

Phenols Degradation by Fenton Reaction in the Presence of Chlorides and Sulfates

E. M. Siedlecka, P. Stepnowski*

Faculty of Chemistry, University of Gdańsk, ul. Sobieskiego 18, PL 80-952 Gdańsk, Poland

Received: 8 November, 2004

Accepted: 26 February, 2005

Abstract

Since they often inhibit abundant bacteriological populations in municipal wastewater treatment plants, alternative treatment methods should be investigated – including advanced oxidation processes. This paper studies the degradation of three representatives of phenolic compounds using the Fenton system in the presence of chlorides and sulfates: phenol, 2-chlorophenol and 2-nitrophenol. The presence of anions influenced degradation rates of all studied compounds, which is attributed to the reduction in hydroxyl radical generation due to the formation of iron-complexes as well as the formation of much less reactive inorganic radicals. Differences between degradation rates of studied compounds and their degradation products in comparison to the rates observed for pure components show higher resistance of formed intermediates in comparison to phenol or 2-nitrophenol. Additionally, it was found that present anions influence further biodegradation of phenolic compounds but not similarly for all the compounds.

Keywords: advanced oxidation processes (AOPs), hydrogen peroxide, Fenton reaction, phenols, oxidation

Introduction

In industry and daily life, phenolic compounds are widely used and have become common pollutants in wastewaters. They are present in high concentrations in wastewater that originates from different branches of industry such as oil-refineries, petrochemical, iron-smelting, food or resin manufacturing. Although the toxicity of phenolic compounds is not as high as heavy metals or biocides, their high contamination often inhibits or even eliminates bacteriological populations in municipal biological wastewater treatment plants. Additional high solubility and stability makes their removal by means of common biological treatment practically impossible. Hence, the introduction of newer technologies to degrade these recalcitrant molecules into smaller molecules that lend themselves to further oxidation by biological methods has become imperative [1]. Advanced oxidation

processes (AOPs) based on the generation of very reactive hydroxyl radicals, which rapidly and non-selectively oxidize a broad range of organic pollutants, have received much attention in recent years. Hydroxyl radicals are generated through different combinations of oxidants as well as a whole range of photocatalytic systems [2-8]. Among these processes, Fenton's reagent ($\text{Fe}^{2+}/\text{H}_2\text{O}_2$) and the Fenton-like reagent ($\text{Fe}^{3+}/\text{H}_2\text{O}_2$) have been the subject of numerous studies in order to study mechanism and the reaction kinetics and to examine the efficiency of the process for the removal of organic pollutants [9-12]. The Fenton process is based on an electron transfer between H_2O_2 and Fe^{2+} acting as homogenous catalyst. The process generates hydroxyl radicals as described by Walling [9]:



The generated $\cdot\text{OH}$ radicals have an oxidizing potential of 2.6V vs. NHE and is capable of oxidizing a wide range of organics in wastewater.

*Corresponding author; e-mail: sox@chem.univ.gda.pl

The Fenton system has been used successfully in the treatment of phenolic compounds like phenol, chlorophenols or nitrophenols [13]. Fenton reaction can additionally be applied for an enhancement of biodegradation of various contaminants [14-18]. Industrial wastewater however, usually contains not only organic pollutants, but also considerable concentrations of common inorganic ions such as chloride, sulfate, nitrate or phosphate. Especially sulfate and chloride ions may have an effect on the efficiency of the $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ and $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ systems due to the formation of complexes with both Fe^{2+} and Fe^{3+} , whose reactivity may be different if compared to free iron species. Furthermore, chloride and sulfate can scavenge $\cdot\text{OH}$ -forming inorganic radicals such as $\text{SO}_4^{\cdot-}$, Cl^- , Cl_2^- , which are less reactive if compared to hydroxyl radicals [19].

Usually, when studying the applicability of AOPs to the degradation of certain groups of contaminants the effect of inorganic salts on the overall rates of decomposition are ignored. Up to now, only a few studies have recognized the importance of this issue and examined the influence of anions on Fenton's reaction [12, 20-23]. This work was therefore undertaken in order to examine the influence of chloride and sulfate anions on the degradation rates of phenol, 2-chloro- and 2-nitrophenol utilizing Fenton system. These three organic solutes are congener representatives of phenolic contaminants ubiquitously present in domestic and industrial wastewater.

