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Oxidation of odor compound indole in aqueous solution with ferrate (VI): Kinetics, pathway, and the variation of assimilable organic carbon

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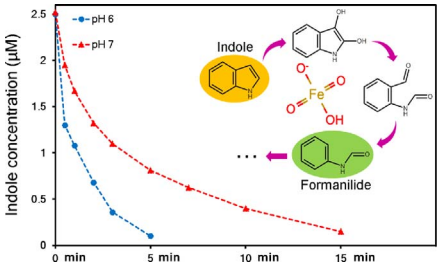
GRAPHICAL ABSTRACT



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ABSTRACT

Indole is a typical fecal odor compound and has negative impact on water quality at low concentrations. Here, the oxidation of indole by ferrate [Fe(VI)] was investigated, in terms of the reaction kinetics, the oxidation products, and the variation of assimilable organic carbon (AOC). The oxidation of indole was pH-dependent (6.0–9.5), and the pH-dependent profile could be well explained by the acid-base equilibrium of Fe(VI). The apparent second-order rate constants (k_{app}) for indole oxidation with Fe(VI) ranged from 692 ± 26 $M^{-1} s^{-1}$ at pH 6.0 to 3.08 ± 0.15 $M^{-1} s^{-1}$ at pH 9.5. The results of experiments conducted under real source water background showed that indole could be effectively removed by Fe(VI) from actual polluted waters. After analyzing the reaction pathway, it was found that the initial steps in the oxidation of indole were the hydroxylation of indole to 2,3-dihydroxyindole, followed by the cleavage of N-heterocyclic ring. Formanilide was a major oxidation product in this process, and it is less reactive with Fe(VI) than that of indole. High concentrations of Fe(VI) could effectively oxidize indole in the water and has little impact on the microbiological stability of the treated water. Based on the results, Fe(VI) can be an effective agent for the control of indole in water treatment.

1. Introduction

Taste and odor compounds would deteriorate the aesthetic property of drinking water, and controlling relevant chemicals is a major work for water suppliers. With the increasing trend of water reuse and projects in which treated wastewater is released into surface water, municipal wastewater effluent has become a potential source of odorous compounds in drinking water. Indole is widespread in nature, and notorious for its fecal odor [1]. Its odor threshold in water is only 0.1 μg L^{-1} [2]. In an odorous tap water crisis which affected two million people for several days in Wuxi, China, 2007, massive bloom and decomposition of cyanobacterium *Microcystis aeruginosa* in Lake Taihu

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led to the release of many kinds of odorous compounds into the water [3]. Among them, indole and its derivatives (mainly methyl indole) were predominant pollutants, and their concentration levels ranged from μg L^{-1} to mg L^{-1} [4]. Considering the globally increased demand for water reuse to meet the growing water crisis [5], exploring relevant controlling method is imperative.

Bio-degradation of indole has been extensively investigated, and its biodegradation time ranged from several days to several weeks. For example, 0.5 g/L of indole could be degraded within 6 days by an isolated thermophilic fungus (*Sporotrichum thermophile*) [6]. Yin et al. reported that 3 μM of indole could be bio-degraded within 84 days [7]. Li et al. reported that 1 mM of indole could be completely degraded within 10 days [8]. Three major bio-degradation pathways of indole were proposed: the catechol pathway, the gentisate pathway and the anthranilate pathway [9]. There also have been some investigations related to the chemical removal of indole [10–13]. Photocatalysis could degrade over 95% of indole within 120 min at the dosage of 1 g/L catalyst (TiO_2) [10]. Iron-alginate bead catalyzed Fenton reaction can oxidize 100% of indole at pH 3.0, and 16% of indole at pH 6.0 within 180 min [11]. Over 60% of indole could be removed by contact glow discharge plasma method within 30 min, at 700 V of applied voltage and 600 μS cm^{-1} of solution electrical conductivity [12]. HSO_5^- was applied for the oxidation of indole in aqueous CH_3CN medium (80:20 v/v), and the observed rate constant was 3.6×10^{-4} s^{-1} when 2 mM HSO_5^- reacted with 20 mM indole at 40 °C [13]. The initial concentrations of indole in reported researches ranged from 10 mg L^{-1} to 100 mg L^{-1}, but the concentration of indole in polluted source water was normally below 1 mg L^{-1}. Exploration for efficient and convenient removal of trace amount of indole in source water is imperative.

Preventing second pollution of drinking water in distribution system is also an important task for water suppliers. Assimilable organic carbon (AOC) is a comprehensive index to evaluate the content of labile dissolved organics which is easy to be bio-consumed [14]. It is also a fundamental factor to study the biological stability of drinking water [15]. However, few investigations focusing on the oxidation of organic pollutants have examined the variation of AOC during oxidation process. Since AOC content is a critical standard for drinking water treatment and the distribution system, relevant studies may offer valuable information about the biological stability of the treated water.

