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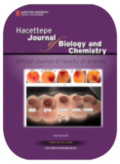

Hydrothermal Synthesis of MIL-53 Catalyst for Liquid Phase Oxidation of Phenol

Fenolün Sıvı Faz Oksidasyonu için Mil-53 Katalizörünün Hidrotermal Sentezi

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ABSTRACT

For the removal of toxic organic phenol pollutants, to find a new alternative oxidation catalyst has been an important topic for a long time. Iron terephthalate (MIL-53) is an efficient catalyst for oxidation processes with high porosity and high surface area. In this study, MIL-53 was used for the oxidation of phenol. The catalyst was synthesized by hydrothermal method at 150°C for 2 h. It was structurally characterized by FT-IR and p-XRD. Thermal properties were also examined. The surface area was found as 152 m^2/g with micropore areas. The liquid phase oxidation of phenol by hydrogen peroxide was performed on MIL-53. The reaction time, reaction temperature, catalyst amount and oxidant amount were also investigated. The phenol was removed with 91% conversion for 3 hours at 80°C. MIL-53 was enhanced as an alternative catalyst for liquid phase oxidation of phenol with high efficiency, selectivity, and conversion.

Key Words
Hydrothermal synthesis; MIL-53; phenol oxidation.

ÖZ

Toksik organik fenol kirleticilerini uzaklaştırmak için yeni bir alternatif oksidasyon katalizörü bulmak uzun zamandan beri önemli bir konudur. Demir tereftalat, yüksek gözenekliliği ve yüksek yüzey alanıyla oksidasyon süreçleri için etkili bir katalizördür. Bu çalışmada, fenol oksidasyonu için MIL-53 kullanılmıştır. Katalizör 2 saatte 150°C'de hidrotermal yöntemle sentezlendi. FT-IR ve toz-XRD ile yapısal olarak karakterize edildi. Termal özellikleri de incelendi. Yüzey alanı, mikrogözenekli alanlarla 152 m^2/g olarak bulundu. Fenolün hidrojen peroksit ile sıvı faz oksidasyonu MIL-53 üzerinde uygulandı. Reaksiyon süresi, reaksiyon sıcaklığı, katalizör miktarı ve yükseltgen miktarı da incelendi. Fenol 80°C'de 3 saatte %91 dönüşümle uzaklaştırıldı. MIL-53, fenolün sıvı faz oksidasyonu için yüksek verimlilik, seçicilik ve dönüşüm ile alternatif bir katalizör olarak geliştirildi.

Anahtar Kelimeler
Hydrothermal sentez; MIL-53; fenol oksidasyonu.

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INTRODUCTION

Developments in urbanization, population growth and industrialization cause pollution in wastewater and threaten human and animal health. Removal of pollutants is a crucial process. Phenol and phenolic compounds are a common organic pollutant and formed in different industries as detergents, plastics, dyes, organic solvents, drugs, petroleum and etc. Several methods like adsorption [1], filtration [2], oxidation [3], degradation [4], precipitation [5] and coagulation [6] have been utilized for the removal of these type of pollutants. Among these methods, oxidation has gained great attention because of economic, simplicity, time and energy saving, high efficiency, reliability [7], high chemical stability and low biodegradability [8]. This process generates strongly oxidizing hydroxyl radicals for the decomposition of phenolic organic pollutants into non-toxic products [9] and it treats as an effective oxidant [10]. Hydrogen peroxide is one of the preferable electron acceptors to form hydroxyl radicals [11] and transition metals [12], UV-irradiation [13], Fe_3O_4 [14], photocatalysts [15], zeolites [16] can also be used as an activator for hydrogen peroxide.

Metal-organic frameworks are used as an efficient oxidation catalyst because of their desirable porosity, tunable pore size and shape, high surface area and easy modification [17]. They are multifunctional inorganic-organic hybrid porous crystalline materials and mostly used in removal, adsorption, and oxidation of pollutants. Chromium terephthalate (MIL-101) was first applied in phenol adsorption by Bhadra and co-authors in 2016 [18]. Cadmium terephthalate was used in highly selective adsorption removal of lead and copper [19]. Toxic metal ions were adsorbed and removed by copper terephthalate [20]. Iron terephthalate was used on different oxidation processes like oxidation of alkenes [21], water oxidation [22], degradation of dye [23] with high selectivity, high conversion and high efficiency.

