บทความวิจัย

จลนพลศาสตร์ของปฏิกิริยาออกซิเดชันสารประกอบคลอโรฟีนอลในน้ำทิ้ง โดยใช้ไฮโดรเจนเปอร์ออกไซด์และซีโอไลต์ชนิด Fe/SUZ-4

Kinetics Oxidation Reaction of Wastewater Containing Phenolic Compounds by H_2O_2 and Fe/SUZ-4 Zeolite

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บทคัดย่อ

การศึกษาปฏิกิริยาออกซิเดชันสารประกอบคลอโรฟีนอลในน้ำโดยใช้ไฮโดรเจนเปอร์ออกไซด์ (H_2O_2) และซีโอไลต์ชนิด Fe/SUZ-4 ที่สังเคราะห์จากเถ้าแกลบ (RHA) เมื่อทำปฏิกิริยากับฟีนอล 2,4-Dichlorophenol และ 4-Chlorophenol โดยใช้ความเข้มข้น 100 40 และ 100 มิลลิกรัมต่อลิตร ตามลำดับ เป็นเวลา 300 นาที ที่ pH 3.0 และจากการวิเคราะห์องค์ประกอบทางเคมีของ RHA พบว่า มีซิลิกา (SiO_2) 99.7 เปอร์เซ็นต์ ส่วน Fe/SUZ-4 มีเหล็ก (Fe) 4.72 เปอร์เซ็นต์โดยน้ำหนัก สำหรับโครงสร้างของ Fe/SUZ-4 ผลึกเป็นรูปเข็มความยาว 5.0 ไมโครเมตร และมีเส้นผ่านศูนย์กลาง 0.2 ไมโครเมตร การศึกษาจลนพลศาสตร์ของปฏิกิริยาพบว่า ใช้ Fe/SUZ-4 เป็นตัวเร่งปฏิกิริยาทำให้ปฏิกิริยาการสลายตัวของฟีนอลและคลอโรฟีนอลเร็วกว่าการใช้ SUZ-4 ที่ไม่มีการแลกเปลี่ยนไอออนกับ Fe โดยที่อัตราการสลายตัวเพิ่มขึ้นตามความเข้มข้นของคลอโรฟีนอล และ H_2O_2 และมีกฎอัตราของปฏิกิริยาการสลายตัวเป็นปฏิกิริยาอันดับหนึ่ง

คำสำคัญ : กฎอัตรา ซีโอไลต์ชนิด SUZ-4 การสังเคราะห์ซีโอไลต์จากเถ้าแกลบ ออกซิเดชั่นคลอโรฟีนอล

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Abstract

By using synthesized Fe/SUZ-4 zeolite catalysts and hydrogen peroxide (H_2O_2) oxidation agent, the degradation reactions of Phenol, 2,4-Dichlorophenol, and 4-Chlorophenol with the concentrations of 100, 40 and 100 mg/l respectively were carried out at pH 3.0 for 300 minutes. The analysis of the rice husk ash (RHA) found that the raw material contained 99.7% SiO_2 and the amount of Fe in SUZ-4 was found to be 4.72 wt. %. The synthesized SUZ-4 has a micro-structure of needle-shaped crystals approximately 0.2 μm in diameter and 5.0 μm in length. The ion-exchanged SUZ-4 zeolite (Fe/SUZ-4) was used since the degradation rate obtained was actually higher than that of the reaction without ion-exchanged zeolite. The rate of reaction were investigated and it was found that the degradation rates slightly increase with increasing the phenol concentration. In the same way, the variation of H_2O_2 was also investigated and the result indicates that the degradation rates also slightly increase as the H_2O_2 concentration increases. The kinetics of the corresponding reactions was found that the degradation reactions of Phenol, 2,4-Dichlorophenol and 4-Chlorophenol can be classified as a first-order reaction.

Keywords: Kinetics, SUZ-4 Zeolite, 2,4-Dichlorophenol, 4-Chlorophenol, Phenol, Catalytic Oxidation.

