13th International Research/Expert Conference
"Trends in the Development of Machinery and Associated Technology"
TMT 2009, Hammamet, Tunisia, 16-21 October 2009

DEGRADATION OF POLYVINYL ALCOHOL (PVA) BY FENTON PROCESS

Marie Dvořáčková, Tu Kim Dung
Department of Environment Protection Engineering, Faculty of Technology,
Tomas Bata University in Zlin,
nám. TGM 275, 762 72 Zlín,
Czech Republic

ABSTRACT
Degradation of polyvinyl alcohol was studied a combination of chemical treatment with Fenton process and biological degradation in anaerobic environment. The experiment was based on different amounts of hydrogen peroxide and of Fe(II) added to water solution of PVA of concentration 200-500 mg.L^{-1}. Fenton process was monitored by analyzing the total organic carbon (TOC) in the solution. Depending on the initial concentration PVA and the amounts of Fe(II) and hydrogen peroxide added an insoluble phase is formed, which was separated by filtration or centrifuging. The test of biodegradability was performed in an aqueous environment under anaerobic condition with digested activated sludge from the municipal wastewater treatment plant. Evaluation of biodegradation was based on methane and carbon dioxide produced in the gas phase. Effect of pH, dosage reactants in Fenton process, time of reaction on the rate of PVA removal was studied. 60 - 68 % PVA was removed by Fenton reaction and then oxidative product was tested under an anaerobic condition. The partial oxidation of polyvinyl alcohol enhances its biodegradability.
Keywords*:* polyvinyl alcohol (PVA), Fenton process, biodegradability, water environment

1. INTRODUCTION
The environmental fate of polyvinyl alcohol (PVA) was investigated due mainly to its large utilization in textile and paper industries, which generate considerable amounts of PVA-containing wastewaters. PVA can be biologically degraded if microorganisms are previously adapted [1]. However, other compounds in the wastewater (mainly salts) can negatively affect the process. One of the most effective technologies to remove organic pollutants from aqueous solutions is the Fenton's reagent treatment. It is well known that organic compounds can easily be oxidized. It consists in a mixture of hydrogen peroxide and iron salts. There are chemical mechanisms that propose hydroxyl radicals as the oxidant species [2] are generated in the following chemical equation:

$$Fe^{2+} + H_2O_2 + H^+ \rightarrow Fe^{3+} + \bullet OH + H_2O \qquad (1)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + \bullet OOH + H+ \qquad (2)$$

•OH is the hydroxyl radical and •OOH is the superoxide radical.
Fenton reagent is very powerful oxidizing agent. Hydroxyl radical due to high oxidation potential (E0 = −2.80 V) can oxidize almost all the organic substances [3]. The degradation rate is influenced by the pH of solution and the amount of hydrogen peroxide and iron salt.

Since both ferrous and ferric ions are coagulants, the Fenton process can therefore have dual functions of oxidation and coagulation in the treatment process. Thus, Fenton treatment has attracted much interest for the destruction of toxic organic compounds in wastewater [4].
This study was conducted to assess the removal efficiency of polyvinyl alcohol from an aqueous solution using Fenton process and anaerobic degradation.

2. EXPERIMENTAL

Materials used for test was currently available commercial products: MOWIOL 5–88 (PVA), viscosity 5.5±0.5 mPas, hydrolysis degree – 88 mol %, produced by Kuraray, CHSK $_{PVA}$ = 1303,73 mg O_2/ g PVA, molecular weight 37 000 g/mol
A partially hydrolyzed polyvinyl alcohol used for the modification of emulsion adhesives and in the production of paper adhesives and remoisten able adhesives. It is also used as a protective colloid in emulsion polymerization, as a binder in paper surface finishing and as a regulator in coating processing. The following analytical reagents were used: pent hydrated ferrous sulfate, hydrogen peroxide (35%, w/w, in water), potassium iodide, anhydrous sodium sulfide, sodium hydroxide, and sulfuric acid.

Experimental conditions of Fenton process

The PVA solution was prepared by gradually dissolving small amounts of solid commercial PVA (Mowiol 5-88) in a beaker with magnetic stirring, at about 50°C, in order to prevent foam formation. The solution was then diluted in water, in order to obtain the desired PVA concentration.
Ferrous sulfate $FeSO_4.7H_2O$ was used to prepare the ferrous solution, which were prepared daily. Hydrogen peroxide H_2O_2 of 35 % purity from Fluka AG was used.
100 ml of polyvinyl alcohol was placed in 250 ml bottle and added sulfuric acid to reach pH 4, then ferrous sulfate and an aliquot of 35% H_2O_2 was added to the mixture of PVA to reach a molar ration (PVA : Fe^{2+} : H_2O_2). The water samples was mixed rapidly for 1 – 120 minute. Taken samples were added solution NaOH 1M or reduction agent (solution of 0,1M - Na_3PO_4, KI, Na_2SO_3) to pH 9. Then an insoluble phase was formed, which was removed by filtration or centrifuging. The filtrate was taken to a TOC analyzer (Shimadzu 5000A). Fenton process was monitored by analyzing the dissolved organic carbon concentration (TOC).
The experiments were carried out with water solutions of PVA of concentrations: 200, 300, 400,500, 5,000 a 15,000 mg.L^{-1}.

