Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2019.24104

154 (2019) 340–346
June

Photocatalytic degradation of catechol in aqueous solutions: a comparison between UV/Fe_2O_3 and Fe_2O_3/sunlight processes

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Received 4 October 2018; Accepted 8 March 2019

ABSTRACT

Phenols and phenolic compounds are widely used in everyday life and industry. Environmental stability, solubility in aqueous medium and high toxicity of these compounds are due to their high attention. The purpose of this study is the removal of catechol from wastewater based on the comparative use of two photocatalytic hematite/UV and hematite/sunlight processes. In this experimental laboratory study, the hematite nanoparticles are used with the separate application of UV and sunlight to reduce 10–50 mg L^{-1} concentration of catechol. The effect of parameters such as hematite concentration, reaction time and pH is studied on the catechol removal efficiency of both processes. The 6-W UV lamp as well as UV-A sunlight is used for radiation on the reactor contents. The remaining catechol concentration in the samples is measured by spectrophotometer within the wavelength of 600 nm. The best catechol removal efficiency by UV/Fe_2O_3 and Fe_2O_3/sunlight processes is 92.3% and 88% obtained at pH = 2, contact time of 60 min, hematite concentration of 4.0 g L^{-1} and catechol concentration of 50 mg L^{-1}. UV/Fe_2O_3 process with 0.4 g L^{-1} Fe_2O_3 obtained COD removal of 71.3%, while sunlight/Fe_2O_3 process achieved lower COD removal of 50.9%. The results showed that UV/Fe_2O_3 and Fe_2O_3/sunlight photocatalytic processes have a good potential in catechol removal from aqueous solutions at pilot scale. However, statistical analysis of results did not show a significant difference between the processes. Therefore, it is proposed to study the performance of these processes as a clean and environmentally friendly practice in full scale with real wastewater.

Keywords: Photocatalyst; Hematite nanoparticles; UV radiation; Catechol; Sunlight

1. Introduction

In recent years, it is necessary to protect water resources from pollution due to the limited water resources for reasons such as drought and rapid population growth [1]. One of the most important global concerns is water pollution caused by organic compounds from agricultural, industrial and urban activities [2]. The majority of them form resistant organic compounds irremovable by conventional treatment methods such as coagulation, adsorption, ion exchange and chemical oxidation [2,3]. As a result, these compounds have been tracked down in water sources such as rivers, lakes, oceans and even drinking water supplies [4]. This leads to environmental health problems such as poisoning and

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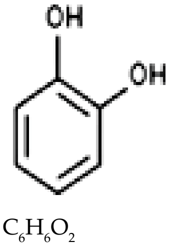
potential health risks of these compounds [2,5]. Phenols and phenolic compound pollution of the water resources as one of the persistent organic compounds has led to great concerns about the individuals' health in recent decades. Phenols and phenolic compounds enter into the environment by industrial effluents. These compounds due to their toxic side effects on the permeability of the cell membrane and cytoplasm coagulation could cause damage to sensitive cells, resulting in irreparable damage to the health and environmental problems [1]. Phenols and phenolic compounds are classified as priority pollutants by the Environmental Protection Agency of the United States [6]. Catechol as a phenolic compound and one of the most important environmental pollutants is found in raw materials or finished products of various industries including the photography, oils and lubricants manufacturer, polymerization inhibitors, dyes, antioxidants, pharmaceuticals, oil refineries and coal conversion [7,8]. This compound is highly toxic and created by replacing two hydrogen atoms in an aromatic nucleus with two hydroxyl groups. Table 1 shows some of the physical and chemical properties of catechol. Also, this compound is one of the intermediate products of phenol ozonation. Catechol is hematotoxic, hepatotoxic, mutagenic and carcinogenic to humans [8]. The International Agency for Research on Cancer has classified this compound in Group B_2 with middle cancer risk to humans [6]. Catechol is much more toxic than phenol that it changes the function of red blood cells at doses even lower than 50 mg L^{-1} while these changes by phenols occur at a concentration of 250 g L^{-1} [9]. Catechol at concentrations of 5–25 mg L^{-1} is highly toxic to fish and it is an inhibitor to the biological growth of microorganisms. The concentration of phenolic compounds in natural waters is 0.01–2 mg L^{-1} [10]. Also, according to the Environmental Protection Agency's standard, the maximum allowable concentration of phenolic compounds discharged to surface waters for agricultural purposes is equal to 1 mg L^{-1} while the concentration of catechol in industrial wastewaters varies between 10 and 1,000 mg L^{-1} and at the lower temperatures of the wastewater from coal carbonization, it is reported up to 5,300 mg L^{-1} [6,9,11,12]. Thus, according to the hazards created by catechol, a study is conducted to treat the wastewaters containing various physical, chemical and biological processes [13]. This process includes up- flow fixed bed biological reactor, up-flow anaerobic sludge blanket, rotating bed biofilm reactor, continuous or steady flow reactor [14], ozonation and photo-Fenton [15]. On the other hand, biodegradation and removing organic compounds from water and wastewater is mainly conducted by the metabolic activity of the living organisms and thus the biological processes usually do not provide satisfactory results in treating the wastewaters that have resistance to toxic compounds [16–19]. Nano-scale photocatalytic approach has the required potential to minimize toxic pollutants in water. This process creates radical electrons and cavities materials and methods by UV radiation to the nanoparticles [18,20–22]. Using titanium nanoparticles in the photocatalytic process limits the photocatalytic activity due to quick electron and cavity pairing. Also the use of magnesium as a catalyst is limited because of the difficulty in removing it from the wastewater [23]. Therefore, the use of hematite nanoparticle is more suitable due to magnetism and easy removal, non-toxicity, eco-friendliness, high surface to volume ratio, lack of need for the bed, chemical stability and inexpensiveness [20,24]. However, this process is completely biocompatible such that Fe_2O_3 nanoparticles are separated from the water by the magnet or separator pump and thus there is a possibility to reuse and recycle pollutants [25]. Also in recent years due to environmental requirements associated with controlling the consumption of form of energy, most professionals are looking for proper solutions to use natural resources such that the use of sunlight has been considered as a clear source of energy for photocatalytic processes because of the abundance and inexpensiveness. This is more important for Iran that enjoys high sunny hours during the year (2,954 h) [26–28]. This method has been considered as a clean method due to no sludge production and no secondary contamination. The purpose of this study is to compare two photocatalytic methods based on the application of industrial UV and sunlight to remove catechol from the aquatic environment.