Materials and Methods

Reagents

Phenol, 2-chlorophenol and 2-nitrophenol (analytical grade) were purchased from POCh (Gliwice, Poland). Sodium sulfate and sodium chloride were obtained from Standard (Lublin, Poland). Hydrogen peroxide was purchased from Techmar (Poland). Monopotassium phosphate, *o*-phosphoric acid 85% and acetonitrile HPLC gradient grade was purchased from POCh (Gliwice, Poland). Iron (II) perchlorate hydrate 98% was purchased from Aldrich. Deionized water was obtained in-house by treating tap water with a carbon filter, reversed osmosis, a mixed bed of ion exchangers and a 0.45 μm filter.

Degradation

The batch experiments were conducted by starting with initial concentrations of the phenolic solute, chloride or sulfate ions in the presence of Fenton reactant. The parameter that varied was the dose of hydrogen peroxide. Reactions were carried out in unbuffered aqueous solutions at $22^\circ\text{C} \pm 1$ in the absence of light and in bath reactor (2L) open to atmosphere. Initial concentrations of phenol (Ph), 2-chlorophenol (2-CL-Ph) and 2-nitrophenol (2- NO_2 -Ph) were 2.66mM, 1.95mM, 1.8mM, respectively. Hydrogen peroxide concentration

was adjusted to the molar ratio of 0.2 to 3.5 mM of H_2O_2 per 1 mM of phenolic compound. The molar ratio of ferrous ion: phenolic contaminant were kept at 0.01:1. This resulted in 0.026, 0.019 and 0.018 mM of iron (II) perchlorate used in the degradation of phenol, 2-chlorophenol and 2-nitrophenol, respectively. Concentrations of inorganic salts were 20mM of NaCl and 7mM of Na_2SO_4 .

The experiments were initiated by adding H_2O_2 to the solution under vigorous magnetic stirring. Residual H_2O_2 was measured after 24h and any residual H_2O_2 was quenched using a slight stoichiometric excess of sodium sulfite. In most cases the residual concentrations of H_2O_2 after 24h were negligible.

Analytical Method

The analyses of phenols were carried out with an assembled system consisting of an LC 10ATvp metering pump (Shimadzu Ltd.), a syringe loading sample injector (Rheodyne) and a UV/Vis variable wavelength detector (Kontron Instruments). Retention times were recorded with a 3390A HPLC integrator (Hewlett Packard). All separations were performed using a Purospher RP-18e column, 125 x 4.6 mm ID, 5 μm (Merck KgaA, Darmstadt, Germany). The analyses were performed at ambient temperature at a flow rate of 1.0 ml min^{-1} . The elution profiles were monitored at 254 and 220 nm. The mobile phase was water-acetonitrile (from 70: 30 v/v) mixed with the $\text{KH}_2\text{PO}_4/\text{H}_3\text{PO}_4$ (40mM) buffer at pH = 3.1.

COD parameter was measured with HACH COD ampoules ($0 \div 1500 \text{ mg O}_2 \text{ L}^{-1}$ range) by colorimetric method (APHA, 1995). The sample was heated for two hours with potassium dichromate in the presence of silver sulfate and mercury sulphate (for chelating chloride ions). The absorbance was measured at 620 nm (HACH method 8000) on a spectrophotometer Odyssey DR/2500 (HACH, Loveland, Colorado).

Hydrogen peroxide concentrations were determined using potassium iodide and dropwise titration with sodium thiosulphate.

Biodegradability was measured in oxidized (after 24h of treatment) and unoxidized wastewater by 5-day biochemical oxygen demand (BOD_5) analysis. As bacterial inoculum a small amount of activated sludge from the bilge/ballast water treatment plant was used. The reason for choosing this wastewater was due to the fact that it was acclimated to the substrates studied (phenols as well as higher concentration of inorganic salts).