Determination of concentration of residual PVA

In Fenton's experiments, the residual polyvinyl alcohol concentration was measured by UV-VIS spectrophotometer (660 nm) UNICAM UV 500, Thermo Spectonic, England.

Anaerobic Biodegradability Test [ČSN EN ISO 11 734]

10 l samples (oxidative product of PVA after Fenton process) was inserted into 300ml flask and 100 ml liquid phase (mineral medium $MgSO_4$; $CaCl_2$; $FeCl_3$; $(NH_4)SO_4$; phosphoric buffer; trace elements: B^{3+}, Fe^{2+}, Zn^{2+}, Mn^{2+}, Cu^{2+}, Co^{2+}, Mo^{6+}) were utilized in the research. Mixed microbial culture was used as a source of microorganisms – activated anaerobic sludge from municipal wastewater treatment. Dry matter of sludge was 3-4 g/l. pH 7, 2. The content of bottles was bubbled with nitrogen 10 min. to eliminate oxygen and then hermetic covered and inserted in thermostat at 35°C.
Gas chromatography was used for determining the biogas production (methane and carbon dioxide).
Gas chromatography - Agilent 7890, column filled with Porapack Q, length 3.6meter, diameter 3 mm
Termal conductivity detector - TCD, temperature 250°C, Carrier gas : helium 99,999%, flow rate 30 ml / min, Termostat: 50°C, injector: 200°C
Calibration: mixed gas 4,05% CH_4, 0,798% CO_2, 95,152% N_2 –Linde Technoplyn a.s., CR
Analysis of actual samples mostly used 0.1-mL quantities of gas phase withdrawn at determined time intervals. Percentage of biologically removed substrate - DC (%) was evaluated through produced carbon dioxide and methane.

3. RESULTS AND DISCUSSION

Degradation of PVA by Fenton Process

In practically all experiments the formation of solid particles, with brownish color, could be visually observed at different reaction times. The nature of the solid particles was not investigated in the present work, and should be the focus of specific studies.

The iron concentration is important for the reaction kinetics. The effect of concentration of H_2O_2 and Fe(II) on oxidative degradation of polyvinyl alcohol by Fenton process is shown in Fig.1. The pH was kept in the range of 3 to 4 the temperature was set at 25 °C. Under such condition, the maximum removal of PVA was max. 60 % after 2 hour.

The effect of molar ratio concentration of PVA: H_2O_2 and Fe(II) on PVA removal by Fenton reaction is presented in Fig.2. The peroxide dose is important in order to obtain better degradation efficiency. The effect of pH was significant, and the degradation of PVA was favorable at lower pH.

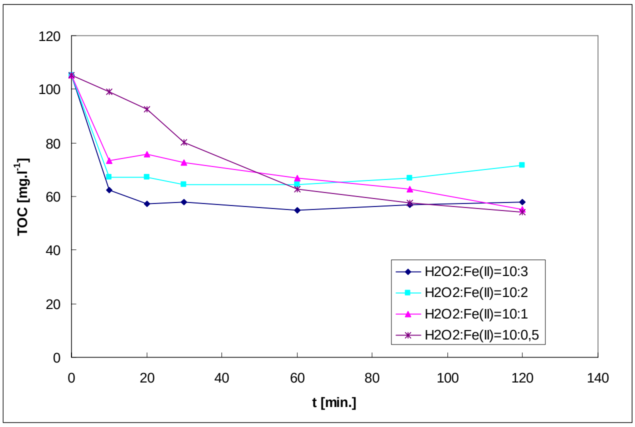

Figure 1. The effect of molar ratio concentration of H_2O_2 and Fe(II) on the oxidation of PVA (TOC removal) by Fenton reaction: The experimental conditions were as follows: pH=4, PVA 200 mg.L^{-1}