Table 1
Some of the physicochemical properties of catechol

Parameters	Catechol
Chemical structure	 $C_6H_6O_2$
Other names	Pyrocatechol; 1,2-benzenediol; 1,2-dihydroxybenzene
Boiling point (°C) at 101.3 kPa	245.5
Density (g cm^{-3})	1.344
Molecular weight (MW; g mol^{-1})	110.11
Water solubility (g L^{-1}) at 25°C (Cs)	430

2. Materials and methods

2.1. Reagents and supplies

Catechol (purity ≥ 98%), alpha hematite (Fe_2O_3; as catalysts), sulfuric acid (H_2SO_4) and sodium hydroxide (NaOH) 0.1 N (to adjust pH), ammonium hydroxide (NH_4OH), potassium ferricyanide ($C_6N_7FeK_4$) and 4-amino anti-pyrene are purchased from Merck company, Germany.

2.2. Photocatalytic reactor

A photo-reactor is designed and built with dimensions of 45 cm × 15 cm × 3 cm to perform a photocatalytic process (Fig. 1). A 6-W UV lamp (middle range-UV-C lamp manufactured by Osram Company, Germany) is devised as the light source inside the reactor. To ensure the absence of reflection,

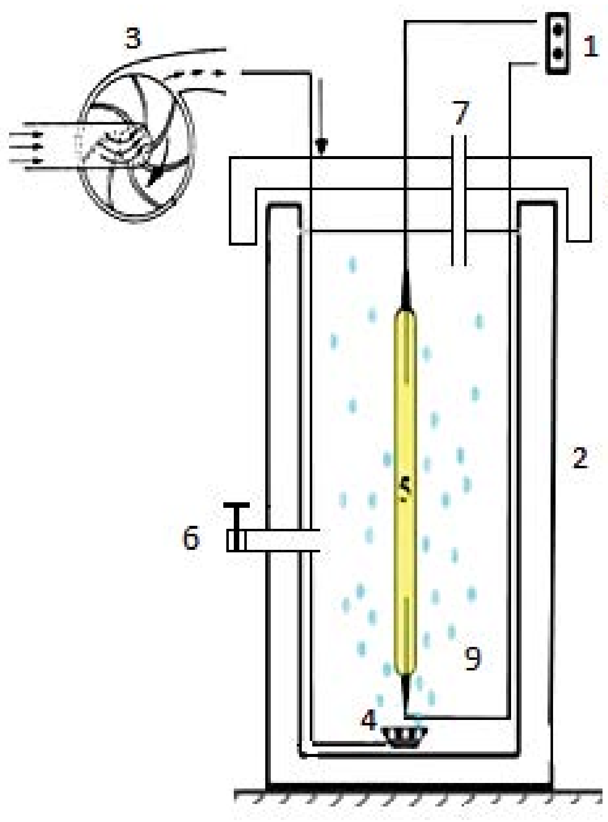


Fig. 1. Schematic of experimental setup. (1) Power supply, (2) glass reactor, (3) air pump, (4) air distributer, (5) UV lamp, (6) sampling port, (7) air exhaust, (8) cap of reactor and (9) synthetic wastewater.

the whole system is located in a dark room. In order to complete mixing and continuous flow of reactor contents, a stirrer is placed under the reactor. All process steps are performed at room temperature.