Introduction

Phenols and related compounds are toxic to human and aquatic life, Chlorinated organic compounds are also another major source of pollution in water. These pollutants are now receiving great concern due to ecological concerns and public health. Pollution in water by phenol-like compounds is a serious problem in both developed and developing countries [1]. Chlorophenols (CPs) have been listed as potential toxic pollutants [2] by United States Environmental Protection Agency (USEPA) in the Clean Water Act [3] and used as preservative agents for agricultural chemicals and biocides as well as widely employed in many industrial processes as synthesized intermediates in the manufacturing of herbicides and of pesticides and in the paper industry [3]. One of chlorophenol in particular, 4 chlorophenol (4–CP), is used for the extraction of sulfur and nitrogen from coal, as intermediate in a synthesis of dyes and drugs, and as a denaturant in alcohol or solvent in a refining of oils [4]. In addition, 2, 4-dichlorophenol (2,4–DCP), is widely used as an intermediate in the production of agricultural chemicals and medicines. This chemical is not only harmful to the environment, but is also very dangerous to human beings, animals and crops [1]. There are several methods for treatments of chlorophenol compounds; for example, pH-adjustment, biological methods, coagulation and chemical oxidation [5]. Particularly, chemical oxidation has been found to be effective in the treatment of wastewater containing high concentration of chlorophenol.

The Fenton reaction is a catalytic process for the generation of hydroxyl radicals from hydrogen peroxide and is based on an electron transfer between H_2O_2 and iron ions acting as homogeneous catalysts. The hydroxyl radicals produced during this activation of hydrogen peroxide are a strong oxidizing agent and able to oxidize organic compounds under ambient conditions [6].

The advantages of Fenton's reagent over other oxidizing treatments are numerous, including high efficiency performance, stability to treat a wide range of substances, and no need of special equipment [1]. Therefore, this oxidation process is considered to be the most promising treatment method for wastewater containing chlorophenol. The Fenton reagent is a mixture of H_2O_2 and ferrous iron, which generates hydroxyl radicals according to the following reaction [5].

$$\text{CPs} + H_2O_2 \longrightarrow \text{Intermediates} + H_2O$$
$$\text{CPs} + HO^{\bullet} \longrightarrow \text{Intermediates}$$
$$\text{Intermediates} + H_2O_2 \longrightarrow CO_2 + H_2O + Cl^-$$
$$\text{Intermediates} + HO^{\bullet} \longrightarrow CO_2 + H_2O + Cl^-$$

The ferrous iron initiates and catalyzes the decomposition of H_2O_2, resulting in a generation of hydroxyl radicals. This generation involves a complete reaction sequence in an aqueous solution [7]. In this study, kinetics of degradation of phenol, 2, 4-dichlorophenol and 4-chlorophenol by the Fenton reaction, using Fe/SUZ-4 Zeolite as a catalyst and H_2O_2 as an oxidation agent, were investigated.

Materials and Methods

Phenol, 2, 4-dichlorophenol, 4-chlorophenol and hydrogen peroxide (H_2O_2, 30%) were purchased from Merck, Ltd. Company. Analytical grade $FeCl_2.7H_2O$, purchased from QRec New Zealand, was used as a source of ferrous ion. HPLC-grade methanol from Sk Chemicals Korea and acetonitrile from Honey well Burdick & Jackson USA were employed as eluents. A mixture of silica sol and rice husk was used as a source of silica for synthesis the SUZ-4 zeolite. All other used chemicals such as tetraethyl ammonium hydroxide 35 %, aluminum powder 97 % were supplied by Mallinck Rodt Baker Inc., USA.

Firstly, potassium aluminate solution was prepared by gradually dissolving potassium hydroxide in water and then aluminum powder was added under continuous stirring for 20 to 25 h. Silica source was prepared by mixing rice husk ash in proportion to the silica sol. the synthesized zeolite SUZ-4 using a rice husk ash to silica sol ratio of 1:1. Then, tetraethyl ammonium hydroxide (TEAOH) and distilled water were added and stirred continuously for 2 h. Subsequently, the prepared potassium aluminate solution was slowly poured into the mixed silica source solution and kept stirring for another 3 h. The pH-value of the mixed solution was adjusted in the range of 13 to 14 by using potassium hydroxide. After that the gel compound was poured into a Teflon cup and put into an autoclave reactor for further hydrothermal processing at 423 K with agitation speed of 250 rpm

(Model M6, CAT Ingenieurbuero M. Zipperer, Germany) for 4 days [8]. Obtained powder was then filtered and rinsed with distilled water until the pH was close to 7. After drying at 393 K and calcining at 773 K, it was kept in a desiccator for further use. The Fe/SUZ-4 catalyst was prepared by a wet impregnation and ion-exchange methods. The synthesized SUZ-4 zeolite was suspended in 150 ml iron (II) chloride solution at room temperature for 24 h. At this stage, Fe^{2+} was expected to exchange with K^+ of SUZ-4 and simultaneously, $FeCl_2$ was impregnated onto the SUZ-4 surface. Next, the suspended solid was filtered, rinsed with deionized water, and dried at 393 K overnight. Finally, the impregnated $FeCl_2$ onto the SUZ-4 was decomposed at 673 K for 4 h to become Fe_2O_3.