In this study, iron terephthalate (MIL-53) was synthesized through the hydrothermal method as an alternative catalyst for the activation of hydrogen peroxide. It was characterized by FT-IR, powder XRD, and TGA techniques. The surface properties were obtained via SEM and BET. The catalyst was used in the liquid phase oxidation of phenol with hydrogen peroxide. The reaction conditions (reaction time, reaction temperature, catalyst amount, oxidant amount) were optimized. The phenol was removed using 10 mg iron terephthalate catalyst at 80°C for 3 hours with 91% conversion. Iron terephthalate (MIL-53) was found as a promising oxidation catalyst for oxidation of phenol and removal of phenol pollutants.

MATERIALS and METHODS

Materials: Terephthalic acid (H2BDC, Aldrich 98%), iron(III) chloride hexahydrate ($FeCl_3.6H_2O$, Aldrich 99%), phenol (C6H5OH, Sigma 99%), hydrogen peroxide (Sigma, 30%) were purchased and used without any further purification.

Synthesis of Catalyst: MIL-53 was synthesized according to previous studies. The mixture of 1 mmol of $FeCl_3.6H_2O$, 1 mmol of terephthalic acid and 5 mL DMF was heated at 150°C for 2 h in reactor vessel modified with Teflon inner chamber. The resulting solid was filtered, the product was purified by washing in hot ethanol and dried in a vacuum oven at 150°C for 12 h [24].

Characterization of Catalyst: Fourier transform infrared (FTIR) spectra were performed Perkin-Elmer Spectrum One instrument using the KBr pellet method (4000-400 cm^{-1}). X-ray powder diffraction was collected in Rigaku DMAX-2200 diffractometer with Cu Kα1 radiation (2θ= 0-60°). N_2 adsorption isotherms were applied at 77 K using Quantachrome Quadrasorb SI Automated Surface Area Analyzer. The thermal behaviors of the samples were studied by TG-DT analysis (Shimadzu DTG-60H) under N_2 atmosphere (T= 25-800°C). The SEM images were obtained using Quanta 200 FEG scanning electron microscopy.

Oxidation of Phenol: 1 mmol phenol and 1 mmol hydrogen peroxide were dissolved in 10 mL acetonitrile and put in a bottom connected reflux. Reaction time, reaction temperature, catalyst amount and hydrogen peroxide amount were optimized under atmospheric pressure. The catalytic results were calculated Thermo DSQ II GC-MS using naphthalene as an internal standard.

RESULTS and DISCUSSION

To investigate the structural properties of iron terephthalate (MIL-53), FT-IR and p-XRD analyses were obtained. From FT-IR spectrum (Figure 1), the broadband seen at 3600-2900 cm^{-1} was the hydroxyl stretching vibrations corresponded to typical of adsorbed water

