

O-Anisidine Degradation by Fenton's Reagent and Reaction Time Estimation

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ABSTRACT: O-Anisidines (OAs) are extensively used as an intermediate for chemical reactions to produce various triphenylmethane and azo dyes, and also in manufacturing numerous pigments. They are found to be highly toxic and have carcinogenic properties, so it is imperative to treat OA solutions before disposal. In this study a promising approach to degrade OA solutions has been carried out using Fenton's reagent. Oxidation trials were conducted for 24 hours and various parameters – OA removal, pH, effect of H₂O₂ and Fe²⁺, and COD removal – were analysed to understand the oxidative degradation of OA. For varying initial OA concentrations, the OA and COD removal efficiencies of 72 to 85% and 62 to 74%, respectively, were obtained at pH = 3, and at different optimum H₂O₂ and Fe²⁺ doses. Lower initial concentrations of OA showed better removal efficiencies. The reaction time was estimated to 360 minutes after which there was negligible degradation occurs.

Keywords: O-Anisidines, Fenton's Oxidation, Ferrous Sulphate, Degradation; Reaction Time.

INTRODUCTION

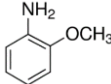
Aniline compounds and their derivatives are major contaminants in industrial and pharmaceutical wastewaters (Datta et al., 2003). These aniline derivatives are highly resistant to microbial degradation due to the complexity in their structure (Kreisberg, 2007). One aniline derivative is O-Anisidine (OA), which is used mostly as an intermediate in pharmaceutical, fragrance, pigment and dye production (Budavari et al., 1996). Numerous triphenylmethane and azo dyes, and most pigments, rely on OA hydrochloride for their production as it is an essential intermediate. They include acid red 4, direct red 72, direct yellow 44 and orange 29. OA is also used to prevent steel corrosion and hinder the oxidation of polymercaptan resins (Desai, 2014). It is a stable chemical and incompatible with many strong oxidizing

agents, chloroformates, acid anhydrides and some acids. Table 1 shows the chemical structure and physical properties of OA.

Acute exposure to OA results in mild irritation of skin in humans. A six-month inhalation exposure to OA can cause vertigo, headaches and methemoglobinemia. Severe effects from chronic exposure have also reported in animal studies – e.g., bladder tumours, blood damage, etc. The revised immediately dangerous to life or health (IDLH) concentration is 50 mg/m³ (Desai, 2014). The International Agency for Research on Cancer (IARC) has categorized OA in Group 2B, probable human carcinogen (IARC, 1982; National Toxicology Program, 2016). It is highly toxic, causing nerve, blood and enzyme damage, with suffocation and risk of cyanosis. Wastewaters containing OA need to be treated prior to disposal.

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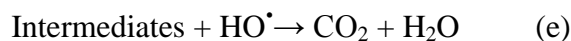
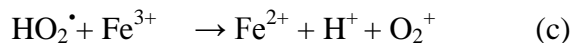
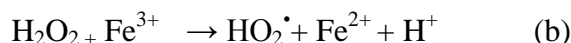
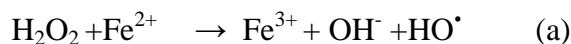
Table 1. Basic properties of OA

Properties	OA
Structure	
Synonyms	O-methoxyphenylamine 2-methoxyaniline, methoxybenzylamine, 2- aminoanisole, O-anisilamine.
Physical state	Yellow liquid; becomes brown when exposed to air
Molecular weight	123.2 g/mol
Formula	C ₇ H ₉ NO
Boiling point	225 °C
Melting point	5 °C
Water solubility	Approximately 14 g/L at 25 °C

Chemical industry and oil refinery wastewaters have been identified as containing OAs (National Library of Medicine, 1998). Aromatic aniline derivatives have been removed from effluents by electrolysis, photodecomposition, ozone oxidation, biodegradation and resin adsorption (Delnavaz et al., 2008; Jing et al., 2015). Complete decomposition has not been achieved by activated sludge processes and their incalculable nature can prevent the biodegradation of several other harmful chemical species in wastewaters (Sun et al., 2008). Most of physical treatment methods, like adsorption, are very sensitive to pH of the wastewater, other methods – e.g., incineration and ultra-filtration – are uneconomic, and thermal incineration can cause air pollution (Ferreira et al., 2002; Sawai et al., 2009; Xie et al., 2012). An environmentally friendly and economic technique is needed to degrade pollutants like OA. Fenton's oxidation can degrade harmful and carcinogenic pollutants like nitroanilines (Amritha and Manu, 2018) and aminopyridines (Karale et al., 2013; 2014) to a large extent, and so was used to oxidise OA at laboratory scale in this study.