The degradation of phenol, 2,4-dichlorophenol and 4-chlorophenol was conducted in a 500 ml glass batch reactor. 200 ml wastewater containing of 2,4-dichlorophenol and 4-chlorophenol was used in each batch reaction. After equilibrating of temperature and pH, the Fe/SUZ-4 catalyst was added, followed by hydrogen peroxide solution (30 % w/w), under rigorous stirring. The concentration of phenol, 2,4-dichlorophenol and 4-chlorophenol was measured by a high performance liquid chromatograph (HPLC Agilent 1200 Infinity Series LC). The analytic conditions of HPLC are as follows: flow-rate of 1.0 ml/min; temperature of chromatogram of 298 K; mobile phase 30% methanol; 30 % acetonitrile and 40 % DI water; wavelength of Photodiode array detector (DAD) of 280 nm.

The chemical composition and crystal structure of the obtained powder were confirmed to be a SUZ-4 zeolite by an X-ray fluorescence Spectrometry (XRF, HORIBA, MESA 500W). The specific surface area and micro pore volume of the product was carried out using a BET–N_2 adsorption (Quantachrome Autosorb-1-C).

Results and Discussion

Before being used as a raw material, the obtained rice husk ash was analyzed its chemical composition by an XRF and was found to contain 99.7% SiO_2 with traces of oxides of aluminum and other metals as shown in Table 1. The total amount of Fe in the synthesized SUZ-4 was also found to be 4.72 wt. % as presented in Table 2.

Table 1. Chemical composition of rice husk ash (RHA).

Chemical Composition	Wt.%
SiO_2	99.7
Al_2O_3	0.2
Others	0.1

Table 2. Chemical composition of synthesized Fe/SUZ-4

Chemical Composition	Wt.%
Si	33.32
K	11.89
Fe	4.72
Al	3.64
Others	46.43

The analysis of micro-structure of synthesized SUZ-4 by a Scanning Electron Microscope (SEM, Jeol Model JSM-5600 LV) is shown in Figure 1. Needle-shaped crystals of SUZ-4 [9] having diameter of approximately 0.2 μm and length of approximately 5 μm can be seen.

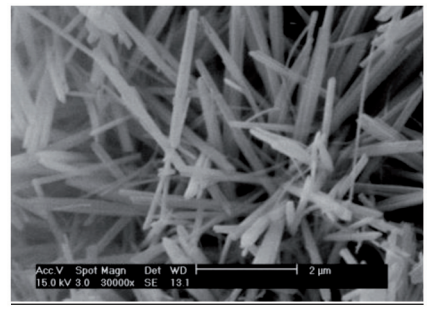

Figure 1. SEM of SUZ-4 zeolite synthesized by using RHA to Silica Sol at the ratio 1:1

In this study, the reaction temperature of the degradation rate of phenolic compounds was maintained at 303 K. The comparison of the degradation rate between the reactions with and without ion-exchanged SUZ-4 was performed. It is clearly seen in Figures 2 that the degradation of the phenolic compounds obtained by using ion-exchanged SUZ-4 is obviously higher than that of without ion-exchanged SUZ-4.

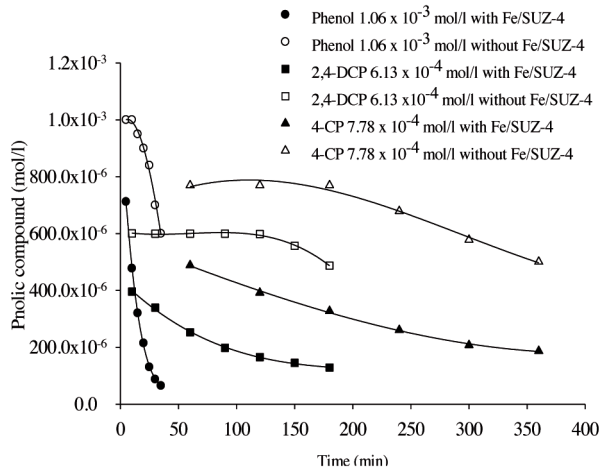

Figure 2. Degradation of phenol, 2,4-DCP and 4-CP using H_2O_2 0.50 g/l, 0.3 % (V/V) and 0.53 g/l, respectively, comparison between the reactions with and without Fe/SUZ-4.