Results and Discussion

Fig. 1 presents the effect of chloride and sulfate ions on the decomposition of phenol, 2-nitro- and 2-chlorophenol for its residual concentration after 24 h of oxidation in the Fenton system. The applied molar ratio

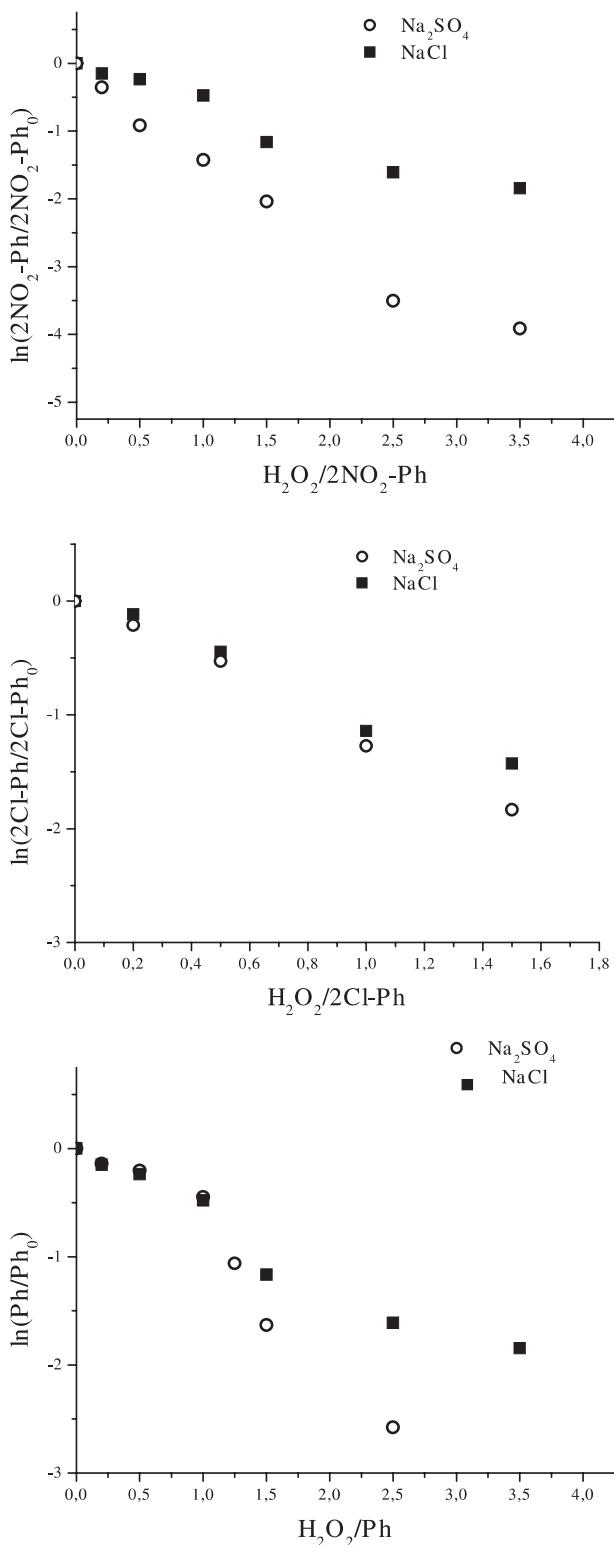


Fig. 1. Decomposition of phenol, 2-nitro- and 2-chlorophenol for its residual concentration after 24 h of oxidation in the Fenton system in the presence of chloride and sulfate ions. ([phenol, 2-chlorophenol and 2-nitrophenol] = 2.66 mM, 1.95 mM, 1.8 mM respectively, $[\text{Fe}^{2+}]/[\text{organic compound}] = 0.01$, $[\text{Na}_2\text{SO}_4] = 7 \text{ mM}$, $[\text{NaCl}] = 20 \text{ mM}$). Correlation coefficients R^2 in the presence of sulfate and chloride, respectively, were: 0.99 and 0.97 for 2-chlorophenol, 0.93 and 0.96 for phenol, 0.97 and 0.94 for 2-nitrophenol.

of hydrogen peroxide to phenolic component were in the range from 0.2 to 3.5. The $\text{Fe}^{2+}/\text{phenolic compound}$ ratio was kept at 0.01.