Fenton's reaction is a type of advanced oxidation process that can degrade organic compounds in aqueous solution (Matavos-Aramyan and Moussavi, 2017). It relies on the production of hydroxyl radicals (HO[•]) by the dissociation of hydrogen peroxide (H₂O₂) in the vicinity of ferrous ions (Fe²⁺) as

catalyst in acidic solution (Equation (a)). The catalyst (Fe²⁺) is restored by the reaction of H₂O₂ and Fe³⁺ (Equation (b)) or HO₂ (Equation (c)) (Sharma et al., 2011). The reaction mechanism is summarized below (Walling, 1975; Temel and Sökmen, 2011):



The organic compound (RH) is oxidised initially into intermediates (Equation (d)), which are subsequently mineralized (Equation (e)).

In this study Fenton's Oxidation was applied for the degradation of OA and the effect of various parameters pH, H₂O₂, Fe²⁺ and OA initial concentration was investigated.

METHODS AND MATERIALS

Chemicals O-Anisidine extra pure (98% assay) were purchased from Loba Chem. Ltd. (India). Ferrous Sulfate (FeSO₄·7H₂O) and Hydrogen peroxide (H₂O₂) (50% w/w purchased from Loba Chem. Ltd. (India). Hydrochloric acid (HCl, Loba, India, 35% purity), Sulfuric acid (H₂SO₄, Loba, India, 98% purity), Hydrochloric acid (HCl,

Loba, India, 35% purity), Sodium hydroxide NaOH, Loba, India, 98% purity), were also applied in this study. UV Vis Spectrophotometer (Product No. G9821A, Agilent Technologies) is used for analysis, COD digester (HACH DRB 200).

OA was characterized using a Double Beam UV-VIS Spectrophotometer (Agilent Technologies) based on absorbance over UV wavelengths from 200 to 500 nm. OA concentration peaks – 0.5 to 2.5 mM – were obtained at 282.5 nm and taken as λ_{max} (Maximum absorbance at this wavelength) for OA. Calibration curves were prepared for the corresponding λ_{max} using known OA concentrations – 0.5, 1.0, 1.5, 2.0 and 2.5 mM. The initial and final (post-treatment) OA concentration and absorbance in the sample for the corresponding λ_{max} were determined using a calibration curve. The laboratory experiments were performed in Erlenmeyer flasks by the batch method at normal room temperature ($27 \pm 3^\circ \text{C}$) (Manu and Mahamood, 2011). 1L solution of OA of known concentration was placed in each of five 2L Erlenmeyer flasks. The pH was changed as necessary using 1N NaOH and 0.5N H_2SO_4 . The required amount of ferrous ion (Fe^{2+}) was added from a freshly prepared solution of ferrous sulphate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$). Finally, hydrogen peroxide

(H_2O_2) was added to the flask to initialize degradation. The reaction solution was stirred constantly for two hours with magnetic stirrers before aliquots from the reactor bath were analyzed using the UV-VIS spectrophotometer. The initial and final COD concentrations in the sample were determined using closed reflux titrimetric method (HACH DRB 200).

RESULTS AND DISCUSSION

pH is significant in Fenton's treatment, as it controls both the rate of hydroxyl radical formation and Fe^{2+} concentration. It was set in the range 2.0 to 4.0 in five separate Erlenmeyer flasks containing $[\text{OA}]_i = 0.5 \text{ mM}$ and $[\text{H}_2\text{O}_2:\text{Fe}^{2+} = 60:1]$ to find the optimum pH (Figure 1).

Maximum OA and COD removals of 84 and 74% were obtained, both at pH 3.0. The effective pH range for OA degradation was 2.5 to 3.5. At $\text{pH} > 3.5$, removal efficiency decreased, perhaps because of deactivation of Fe^{2+} catalyst with the production of ferric hydroxide [$\text{Fe}(\text{OH})_3$], leading to reduced amounts of hydroxyl radical (Lucas and Peres, 2006; Sun et al., 2007). At $\text{pH} < 2.5$, the reaction between hydrogen peroxide and Fe^{2+} was affected seriously as hydrogen ions [H^+] were consumed by hydroxyl radicals (Michael et al., 2010).

