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Porous ferrite synthesis and catalytic effect on benzene degradation

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In this study, feasibility of porous ferrite (MFe₂O₄) synthesis and catalytic effect on benzene degradation was evaluated. Various types of ferrites were synthesized by CuO, ZnO, NiO, and Fe₂O₃ under different Fe/M molar ratios and sintering temperatures. Porous ferrite synthesized by NiO, Fe₂O₃, polyvinyl alcohol (PVA) and kaolinite addition with appropriate sintering conditions were used in column tests to simulate benzene degradation in permeable catalyst barriers. Results from this research showed NiFe₂O₄ sintered with Fe/M molar ratio of 2 at 1000 °C had highest removal efficiency on Fenton-like benzene degradation. The removal efficiency of different ferrites on benzene degradation is in the order of: NiFe₂O₄ > ZnFe₂O₄ > CuFe₂O₄ > Fe₃O₄. Significant removal of benzene was observed when benzene/H₂O₂ (w/w) ratio = 1/32 and hydraulic retention time of 330 s. Under such reaction conditions, 94.98% of benzene was degraded at a relative liquid volume of 120. According to this study, porous Ni ferrite synthesized with Fe/M molar ratio = 2, 5% PVA, 10% kaolinite and sintered at 1000 °C under nitrogen atmosphere for 3 h was a favorable catalyst in generating Fenton-like reaction. It was regarded as potential catalytic material with environmental friendly characteristics that can be used in permeable catalytic barriers.

Key words: Ferrite, Fenton-like, benzene, permeable catalytic barriers.

INTRODUCTION

Soil and groundwater contaminations caused by organic pollutants had been a great concern in industrialized countries. Underground pipelines and storage tanks of petroleum refining industry and gas stations often have leakage problems, thus regarded as the main pollution source of soil and groundwater contamination (Johnson et al., 2000). These problems often result in huge disturbances and disastrous consequences for the biotic and abiotic components of ecosystems (Mueller et al., 1992). Permeable reactive barriers are emerging as an

in situ contaminant remediation technology. Reactive material is placed in the subsurface where a plume of contaminated ground water flows through, the ground water can be treated as it flows through the reactive material. The main advantage of a reactive barrier is the passive nature of the treatment, and the majority reactive media used so far has been granular iron (USEPA, 1998). In order to reduce the consumption of reactive media and make the installation easy to maintain, catalysts utilized in reactive media for permeable reaction barriers were new remediation technology which was firstly introduced in MTBE conversion (Centi et al., 2003). The catalysts used as the reactive material of permeable reactive barriers are often commercial product synthesized from pure chemical. However, if they can be

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synthesized from inorganic wastes, it will reduce the cost of contaminant remediation and enhance the value of wastes materialization.

The mechanism of Fenton reaction works as ferrous iron and hydrogen peroxide forms highly reactive hydroxyl radicals (OH^\cdot), which is used to oxidize contaminants under acidic condition (Kim and Huh, 1997; Kitis et al., 1999). Nowadays, Fenton reaction is used to treat a large variety of water pollutions such as phenols, dyes, tannery wastewaters and so on (Schrank et al., 2005; Xu et al., 2004). Unlike Fenton reaction, Fenton-like reaction works by generating hydroxyl radical from metal oxides instead of Fe^{2+} dissolved in solutions. In recent research, ferrite has been chosen to carry out Fenton-like reaction with H_2O_2 as it contained both Fe^{3+} and M^{2+} ($\text{M} = \text{Ni}, \text{Mn}, \text{Co}$, etc.) in heterogeneous system which would enhance the reactivity of H_2O_2 and remove the contaminants (Costa et al., 2006). Spinel ferrite structure, which had a chemical formula of AB_2O_4 (MFe_2O_4), is a cubic formed with a closely packed array of octahedral and tetrahedral structures. Where A is divalent ions for Mg^{2+} , Fe^{2+} , Mn^{2+} , Ni^{2+} , Zn^{2+} , etc., while B can be substituted with trivalent ions Al^{3+} , Cr^{3+} , among other chemicals. High temperature ferritization is one of the traditional methods for ferrite synthesis. Divalent and trivalent ions diffuse into the ferrite lattice after sintering. By controlling Fe/M molar ratio of the incoming material and sintering temperature, different types of ferrite (MFe_2O_4 , $\text{M} = \text{divalent metal}$) could be synthesized (Ahmed et al., 2000; Chen et al., 2000). In the field of heavy metal containing waste solidification/stabilization, the complicated composition of heavy metal containing waste (e.g. electroplating sludge) makes it difficult to process, thus by adjusting the Fe/M molar ratio in ferrite synthesis could reduce the mobility of heavy metals (Lu et al., 2008).

Ferrite is chemically stable because of the lattice bonding between heavy metal ions and Fe ion. The structure of ferrite is very similar to that of natural mineral, which has limited ions exchangeability, thermal stability and chemical stability. Together with its distinguished chemical and stabilizing characteristics, ferrite is applied in (a) inorganic waste ferritization (Lu et al., 2008), (b) adsorption of contaminants (Parsons et al., 2009), (c) catalytic reaction (Faunagnawakij et al., 2008), (d) electric conductor (Saxena et al., 2010), (e) magnetic device (Yamamoto et al., 2004), (f) gas sensor (Rezlescu et al., 2008), etc. Therefore, ferrite is considered as a potential catalytic material because of its high chemical stability as well as the presence of Fe^{3+} and M^{2+} which favours Fenton-like reaction. However, further discussion is needed for special requirements of catalysts utilized in permeable catalytic barriers, such as the catalysts activity, hydraulic conductivity of sintered specimens, environmental compatibility etc.

In this research, different types of ferrites are synthesized by pure chemicals to verify the feasibility of

ferrites utilization in permeable catalyst barrier. Optimum sintering parameters and pore former addition for different ferrites synthesis are evaluated to obtain the suitable catalyst utilized in permeable catalytic barriers. The conclusion can be used as reference to evaluate the feasibility of ferrites synthesized from waste materials utilization in permeable catalyst barriers. Benzene is selected to represent the organic contamination, as it is considered as the most problematic petroleum hydrocarbon due to its high toxicity and relatively high water solubility (Johnson et al., 2003). Fenton-like reaction generated by ferrite with permeable catalytic barriers was then involved in the discussion for benzene degradation. Environmental compatibility should be taken into consideration for all catalytic reaction proposed.