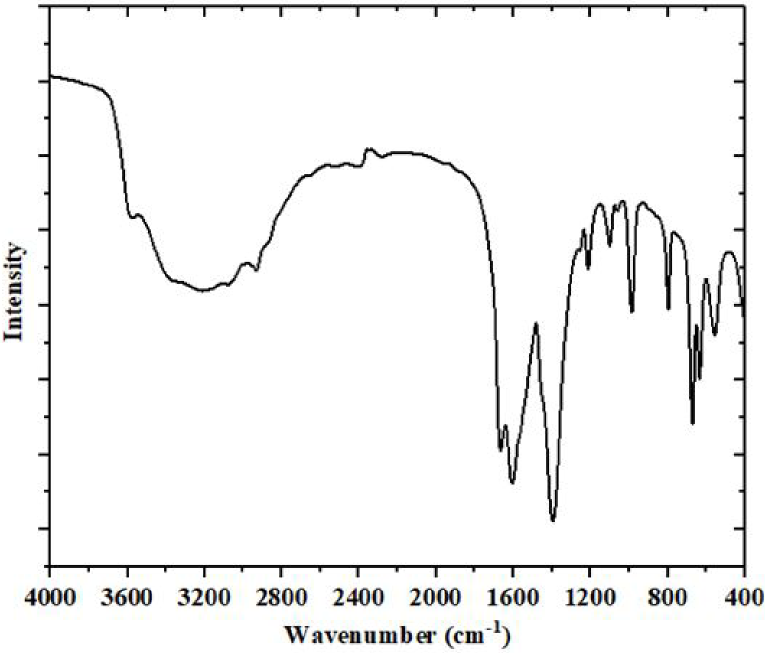

Figure 1. FT-IR spectrum of iron terephthalate.

molecules [25]. The two sharp peaks at 1671 cm^{-1} and 1606 cm^{-1} were the C-O asymmetric vibrations and the peak at 1400 cm^{-1} was assigned to the C-O symmetric vibration confirming the presence of the dicarboxylate ligand. The peaks at 636 cm^{-1} and 676 cm^{-1} were the C-H stretching vibrations of benzene rings. All peaks were correlated with the formation of iron terephthalate.

The XRD pattern of catalyst was shown in Figure 2 and highly crystalline product was obtained via the hydrothermal method. The characteristic XRD peaks (2Ө=9.2, 12.26, 17.94, 18.46, 24.46 and 26.48) were found and the pattern was identical with previous studies [26]. The results of structural analyses clearly conform the formation of iron terephthalate (MIL-53).

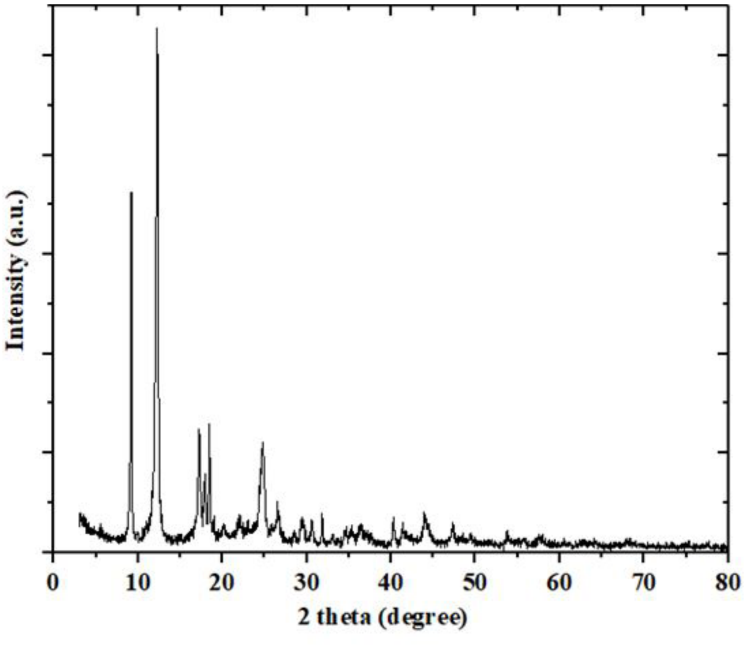

Figure 2. p-XRD diffractogram of iron terephthalate.