The calculation on the degradation of phenol, 2,4-dichlorophenol and 4-chlorophenol was done by applying equation (1) [1].

$$\eta = \frac{C_1 - C_2}{C_1} \times 100 \qquad (1)$$

Where η is degradation of phenolic compounds, C_1 and C_2 are the concentrations of phenolic compounds before and after reaction, respectively. The results show that the degradation rate of phenol, 2,4-dichlorophenol and 4-chlorophenol without ion-exchanged SUZ-4 and with Fe/SUZ-4 are 34.12, 20.55, 35.61 % and 93.92, 79.03, 75.95 %, respectively. Consequently, the ion-exchanged SUZ-4 (Fe/SUZ-4) was chosen to be used for the rest of experiment.

The degradation reaction of phenol, 2,4-dichlorophenol and 4-chlorophenol degradation were investigated and the obtained results are shown in Figures 3 – 5. It is evident that the rate of degradation ($-r_d$) (i.e., slope of each curve) increases when the initial concentration of phenolic compound increases. This is just consistent with a kinetic behavior-the more concentration of reactant presents in the system, the higher rate of reaction occurs.

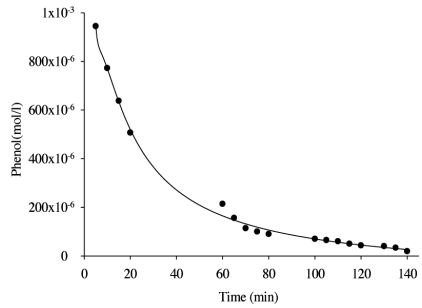

Figure 3. Degradation of phenol using H_2O_2 0.50 g/l and Fe/SUZ-4 0.026 g/l at 303 K, pH 3.0.

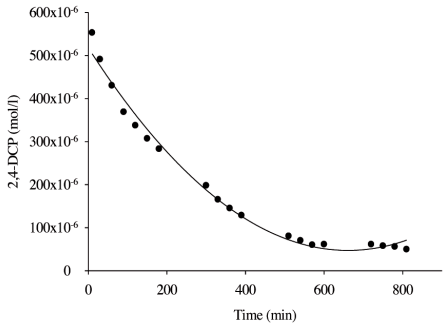

Figure 4. Degradation of 2,4-DCP using H_2O_2 0.3 % (V/V) and Fe/SUZ-4 0.2 g/l at 303 K, pH 3.0.

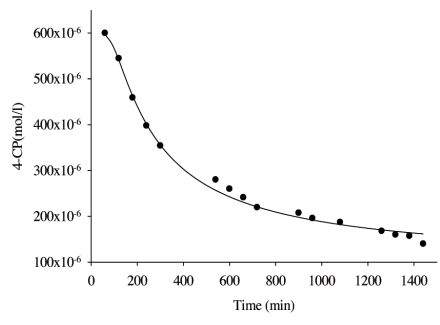

Figure 5. Degradation of 4-CP using H_2O_2 0.53 g/l and Fe/SUZ-4 0.1 g/l at 303 K, pH 3.0.

When the slope of each curve was taken at time approaching zero, the plot of phenolic compound concentration versus ln ($-r_d$) for phenol, 2,4-DCP and 4-CP degradation was obtained as shown in Figure 6.

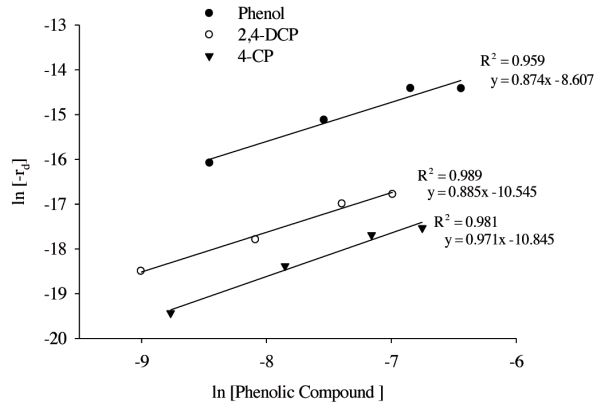

Figure 6. Plot of ln [Phenolic Compound] versus ln[-rd] for phenol, 2,4-DCP and 4-CP degradation

The slope of each plot is, in fact, an order of degradation reaction, following these equations:

$$r_d = \frac{dC_{CPs}}{dt} = kC_{CPs}^{n}C_{H_2O_2}^{m} \quad (2)$$

$$\ln \frac{dC_{CPs}}{dt} = n \ln C_{CPs} + \ln(kC_{H_2O_2}^{m}) \quad (3)$$

Where C_{CPs} : concentration of corresponding phenolic compound , $C_{H_2O_2}$ concentration of H_2O_2 that was kept constant, n : order of reaction with respect to C_{CPs} and k : rate constant.