MATERIALS AND METHODS

Materials

Ferrite was synthesized from pure chemical powders such as copper (II) oxide (99%, Showa), iron (III) oxide (98%, Showa), nickel (II) oxide (97%, Showa) and Zinc oxide (99%, Merck). Kaolinite (EP grade, Hayashi) and polyvinyl alcohol (PVA) (EP grade, Sigma) were used as binder and pore former for porous ferrite synthesis. Reagents utilized in benzene (99.5%, Merck) degradation included porous ferrite and hydrogen peroxide (30%, Showa).

Ferrite synthesis

ZnO , CuO , NiO , and Fe_2O_3 were mixed using a ball miller with Fe/M ($\text{M} = \text{Cu}, \text{Ni}$ and Zn) molar ratio of 2 and 2.5. The obtained powders were then pelletized into pellet with 30 mm diameter and uniaxial compression at 27 MPa. The pellets were taken into tubular furnace for sintering. Tubular furnace composed of electronic controller, gas flow meter, heating area and quartz tube as combustion chamber. Nitrogen (N_2) controlled by flow meter at 1.5 L/min to maintain an inert atmosphere inside the furnace. Sintering temperature ranged from 800 to 1000°C for 3 h. By the end of the sintering process, furnace was naturally cooled to room temperature and the sintered specimens were first crushed and ball milled to pass through 200 mesh sieve for further microstructure and composition analysis.

Batch test for benzene degradation

Experimental conditions of batch test for benzene degradation were 1 L solution of benzene/ H_2O_2 (w/w) ratio = 1/32 and addition of 5 g ferrites, then rotated at 30 rpm for 24 h at room temperature. The concentration of benzene and H_2O_2 reagent were controlled at 12.2 and 390 ppm, respectively. The solution was then filtered with syringe filter (Pall AP-4518). Divalent metals and Fe concentration in solution were analyzed thereafter by ICP-OES. Benzene analysis by gas chromatography-flame ionization detector (GC-FID, Hewlett Packard 6890 series GC system) was carried out immediately after sample collection. Nitrogen was used as carrier gas in GC-FID. The peak of benzene would appear within the range of 7.5 to 8 min retention time. Solid-phase micro-extraction (SPME, 75 μm PDMS/Carboxen fiber, Supelco) was used to extract compounds that adsorb on the carbon fiber of SPME at 18°C water bath for 30 min. Sodium chloride with concentration of 25% was added in the sample to drive the analysed compounds into gas phase for SPME

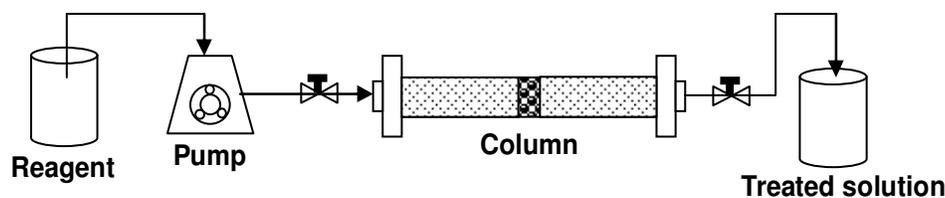


Figure 1. Scheme of the apparatus for column test.

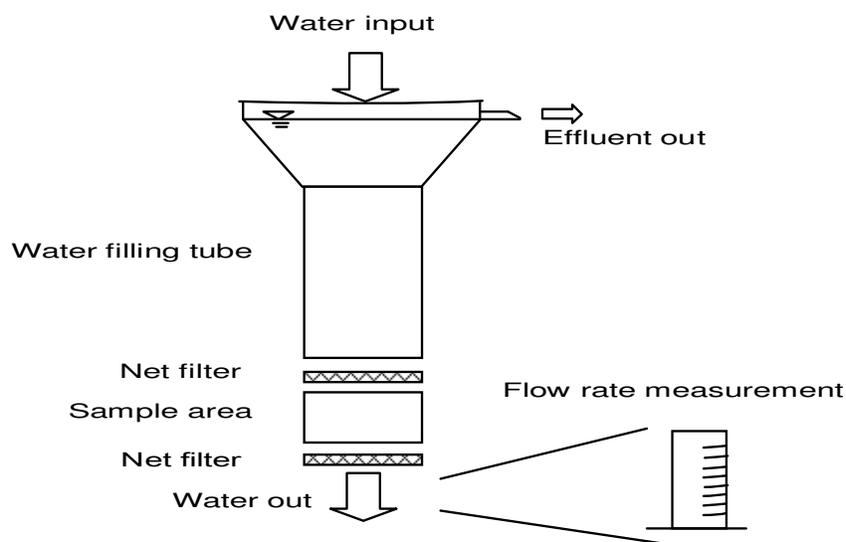


Figure 2. Scheme of the apparatus for hydraulic conductivity measurement.

extraction. Compounds would release after carbon fiber was inserted into the injection chamber (Vas and Vékey, 2004).

Porous ferrite synthesis

NiO and Fe₂O₃ were mixed with 10% (wt) of kaolinite for ferrite binding. 5 to 20% of PVA were added respectively into the mixed powder to assist pore formation in ferrite during sintering. Mixed powders were pelletized and sintered at 1000°C for 3 h under N₂ atmosphere. Obtained samples were crushed and ball milled to pass through 200 mesh sieve for further analysis.

Column test for benzene degradation

For permeable catalytic barriers simulation, benzene degradation was carried out using rapid small-scale column tests (Westerhoff et al., 2005) with the following displacement (Figure 1). A column of 2 cm in diameter and 19 cm in length was used to set up the column tests. 2 cm thick sample was filled in the column in all tests. Other spaces in the column were filled with 2 mm glass balls to conduct a uniform flow of benzene containing solution came in contact with the catalyst. Sintered specimens were crushed with jaw crusher and the finished product with particles size of 1 to 2 mm (18 to 10 mesh) were collected for column test sample. Benzene and H₂O₂ solution was mixed with benzene/H₂O₂ wt ratio of 1/24, 1/32 and 1/64 respectively, and then the solution was pumped passing through the filled column by peristaltic pump (Eyela, MP1000). Treated solution

was collected in the end at different relative liquid volumes (liquid/pore volume) for benzene and metals concentration analysis.