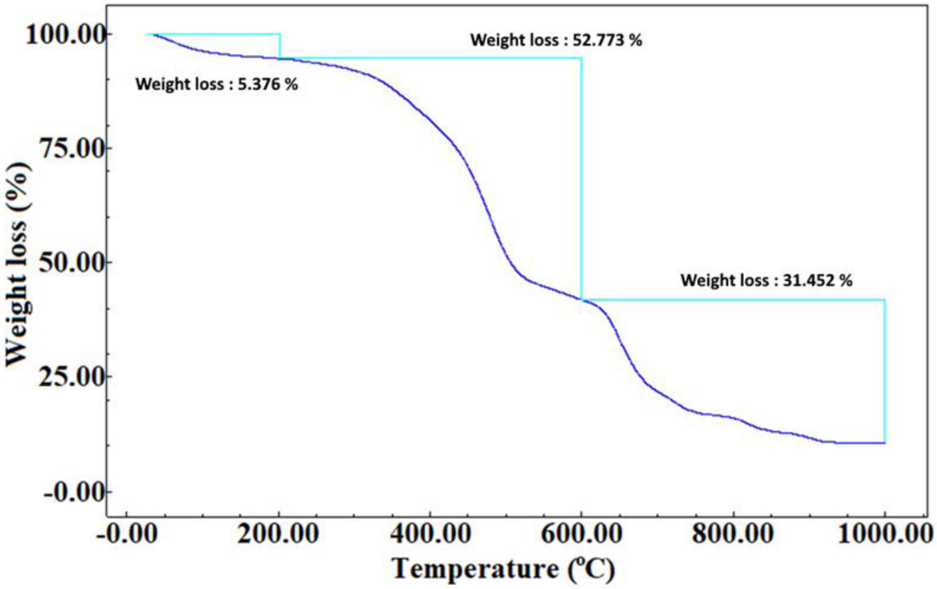

Figure 3. TG analysis of iron terephthalate.

The thermal properties of the catalyst were also investigated and shown in Figure 3. Iron terephthalate (MIL-53) possessed three gradual steps which are totally 90% weight loss. 5.4% weight loss of iron terephthalate between 25-200°C was attributed to moisture, water absorbed on the surface of the catalyst and water adsorbed to the molecular cavities. The other weight loss from 200°C to 600°C of 52.8 % was due to the burning of terephthalate ligand in the structure. The last weight loss of 31.5% up to 1000°C corresponded to the removal of all remaining ligand from the structure. The last residual mass (nearly 10%), as seen in the TGA curve, was the result of iron oxide formation owing to increasing temperature.

According to TG analyses, the removal of water was finished at 200°C and to find surface area of the iron terephthalate, it was degassed at 200°C. The Brunauer-Emmett-Teller surface area of the catalyst was calculated as 152.13 m^2/g and total pore volume was 0.046 cm3/g. The isotherm of MIL-53 (Figure 4) represented Type I isotherm characteristic of microporous solid, which was concave to relative pressure (P/P°). Type 1 isotherm has powerful adsorbate-adsorbent interactions and its pore volume is based on the saturation value according to the International Union of Pure and Applied Chemistry (IUPAC) in terms of isotherm shapes [27].

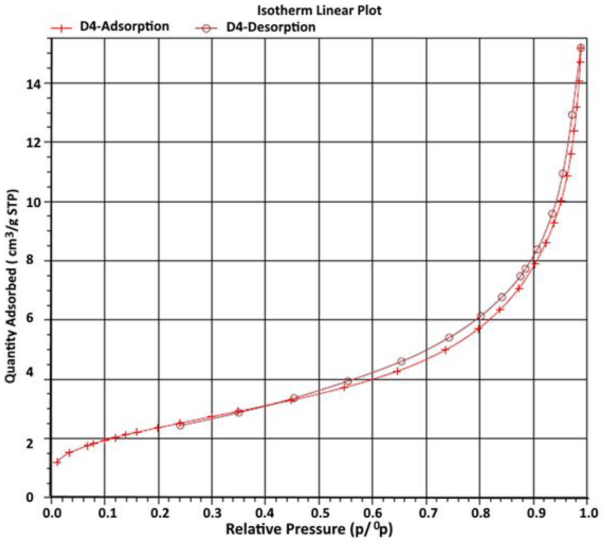

Figure 4. N_2 sorption isotherm of iron terephthalate.

