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Yerkanat N Kanafin[1,3], Ardak Makhatova[1], Elizabeth Arkhangelsky[2] and Stavros G Poulopoulos[1]

[1]Chemical and Materials Engineering Department, School of Engineering and Digital Sciences, Environmental Science and Technology Group (ESTg), The Environment and Resource Efficiency Cluster (EREC), Nazarbayev University, 010000, Nur-Sultan, Kazakhstan
[2]Civil and Environmental Engineering Department, School of Engineering and Digital Sciences, Environmental Science and Technology Group (ESTg), The Environment and Resource Efficiency Cluster (EREC), Nazarbayev University, 010000, Nur-Sultan, Kazakhstan

[3]Corresponding author, Email: yerkanat.kanafin@nu.edu.kz

Abstract. The photochemical treatment of an actual municipal wastewater (MWW) from wastewater treatment plant (WWTP) in Kazakhstan has been studied in the present work. The MWW has been taken after mechanical treatment stage and characterized. The photochemical treatment included the use of the photo-Fenton-like process in the batch photoreactor with a UV irradiation at 254 nm for 120 min. Experiments have been done without adjusting the initial pH of wastewater, which was around 7.7. Potassium persulfate ($K_2S_2O_8$) was activated by means of UV and ferric ions, which led to generation of highly oxidative sulfate and peroxymonosulfate radicals. The concentration of Fe^{2+} ions ranged from 20 to 100 ppm, while the concentration of $K_2S_2O_8$ was in between 5 and 25 mmol/L. 83% removal of total organic carbon (TOC) was achieved after 120 min of treatment using 15 mmol/L $K_2S_2O_8$ and 20 ppm Fe^{2+}, while 75% removal of total carbon (TC) was observed at 15 mmol/L $K_2S_2O_8$ and 100 ppm Fe^{2+}. As the carboxylic acids are common organic intermediates after photochemical treatment, the presence of formate and acetate anions in effluents were further detected on the ion chromatography.

1. Introduction

Nowadays, development of countries through urbanization and industrialization is contributing to the rapid generation of municipal wastewater globally [1]. Conventional municipal wastewater treatment plants (WWTP) mainly rely on biological treatment methods [2]. As the efficient operation of conventional WWTPs involves considerable investment on construction and maintenance, the search for other wastewater treatment technologies should be conducted. In this regards, advanced oxidation processes (AOPs) are gaining increasing interest in wastewater treatment research. Among different AOPs, sulfate-radical based systems (SR-AOPs) are being recognized as a promising technique for the degradation of organic pollutants. Potassium, sodium and ammonium persulfate can be used as a source of the sulfate radicals ($SO_4^{\bullet-}$) [3]. Generally, persulfate (PS) is activated into sulfate radicals using photolysis, sonolysis, thermolysis as well as with homogeneous or heterogeneous catalysts, where photo-activation is considered as the most practically approachable [1]. The mechanism of PS activation by UV light and ferrous iron are shown in equations 1 and 2 below:

$$S_2O_8^{2-} + hv \rightarrow 2SO_4^{\bullet -} \quad (1)$$

$$S_2O_8^{2-} + Fe^{2+} \rightarrow SO_4^{\bullet -} + SO_4^{2-} + Fe^{3+} \quad (2)$$

The present work studied the use of photo-Fenton-like process ($UV/S_2O_8^{2-}/Fe^{2+}$) for the treatment of a real municipal wastewater.

2. Materials and Methods

2.1. Wastewater characteristics

The real wastewater was sampled from the municipal WWTP "Astana su arnasy" (Nur-Sultan city, Kazakhstan). The wastewater was filtered through a glass microfiber filter paper (0.7 µm, Whatman, Grade GF/F) and stored in the fridge at 4°C prior the experiments. The characteristics of wastewater are shown in Table 1.

Table 1. Characteristics of a real municipal wastewater.

Parameter	Unit	Value
Total carbon (TC)	ppm	117.66 ± 1.44
Total inorganic carbon (TIC)	ppm	95.23 ± 2.78
Total organic carbon (TOC)	ppm	22.43 ± 3.01
pH		7.60 ± 0.17

2.2. Chemicals

Potassium persulfate ($K_2S_2O_8$) was used as a source of sulfate radicals and purchased from Sigma-Aldrich. Ammonium iron (II) sulfate hexahydrate ($(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$) was obtained from Fisher Chemical and utilized as a source of ferrous iron. Both reagents had purity more than 99% and applied without further purification.