2.3. Photocatalytic process

The parameters examined in this study are the effects of pH, Fe_2O_3 concentration, initial catechol concentration and reaction time on the UV/Fe_2O_3 and Fe_2O_3/sunlight processes. In each of the cases, the removal of catechol with and without catalyst, UV and sunlight is investigated. The stock solution (100 ppm) is used to prepare 10, 20, 30 and 50 mg L^{-1} concentrations of catechol. In order to achieve comparable results, the samples are exposed to UV, alpha hematite and sunlight under controlled conditions in separate processes. The concurrent effects of UV/Fe_2O_3 and Fe_2O_3/sunlight are studied on catechol oxidation in 10, 20, 30 and 50 mg L^{-1} catechol solutions. Accordingly, the 0.2, 0.3 and 0.4 g L^{-1} concentrations of alpha hematite are used. After adjusting pH on each of 2, 3, 4, 5 and 7 values within 15, 30 and 60 min intervals, reactor sampling is conducted. At the end of each stage of the experiment, alpha hematite in the samples is separated by the magnet and filtration of each sample is conducted by Buchner funnel and passing through Whatman filter paper with 0.45 mm mesh made of cellulose acetate. In this study, the UV-A in the sunlight is used for radiation to reactor contents. UVA rays contain waves with a wavelength between 320 and 4,000 nm and pass the glass. During a summer day, about 96.5% of the ultraviolet spectrum that reaches the Earth's surface is UVA type. 90% of visible light, above 70% of the UVA (300–400 nm) and more than 80% of solar heat passes through the transparent glass. Fe_2O_3/sunlight process experiments are conducted in ShahreKord in a mountainous area at 32°–20° N, 51°–50° East in July between 10 am and 2 pm.

2.4. Analysis

Catechol remaining in the filtered sample is measured by adding 2 mL of ammonium hydroxide, adjusting the pH by phosphate buffer in the range of 7–9, adding 2 mL 4-amino anti-pyrene and 2 mL potassium ferricyanide after 15 min with a spectrophotometer at a wavelength of 600 nm. All experiments in this study are conducted according to the experiment protocol in "standard methods for water and wastewater experiments". COD was measured by dichromate oxidation according to the standard method [29]. The catechol removal rate is calculated using the following equation:

$$\text{Degradation efficiency}(\%) = \left(1 - \frac{C_t}{C_0}\right) \times 100 \qquad (1)$$

where C_0 and C_t are the initial and final catechol concentrations [29].

3. Results and discussion

3.1. Effect of pH0

Photocatalytic degradation of catechol in pH between 2 and 7 for UV/Fe_2O_3 and Fe_2O_3/sunlight processes is shown in Fig. 2. The highest catechol degradation for all concentrations in both processes has occurred at pH = 2 and the removal efficiency has a downward trend by increasing pH from 2 to 7. In other words, the photocatalytic reaction has the highest efficiency in acidic pH. This is due to the presence of hydrogen ions in the acid environments that serves as a precursor to hydrogen radicals. Then the radicals form $HO_2^\bullet$ through the reaction with oxygen in the solution and finally they lead to the formation of $OH^\bullet$ radicals [30]. In confirming the present study, Mandal et al. [31] showed that in the photo-Fenton process the hydroxyl radicals are produced through reaction with H_2O_2 in the optimal pH of 2.7. Also the obtained results are consistent with Chen et al. [32]. Gogoi et al. [33] showed that the highest catechol degradation happens at acidic pH of 2.4 because hydroxyl radicals are produced to a greater extent in acidic conditions and the presence of magnetic nanoparticles. But in alkaline conditions $O_2^{\bullet-}$anionic radical is produced. $OH^\bullet$ radicals have a much greater ability to break down catechol and phenolic compounds [33]. However the results of Li et al. [34] are in contrast with the results of the present study. In their study, the increase in pH raised the level of catechol degradation. They concluded that the impact of initial pH on catechol degradation is dependent on reaction time; thus pH of the solution reduced by increasing

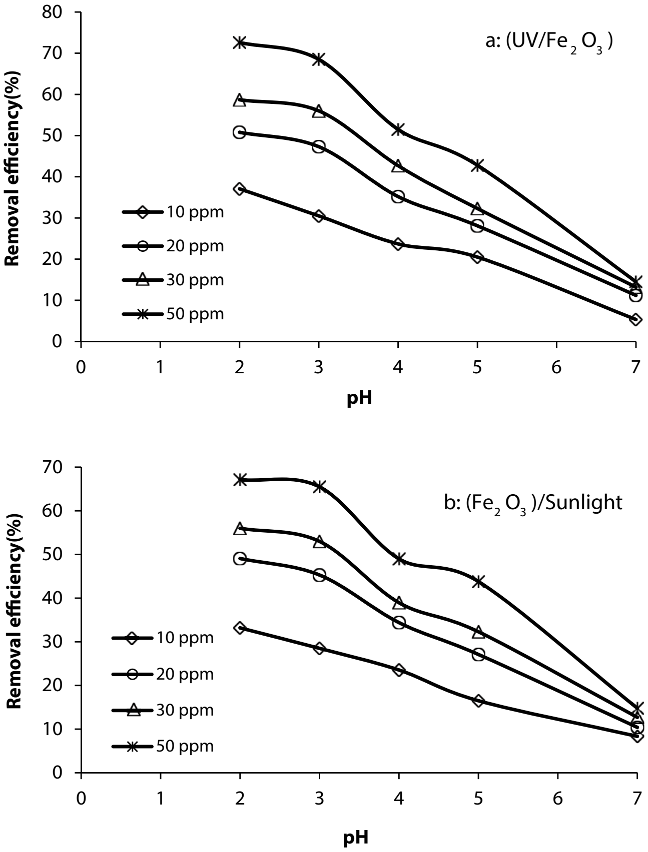


Fig. 2. Effect of pH on photocatalytic removal of catechol. (a) UV/Fe_2O_3 and (b) Fe_2O_3/sunlight (time = 60 min and Fe_2O_3 = 0.4 g L^{-1}).

