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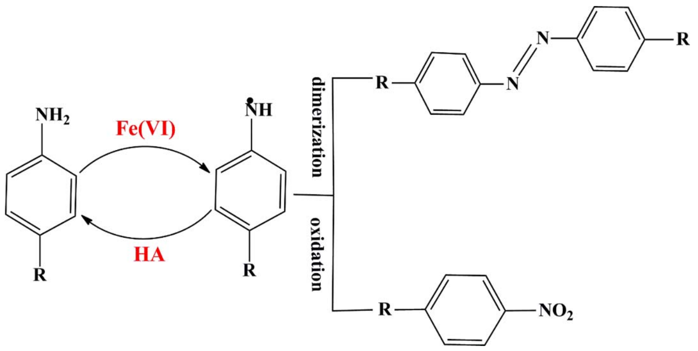
Transformation of substituted anilines by ferrate(VI): Kinetics, pathways, and effect of dissolved organic matter

Shaofang Sun[a], Yulei Liu[a], Jun Ma[a,*], Suyan Pang[b,*], Zhuangsong Huang[a], Jia Gu[a], Yuan Gao[a], Mang Xue[a], Yixing Yuan[a], Jin Jiang[a]

[a] State Key Laboratory of Urban Water Resource and Environment, School of Municipal and Environmental Engineering, Harbin Institute of Technology, Harbin 150090, China

[b] College of Chemical and Environmental Engineering, Harbin University of Science and Technology, Harbin 150040, China

GRAPHICAL ABSTRACT



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ABSTRACT

This study showed that substituted anilines of environmental concerns could be appreciably degraded by potassium ferrate (K_2FeO_4) in the pH range of 6–10 with apparent second-order rate constants (k_{app}) varying from 0.32 to 36,500 $M^{-1}\,s^{-1}$. The pH-dependence rate curves were well fitted via a kinetic model, which involved the formation of intermediates between Fe(VI) and substituted anilines. The plausible degradation pathways were proposed including the generation of aniline radical cations and their further oxidation to nitrobenzene compounds or dimerization to azobenzene compounds. Humic acid (HA) significantly reduced the transformation rates of substituted anilines with Fe(VI) even though considering the effect of oxidant consumption. This suppression effect likely resulted from the reaction between HA and the aniline radical cation, where the aniline radical cation was turned back to parent compound. Meanwhile, it was found that HA also had an impact on the formation kinetics of oxidation products. The effectiveness of Fe(VI) for degradation of substituted anilines in natural water was evaluated, where background matrix constituents could affect both the kinetics of contaminants degradation and products formation, similar to the case of HA. These results have advanced the understanding of Fe(VI) chemistry involved in water and wastewater treatment.

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* Corresponding authors.
E-mail addresses: majun@hit.edu.cn (J. Ma), psyhit@126.com (S. Pang).

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1. Introduction

Substituted anilines are widely applied in many industries including the production of pharmaceuticals and pesticides as well as textile mill [1–3]. The extensive utilization of substituted anilines leads to their frequent occurrence in aquatic environments at concentrations up to 1 mg L^{-1} [4,5]. Some substituted anilines (e.g., *p*-chloroaniline, *o*-toluidine, 5-nitro-*o*-toluidine) are categorized as prohibited contaminants in the European Union 1907/2006 because of their potential carcinogensis and genotoxic effects [1,6]. Therefore, it is imperative to explore various treatment technologies to degrade substituted anilines contaminants. Previous researches have demonstrated that a few oxidants such as ozone, hydrogen peroxide, and manganese dioxide are effective in treating substituted anilines [3,7–9]. For instance, Tekle-Rottering et al. [3] reported that ozone could considerably degrade aniline with $k_{app} = 1.3 \times 10^6\ M^{-1}\ s^{-1}$ at room temperature. Salter-Blanc et al. [9] found that substituted anilines could be oxidized by manganese dioxide with a pseudo-first-order rate constant of $2.16 \times 10^{-2}\ s^{-1}$ at pH 6.

Recently, Fe(VI) has attracted increasing attention because it can be used not only as an environmentally-friendly oxidizing agent but also as a good coagulant [10–14]. Numerous studies have researched on reaction mechanisms and products for the reactions between Fe(VI) and a variety of environmental micropollutants (e.g., pharmaceuticals, nitrogen-containing compounds, alcohols), indicating that organic micropollutants comprising electron-rich moieties (e.g., phenols, thiol thioesters, amines) have a high reactivity with Fe(VI) [15–19]. Nevertheless, up to now, little knowledge is established on the degradation of substituted anilines with Fe(VI). Few studies have been conducted to investigate the degradation kinetics and products of aniline with Fe(VI) [20–23]. The influences of ring substituents on the transformation of substituted anilines with Fe(VI) have not been studied yet.

As a classic representative of water matrix constituents, dissolved organic matters (DOM) have a significant impact on the transformation of contaminants during water treatment. Several studies have shown that DOM can compete for Fe(VI) with organic pollutants, resulting in the decrease of the transformation efficiency of contaminants. For instance, Feng et al. [24] found that the removal of flumequine (FLU) was considerably inhibited with the increase of DOM concentration due to its competition for Fe(VI). Yang et al. [25] also reported that DOM could compete for Fe(VI), thus decreasing the removal efficiency of tetrabromobisphenol A (TBrBPA). Interestingly, a recent study found that DOM could affect the k_{app} of Fe(VI) with TBrBPA by reducing radical intermediate formed via one electron transfer to its parent form [26]. This repressive effect of DOM was also found in excited triplet states and laccase catalyzed oxidation of pollutants [27,28]. As far as we know, no systematic researches on the effect of DOM on the substituted anilines oxidation by Fe(VI) have been conducted yet.