Ferrate [Fe(VI)] has drawn extensive attentions in recent years for the control of organic pollutants in water treatment [16,17]. Fe(VI) is a strong oxidant and can react with electron-rich moieties such as phenols, amines and alcohols [18,19]. The *in-situ* formed ferric oxides can absorb chemicals and metal ions in the water [20–22], thus facilitate the following coagulation, flocculation and filtration process [23]. Besides, Fe(VI) has low reactivity with bromide [24,25], and could decrease the disinfection byproduct formation potentials in raw water [26,27]. However, there is not any study reporting the oxidation of indole by Fe(VI), and evaluating the variation of AOC content during Fe (VI) treatment process. The objectives of this study were to: (1) investigate the reaction kinetics between indole and Fe(VI) as a function of pH (from 6.0 to 9.5), and explain the oxidation mechanism; (2) identify the oxidation products and propose the degradation mechanism; (3) examine the degradation of indole under the condition of real source water background, and (4) assess the AOC variation during the reaction process.

2. Materials and methods

2.1. Chemicals and agents

Indole (98% purity) was purchased from Sigma Aldrich Chemical Inc. Chromatography grade n-hexane was obtained from Thermo Fisher Scientific Inc. Formanilide (98% purity) and methanol (HPLC grade) were purchased from Aladdin Chemical Inc. (Shanghai, China). Other chemicals were of analytical grade and used without purification. Potassium ferrate (K_2FeO_4, purity = 93%) was prepared in the lab according to the previously described method [28,29]. Briefly, KClO solution was prepared by the oxidation of KOH with Cl_2. Pulverized Fe $(NO_3)_3{\cdot}9H_2O$ was added into the KClO solution and reacted for over 1 h under cooling conditions (< 5 °C). A quantity of 0.5 mol of KOH was then added into the solution and stirred for 20 min. The resulting slurry was filtered through a glass filter, and the precipitate was washed with 25 ml of cold 1 M aqueous KOH solution. The filtrate from the washings was collected and added to a flask containing 300 ml of a chilled saturated KOH solution. The solution was mixed, allowed to stand for 10 min and then filtered initially with a glass filter (P-3), followed by double filtering with GF/A filter papers (Whatman ∅70 mm). The precipitate was flushed with n-hexane (3 times × 30 ml), n-pentane (3 times × 30 ml), methanol (3 times × 30 ml), and diethyl ether (3 times × 20 ml). The final product (K_2FeO_4) was stored in a vacuum desiccator prior to use.

To determine the purity of Fe(VI), definite amount of solid Fe(VI) was dissolved in 1 mM borate/5 mM phosphate buffer solution (pH = 9.2), and immediately filtered through an acetate cellulose membrane of 0.22 μm pore size (Shanghai ANPEL, China). The K_2FeO_4 solution concentration was determined at 510 nm with $\varepsilon_{510\ nm}$ = 1150 cm^{-1} M^{-1} on a UV–Visible spectrophotometry. The purity of Fe(VI) was calculated based on the concentration of the solution and the amount of the dissolved Fe(VI) powder.

Before experiment, indole stock solution was prepared. Indole powder (58.5 mg) was dissolved in 500 μL methanol. After that, pure water was added into the solution, and the solution volume was adjusted to 10 mL.

Two source water samples were collected to study the removal of indole under the condition of real water background. A reservoir water was collected from Mopanshan reservoir in Harbin. A ground water sample was collected from a well in Harbin Dashen Food Corporation. Water samples were filtered through a glass-fiber membrane (Whatman) of 0.75 μm pore size and stored at 4 °C prior to use. The water samples did not contain indole after HPLC analysis, and definite amount of indole stock solution was added into the water samples in the experiment (end concentration: 0.5 μM and 2.5 μM). The properties of the collected water samples are listed in Table S1.

2.2. Analytical methods

Before experiment, desired amount of Fe(VI) powder was dissolved into a 1 mM borate/5 mM phosphate buffer solution at pH 9.2, and immediately filtered through a hydrophilic acetate fiber membrane (Shanghai ANPEL, China) of 0.22 μm pore size. The concentration of Fe (VI) was measured spectrophotometrically at the wavelength of 510 nm ($\varepsilon_{510\ nm}$ = 1150 $M^{-1}cm^{-1}$) [30,31].

The indole concentration was determined with high-performance liquid chromatography (HPLC, Waters 2695) with a symmetry C18 column (4.6 × 150 mm, 5 mm particle size, Waters) and a photodiode array detector (PDA, Waters 2998) at the wavelength of 215 nm. The mobile phase consisted of methanol and water (0.5‰ (v/v) acetic acid) at a ratio of 45:55 (v/v), and a flow rate of 1.0 mL min^{-1} was used. The concentration of formanilide was determined with the HPLC at the wavelength of 239 nm. The mobile phase consisted of methanol and water [0.5‰ (v/v) acetic acid] at a ratio of 35:65 (v/v), and a flow rate of 1.0 mL min^{-1} was used.

The reactions were started by adding Fe(VI) stock solution to the solutions containing indole under rapid mixing. At certain time intervals, 5 mL of the solution was sampled for the determining of Fe(VI) concentrations using a ABTS method at 415 nm, and 2 mL of the solution was sampled and quenched with a hydroxylamine hydrochloride solution (10 wt%) to measure residual concentrations of indole by HPLC. The pH variation was below 0.1 units during the experiments, and all kinetic experiments were carried out in triplicate.

Different volume of Fe(VI) stock solution was added into reactors