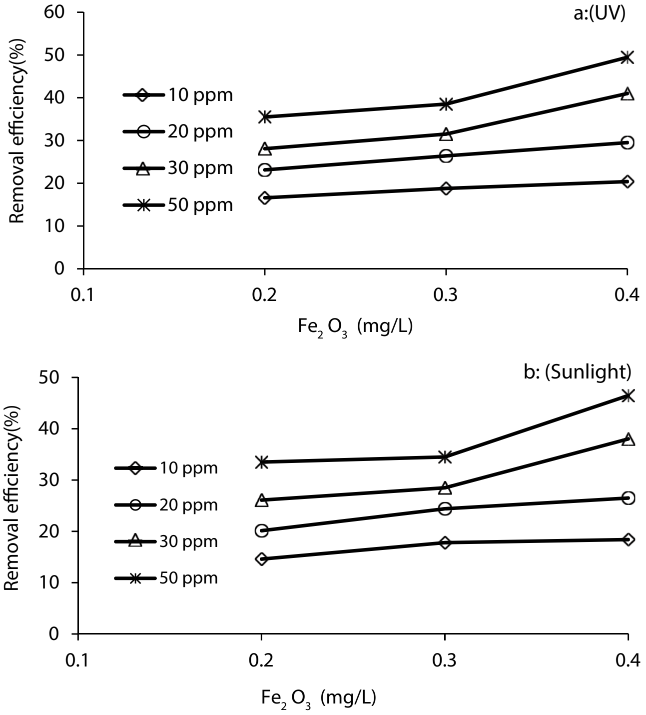


Fig. 3. Effect of Fe_2O_3 concentration on photocatalytic removal of catechol. (a) UV/Fe_2O_3 and (b) Fe_2O_3/sunlight (pH = 2 and time = 60 min).

the reaction time. This is associated with the production of some intermediate acidic compounds (formic acid, acetic acid, oxalic acid and maleic acid). In fact the production of intermediate acidic compounds reduces the pH of the solution and decreases the efficiency of the oxidation process [34]. In a study by Boruah et al. [35], the maximum phenol degradation efficiency was obtained in pH = 7 which is not consistent with the present study. They concluded that the maximum degradation of phenolic compounds happens in the pH range between 5 and 11. Boruah et al. [35] attributed this to the reduced catalytic activity of ammonia-modified graphene (AG)/Fe_3O_4 in acidic solutions.

3.2. *Effect of Fe_2O_3 concentration*

Fig. 3 indicates the change in removal efficiency of catechol for UV/Fe_2O_3 and Fe_2O_3/sunlight processes vs. varying concentrations of Fe_2O_3. According to this graph, it can be concluded that by increasing the Fe_2O_3 concentration, catechol removal is increased for both processes. This increased removal rate follows an almost similar pattern at lower concentrations of Fe_2O_3, and whatever Fe_2O_3 concentration increases, the curves for both processes have been further apart. The reason could be the availability of more absorption active sites in the solution. The results of this study are consistent with Kadirova et al [36] on the effect of Fe_2O_3 loading on methylene blue photocatalytic degradation. The study suggests that by increasing the catalyst concentration, the number of absorbed photons increases and finally increases the number of active sites on the surface of the photocatalyst. Therefore, by increasing Fe_2O_3, the photocatalytic degradation of methylene blue increases [36]. Mandal et al. [31] showed that in case of using ferrous sulfate catalyst, the hydroxyl radicals' production increases significantly and this leads to further catechol degradation [31]. Also Masomboon et al. [37] studied 1 and 6-dimethyl amine oxidation by Fenton process. They concluded that the catalyst concentration should be increased to raise the rate of pollutant degradation, but more than one mg per liter increase of hematite leads to the formation of an inhibiting effect in hydroxyl radicals which results in reducing pollutant's degradation [37]. But Gogoi et al. [33] concluded that increasing CeO_2/Fe_3O_4 catalyst to 50 mg in acidic medium leads to greater catechol degradation which is due to smaller particle size, more active sites and greater contact surfaces of Fe_3O_4.