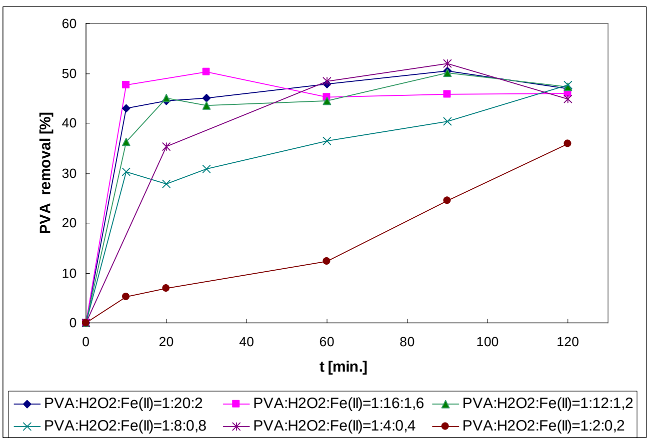

Figure 2. The effect of molar ratio concentration of PVA: H_2O_2 and Fe(II) on PVA removal by Fenton reaction: The experimental conditions were as follows: pH=4, PVA 200 mg.L^{-1}

The molar ratio of PVA: H_2O_2 and Fe(II) 1 : 2,22 : 0,11 were evaluated as the most appropriate from the perspective of ecological and economical of this process.

Degradation of oxidative products of Fenton process in anaerobic sludge

The solutions of polyvinyl alcohol concentration 5 $g.L^{-1}$ and 15 $g.L^{-1}$ were treated by Fenton process. The solid particles created during degradation reaction were separated by filtration and residual product was tested in an anaerobic sludge. Natrium acetate (NaAc) was used as a standard . In the Fig. 3 can see that biogas production from these samples was low. Oxidative products of Fenton process inhibit the reaction in the anaerobic environment.

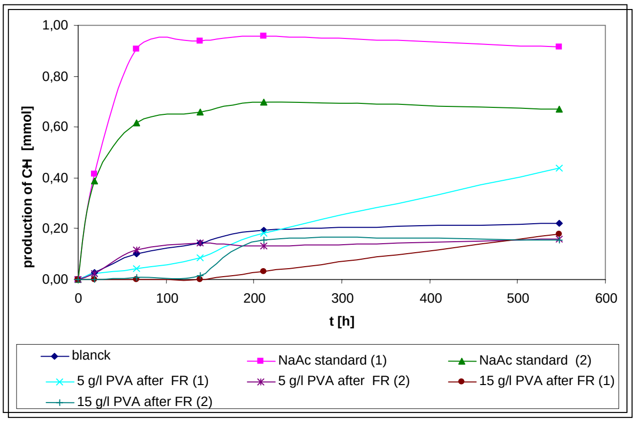

Figure 3. Test biodegradability of oxidative products PVA after Fenton process in anaerobic environment (production of methane)

4. CONCLUSION

In this study, the degradation of polyvinyl alcohol (PVA) was investigated under combination Fenton reagent H_2O_2 and Fe(II) and biological degradation in an anaerobic condition. There are two important factors affecting the rate of Fenton's reaction: hydrogen peroxide dose and iron concentration. The peroxide dose is important in order to obtain a better degradation efficiency the iron concentration is important for the reaction kinetics. Using a molar ratio PVA : H_2O_2 : Fe(II) (1 : 2,22 : 0,11) almost 68% PVA was remove during 23 hours, but the same result was achieved at higher concentration of Fenton reagent for two hours.

It was found that the partial oxidation of PVA enhances biodegradability in anaerobic environment, but it would be more appropriate to use an aerobic environment.

Acknowledgements: This work was supported by Research Project of the Ministry of Youth, Education and Sports of the Czech Republic No. MSM 7088352101.

5. REFERENCES

[1] K. Schluter, Ullmann's Encyclopedia of Industrial Chemistry vol. A26, Textile Auxiliary—Sizing Agents, Weinheim (1995) pp. 244–253.

[2] Walling C., El-Taliawi, G.M. and Johnson, R.A., 1974. Fenton's reagent IV: structure and reactivity relations in the reaction of hydroxyl radicals and the redox reactions of radicals. Journal of Amercian Chemical Society 96, pp. 133–139.

[3] S. Gartiser, M. Wallrabenstein and G. Stiene, Assessment of several test methods for the determination of the anaerobic biodegradability of polymers. J Environ Polym Degrad 6 (1998), pp. 159–173

[4] Barb W.G., Baxendale J.H., Georgie P., Hargrave K.R.: Reactions of ferrous and ferric ions with hydrogen peroxide. Part I. The ferrous ion reaction. Trans. Faraday Soc., Vol. 47, 462-500 (1951).

[5] Halmann MM (1996) Photodegradation of water pollutants. CRC, Boca Raton, pp 1–19