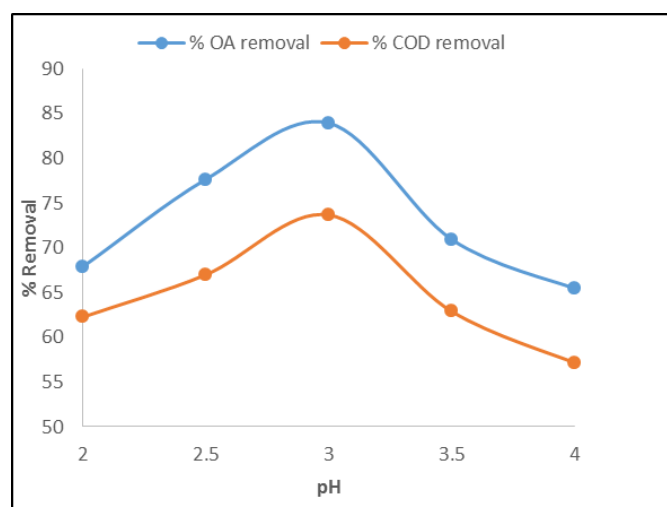


Fig. 1. Influence of pH on OA and COD removal (%) using Fenton's treatment. $[\text{OA}]_i = 0.5 \text{ mM}$; $[\text{H}_2\text{O}_2] = 3 \text{ mM}$; $[\text{Fe}^{2+}] = 0.05 \text{ mM}$.

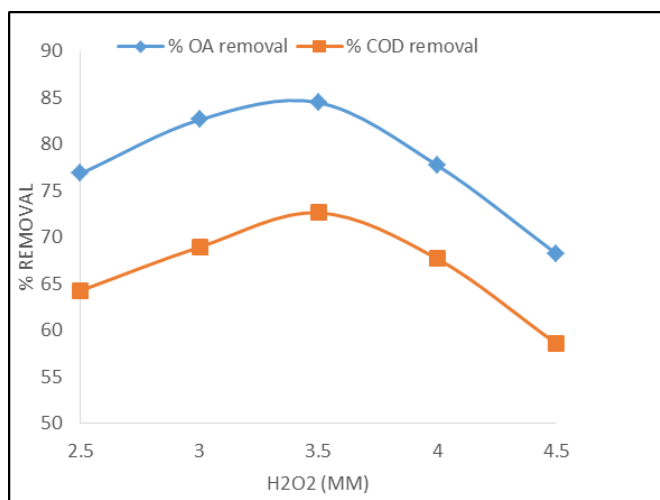


Fig. 2. Influence of H₂O₂ concentration on OA and COD removal (%) using Fenton's treatment. [OA]_i = 0.5 mM; pH = 3; [Fe²⁺] = 0.05 mM.

The H₂O₂ dosage was also optimized by varying the H₂O₂ concentration from 2.5 to 4.5 mM at pH 3.0, while keeping the iron concentration constant at 0.05 mM (Figure 2).

Maximum removal occurred when the H₂O₂ concentration was 3.5 mM, with 84 and 73% OA and COD removal, respectively. When H₂O₂ concentrations were 3.0 and 4.0 mM, respectively, the OA and COD removal rates were 80 and 77%, and 67 and 65%, respectively. (At 4.5 mM initial H₂O₂ concentration, the OA and COD removal rates were 69 and 53%, respectively.)

The proportional removal of OA and COD decreases with increased H₂O₂ concentration because of the decreased

catalytic activity. As the H₂O₂ concentration increased, some reduction in the degradation rate of OA might have occurred due to the scavenging of hydroxyl radicals by H₂O₂ in generating OOH radicals, which are far less reactive than the HO[•] radical (Chen and Pignatello, 1997; Kang et al., 2002; Walling and Kato, 1971; Hassan and Hameed, 2011).

The iron concentration was varied from 0.025 to 0.125 mM while maintaining that of H₂O₂ constant at 3.5 mM for the same pollutant dosage. The maximum OA and COD removals from solution were 85 and 74% respectively at 0.05 mM Fe²⁺ concentration (Figure 3).

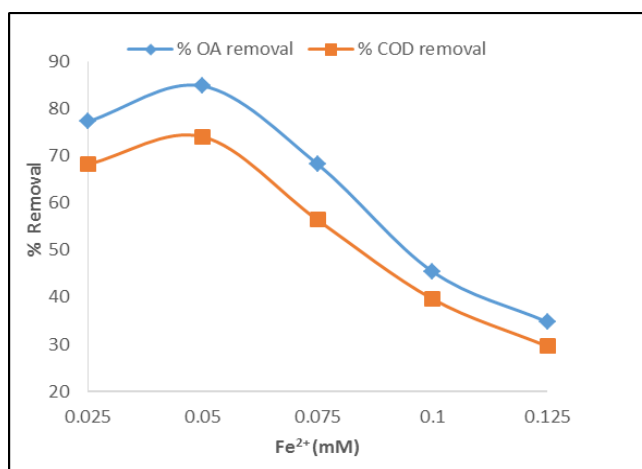


Fig. 3. Effect of iron concentration on OA and COD removal (%) using Fenton's Oxidation. [OA]_i = 0.5 mM; [H₂O₂] = 3 mM; pH = 3.