In this study, twelve substituted anilines including aniline (AN), *m*-methylaniline (*m*-MA), *p*-methylaniline (*p*-MA), *o*-bromoaniline (*o*-BA), *m*-bromoaniline (*m*-BA), *p*-bromoaniline (*p*-BA), *o*-chloroaniline (*o*-CA), *m*-chloroaniline (*m*-CA), *p*-chloroaniline (*p*-CA), *p*-nitroaniline (*p*-NA), *p*-aminobenzoic acid (*p*-ABA) and *o,p*-dichloroaniline (*o,p*-DCA) were taken as model compounds. First, the oxidation kinetics of substituted anilines by Fe(VI) were investigated in buffered solutions over the pH range of 6–10, and the effect of ring substituents was explored. Then, oxidation products from substituted anilines treated by Fe(VI) were identified, and the plausible degradation pathways were suggested. Further, the influence of HA on the kinetics of substituted anilines degradation and products formation was evaluated. At last, the degradation kinetics of substituted anilines by Fe(VI) in nature water were performed.

2. Materials and methods

2.1. Reagents

Twelve substituted anilines of high purity were obtained from J & K Scientific Ltd. Potassium ferrate (K_2FeO_4, > 93%) was prepared using the previously described method by Thompson et al. [29]. A commercial humic acid (HA) and 2,2-azino-bis(3-ethylbenzothiazoline)-6-sulfonate (ABTS, > 98%) were obtained from Sigma-Aldrich. Other chemicals with high purity were purchased from Sinopharm Chemical Reagent Co. Ltd. china. Stock solutions of Fe(VI) were freshly prepared by dissolving weighed amounts of solid K_2FeO_4 in 5 mM Na_2HPO_4/1 mM borate buffer (pH = 9.2), in which aqueous Fe(VI) was known to be most stable [17]. Stock solutions of substituted anilines were prepared in acetonitrile-water mixture (2/98%) due to their low aqueous solubility. The concentration of acetonitrile in the reaction solutions was < 0.5‰, which had no impact on the consumption of Fe(VI) during kinetic experiments. HA was purified by repeated pH adjustment, precipitation, and filtration according to the procedure described in the literature [30]. Some properties of purified HA was shown in Table S1.

2.2. Determination of rate constants

Kinetics for the reactions of substituted anilines with Fe(VI) were studied at 25 ± 1 °C over the pH range of 6–10 by monitoring the decay of Fe(VI) using stopped-flow spectrophotometer or ABTS method under substituted anilines in excess ([compound] > 10[Fe(VI)]). For rapid kinetics (t = 30 ms-10 s), a stopped-flow spectrophotometer (Applied Photophysics SX20) was used to monitor the decay of Fe(VI) at 510 nm under various pH, where the pseudo-first order conditions with substituted anilines in excess were maintained ([Fe(VI)] = 50 μM − 100 μM, [compound] > 10[Fe(VI)]) (for details see Supplementary Material (SM) Text S1). For slow kinetics (t > 10 s), the reaction of substituted anilines with Fe(VI) was studied in a 250 mL conical flask under the conditions of the target compound in excess ([Fe(VI)] = 1 μM − 10 μM, [compound] > 10[Fe(VI)]) (for details see SM Text S1). 10 mM phosphate for pH 6–8 and 10 mM phosphate/10 mM borate for pH 9–10 were used as buffers. The pH shift (< 0.1 units) was negligible during the kinetic runs. Fe(VI) self-decomposition, which was less than 5% of the initial Fe(VI) concentration in control experiments, was ignored during the kinetic runs (for details see SM Text S2 and Fig. S1).

2.3. Oxidation products

For identification of reaction products, pH-buffered solutions (pH = 8) containing a relatively high concentration of one model compound (i.e., AN, *m*-MA or *p*-CA at 20 μM) were treated by various concentration of Fe(VI) (5–100 μM). When the purple color of Fe(VI) completely disappeared, the solutions were filtered and extracted with hexane (see Table S2). Then, the samples were analyzed by Gas Chromatography/Mass Spectrometer-Mass Spectrometer (GC/MS-MS).

2.4. Effect of HA

The oxidation kinetics of AN and *p*-NA were conducted at pH 8 in the absence/presence of HA (0.5–2.0 mgC L^{-1}). The kinetic runs were started with adding excess Fe(VI) (30 μM) to reaction solutions including 2 μM AN or *p*-NA (for details see SM Text S3). Two parallel samples (3 mL) were simultaneously collected at predetermined time intervals with one being quenched with excess ABTS to measure residual Fe(VI) and the other being quenched with excess $NaAsO_2$ (20 mM) and then filtered through 0.22 μm glass fiber membrane to monitor residual compounds by high performance liquid chromatography (HPLC), respectively. In addition, the formation profiles of two