3.3. *Impact of the initial concentration of catechol*

Fig. 4 shows the effect of initial concentrations of catechol in photocatalytic degradation. According to this chart, increasing initial concentration of catechol from 10 to 50 mg/L^{-1} has increased the photocatalytic degradation of catechol in UV/$Fe_2O_3$and Fe_2O_3/sunlight processes by 22.5% and 20%, respectively. In this study, the highest catechol removal concentration is obtained in 50 mg L^{-1}. In fact, by increasing the catechol concentration from 10 to 50 mg L^{-1}, the number of catechol particles' collision with the hydroxyl oxidizing agent is increased which increases the removal efficiency. But studies have shown that increasing catechol

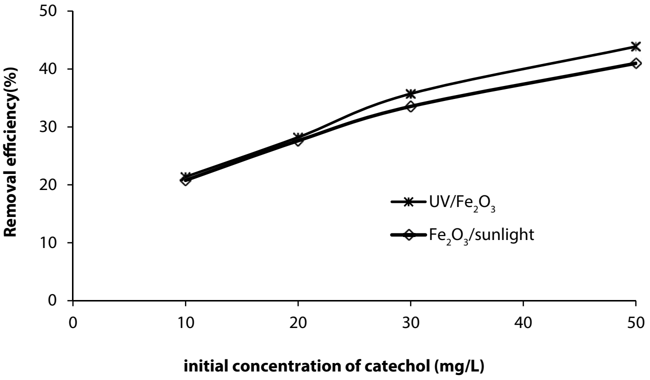


Fig. 4. Effect of initial concentration of catechol on photocatalytic removal (pH = 2, time = 60 min and Fe_2O_3 = 0.4 g L^{-1}).

concentration to greater than 50 mg L^{-1} produces intermediate products more reactive than the pollutant that react with the free radicals and reduce catechol removal efficiency [15,31]. Lofrano et al. [15] studied the advanced oxidation of catechol with the photocatalytic process and concluded that by increasing catechol concentration 50–200 mg L^{-1} the rate of catechol degradation is reduced because of the increase in intermediate products and their competition with catechol. Generally the photocatalytic process is not effective for the degradation of high concentrations of catechol [15]. Mandal et al. [31] found that by increasing the initial concentration of catechol more time is required for catechol degradation. So that at low concentrations about 90% of the catechol is removed by the photo-oxidation process in the first 5 min of contact time [31].

3.4. Effect of reaction time

Catechol removal rate as a function of time is shown in Fig. 5. According to this chart, with an increase in time, the rate of photocatalytic degradation of catechol increases. This is due to increased interaction between hydroxyl and catechol radicals. Mandal et al. [31] studied catechol removal from aqueous solutions by advanced photo-oxidation processes. Their results showed that about 90%–95% of catechol was removed in 60 min. They have associated this with higher production of hydroxyl radicals by increasing the reaction time [31]. Kadirova et al. [36] in a study on the absorption and degradation of methylene blue by active hematite - carbon under UV showed that by increasing the reaction time, removal efficiency increases. The same results were obtained by Lofrano et al. [15].

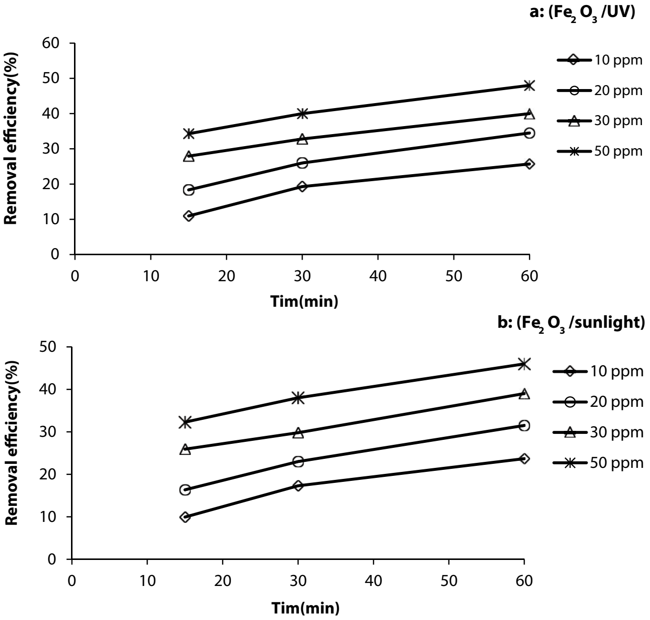


Fig. 5. Effect of contact time on photocatalytic removal of catechol. (a) UV/Fe_2O_3, (b) Fe_2O_3/sunlight (pH = 2 and Fe_2O_3 = 0.4 g L^{-1}).

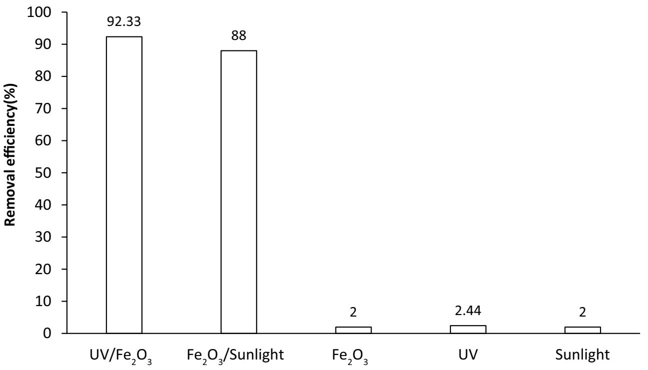


Fig. 6. Degradation and oxidation curves of catechol (50 mg L^{-1} catechol. pH = 2, time = 60 min and Fe_2O_3 = 0.4 g L^{-1}).