Crystalline phase identification

X-ray diffractometer was used to identify the types of ferrites by their crystalline phases. Sieved samples were pressed flat on a disc, all XRD analysis were performed under the following parameters (1) scanning range of 20°–60° (2θ), (2) step size = 0.05° and (3) time of each step = 2 s. The characteristic spectrum of the samples was compared with ICDD-JCPDS (The International Centre for Diffraction Data, Joint Committee on Powder Diffraction Standards) standard spectrum for crystals identification. Peak intensity was often examined to quantify the crystalline compound as it represented all the scattering of specific compound detected, thus related to both structure and composition of the compound. Internal standard method was one of the quantitative methods. With internal standard used, the intensity ratio would be used to represent the change of relative quantity in compound (Connolly, 2010). In this study, 20% of high crystallinity TiO₂ with an identified diffraction pattern was added as internal standard.

Hydraulic conductivity measurement

The apparatus for hydraulic conductivity of ferrite measurement was shown in Figure 2. Hydraulic conductivity replicated the permeability of material as liquid phase pass through it. Under room

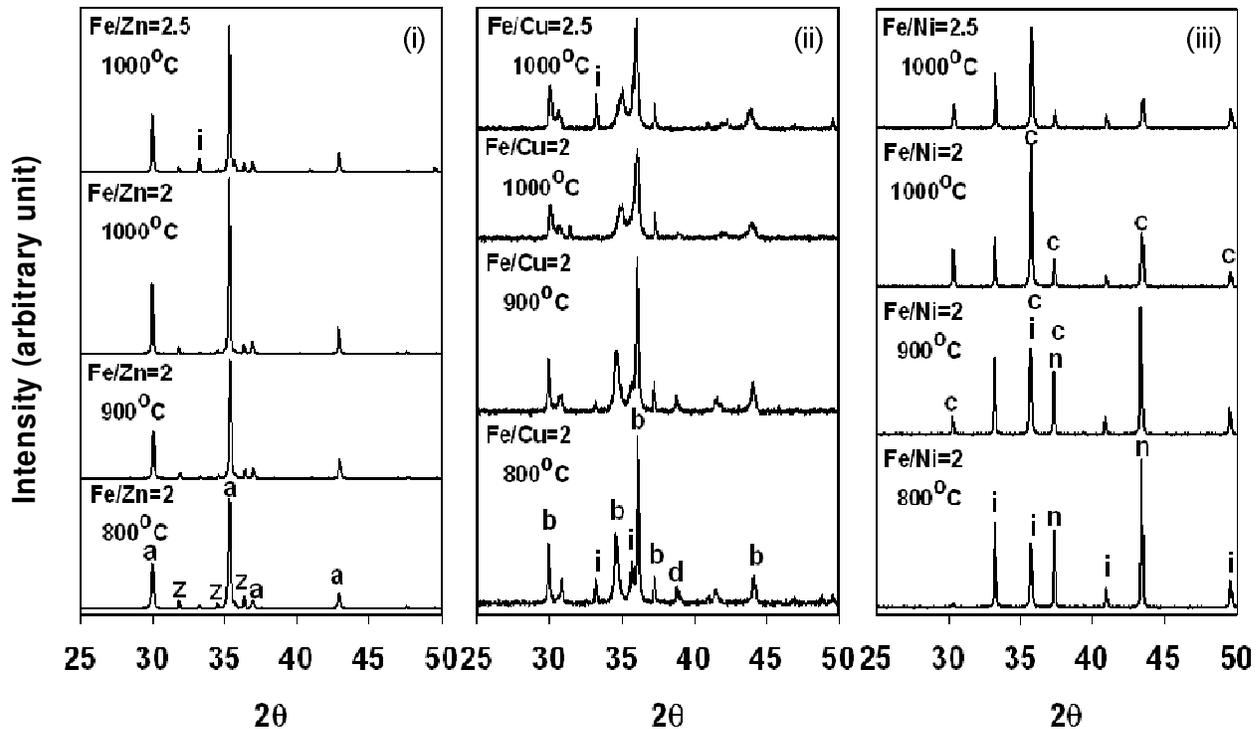


Figure 3. X-ray powder diffraction patterns of ferrites with different synthesis temperatures and Fe/M molar ratios (i) M=Zn; (ii) M=Cu; (iii) M=Ni (nitrogen atmosphere, isothermal time for 3 h). Note: a=ZnFe₂O₄; b=CuFe₂O₄; c=NiFe₂O₄; d=CuO; i=Fe₂O₃; n=NiO; z=ZnO.

temperature, hydraulic conductivity (K_T) was derived from Darcy's law as Equation (1),

$$K_T = \frac{L}{h} \cdot \frac{Q}{A(t_2 - t_1)} \quad (1)$$

Where K_T =hydraulic conductivity, cm/s; L=height of sample, cm; A=surface area of samples, cm²; h=constant head, cm; Q=quantity of water discharged within t_2 and t_1 , cm³; t_1 =starting time, s; t_2 =ending time, s.

Samples were filled in sample area with two barriers to hold samples in place. Constant head was the distance between the water surface and the end of water filling tube. As water input from the top, the water flow would waited until reached a stable condition, then the flow rate could be measured.

RESULTS AND DISCUSSION

Effect of sintering temperature and Fe/M molar ratio for manufacturing different types of ferrites

CuO, NiO, and ZnO were chosen as the divalent metals while Fe₂O₃ was chosen as the trivalent metal to synthesize three types of ferrite. In order to verify suitable synthesis conditions for ferritization, parameters, such as

temperature and Fe/M molar ratio were discussed here. Figure 3 showed X-ray diffraction (XRD) patterns of specimens sintered at 800, 900 and 1000°C with Fe/M molar ratios of 2 and 2.5 under nitrogen atmosphere. ZnFe₂O₄ was found to be the major crystalline phase in Fe/Zn=2 samples at all sintering temperatures.

As sintering temperature increased from 800 to 1000°C, stronger peak intensity of ZnFe₂O₄ was revealed. The XRD pattern of Fe/Cu=2 at 800°C indicated the presence of CuFe₂O₄, Fe₂O₃ and CuO, but the peak of Fe₂O₃ and CuO disappeared, as the sintering temperature increased. The formation of NiFe₂O₄ was not observed until 900°C. Fe₂O₃ and NiO were still the dominant phase at 800°C and their peak intensity gradually decreased with increasing sintered temperature. At 1000°C, only the crystalline phase of NiFe₂O₄ and Fe₂O₃ was observed. ZnFe₂O₄ and CuFe₂O₄ could be synthesized at 800°C while NiFe₂O₄ only appeared at 900°C or above. All types of ferrite showed the trend of stronger crystalline intensity as sintering temperature increased from 800 to 1000°C. At 1000°C, ferrite was the dominant crystalline phase in all types of sintered specimens.