As can be seen from Fig. 1, the concentrations of all compounds decrease with an increase of H_2O_2 levels. Log values of the degradation rates of phenolic components ($\ln C/C_0$) can be linearly correlated with the concentration of H_2O_2 . Obtained correlation coefficients in the presence of sulfate and chloride, respectively, were: 0.99 and 0.97 for 2-chlorophenol, 0.93 and 0.96 for phenol, 0.97 and 0.94 for 2-nitrophenol. The presence of inorganic salts in the system influences this process significantly. In the case of the chloride ions used, distinctive inhibition of oxidation can be seen for all treated phenolic contaminants, whereas the addition of sulfates influence these rates to a much smaller extent. The absolute difference in slopes (degradation rates) of plotted correlations between those registered in the presence of chloride and sulfate are 0.71 and 0.55 for phenol and 2-nitrophenol, respectively, and only 0.16 for 2-chlorophenol.

Higher retardation of the degradation rates in the presence of chlorides is most likely due to the inhibiting influence of hydroxyl radical formation. In solutions containing chloride, certain amounts of free radicals are scavenged and various chlorinated inorganic radicals are formed ($\text{Cl}\cdot$, $\text{HClOH}\cdot/\text{ClOH}\cdot$, $\text{Cl}_2\cdot$) among which the dichloride anion radical is the predominant one [24]. However, sulfates are also good scavengers of H_2O_2 , the overall effect on the degradation rates in their presence were much lower in comparison to chloride ions. Firstly, formed sulfate radicals ($\text{SO}_4\cdot$) are more reactive than dichloride anion radicals, and can therefore take part in the oxidation of phenolic components more efficiently. Further, reaction constant of the formation of $\text{HO}_2\cdot$ radicals is three orders of magnitude higher in the reaction of H_2O_2 with sulfate radicals in comparison to chloride ones (1.2×10^7 vs. $4.1 \times 10^4 \text{ M}^{-1}\text{s}^{-1}$) [19]. Moreover, it is believed that sulfato-iron (II) complex (FeSO_4) is more reactive towards H_2O_2 than Fe^{2+} alone, which can additionally balance inhibitory potential of sulfate ions [12]. The relatively low degradation rates (practically independent of type of anion used) observed for 2-chlorophenol are likely to be caused by the presence of additional chloride radicals originating from the abstraction reactions. These entities can undergo several reactions with H_2O_2 , Fe^{2+} or free electrons subsequently decreasing net reaction rates.

Because of the indiscriminate nature by which generated radicals degrade organic pollutants, it is necessary to profile the decomposition of each waste to be treated. Each transformation in the series of phenolic degradation may generate several intermediate compounds (carboxylic acids, quinones) which have their own reaction rates, thus require sufficient hydrogen peroxide to be added to push reaction beyond the point of build-up of undesirable intermediaries. Fig. 2 summarizes results of changes in Chemical Oxygen Demand (COD) value obtained while applying hydrogen peroxide in the given concentration range in the presence of