3.5. Use of UV radiation and Fe_2O_3 catalysts in catechol degradation separately

Fig. 6 presents the comparison between Fe_2O_3 catalysts, UV radiation, sunlight, UV/Fe_2O_3 and Fe_2O_3/sunlight on catechol removal in optimal conditions (50 mg L^{-1} catechol, pH = 2, contact time of 60 min, hematite concentration of 0.4 g L^{-1}). The maximum catechol removal efficiency by Fe_2O_3 is only 2%, which is minimal compared with the photocatalytic degradation of catechol in the Fe_2O_3/UV process (92.33% efficiency). The reason for this could be the low amount of hematite in the sample which is not capable of initiating photocatalytic reaction and adsorption. Moreover, the hematite containing sample has a very weak absorption band that is not capable of catechol adsorption. In fact, when hematite is used alone, the radical reactions will not happen, thus the removal is very low. According to Fig. 6, the maximum catechol removal by UV radiation alone is about 2.5%. The study conducted by Sun (2012) titled "the hematite effect on the photocatalytic activity of phenols" confirms this issue [23]. In a study by Araña et al. [38], no catechol adsorption was observed at the first 45 min of contact time. In the present study using sunlight, catechol degradation is only 2% in optimal conditions. Boruah et al. [35] showed that in the absence of AG/Fe_3O_4 catalysts and using sunlight alone, only 6% of the phenol is biodegraded. Also in case of using the catalysts in the dark, 17% of phenol was degraded. However, the concurrent use of catalysts and sunlight at pH = 7 and contact time of 120 min increases phenol degradation to 92.43% [35].

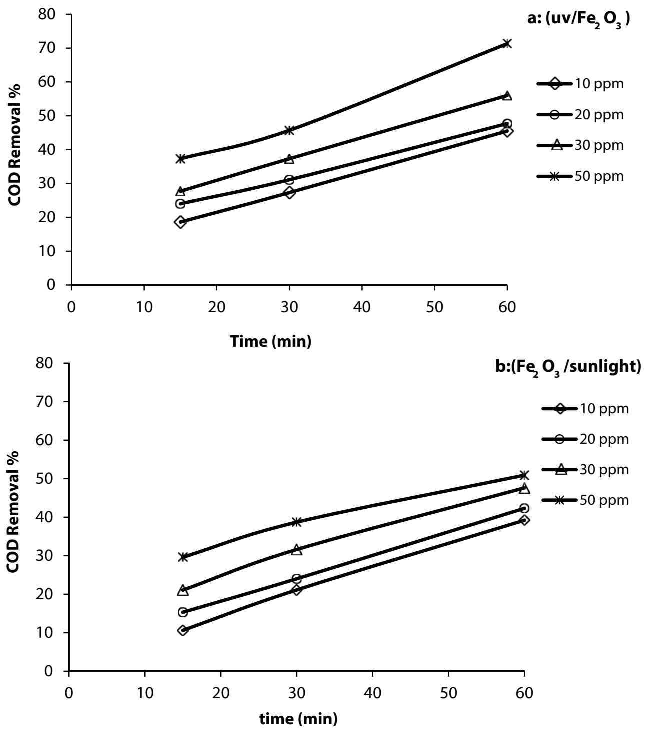


Fig. 7. Oxidation of catechol by different processes. (a) UV/Fe_2O_3 and (b) Fe_2O_3/sunlight (pH = 2 and Fe_2O_3 = 0.4 g L^{-1}).

In this study, UV/Fe_3O_4 process had higher efficiency than other processes for catechol removal (92.3%). Unlike the present study, the results of Kunduz and Soylu [39] for phenol removal from wastewater using photocatalytic activity of $BiVO_4$ nanoparticles showed that the sunlight has a better efficiency in the phenol removal than UVB and mercury lamp. It is stated that in a contact time of 90 min, 100% phenol is removed in the presence of sunlight and $BiVO_4$ nanoparticles while the removal efficiency by UVB and mercury lamp is 74% and 34%, respectively [39].

3.6. Oxidation of catechol by UV/Fe_2O_3 and sunlight/Fe_2O_3 processes

Control experiments were conducted to compare the oxidation performance of various processes including UV/Fe_2O_3 and Fe_2O_3/sunlight. The results in Fig. 7 show that COD removal of 58% within 60 min and no COD removal was found by Fe_2O_3 adsorption alone, showing surface adsorption of Fe_2O_3 did not contribute to COD removal in catechol oxidation. However, in the presence of UV irradiation, heterogeneous UV/Fe_2O_3 with 0.4 g L^{-1} Fe_2O_3 obtained COD removal of 71.3%, while Fe_2O_3/sunlight achieved lower COD removal of 50.9%. The oxidation efficiency in heterogeneous UV/Fe_2O_3 was larger than the Fe_2O_3/sunlight. Hence, the following experiments were performed on catechol oxidation by UV/Fe_2O_3 and Fe_2O_3/sunlight processes. Li et al. [34] showed that heterogeneous UV–Fenton with 0.5 g L^{-1} nano-Fe_3O_4 obtained COD removal of 84% while photolysis of H_2O_2 achieved lower COD removal of 32%.