Unlike sintering temperature, the XRD pattern of sintered specimens revealed stronger peak intensities of Fe₂O₃ when Fe/M molar ratio increased from 2 to 2.5 at 1000°C. This phenomenon was due to an overdose of

Table 1. Comparison of different ferrites in benzene degradation with batch test and metal concentration after reaction.

MFe ₂ O ₄	Benzene removal efficiency (%)	Metal leaching concentration* (mg/L)	
		M	Fe
Fe ₃ O ₄	78.13 ± 0.4	N.D.	N.D.
NiFe ₂ O ₄	85.07 ± 0.9	N.D.	N.D.
ZnFe ₂ O ₄	84.62 ± 0.6	0.21	N.D.
CuFe ₂ O ₄	83.74 ± 1.0	0.13	N.D.

N.D.: under detection limit 0.1 mg/L. Metal leaching concentration*: the concentration of metal ions in solution after Fenton-like reaction.

iron (III) oxide in ferrite formation. However, increase Fe/M molar ratio in raw mixed powders would not significantly increase the peak intensity of ferrite. In order to prevent the formation of other metal oxides that might react with H₂O₂ to generate Fenton-like reaction during catalytic reaction. Ferrite should be synthesized with high peak intensity and limit the formation of other crystalline phase. The results indicated suitable sintering conditions occurred at 1000 °C under the stoichiometric Fe/M molar ratio of 2 for ZnFe₂O₄, CuFe₂O₄, and NiFe₂O₄ synthesis.

Effect of different ferrites in benzene degradation

Here, batch test was conducted to evaluate the ability of different ferrites on benzene degradation. The batch tests were performed with 5 g/L of each type of ferrite in brown glass bottle with benzene/H₂O₂ ratio of 1/32 which rotated for 24 h. Table 1 indicated the results of batch test conducted by different types of ferrite on benzene degradation. The removal efficiency of NiFe₂O₄, ZnFe₂O₄, CuFe₂O₄, and commercial Fe₃O₄ (98%, Showa) on benzene was, 85.07, 84.62, 83.74 and 78.13% respectively. Benzene removal efficiency of ferrite decreased in the following order: NiFe₂O₄ > ZnFe₂O₄ > CuFe₂O₄ > Fe₃O₄. The results showed substitution of cations such as divalent metals Ni, Zn and Cu in octahedral site of ferrite would lead to higher catalytic activity than Fe.

To investigate the environmental compatibility of ferrite to the environment during catalytic reaction, metals concentration in treated solution was analyzed by ICP-OES. The analyzed results were also constructed in Table 1. There were no ions released into liquid phase from all types of ferrite. Regarding to the high removal efficiency of NiFe₂O₄ on benzene, concentration of Ni in solution after reaction was also under detection limit. In contrast, other types of ferrite had minor amount of cations released into the solution, with a concentration of 0.2 mg/L for ZnFe₂O₄ and 0.1 mg/L for CuFe₂O₄. Therefore, NiFe₂O₄ would be an appropriate catalyst to utilize in permeable catalytic barriers, due to its high benzene removal efficiency and limited Ni dissolution during catalytic reaction.

The effect of pore former addition on porous Ni ferrite synthesis

The permeable catalytic barriers worked when contaminants in soil and groundwater flow through it after uptake of H₂O₂ in oxidation injection well. Porous material should therefore encounter, to ensure a flow of contaminants occurred. This point of view extends the requirement of porous materials formation. In this study, pore formers and binders were considered as additives in raw materials. By high temperature ferritization, Ni ferrite synthesis would occur together with pore formation. Different percentages of pore former polyvinyl alcohol (PVA) were added and examined in specimens, in order to acquire appropriate PVA addition. From 5 to 20% of PVA were added together with 10% of binder kaolinite in raw mixed powders (Fe/Ni = 2). The raw mixed powders was then pelletized and sintered at 1000 °C for 3 h under N₂ atmosphere. The specimens obtained then carried out XRD analysis and hydraulic conductivity measurements.

According to Figure 4, crystalline phase in XRD patterns with different PVA additions were similar. Only the crystalline phases of NiFe₂O₄, Ni and SiO₂ were observed with different PVA additions. The SiO₂ phase came from the transformation of heating kaolinite at 1000 °C (Chen et al., 1999). There was a significant decrease in peak intensity of NiFe₂O₄ as PVA increased from 5 to 20%. On the contrary, the peak of Ni phase was stronger with more PVA addition. Polyvinyl alcohol (PVA) is a type of organic solid. When porous ferrite synthesized at high temperature, oxygen would be consumed by burning out PVA and created a reduction atmosphere. Therefore, increasing the amount of PVA in raw mixed powders, stronger reduction atmosphere would be revealed at high temperature. Instead of synthesized NiFe₂O₃ by NiO and Fe₂O₃, stronger reduction would cause NiO reduce to Ni and interrupted the formation of NiFe₂O₃. The relative quantitative analysis of NiFe₂O₄ crystalline phase in Figure 5 further quantified this phenomenon.

In this study, the specific 2θ of X-ray diffraction selected for relative quantitative analysis of NiFe₂O₄ and TiO₂ (Internal standard) were 35.68° and 27.43°. I and I₀ stand for the selected peak intensity of NiFe₂O₄ and TiO₂