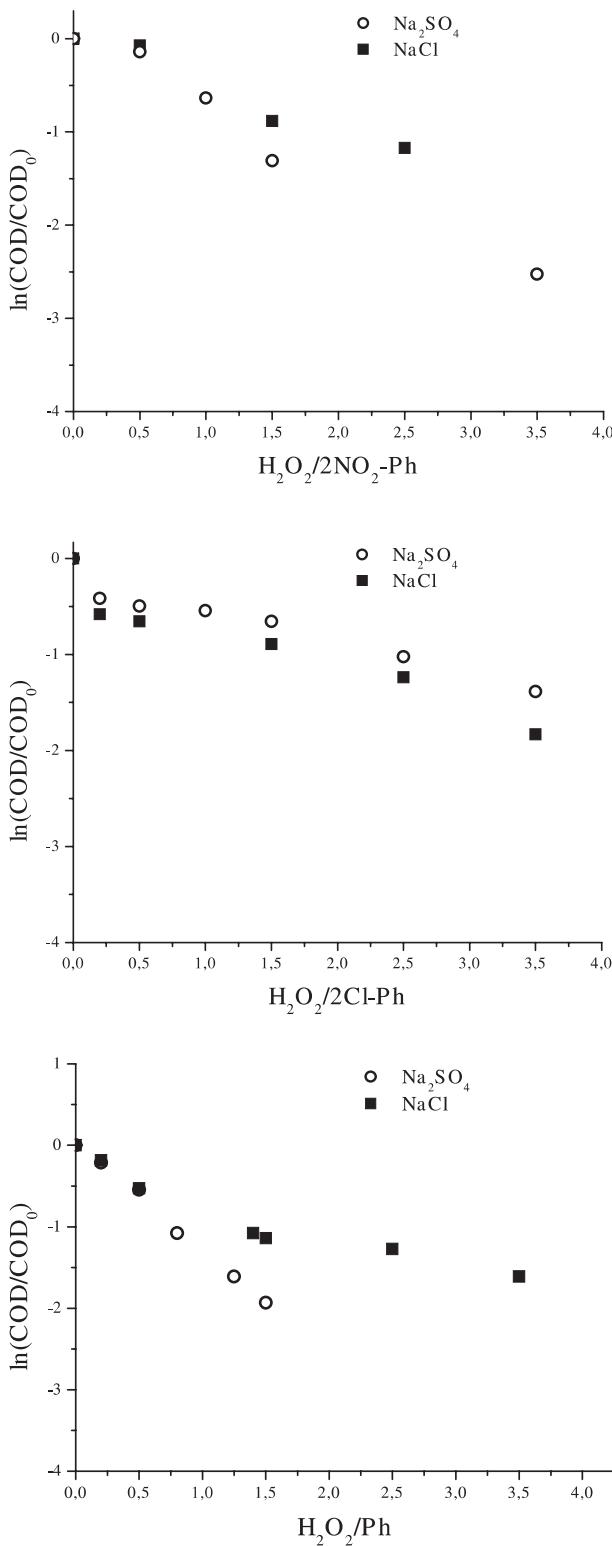


Fig. 2. Effects of chloride and sulfate ions on the changes in chemical oxygen demand value after 24 h of oxidation in the Fenton system. ([phenol, 2-chlorophenol and 2-nitrophenol] = 2.66mM, 1.95mM, 1.8mM respectively, $[Fe^{2+}]/[organic\ compound] = 0.01$, $[Na_2SO_4] = 7mM$, $[NaCl] = 20mM$). Correlation coefficients R^2 in the presence of sulfate and chloride, respectively, were: 0.98 and 0.96 for 2-chlorophenol, 0.99 and 0.94 for phenol, 0.97 and 0.93 for 2-nitrophenol

sulfate and chloride ions. Inhibitory potential of chloride ions on decomposition of 2-nitrophenol and its degradation products is lower in comparison to the rates observed for pure component. Net degradation of phenol and its degradation intermediates is retarded greatly by the presence of chloride ions, whereas the addition of sulfates influences degradation in the same manner as in the reaction with pure phenol. Degradation of 2-chlorophenol and its decomposition products are inhibited almost similarly either by sulfates or chloride ions. The additional, comparably low, degradation rate shows higher resistance of formed intermediates in comparison to phenol or 2-nitrophenol.