When the Fe^{2+} concentration was increased from 0.025 to 0.05 mM, the OA and COD removal rates rose from 77 to 86% and 68 to 71%, respectively. When it was further increased to 0.075 and then 0.1 mM, the removal rates fell to 66 and 45% (OA), 56 and 40% (COD). For $[\text{OA}]_i = 0.5$ mM, maximum degradation was achieved at $\text{H}_2\text{O}_2 = 3.5$ mM, and $\text{Fe}^{2+} = 0.05$ mM, at pH 3.0. At high Fe^{2+} concentrations, the Fe^{3+} produced from the reaction between H_2O_2 and Fe^{2+} – Equation (a) – precipitated as $\text{Fe}(\text{OH})_2^+$ resulting in sharp decline in % removal of OA and COD (Tamimi et al., 2008).

For higher concentrations of OA – i.e., 1.0, 1.5, 2.0 and 2.5 mM – the hydrogen peroxide and iron dosages were optimized in a similar way. The optimum Fenton’s reagent dosages for were used as starting

dosages and then increased gradually to find their respective optimums for higher concentrations.

At initiation the reaction mixture turned very dark and took 24 hours to clear, as the precipitates settled. The OA and COD concentrations were determined after 24 hours – i.e., when it had cleared. The effect of varying the OA concentration on Fenton’s Oxidation (Figure 4).

The optimum Fenton’s reagent dosages for each $[\text{OA}]_i$ and their respective OA and COD removals are summarized in Table 2. It is clear that the lower the OA concentration higher it’s proportional removal – Figure 4. At higher OA concentrations, more hydrogen peroxide is consumed than expected while the iron requirement increases in the usual order.

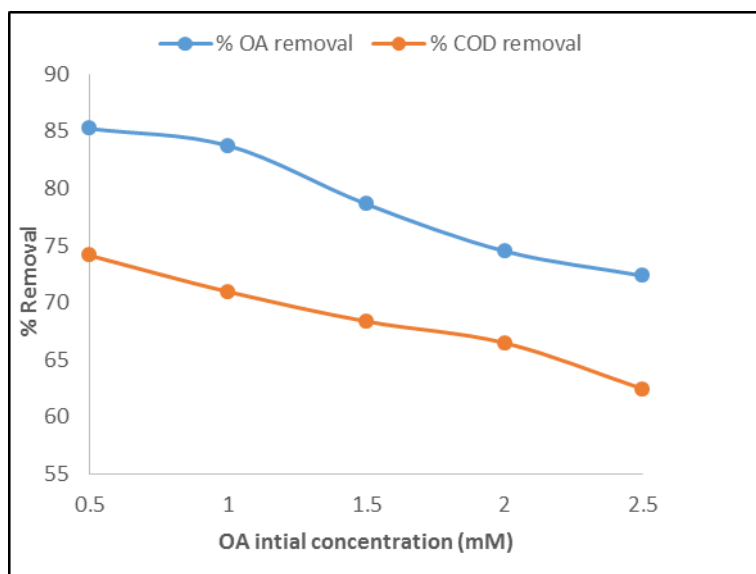


Fig. 4. OA and COD removal (%) with varying dosages of OA using Fenton’s oxidation reaction (pH = 3.0).

Table 2. Fenton’s oxidation of OA at different initial concentrations

$[\text{OA}]_i$ (mM)	H_2O_2 (mM)	Fe^{2+} (mM)	OA removal (%)	COD removal (%)
0.5	3.5	0.05	85	74
1.0	5.5	0.075	84	71
1.5	9.5	0.125	79	68
2.0	13.5	0.175	75	66
2.5	17.0	0.225	72	62

At relatively higher initial OA concentrations the relative proportion of OA adsorbed onto the catalyst's surface was greater, leading to a relatively lower proportional rate of degradation.

The study of Fenton's oxidation of OA suggested a first-order kinetic model (Equation (f)):

$$\ln(C_t/C_0) = -Kt$$

Where, C_0 = initial concentration of OA when the reaction started

C_t = OA concentration after time t ,

K = rate constant for first-order chemical reaction (min^{-1}), and

T = time (min).