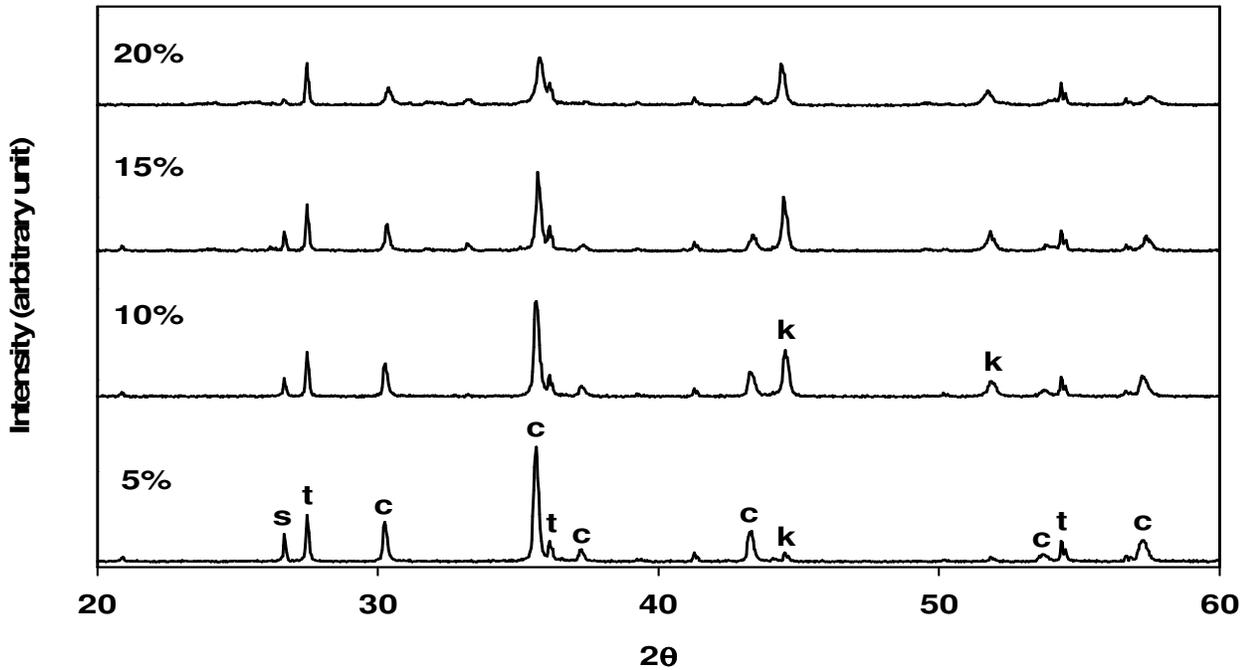


Figure 4. X-ray powder diffraction patterns of sintered specimens with different amounts of PVA addition (Fe/Ni = 2, Kaolinite = 10%, sintered at 1000 °C, nitrogen atmosphere, isothermal time for 3 h). c = NiFe_2O_4 ; k = Ni; s = SiO_2 ; t = internal standard TiO_2 .

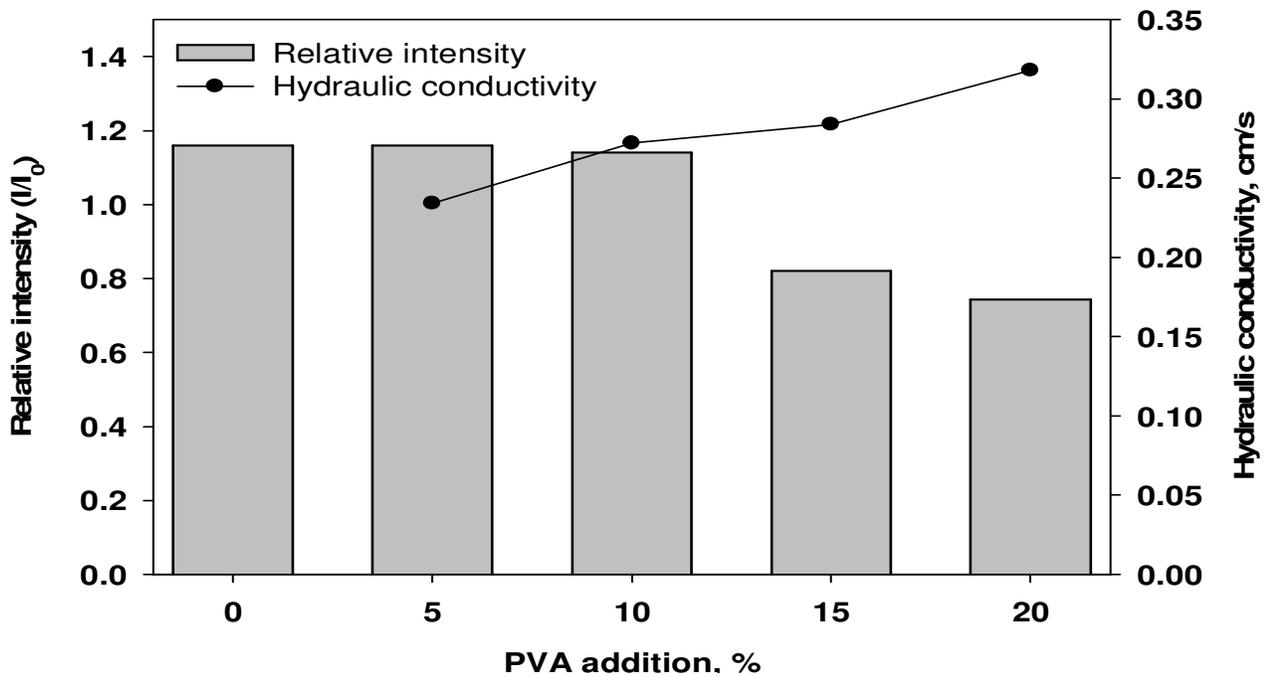


Figure 5. X-ray powder diffraction relative intensity and hydraulic conductivity of porous Ni ferrite with different amounts of PVA addition.

with different amount of PVA addition. 5% of PVA addition did not have significant effect towards NiFe_2O_4 synthesis

with the same relative intensity of NiFe_2O_4 ($I/I_0 = 1.16$) as original Ni ferrite sintered without binder and pore former