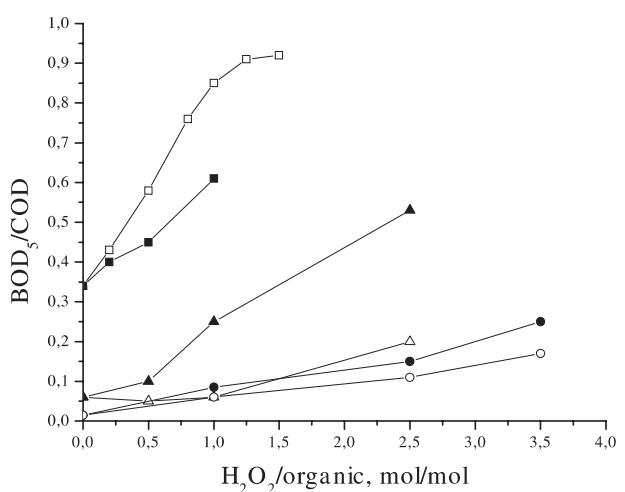


Fig. 3. Changes of BOD_5/COD ratio after 24 h of Fenton's reaction using different concentrations of hydrogen peroxide applied in the presence of sulfate and chloride ions. ■ Ph, ▲ $2NO_2\text{-Ph}$, ● $2Cl\text{-Ph}$ in the presence of $NaCl$ (20mM) and □ Ph, △ $2NO_2\text{-Ph}$, ○ $2Cl\text{-Ph}$ in the presence of Na_2SO_4 (7mM). ($[phenol, 2\text{-chlorophenol and } 2\text{-nitrophenol}] = 2.66mM, 1.95mM, 1.8mM$ respectively, $[Fe^{2+}]/[organic\ compound] = 0.01$)

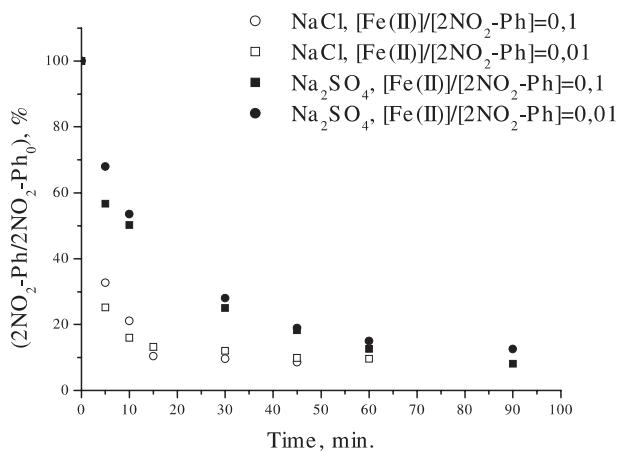


Fig. 4. Kinetics of the 2-nitrophenol degradation in the presence of chlorides and sulfates in the Fenton system. ($[2NO_2\text{-Ph}] = 1.8mM$ $[H_2O_2]/[2NO_2\text{-Ph}] = 14\ mol\ mol^{-1}$, $[NaCl] = 20mM$, $[Na_2SO_4] = 7mM$)

Table 1. Comparison between Ph, 2Cl-Ph and 2NO₂-Ph removal [%], COD removal [%] and value of BOD/COD ratio in the presence of the sulfate and chloride ions [initial concentration].

H ₂ O ₂ /organic	Removal % [Na ₂ SO ₄] = 7mM			Removal % [NaCl] = 20mM		
	Ph	2NO ₂ -Ph	2Cl-Ph	Ph	2NO ₂ -Ph	2Cl-Ph
0.5	18.3	59.9	40.9	20.9	21.5	35.9
1.5	80.3	86.9	83.9	68.7	69.9	75.9
2.5	92.4	96.9	-	79.9	80.1	-
	COD removal, % [Na ₂ SO ₄] = 7mM			COD removal, % [NaCl] = 20mM		
0.5	41.0	12.9	34.3	42	6.9	44.5
1.5	67.9	72.7	42.3	85.3	58.5	55.9
2.5	72.4	84.1	59.3	87.9	68.9	66.7
	BOD _s /COD [Na ₂ SO ₄] = 7mM			BOD _s /COD [NaCl] = 20mM		
0.5	0.58	0.04	0.05	0.45	0.10	0.05
1.5	0.92	-	-	-	-	-
2.5	-	0.20	0.11	-	0.53	0.15