The correlation coefficient (R^2) was between 97 and 99%. R^2 was calculated by fitting the data by linear regression to a pseudo-first-order kinetic model.

The values of the rate constant (K), half-life period ($T_{1/2}$) and correlation coefficient (R^2) are presented in Table 3.

The kinetic OA degradation profiles for

OA_i in the range 0.5 to 2.5 mM, with ferrous sulphate as the iron source, are shown in Figure 5. The OA kinetic studies were conducted pre-determined optimized Fenton's doses, with 2 hours' rapid mixing initially then followed by 6 hours reaction time. The studies showed that OA degradation started as early as 10 to 15 minutes after initiation and that about 50% OA removal occurred in the first 120 to 150 minutes of reaction. This is due to the fact that more hydrogen peroxide was consumed in the first 180 min with constant (H_2O_2) and (Fe^{2+}). Degradations were faster in first 120 minutes as the mixture was agitated constantly then. When mixing stopped, degradation slowed significantly. Further degradation of about 30 to 35% of the initial OA load was observed in the 240 minutes after mixing ceased, after which no significant degradation occurred – i.e., only about 3 to 5% of total removal occurred between 240 and 360 minutes.

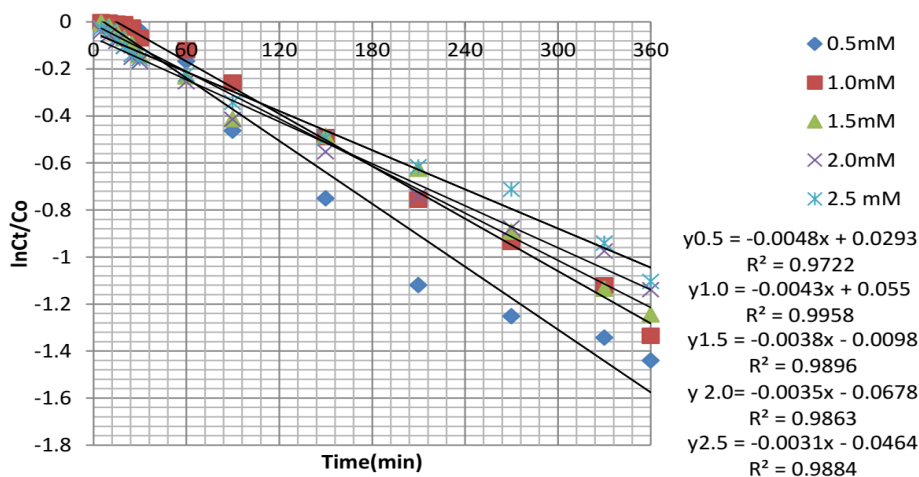


Fig. 5. Plot of $\ln(C_t/C_0)$ with respect to time during the Fenton oxidation of $[\text{OA}]_i = 0.5$ to 2.5 mM; pH 3.0.

Table 3. Rate constant (K) and half-life period ($T_{1/2}$) during Fenton's oxidation.

[OA] _i (mM)	Fenton's Oxidation	
	K (min^{-1})	$T_{1/2}$ (min)
0.5	-0.0047	143.6
1.0	-0.0044	162.5
1.5	-0.0039	180.7
2.0	-0.0034	199.2
2.5	-0.0030	222.7

CONCLUSIONS

- The study showed that lower OA_i concentrations are favored by Fenton's treatment method – i.e., removal efficiency decreases with increasing OA_i.
- The maximum OA and COD removals of 85 and 74% were observed at pH 3.0, H₂O₂ concentration 3.5 mM and Fe²⁺ concentration 0.05 mM, for 0.5 mM OA_i.
- First-order reaction kinetics was suggested for OA degradation and the estimated reaction time was 360 minutes (6 hours).
- Fenton's oxidation process is generally effective in degrading OA and removing it from aqueous solution to a large extent. The treated effluent produced has low toxicity and can be treated further biologically to remove more OA.

GRANT SUPPORT DETAILS

The present research did not receive any financial support.

CONFLICT OF INTEREST

The authors declare that there is not any conflict of interests regarding the publication of this manuscript. In addition, the ethical issues, including plagiarism, informed consent, misconduct, data fabrication and/ or falsification, double publication and/or submission, and redundancy has been completely observed by the authors.

LIFE SCIENCE REPORTING

No life science threat was practiced in this research.

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