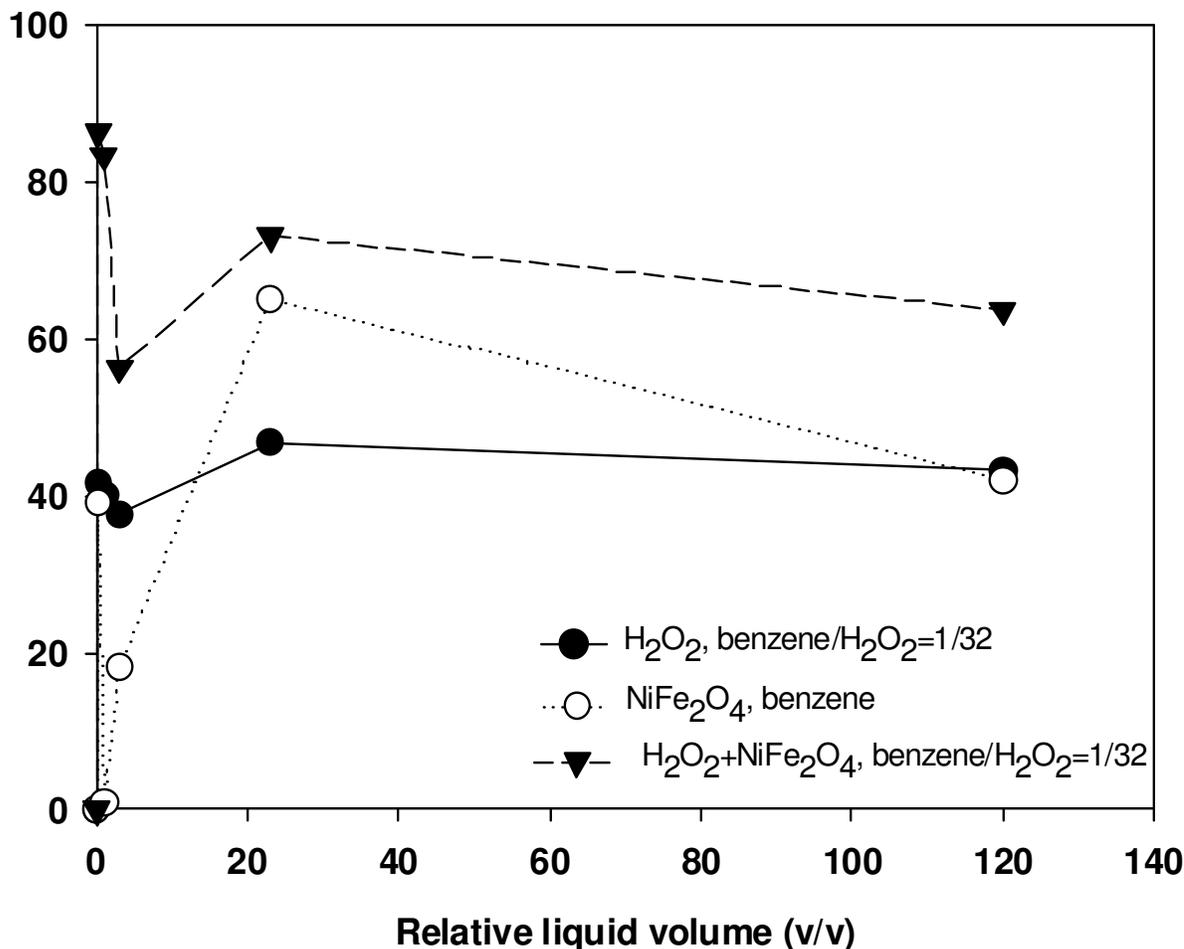


Figure 6. Benzene degradation in column tests ($Q = 0.048$ ml/s, HRT = 130 s).

addition. However, a decreased relative intensity of NiFe_2O_4 was observed, from original 1.16 decreased to 0.74 with 20% PVA addition.

Further characteristics affected by PVA addition on porous Ni ferrite was hydraulic conductivity (Figure 5). Without addition of PVA and kaolinite, sintered specimen existed in powdered form after being crushed and hydraulic conductivity was too low to be measured. As it was not detectable, the hydraulic conductivity was not presented in Figure 5. A rise of hydraulic conductivity was shown with increased PVA addition, ranging from 0.234 cm/s with 5% PVA addition to 0.318 cm/s with 20% PVA addition. Owing to permeable catalytic barriers required catalytic materials to have a hydraulic conductivity above 10^{-2} cm/s and particle size greater than 0.5 mm. Sieve analysis was done on porous Ni ferrite sintered with 5% PVA and 10% kaolinite. After crush, around 40% (wt) of sample was within particle size range of 1 to 2 mm. Summarized from the aforesaid results, 5% PVA addition was the suitable amount to fulfill the hydraulic conductivity and particle size requirements of permeable

catalytic barriers, which has the crystalline intensity of NiFe_2O_4 similar to the original NiFe_2O_4 sintered without binder and pore former addition.

Verification of Fenton-like reaction on benzene degradation by porous ferrite

Rapid small-scale column tests were used to simulate the degradation of soil and groundwater contaminants, as they flow through permeable catalytic barriers. In order to verify catalytic and adsorption reaction of NiFe_2O_4 in benzene degradation, column tests under three circumstances were conducted. The porosity of column filled with ferrite catalytic material was 37% and the benzene/ H_2O_2 ratio (w/w) of column tests was set at 1/32, unless otherwise stated. In Figure 6, the relative liquid volume represented the liquid volume (liquid/pore volume) passing through the pores of porous ferrite. The flow rate was controlled at 0.048 ml/s and obtained hydraulic retention time (HRT) of benzene in catalytic

