AP, an adsorption mechanism can be suggested. In the α-Fe_2O_3 crystal, the known Fe−Fe atomic distances are, for the face-shared arrangement, 2.89 Å; for the edge-shared octahedra, 2.97 Å; and for the corner-shared octahedra, 3.39 Å. The atomic distances were calculated using CAChe software using semiempirical methods to optimize the molecular geometry.[14] In free 2-AP, the distance between the N and O atoms is 2.83 Å. The matching of atomic distances between pairs of Fe atoms in the α-Fe_2O_3 crystal and the N and O atoms of 2-AP allows for the formation of a bridging bidentate bond.[13] Further, the bridging bidentate formation is supported by the shifts of the vibrational frequencies of C═C from 1513 to 1501 cm^{-1} and from 1403 to 1395 cm^{-1}. As the vibrational shifts are extremely small, the formation of a chelate bidentate complex can be excluded. If a bidentate chelate were indeed formed, then a more strained surface species would appear, involving more significant vibrational shifts than observed in the present case.

The IR spectrum of 4-AP on the hematite surface is shown in Figure 7. As shown earlier, 4-AP adsorbs poorly on hematite, and the IR spectrum confirms the weak adsorption of 4-AP. The presence of broad and less intense peaks makes the assignment for the experimental peaks difficult. 3-AP does not adsorb on iron oxide, and hence, its IR spectrum is not shown.

Figure 8 shows the temporal change of the IR pattern of 2-AP adsorbed on α-Fe_2O_3 under light irradiation. The IR patterns of the dark and light experiments were the same, but the intensities of the peaks differs. This indicates that the same intermediate products are formed under light and dark conditions. In the case of 4-AP under light, the observed IR spectrum changed with time. In the dark, little change was observed, which is consistent with the poor 4-AP degradation under these conditions because of its low adsorption on hematite.

(13) Nakatsuji, H.; Yoshimota, M.; Umemura, Y.; Takagi, S.; Hada, M. *J. Phys. Chem.* **1996**, *100*, 694.

(14) The CAChe MOPAC application determined the optimum geometry and the electronic properties using MINDO.

Table 1. Oxidation Potentials[a] of Aminophenols at Different pH Values

pH	2-AP	3-AP	4-AP
1.5	0.94	1.22	0.95
4.0	0.86	1.05	0.69
7.4	0.72	0.96	0.65
11.5	0.39	0.69	0.54

[a] In units of eV vs NHE.

Pulgarin and Kiwi[15] have shown that α-Fe_2O_3 acts as a photocatalyst in the case of 2-AP. Photoproduced electrons and holes participate in reduction and oxidation reactions.

$$Fe_2O_3 \xrightarrow{h\nu} Fe_2O_3\,(e^-_{CB}, h^+_{VB}) \quad (8)$$

$$e^- + \text{2-AP} \rightarrow \text{2-AP}^- \text{ (reduction)} \quad (9)$$

$$h^+ + \text{2-AP} \rightarrow \text{2-AP}^+ \text{ (oxidation)} \quad (10)$$

According to ref 14, a photochemical reaction involving a surface-complex of α-Fe_2O_3 accounts for the observed photodegradation. According to the potential levels, a reaction between e^-_{CB} and O_2 is not possible, as the potential necessary for the reaction $O_2/O_2^{\bullet-}$ ($E = -0.16$ eV vs NHE) is higher than that for e^-_{CB} ($E = 0.02$ eV vs NHE) at pH 6.0. Instead, e^-_{CB} reacts with lattice $>Fe^{3+}$ ($>$ = surface site), leading to a reduced surface site, $>Fe^{2+}$, which reacts with O_2 to produce $O_2^{\bullet-}$ radical.[16]

$$>Fe^{2+} + O_2 \rightarrow >Fe^{3+} + O_2^{\bullet-} \quad (11)$$

Reaction 11 is found to be competitive with the detachment of Fe^{2+} from the oxide surface. It has been reported[17] that, for an oxygen concentration of 2.7×10^{-4} M, the first-order rate constant of Fe^{2+} with O_2 is 6.0×10^{-9} s^{-1}, and the rate constant for detachment of Fe^{2+} from the α-Fe_2O_3 surface is 5.04×10^{-5} s^{-1} for a low surface coverage of azo dye on the α-Fe_2O_3 surface.[10]

The $O_2^{\bullet-}$ radicals present in solution can react directly with aminophenol and oxidize the substrate, or they can react with H^+ to form $HO^{\bullet}_2$ (H_2O_2) and $HO^{\bullet}$ radicals that oxidize the aminophenols.

$$O_2^{\bullet-} + H^+ \rightarrow HO_2^{\bullet} \rightarrow H_2O_2 \quad (12)$$

$$H_2O_2 \rightarrow HO^{\bullet} + HO^- \quad (13)$$

Photogenerated holes are also capable of oxidizing the substrate if the thermodynamics of the process is allowed. The oxidation potential of the h^+ (α-Fe_2O_3) is 2.5 eV (NHE), and the oxidation potentials of the aminophenols at different pH values are given in Table 1. The holes of α-Fe_2O_3 are capable of oxidizing the aminophenols. For a hole (h^+) to react effectively with an aminophenol, the aminophenol should adsorb strongly on the α-Fe_2O_3 surface because the hole lifetime is very short.[5] Because 3-AP and 4-AP adsorb very poorly on the α-Fe_2O_3 surface, the probability of these two compounds undergoing oxidative degradation is low. In contrast, 2-AP is capable of undergoing bridging bidentate formation with the α-Fe_2O_3 surface (IR data above) and can undergo both degradation paths.

$$O_2^{\bullet-} + \text{AP} \rightarrow \text{oxidized products} \quad (14)$$

$$h^+ + \text{AP} \rightarrow \text{oxidized products} \quad (15)$$

Degradation carried out under O_2- and Ar-saturated conditions confirm the above results. As expected, high degradation rates of 2-AP were observed under O_2-saturated conditions as both reactions 14 and 15 lead to degradation. Under Ar-saturated conditions, lower degradation rates were observed because reaction 14 cannot proceed. Nevertheless, some degradation was still observed under Ar, suggesting that reaction 15 is operative even in the absence of O_2.

A modest degradation of 2-AP, and of 4-AP to a lesser extent, was observed in the dark. A surface-catalyzed hydrolysis reaction has been reported for compounds such as phenyl picolinate (PHP) on different oxide surfaces.[18] The two ligand-donor groups of PHP chelate with the surface metal, facilitating the hydrolysis. The nature and relative positions of the donor groups are an important factor determining the degradation of PHP. The observed 2-AP degradation on the α-Fe_2O_3 surface in the dark suggests a degradation route involving chelation of aminophenol onto the hematite surface via N and O groups.

Conclusions

2-Aminophenol adsorbs on the α-Fe_2O_3 surface via bridged chelate surface−complex formation through the $-OH$ and $-NH_2$ groups. A hydroxyl group in the ortho position to the amino group favors chelation to a greater extent than hydroxyl groups in the meta or para positions. The chelation of aminophenols on hematite mediates the dark degradation. The degradation kinetics was accelerated by light, suggesting additional photochemical degradation involving light-induced charge transfer. The photochemical degradation of 2-AP on the α-Fe_2O_3 surface suggests the participation of both holes and electrons. Photodegradation of 2-AP was more efficient than that of 3-AP and 4-AP because of the more favorable surface chelation with the hematite surface. The degradation products (intermediates) were observed to be less toxic than the initial compounds for 2-AP and 4-AP.

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