4. Conclusion

This study proved the catechol removal of 92.3% and 88% for UV/Fe_2O_3 and Fe_2O_3/sunlight reactions in the best operation conditions (pH = 2, contact time of 60 min, hematite concentration of 4.0 g L^{-1} and catechol concentration of 50 mg L^{-1}). The results of the study showed that there is no significant difference in the catechol removal between two processes with $p > 0.05$, therefore replacing the sunlight instead of UV lamps will be a step towards economic optimization and sustainable development.

Competing interests

The authors declare that they have no competing interests.

Acknowledgment

The authors are grateful to Deputy of Research and Technology of Shahrekord University of Medical Sciences (SKUMS) for financial support and laboratory assistance of Department of Environmental Health and Engineering, School of Health, SKUMS.

References

[1] R. Subramanyam, I. Mishra, Biodegradation of catechol (2-hydroxy phenol) bearing wastewater in an UASB reactor, Chemosphere, 69 (2007) 816–824.

[2] F.C. Moreira, R. Boaventura, E. Brillas, V. Vilar, Electrochemical advanced oxidation processes: a review on their application to synthetic and real wastewaters, Appl. Catal., B, 202 (2017) 217–261.

[3] M. Qasemi, M. Afsharnia, A. Zarei, A.A. Najafpoor, S. Salari, M. Shams, Phenol removal from aqueous solution using *Citrullus colocynthis* waste ash, Data in Brief, 18 (2018) 620–628.

[4] C.A. Damalas, I.G. Eleftherohorinos, Pesticide exposure, safety issues, and risk assessment indicators, Int. J. Environ. Res. Public Health, 8 (2011) 1402–1419.

[5] M. Ghaderpoori, M. Paydar, A. Zarei, H. Alidadi, A.A. Najafpoor, A.H. Gohary, M. Shams, Health risk assessment of fluoride in water distribution network of Mashhad, Iran, Hum. Ecol. Risk Assess., (2018) p. 1–12.

[6] A.A. Aghapour, G. Moussavi, K. Yaghmaeian, Biological degradation of catechol in wastewater using the sequencing continuous-inflow reactor (SCR), J. Environ. Health Sci. Eng., 11 (2013) 1–10.

[7] M. Bajaj, C. Gallert, J. Winter, Biodegradation of high phenol containing synthetic wastewater by an aerobic fixed bed reactor, Bioresour. Technol., 99 (2008) 8376–8381.

[8] G. Moussavi, A.A. Aghapour, K. Yaghmaeian, The degradation and mineralization of catechol using ozonation catalyzed with MgO/GAC composite in a fluidized bed reactor, Chem. Eng. J., 249 (2014) 302–310.

[9] S. Suresh, V.C. Srivastava, I.M. Mishra, Adsorption of catechol, resorcinol, hydroquinone, and their derivatives: a review, Int. J. Energy Environ. Eng., 3 (2012) 1–19.

[10] J. Michałowicz, W. Duda, Phenols sources and toxicity, Pol. J. Environ. Studies, 16 (2007) 347–362.

[11] M. Ahmadi, F. Vahabzade, E. Moffarrah, M. Aliabadi, Application of Advanced Oxidation of Dephenolization of Olive Oil Mill Wastewater Processing by Fenton's Reagent, Proc. 9th National Congress of Chem, Eng., 2004.

[12] R. Subramanyam, I. Mishra, Treatment of catechol bearing wastewater in an upflow anaerobic sludge blanket (UASB) reactor: sludge characteristics, Bioresour. Technol., 99 (2008) 8917–8925.

[13] A. Kumar, S. Kumar, S. Kumar, Adsorption of resorcinol and catechol on granular activated carbon: equilibrium and kinetics, Carbon, 41 (2003) 3015–3025.

[14] A.A. Aghapour, G. Moussavi, K. Yaghmaeian, Investigating the performance of a novel cyclic rotating-bed biological reactor compared with a sequencing continuous-inflow reactor for biodegradation of catechol in wastewater, Bioresour. Technol., 138 (2013) 369–372.

[15] G. Lofrano, L. Rizzo, M. Grassi, V. Belgiorno, Advanced oxidation of catechol: a comparison among photocatalysis, Fenton and photo-Fenton processes, Desalination, 249 (2009) 878–883.

[16] I. Oller, S. Malato, J. Sánchez-Pérez, Combination of advanced oxidation processes and biological treatments for wastewater decontamination—a review, Sci. Total Environ., 409 (2011) 4141–4166.

[17] M. Lapertot, C. Pulgarin, I. Oller, W. Gernjak, S. Malato, Enhancing biodegradability of priority substances (pesticides) by solar photo-Fenton, Water Res., 40 (2006) 1086–1094.

[18] A. Fadaei, M.H. Dehghani, A. Rahimi, M. Sadeghi, Using sonophotodegradation technology for removal of organophosphorus pesticides in aqueous solution, Asian J. Chem., 25 (2013) 7517.