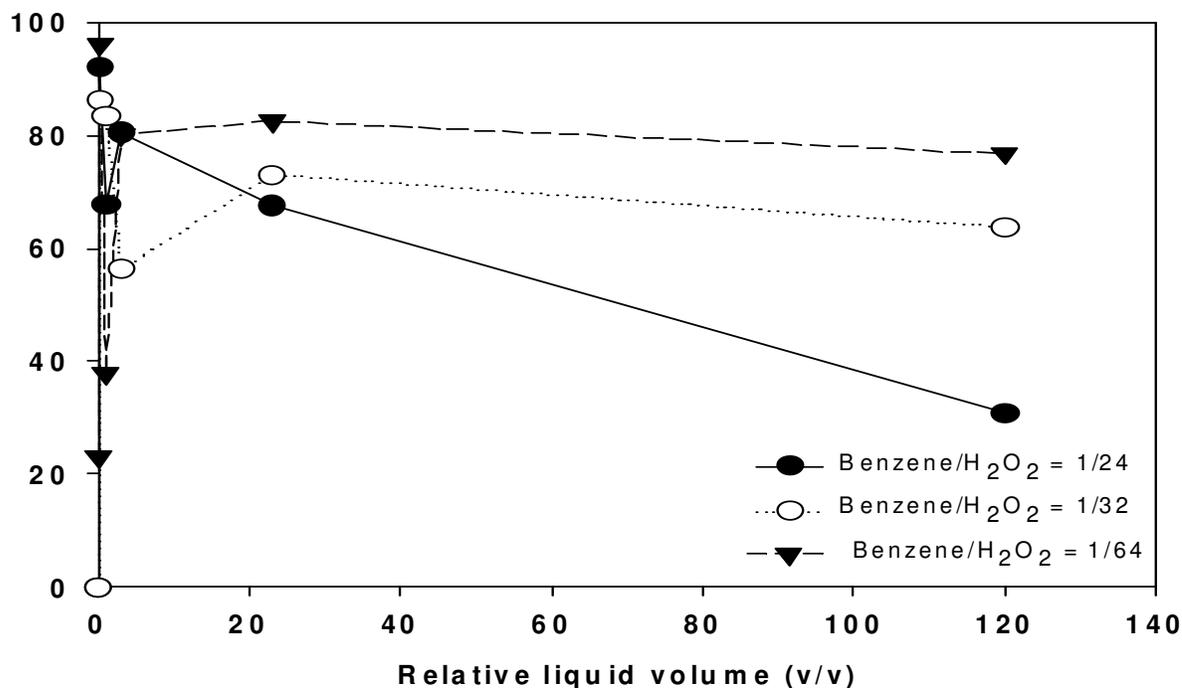


Figure 7. Effect of benzene/H₂O₂ ratio on benzene degradation in column tests (Q = 0.048 ml/s, HRT = 130 s).

material was 130 s. First column test act as blank test (marked as H₂O₂ in Figure 6) with benzene and H₂O₂ under the ratio of 1/32 passing through the column filled with 2 mm glass balls. No Ni ferrite was filled in the column during blank test. Second column test represented adsorption of benzene on porous Ni ferrite (marked as NiFe₂O₄ in Figure 6). The column was filled with 2 cm thickness of Ni ferrite. Benzene solution of 60 mg/L was pumped through the column without H₂O₂. The third column test represented catalytic reaction enhanced with H₂O₂ on benzene degradation using porous Ni ferrite (marked as H₂O₂+NiFe₂O₄ in Figure 6). The column filled with 2 cm thickness of NiFe₂O₄ and solution of 1/32 benzene/H₂O₂ ratio was used during the reaction.

From Figure 6, catalytic degradation of benzene was predominant in the column test with H₂O₂ and porous Ni ferrite as higher removal efficiency was observed. In the presence of H₂O₂ and NiFe₂O₄, catalytic reaction on benzene had been rapid. Initially, high removal efficiency of 86.68% was observed at liquid volume less than 3, which then decreased to 73% at liquid volume of 23. Gradual decrease in removal efficiency was observed though the reaction; the efficiency reduced to 64% at liquid volume of 120. A similar reaction pattern was also noted in blank test of H₂O₂ and benzene with removal efficiency of 47% at liquid volume of 23. Benzene adsorption on porous Ni ferrite showed an increase of removal efficiency when liquid volume was less than 23. Fluctuation observed at liquid volume of less than 3, indicated the reaction system had not yet reached the

equilibrium. Reaction generated by H₂O₂ and NiFe₂O₄ had higher removal efficiency of benzene than the adsorption by porous Ni ferrite alone. Although catalytic reaction generated from metal oxides were complicated, and contribution of benzene adsorption in this system was difficult to clarify. However, higher removal efficiency of benzene conducted by NiFe₂O₄ and H₂O₂ ensured this combination could enhance the degradation.

Effect of benzene/H₂O₂ ratio on benzene degradation

In order to improve the removal efficiency of benzene, reaction parameters such as hydraulic retention time and benzene/H₂O₂ ratio of column tests were discussed. The column was filled with 2 cm thick of porous Ni ferrite in all column tests. Benzene/H₂O₂ ratio represented a change of benzene concentration towards H₂O₂ dosage in this reaction system. Column tests with 1/24, 1/32 and 1/64 benzene/H₂O₂ ratio were considered for investigation. Figure 7 showed that with benzene/H₂O₂ ratio of 1/64, the removal efficiency was maintained around 80%. At a ratio of 1/32, a rise of removal efficiency to 73.06% was observed at a liquid volume from 3 to 23 which then decreased gently until liquid volume of 120. Benzene/H₂O₂ ratio of 1/24 had a reducing trend in removal efficiency on benzene, since liquid volume of 3. Removal efficiency of benzene at liquid volume of 120 with benzene/H₂O₂ ratio of 1/24, 1/32 and 1/64 were 30.91, 73 and 82.54%, respectively.

Table 2. Ni concentration in solution after Fenton-like reaction under different benzene/H₂O₂ ratio (Q = 0.048 ml/s, HRT = 130 s).

Benzene/H ₂ O ₂ ratio	Ni concentration under different liquid volume (mg/L)				
	0.2	1	3	23	120
1/24	N.D.	N.D.	N.D.	5.34	5.21
1/32	N.D.	N.D.	N.D.	N.D.	1.01
1/64	N.D.	N.D.	N.D.	4.32	12.38

N.D.: under detection limit 0.1 mg/L.

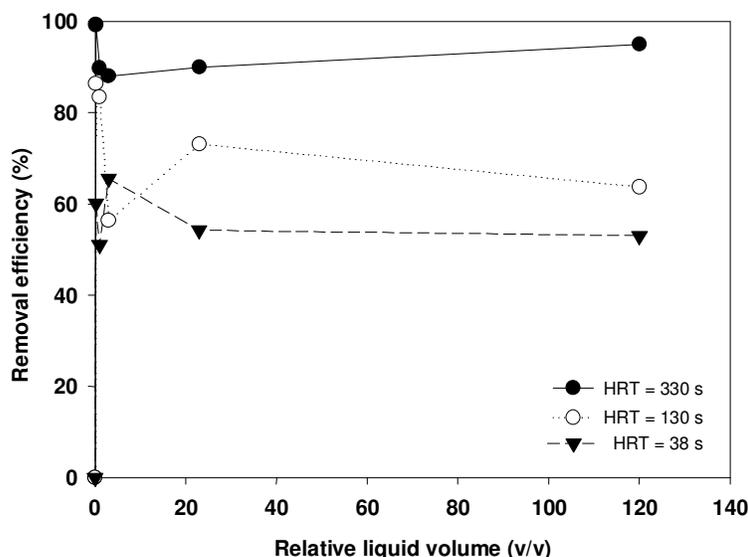


Figure 8. Effect of hydraulic retention time on benzene degradation in column tests (benzene/H₂O₂ = 1/32).