2.3. Batch experiments

A batch photochemical reactor was used for all experiments (Toption Instrument Co., Ltd, China). Reactor was equipped with 30 W lamp with an ultraviolet irradiation at 254 nm. 400 mL of wastewater was used for each run. The reaction solution was continuously mixed using a magnetic stirrer. Aliquots were taken using syringe and filtered through a membrane filters with the pore size of 0.2 µm (Chromofil Xtra RC-20/25) prior to analysis. TC, TIC and TOC of the sample were determined using the Multi N/C 3100 instrument by Analytik Jena AG (Germany). The details of analysis are provided in the previous work [2]. Ion chromatography (IC, the 930 Compact IC Flex, Metrohm) was employed to detect trace concentrations of formic and acetic acids in the wastewater solutions.

3. Results and Discussion

3.1. Photochemical treatment of municipal wastewater

Photo-Fenton-like oxidation involves the use of UV light, persulfate and iron for generation of sulfate radicals. Moreover, other oxidizing radicals such as hydroxyl and persulfate radicals can be formed during this process (Equations 3 and 4) [4], which makes persulfate more efficient oxidant source than hydrogen peroxide (H_2O_2).

$$SO_4^{\bullet -} + H_2O \rightarrow SO_4^{2-} + H^+ + HO^\bullet \quad (3)$$

$$SO_4^{\bullet -} + S_2O_8^{2-} \rightarrow SO_4^{2-} + S_2O_8^{\bullet -} \quad (4)$$

In this work, the concentration of persulfate (PS) ranged from 5 to 25 mM and concentrations of Fe^{2+} were between 20 ppm and 100 ppm. The removal of TC and TOC and pH evolution during photo-Fenton-like treatment of wastewater are shown in Figures 1, 2 and 3, respectively.

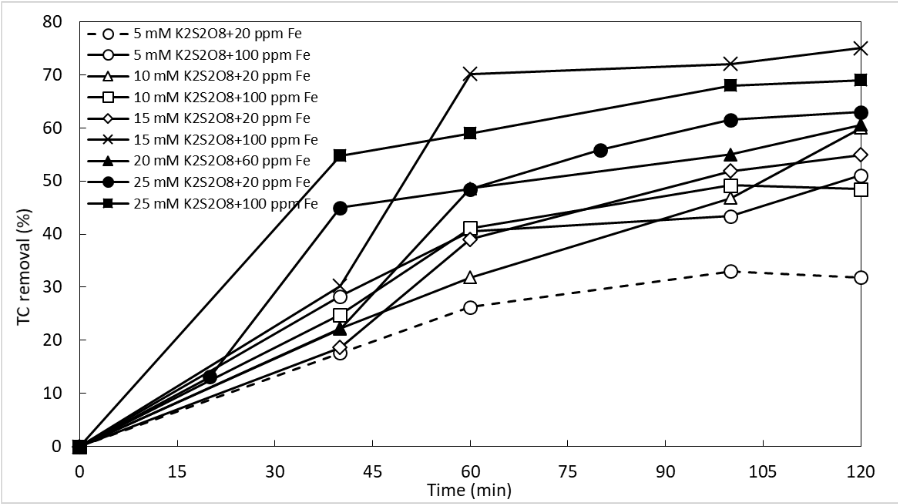

Figure 1. TC removal during photochemical treatment of municipal wastewater.

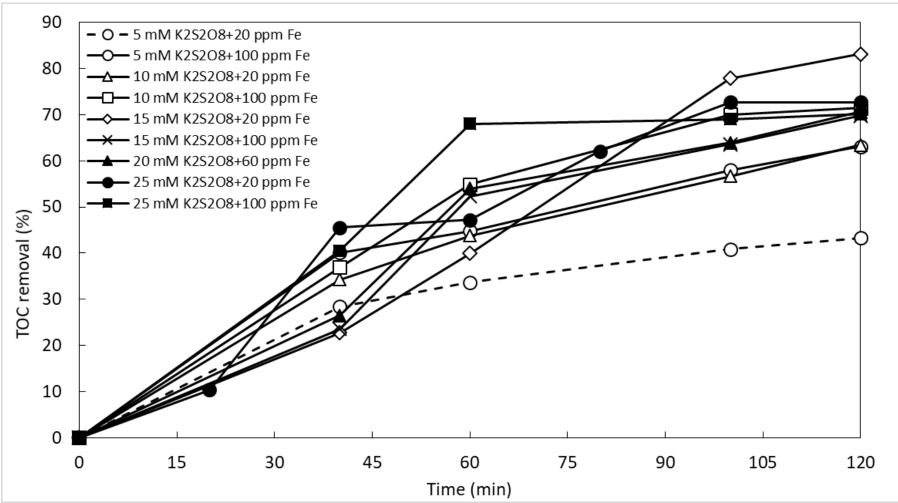

Figure 2. TOC removal during photochemical treatment of municipal wastewater.