From Figure 6, since the obtained slopes are close to 1, it can be concluded that the degradation of phenolic compounds follow the 1st-order reaction scheme. Then, the degradation of phenolic compounds repeated by varying H_2O_2 concentration and fixing phenolic compound concentration. The obtained results are presented in Figures 7 – 9.

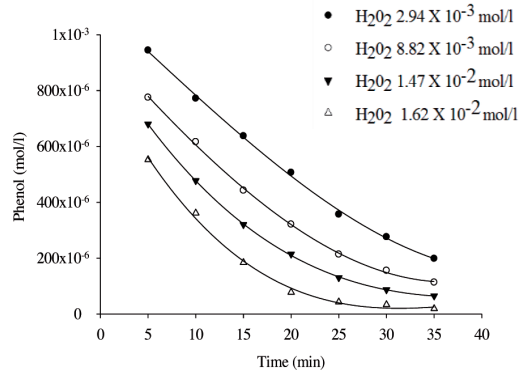

Figure 7. Degradation of phenol 0.10 g/l when [H_2O_2] was varied, using Fe/SUZ-4 0.026 g/l, 303 K, pH of 3.0.

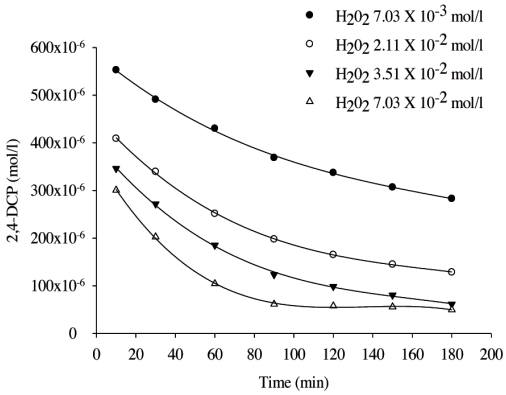

Figure 8. Degradation of 2,4-DCP 0.10 g/l when $[H_2O_2]$ was varied, using Fe/SUZ-4 0.2 g/l, 303 K, pH of 3.0.

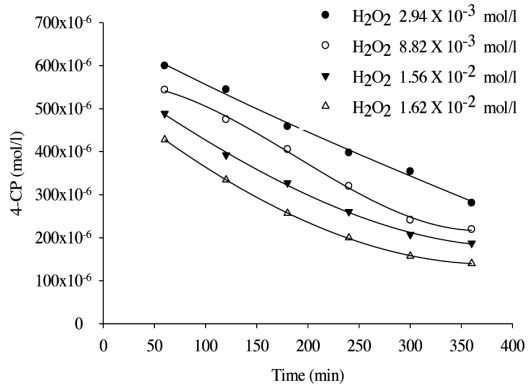

Figure 9. Degradation of 4-CP 0.10 g/l when $[H_2O_2]$ was varied, using Fe/SUZ-4 0.1 g/l, 303 K, pH of 3.0.

When the slope of each curve (i.e., $-r_d$) was determined and plotted against $[H_2O_2]$ in logarithmic scale as shown in Figure 10,.

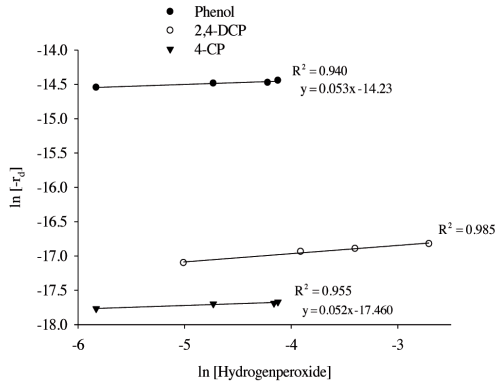

Figure 10. Plot of ln $[H_2O_2]$ versus ln$[^{-}r_d]$ for phenol, 2,4-DCP and 4-CP degradation.

it obviously shows that the slopes of all three lines are close to zero. These slopes are corresponded to the order of reaction with respect to H_2O_2. This means the rate of degradation does not depend on the hydrogen peroxide concentration.

Conclusions

Catalytic degradation of phenol, 2,4-DCP and 4-CP by the heterogeneous Fenton reaction using self prepared Fe/suz-4 zeolite catalysts was performed, and it was determined that the optimal reaction conditions were maintained at pH 3.0 and a reaction temperature at 303 K. The reaction kinetics study illustrated that the degradation of phenol, 2,4-DCP and 4-CP follow a first-order reaction scheme.` The rate law of reaction, following these equations $\ln \frac{dC_{CPs}}{dt} = \ln C_{CPs} + \ln k.$

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