While studying enhanced oxidative degradability of any pollutant it is also important to evaluate biodegradability of degradation products [25]. A BOD_s/COD ratio of 0.4 is generally considered the cut-off point between biodegradable and difficult-to-biodegradable. As for industrial wastewaters there are no reference ratios reported, those for municipal wastewater are taken as reference, which have a BOD_s/COD ratio between 0.4 to 0.8 and is considered to be substantially biodegradable [26]. Fig. 3 shows changes of this ratio after 24 h of Fenton's reaction using different concentrations of hydrogen peroxide applied in the presence of sulfate and chloride ions. It can be seen that the treatment of phenol in both systems will greatly support its biodegradation whereas oxidizing chloro- and nitro-derivatives is much less effective in obtaining more biodegradable entities. However, it can be observed that biodegradation tendency increased with the increase of H₂O₂ concentration applied for all contaminants studied. The influence of the type of anion is different for different compounds. The presence of chloride suppressed the biodegradability of phenol but enhanced the biodegradability of nitro- and chlorophenols. The largest differences in biodegradation of pre-oxidized phenols while using sulfates and chlorides were found for 2-nitrophenol.

Exemplary kinetics of 2-nitrophenol degradation in the presence of chlorides and sulfates is presented in Figure 4. Data obtained while using Fe²⁺/2-NP ratio of 0.1 and 0.01 and H₂O₂/2-NP ratio of 14, according to the calculated stoichiometric demand for complete mineralization to CO₂. The degradation pattern follows the pseudo-first order rate of reaction.

Conclusions

It was found that the presence of chloride and sulfate anions have a significant influence on the degradation rates of phenol, 2-chloro- and 2-nitrophenol utilizing the Fenton system. The addition of sulfates influences these rates to a much smaller extent when compared to chlorides. Relatively low degradation rates are observed for 2-chlorophenol, which is likely to be caused by the presence of additional chloride radicals originating from the abstraction reactions. It was also noticed that there are distinctive differences between degradation rates of studied compounds and their degradation products in comparison to the rates observed for pure components. Comparably low degradation rates show higher resistance of formed intermediates in comparison to phenol or 2-nitrophenol.

Finally it was found that chlorides and sulfates influence biodegradation of phenolic compounds differently: biodegradability of phenol is enhanced by chlorides, whereas that one of 2-nitrophenol and 2-chlorophenol by sulfates.

Acknowledgements

This study was supported by the Polish Ministry of Scientific Research and Information Technology under grants BW 8000-5-0192-4, DS 8390-4-0141-5 and DS-8270-4-0093-5.