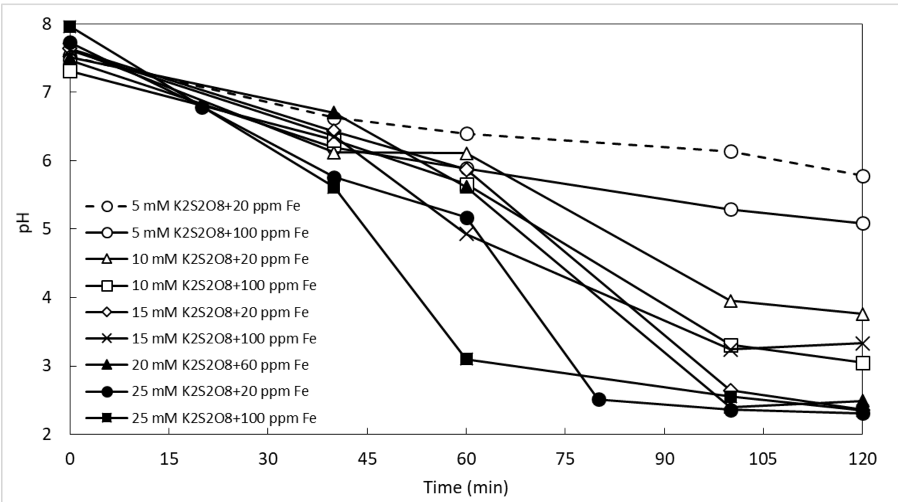

Figure 3. pH evolution during photochemical treatment of municipal wastewater.

As it can be seen from Figure 1, TC removal rose from 51% at 5 mM PS and 100 ppm Fe^{2+} to 75% after 15 mM PS and 100 ppm Fe^{2+}. Further increase of PS concentration, to 20 and 25 mM resulted in decrease of TC removal. The increase of Fe^{2+} concentration from 20 ppm to 100 ppm improved TC removal at 5, 15 and 15 mM PS.

The highest TOC removal rate of 83% has been obtained at 15 mM PS and 20 ppm Fe^{2+}, while increase of Fe^{2+} concentration to 100 ppm resulted in 70% removal of TOC. This might be linked to the consumption of sulfate radicals with the excess of Fe^{2+} (Equation 5). Similar to TC removal, TOC removal decreased with further increment in PS concentration.

$$SO_4^{\bullet -} + Fe^{2+} \rightarrow SO_4^{2-} + Fe^{3+} \quad (5)$$

In the previous work, UV/$S_2O_8^{2-}$/Fe^{2+} process was applied to treat synthetic wastewater effluents and 78% removal of TOC was achieved with 5 mM of PS and 5 ppm of Fe^{2+} [5]. In comparison, the use of 5 mM of PS and 20 ppm of Fe^{2+} in the present work resulted in only 43% TOC removal. This difference could be explained by the abundance of TIC (81% of TC) in a real wastewater, which contains radical scavenging compounds and stagnates the removal of contaminants. The issue with TIC could be easily solved by acidification of wastewater [6].

As it is shown in Figure 3, photo-Fenton-like oxidation of wastewater lead to decrease of pH in all cases. It should be noted that Fe^{3+} ions produced after generation of $SO_4^{\bullet -}$ radicals, mainly exist in the form of ferric hydroxide ($Fe(OH)^{2+}$). In the presence of UV irradiation, ferric hydroxide absorbs the light, regenerates into Fe^{2+} ions and produces hydroxyl radicals (Equation 6) [1].

$$Fe(OH)^{2+} + hv \rightarrow Fe^{2+} + HO^{\bullet} \quad (6)$$

The conditions, where the most efficient removal of TC and TOC were observed, had final pH of 2.4-3.3. Both ferrous and ferric iron are highly soluble in this pH range, which accelerates the regeneration of Fe^{2+}.