[19] V. Oskoei, M.H. Dehghani, S. Nazmara, B. Heibati, M. Asif, I. Tyagi, S. Agarwal, Removal of humic acid from aqueous solution using UV/ZnO nano-photocatalysis and adsorption, J. Mol. Liq., 213 (2016) 374–380.

[20] P. Xu, G.M. Zeng, D.L. Huang, C.L. Feng, Z. Wei, G. Xie, Use of iron oxide nanomaterials in wastewater treatment: a review, Sci. Total Environ., 424 (2012) 1–10.

[21] M. Farzadkia, Degradation of metronidazole in aqueous solution by nano-ZnO/UV photocatalytic process, Desal. Wat. Treat., 52 (2014) 4947–4952.

[22] A. Fadaei, Mh. Dehghani, A.H. Mahvi, S. Nasseri, N. Rastkari, M. Shayeghi, Degradation of organophosphorus pesticides in water during UV/H_2O_2 treatment: role of sulphate and bicarbonate ions, J. Chem., 9 (2012) 2015–2022.

[23] Q. Sun, W. Leng, Z. Li, Y. Xu, Effect of surface Fe_2O_3 clusters on the photocatalytic activity of TiO_2 for phenol degradation in water, J. Hazard. Mater., 229 (2012) 224–232.

[24] M. Sadeghi, Efficacy study on Advanced Oxidation Processes (AOPs) application for pesticides removal from water with emphasis on their cost aspects, J. Shahrekord Univ. Med. Sci., 15 (2013) 80–89.

[25] H. Hildebrand, K. Mackenzie, F. Kopinke, Novel nano-catalysts for wastewater treatment, Global NEST J., 10 (2008) 47–53.

[26] G.M. Titato, F.M. Lanças, Optimization and validation of HPLC-UV-DAD and HPLC-APCI-MS methodologies for the determination of selected PAHs in water samples, J. Chromatogr. Sci., 44 (2006) 35–40.

[27] F. Mojarad, K. Moradi, Brnamvzvny attitudes and trends sunlight hours in Iran, Geogr. Dev., 34 (2014) 153–166.

[28] R. Rezaei Kalantary, Y. Dadban, M. Farzadkia, A. Esrafili, Photocatalytic degradation and mineralization of diazinon in aqueous solution using nano-TiO_2(Degussa, P25): kinetic and statistical analysis, Desal. Wat. Treat., 55 (2015) 555–563.

[29] WEF, APHA, Standard Methods for the Examination of Water and Wastewater, American Public Health Association (APHA), Washington, D.C., USA, 2005.

[30] M. Aslam, I. Ismail, N. Salah, M. Qamar, A. Hameed, Evaluation of sunlight induced structural changes and their effect on the photocatalytic activity of V_2O_5 for the degradation of phenols, J. Hazard. Mater., 286 (2015) 127–135.

[31] A. Mandal, K. Ojha, K. Deasim, S. Bhattacharjee, Removal of catechol from aqueous solution by advanced photo-oxidation process, Chem. Eng. J., 102 (2004) 203–208.

[32] M. Chen, X. Li, X. Ma, Selective determination of catechol in wastewater at silver doped polyglycine modified film electrode, Int. J. Electrochem. Sci., 7 (2012) 2616.

[33] A. Gogoi, M. Navgir, K. Sarma, P. Gogoi, Fe_3O_4-CeO_2 metal oxide nanocomposite as a Fenton-like heterogeneous catalyst for degradation of catechol, Chem. Eng. J., 311 (2016) 153–162.

[34] Y. Li, Y. Wang, A. Irini, Effect of pH and H_2O_2 dosage on catechol oxidation in nano-Fe_3O_4 catalyzing UV–Fenton and identification of reactive oxygen species, Chem. Eng. J., 244 (2014) 1–8.

[35] P.K. Boruah, B. Sharma, I. Karbhal, M. Shelke, M. Das, Ammonia-modified graphene sheets decorated with magnetic Fe_3O_4 nanoparticles for the photocatalytic and photo-Fenton degradation of phenolic compounds under sunlight irradiation, J. Hazard. Mater., 325 (2016) 90–100.

[36] Z.C. Kadirova, K. Katsumata, T. Isobe, N. Matsushita, A. Nakajima, Adsorption and photodegradation of methylene blue with Fe_2O_3-activated carbons under UV illumination in oxalate solution, J. Environ. Chem. Eng., 2 (2014) 2026–2036.

[37] N. Masomboon, C. Ratanatamskul, M.-C. Lu, Chemical oxidation of 2,6-dimethylaniline by electrochemically generated Fenton's reagent, J. Hazard. Mater., 176 (2010) 92–98.

[38] J. Araña, J.M. Rodriguez, G. Diaz, J.A. Melian, P. Pena, The effect of acetic acid on the photocatalytic degradation of catechol and resorcinol, Appl. Catal., A, 299 (2006) 274–284.

[39] S. Kunduz, G.S.P. Soylu, Highly active $BiVO_4$ nanoparticles: the enhanced photocatalytic properties under natural sunlight for removal of phenol from wastewater, Sep. Purif. Technol., 141 (2015) 221–228.