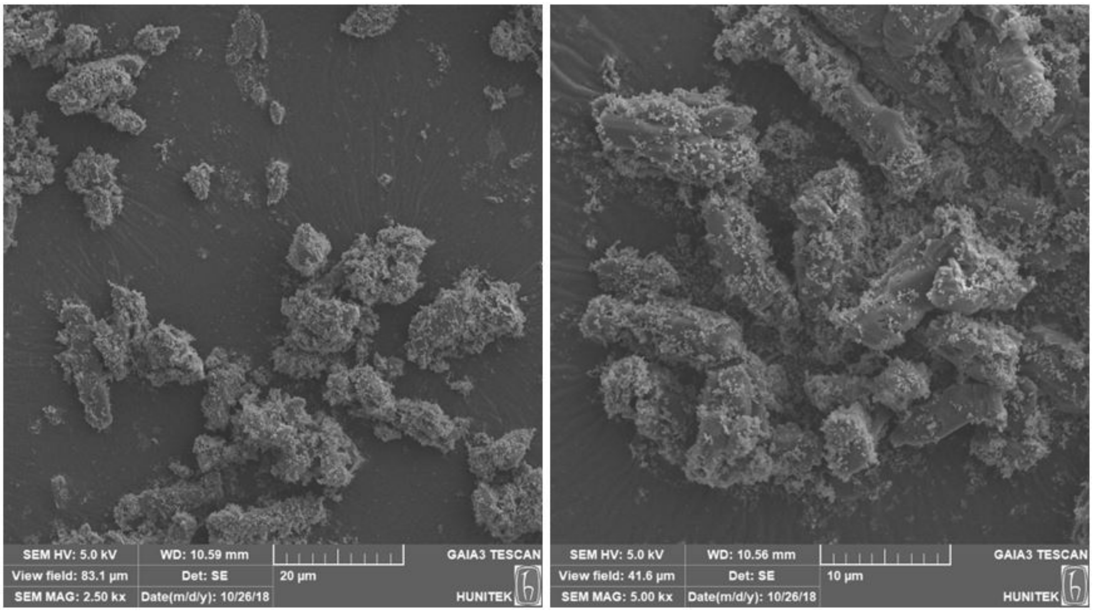

Figure 5. SEM images of iron terephthalate.

The morphology and particle size of the catalyst were observed from the SEM picture (Figure 5) with different view fields. As seen in Figure 4, iron terephthalate (MIL-53) consisted of nano-sized spherical particles adhered on the surface of aggregate micro-particles that are irregular shapes. The whole structure formed as nano- and micro-particles would contribute to the catalytic reaction for liquid phase oxidation of phenol as a catalyst.

The oxidation of phenol reaction was applied on hydrothermal synthesized iron terephthalate (MIL-53). To obtain maximum phenol conversion, the reaction parameters (reaction temperature, reaction time, catalyst amount and oxidant amount) were optimized. First, different reaction temperatures were performed and shown in Figure 6. The phenol conversion was increased up to 80°C which is the boiling point of acetonitrile. After that, hydrogen peroxide decomposed faster and the conversion was started to decrease. The reaction temperature was found as 80°C with the maximum conversion. In the second, reaction time was optimized. As the reaction time increased, the phenol conversion was also increased. After 180 minutes, no significant change was observed. The catalyst amount was investigated and increasing catalyst amount (20 mg, 30 mg, and 40 mg) did not change the conversion. It was said that 10 mg catalyst was enough to 1 mmol phenol. The last parameter was the oxidant amount and hydrogen peroxide/phenol mole ratio was raised to 2:1. The maximum phenol conversion was obtained as 91% with hydrothermal synthesized iron terephthalate (MIL-53). The ad-

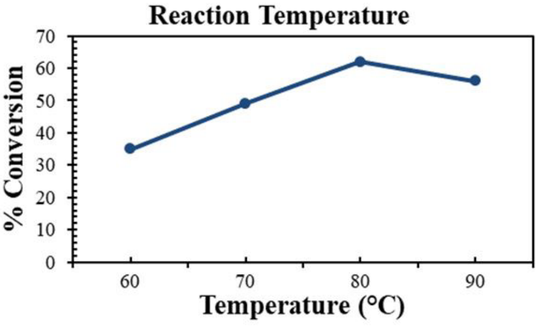

Figure 6. Different reaction temperatures for oxidation of phenol (1 mmol phenol; 1 mmol H_2O_2; 10 mg catalyst; 120 min).