Environmental compatibility of porous Ni ferrite during catalytic reaction with different benzene/H₂O₂ ratios were analyzed by metals concentration detection on benzene treated solution. The analyzed results from ICP-OES were shown in Table 2. Iron was not detected in any solution with different benzene/H₂O₂ ratios. However, Ni had leached since liquid volume of 23 with benzene/H₂O₂ ratio of 1/64 and 1/24, with the value of 4.32 and 5.34 mg/L, respectively. All ratios had Ni leaching at liquid volume of 120; the highest leaching occurred at 1/64 with 12.38 mg/L of Ni concentration in the solution. At benzene/H₂O₂ ratio of 1/32, 1.01 mg/L of Ni leaching was detected at liquid volume of 120. It was observed that leaching of Ni in treated solution increased with the liquid volume, thus affected the removal efficiency of Ni ferrite on benzene resulted in a decreasing trend. Dissolution of Ni from sintered Ni ferrite into solution during catalytic reaction was unfavorable. Divalent metal Cu dissolution from copper and iron exchanged zeolite (CuFeZSM-5) during Fenton-like reaction was proposed by other researchers. Activity of CuFeZSM-5 was lowered due to Cu leaching from catalyst (Dükkanci et al., 2010).

Dissolution of metals in Fenton-like reaction was suggested to be an attribute to the coordination of intermediate compounds during surface complex formation and electron transfer in organic degradation (Zhang et al., 2010). When considered, the removal efficiency of benzene and environmental compatibility of Ni ferrite, Benzene/H₂O₂ ratio of 1/32 could be qualified as an appropriate parameter in Fenton-like reaction system, with low leaching of Ni and second highest removal efficiency of benzene.

Effect of hydraulic retention time on benzene degradation

To determine the effect of hydraulic retention time towards benzene degradation, column tests under flow rate of 0.019 ml/s (HRT = 330 s), 0.048 ml/s (HRT = 130 s) and 0.167 ml/s (HRT = 38 s) with benzene/H₂O₂ ratio of 1/32 was conducted and results were presented in Figure 8. Two flow rates (0.019 and 0.048 ml/s) were chosen to simulate the flow of benzene contaminant in

Table 3. Ni concentration in solution after Fenton-like reaction under different hydraulic retention time (benzene/H₂O₂ = 1/32).

Hydraulic retention time (s)	Ni concentration under different liquid volume (mg/L)				
	0.2	1	3	23	120
330 (Q = 0.019 ml/s)	N.D.	N.D.	N.D.	1.29	5.68
130 (Q = 0.048 ml/s)	N.D.	N.D.	N.D.	N.D.	1.01
38 (Q = 0.167 ml/s)	N.D.	N.D.	N.D.	N.D.	N.D.

N.D.: Under detection limit 0.1 mg/L.

ground and groundwater with hydraulic gradient of 0.026 and 0.065, respectively. Typical hydraulic gradient in ground and groundwater would range from 0.005 to 0.1. A high flow rate of 0.167 ml/s was also chosen to represent the flow in loose coarse or compressed aquifer, that was, with high hydraulic gradient at 0.277. Hydraulic gradient in loose coarse sand was suggested to be not greater than 0.8 (Smith et al., 1992).

Figure 8 showed that the degradation of benzene under different hydraulic retention times reached equilibrium after a liquid volume of 23.

As the hydraulic retention time increased from 38 to 330 s with a reduced flow rate, removal efficiency on benzene increased from 53 to 95% at liquid volume of 120. At HRT of 330 s, the removal efficiencies on benzene were all greater than 89% at different liquid volumes. The analysis of Ni leaching after catalytic reaction under different hydraulic retention time in Table 3 conducted low leaching concentration of Ni in the solution. Ni was not detected at any liquid volume with HRT of 38 s. Minor Ni concentration was detected at liquid volume of 120 as the HRT increased to 130 and 330 s. HRT of 330 s resulted in 5.68 mg/L of Ni released into the solution while 1.01 mg/L of Ni leached with HRT of 130 s. Ni released into the solution would increase accordingly to longer contact time of benzene and H₂O₂ with NiFe₂O₄ in the column. To compare the removal efficiency and Ni leaching between benzene/H₂O₂ ratio of 1/64 with HRT of 130 s and benzene/H₂O₂ ratio of 1/32 with HRT of 330 s. Prolonged hydraulic retention time had higher removal efficiency with smaller dosage of H₂O₂. Although HRT of 330 s at benzene/H₂O₂ of 1/32 also resulted in 5.68 mg/L leaching of Ni, the leaching concentration was lower than that of benzene/H₂O₂ ratio of 1/64.

Compared with the work of Chen et al. (2009), a 60-cm thick column was required to degrade 93% of benzene with column test using Mn coated zeolite. In this research, reaction conditions of 330 s HRT with benzene/H₂O₂ ratio of 1/32, resulted in 95% removal efficiency on benzene degradation with 2 cm thickness of sintered porous Ni ferrite filled in the column. In conclusion, a hydraulic retention time of 330 s with benzene/H₂O₂ ratio of 1/32 would be favorable reaction conditions for benzene degradation in Fenton-like reaction system.

Conclusions

The porous ferrite sintered from pure metal oxides, kaolinite and PVA was utilized as catalysts in rapid small-scale column tests for benzene degradation. The summarized conclusions would be described as follows:

1. Fe/M molar ratio of 2 sintered at 1000°C for 3 h under N₂ atmosphere was suitable sintering conditions for ZnFe₂O₄, CuFe₂O₄ and NiFe₂O₄. From the results of batch tests on benzene degradation, NiFe₂O₄ had the highest removal efficiency. The removal efficiency of different ferrites was in the order of: NiFe₂O₄ > ZnFe₂O₄ > CuFe₂O₄ > Fe₃O₄.
2. 5% of PVA pore former addition did not have significant influence on ferrite formation, resulting in the same XRD relative intensity of NiFe₂O₄ (1.16) as original NiFe₂O₄ sintered. Hydraulic conductivity of sintered ferrite fulfilled the requirement of 10⁻² cm/s with a value of 0.234 cm/s.
3. Porous Ni ferrite synthesized with Fe/M molar ratio of 2, 5% PVA and 10% kaolinite, 1000°C sintering temperature under nitrogen atmosphere for 3 h was favorable catalyst, which had high chemical stability in generating Fenton-like reaction.
4. The column tests proposed by porous Ni ferrite with benzene/H₂O₂ ratio of 1/32 and prolonged hydraulic retention time of 330 s resulted in 94.98% removal efficiency and only 5.68 mg/L of Ni leaching, which identified the suitable reaction condition for benzene degradation.

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