3.2. Formation of intermediates

Degradation products after photochemical treatment of municipal wastewater has been analyzed using ion chromatography. Concentration of unidentified organic intermediates has been calculated by subtracting mineralized organic carbon (CO_2), organic carbons of formic and acetic acids from initial TOC. The results are depicted in Figure 4.

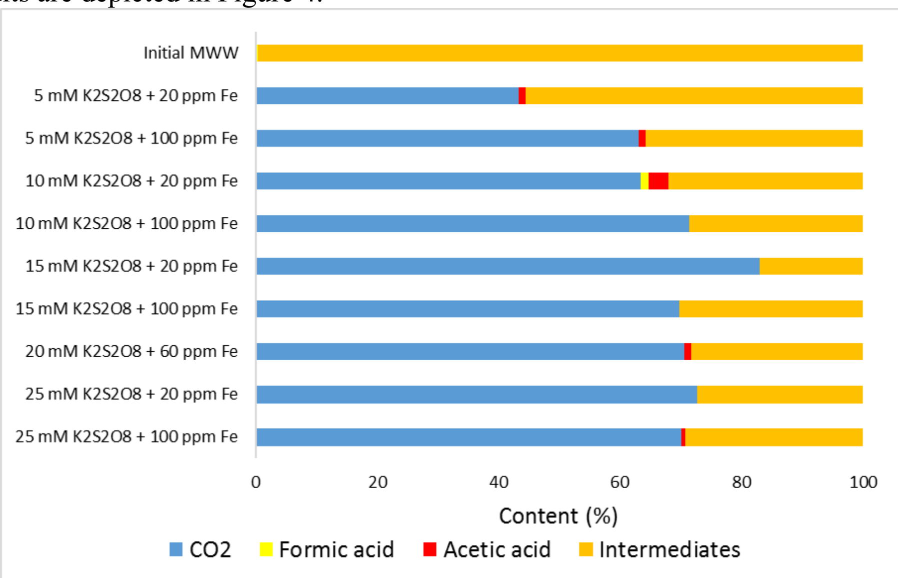

Figure 4. The content of formic acid, acetic acid, intermediates and CO_2 for each process.

According to Figure 4, the least proportion of unidentified intermediates (16.9%) was determined in final solution after 15 mM of PS and 20 ppm of Fe^{2+}.

4. Conclusions

The treatment of a real municipal wastewater was studied by photo-Fenton-like process. The efficiency of the treatment was assessed in terms of TC and TOC removal rates. Potassium persulfate was used in the range from 5 to 25 mM and concentration of Fe^{2+} was between 20 to 100 ppm. The main results of this work are following:

(a) The highest removal of TC (75%) was achieved when 15 mM of PS and 100 ppm of Fe^{2+} was used;

(b) The combination of 15 mM of PS and 100 ppm of Fe^{2+} resulted in 83% TOC removal after 120 min;

(c) The organic content of wastewater solutions after each photochemical treatment has been analyzed using ion chromatography.

Acknowledgements

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References

[1] Yang J, Zhu M and Dionysiou D D 2021 What is the role of light in persulfate-based advanced oxidation for water treatment? *Water Research* **189**

[2] Kanafin Y N, Kakimov Y, Adamov A, Makhatova A, Yeshmuratov A, Poulopoulos S G, Inglezakis V J and Arkhangelsky E 2021 The effect of caffeine, metronidazole and ibuprofen on continuous flow activated sludge process *Journal of Chemical Technology & Biotechnology* **96** 1370–80

[3] Izadifard M, Achari G and Langford C H 2017 Degradation of sulfolane using activated persulfate with UV and UV-Ozone *Water Research* **125** 325–31

[4] Velo-Gala I, López-Peñalver J J, Sánchez-Polo M and Rivera-Utrilla J 2014 Comparative study of oxidative degradation of sodium diatrizoate in aqueous solution by H2O2/Fe2+, H2O2/Fe3+, Fe (VI) and UV, H2O2/UV, K2S2O8/UV *Chemical Engineering Journal* **241** 504–12

[5] Kanafin Y N, Satayeva A, Arkhangelsky E and Poulopoulos S G 2021 Treatment of a Biological Effluent Containing Metronidazole *Chemical Engineering Transactions* **86** 595–600

[6] Philippopoulos C J and Poulopoulos S G 2003 Photo-assisted oxidation of an oily wastewater using hydrogen peroxide *Journal of Hazardous Materials* **98** 201–10