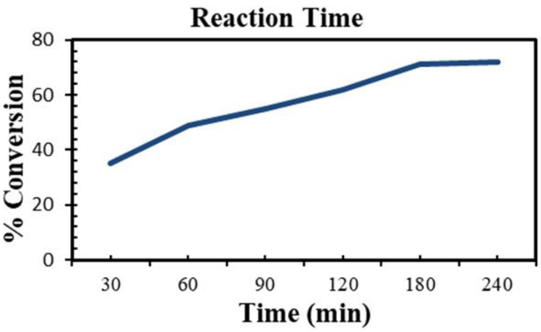

Figure 7. Different reaction times for oxidation of phenol (1 mmol phenol; 1 mmol H_2O_2; 10 mg catalyst; 80°C).

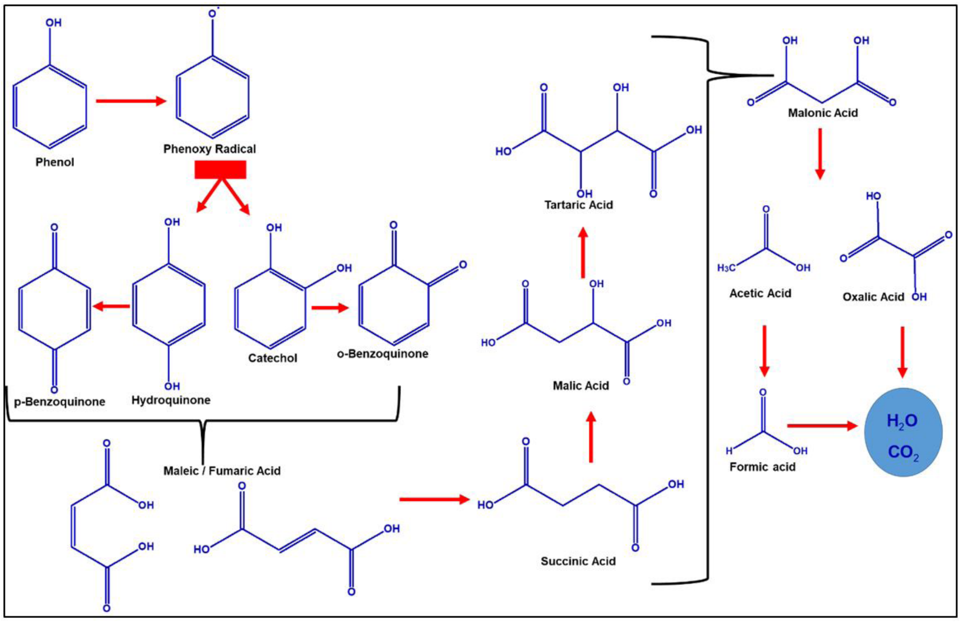

Figure 8. The proposing mechanism for oxidation of phenol.

sorbate-adsorbent interactions and hydrogen bonding of adsorbate molecules with Brönsted acid sites of the metal-organic framework have increased the efficiency [28] and the catalyst was improved as an alternative oxidation catalyst for phenol removal. The proposing reaction mechanism was shown in Figure 8 and the phenol was successfully removed as nontoxic chemicals [29].

CONCLUSION

Iron terephthalate was successfully synthesized via the hydrothermal method as an alternative catalyst for oxidation of phenol to nontoxic chemicals. The catalyst was structurally characterized and thermal properties were also investigated. The catalytic reaction parameters were optimized and 91% conversion was obtained at 80°C for 3 hours. The hydrothermal synthesized of iron terephthalate supplied higher conversion and higher efficiency than the solvothermal synthesized iron terephthalate [30]. The difference came from the surface properties which was changed the surface properties. The hydrothermal synthesized MIL-53 has 152.13 m^2/g surface area and 0.046 cm^3/g pore volume with the shape of nano-sized spherical particles adhered on the surface of aggregate micro-particles. As a result, an alternative catalyst for the oxidation of phenol was determined.

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