References

1. GOGATE P. R., PANDIT A. B. A review of imperative tech-

- nologies for wastewater treatment I: oxidation technologies at ambient conditions, *Adv. Environ. Res.* **8** (3-4) 501, **2004**.
2. CAREY J. H. An introduction to advanced oxidation processes (AOP) for destruction of organic wastewater. *Water Pollut. Res. J. Canada.* **27** (1), 1, **1992**.
 3. ALHAKIMI G., GEBRIL S., STUDNICKI L. H. Comparative photocatalytic degradation using natural and artificial UV-light of 4-chlorophenol as a representative compound in refinery wastewater. *J. Photochem. Photobiol. A: Chem.* **157**, 103, **2003**.
 4. GLAZE W. M., KANG J. W. AND CHAPIN D. H. The chemistry of water treatment processes involving ozone, hydrogen peroxide and ultraviolet radiation. *Ozone Sci. Eng.* **9**, 335, **1987**.
 5. GULYAS H. Processes for the removal of recalcitrant organics from industrial wastewaters. *Water. Sci. Technol.* **36** (2-3) 9, **1997**.
 6. MARTIN M. A., RAPOSO F., BORJA R., MARTIN A. Kinetic study of the anaerobic digestion of vinasse pretreated with ozone, ozone plus ultraviolet light, and ozone plus ultraviolet light in the presence of titanium dioxide. *Proc. Biochem.* **37**, 699, **2002**.
 7. STEPNOWSKI P., SIEDLECKA E. M., BEHREND P., JASTORFF B. Enhanced photo-degradation of contaminants in petroleum refinery wastewater. *Water Res.* **36** (9) 2167, **2002**.
 8. STEPNOWSKI P., ZALESKA A. Comparison of different advanced oxidation processes for the degradation of room temperature ionic liquids, *J. Photochem. Photobiol. A: Chem.* **170**, 45, **2005**.
 9. WALLING C. Fenton reagent revisited, *Acc. Chem. Res.*, **121**, **1975**.
 10. SYCHEV A. Y., ISAAK V. G. Iron compounds and the mechanisms of the homogenous catalysis of the activation of O_2 and H_2O_2 and of oxidation of organic substrates. *Russ. Chem. Rev.*, **64**, 1105, **1995**.
 11. SAFARZADEH-AMIRI A., BOLTON J. R., CATER S. R. The use of iron in advanced oxidation processes, *J. Adv. Oxid. Technol.*, **1** (1) 18, **1996**.
 12. DE LAAT J., TRUONG G. L., LEGUBE B. A comparative study of the effects of chloride, sulfate and nitrate ions on the rates of decomposition of H_2O_2 , and organic compounds by Fe (II)/ H_2O_2 and Fe (III)/ H_2O_2 . *Chemosphere* **55**, 715, **2004**.
 13. PERA-TITUS M., GARCIA-MOLINA V., BANOS M. A., GIMENEZ J., ESPLUGAS S. Degradation of chlorophenols by means of advanced oxidation processes: a general review. *Appl. Catal. B: Environ.* **47**, 219, **2004**.
 14. CHAMARRO E., MARCO A., ESPLUGAS S. Use of Fenton reagent to improve organic chemical biodegradability. *Wat. Res.* **35**, 1047, **2001**.
 15. KIWI J., PULGARIN C., PERINGER P. Effect of Fenton and photo-Fenton reaction on the degradation and biodegradability of 2- and 4-nitrophenols in water treatment. *Appl. Catal. B: Environ.* **3**, 335, **1994**.
 16. MARCO A., ESPLUGAS S., SAUM G. How and why combine chemical and biological processes for wastewater treatment. *Water Science and Technology* **35** (4), 321, **1997**.
 17. KITIS M., ADAMS C. D., DAIGGER G. T. The effects of Fenton's reagent pretreatment on the biodegradability of nonionic surfactants. *Water Research* **33**, 2561, **1999**.
 18. NAM K., RODRIGEZ W., KUKOR J. J. Enhanced degradation of polycyclic aromatic hydrocarbons by biodegradation combined with a modified Fenton reaction. *Chemosphere*, **45**, 11, **2001**.
 19. NETA P., HUIE R. E., ROSS A. B. rate constants for reactions for inorganic radicals in aqueous solution. *J. Phys. Chem. Ref. data* **17**, 1027, **1988**.
 20. KING D. W., FARLOW R. Role of carbonate speciation on the oxidation of Fe (II) by H_2O_2 . *Mar. Chem.*, **70**, 201, **2000**.
 21. LIPCZYŃSKA-KOCHANY E., SPRAH G., HARMS S. Influence of some groundwater and surface waters constituents on the degradation of 4-chlorophenol by the Fenton reaction. *Chemosphere* **30** (1), 9, **1995**.
 22. LU M. C., CHEN J. N., CHANG C. P. Effect of inorganic ions on the oxidation of dichlorvos insecticide with Fenton's reaction. *Chemosphere* **35**, 2285, **1997**.
 23. PIGNATELLO J. J. Dark and photoassisted Fe^{3+} -catalysed degradation of chlorophenoxy herbicides by hydrogen peroxide. *Environ. Sci. Technol.*, **26**, 944, **1992**.
 24. TRUONG G. L., DE LAAT J., LEGUBE B. Effect of chloride and sulfate on the rate of oxidation of ferrous ion by H_2O_2 . *Water Research* **38**, 2383, **2004**.
 25. SIEDLECKA E. M., STEPNOWSKI P., JASTORFF B. Effect of H_2O_2 on characteristics and biological treatment of petroleum refinery wastewater. *Fresenius Environ. Bull.*, **11** (5), 223, **2002**.
 26. METCALF AND EDDY INC. *Wastewater Engineering – treatment disposal and reuse*, Int. ed.; McGraw-Hill Book Company, New York, **1991**.