

ORIGINAL RESEARCH PAPER

Influence of Calcination Temperature and Operational Parameters on Fe-ZSM-5 Catalyst performance in Sonocatalytic Degradation of Phenol from wastewater

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ABSTRACT

Nowadays, the lack of water sources and water pollution by industrial wastewater has become a significant challenge. One of the pollutants of water resources, which threatens water resources, is the phenol that enters the environment through wastewater from various industries such as petrochemicals, refineries, pharmaceuticals, etc. Due to the phenol toxicity, high stability, and solubility in water caused many problems; it is essential to remove it from industrial wastewater. Therefore, the primary purpose of this study is to remove phenol from wastewater by using catalytic oxidation. Fe-ZSM-5 catalyst was synthesized by precipitation method, and its characteristics were determined by XRD, FTIR, SEM, and BET analyses. The results of the XRD analysis showed that the iron ions are in the MFI structure, and the catalyst has a good crystallinity phase so that it retains its MFI structure. BET analysis showed that the specific surface area of the synthesized catalyst is 293g/m². The catalytic activity of Fe-ZSM-5 was investigated in the degradation of phenol, and the results showed that the mentioned catalyst had the highest removal percentage (85.82%) in 90 min at pH = 4.25 and T= 70 °C. The effect of various parameters such as ultraviolet radiation, initial pollutant concentration, catalyst loading, and H₂O₂ concentration on the catalytic activity was also investigated.

Keywords: Catalytic oxidation, Fe-ZSM-5, Phenol, Wastewater treatment, Ultrasound Waves.

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INTRODUCTION

Nowadays, discharge of toxic compounds from different industries such as dyeing, polymer, and refineries, petrochemical industries to water sources has caused many problems[1, 2]. Discharge of wastewater to the environment has irreversible consequences such as surface water pollution,

threat human, animal health also harmful effects on the land and agricultural products[3]. Therefore, industrial wastewater treatment causes the reuse of this treated wastewater and intercepts the increase of illness causes and the destruction of plant and animal ecosystems and genetic mutations[4]. One of the major pollutants that makes pollution in water sources is phenol. It is a white solid with the

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chemical structure of (C_6H_5OH), one of the most common pollutants, which observable in the sillage of petroleum refineries, petrochemical industries, phenolic production resins, dyes, and pesticides[5]. It is mortal due to its high toxicity (doses above 500 ppm) and has caused many problems[6]. Phenol degradation from industrial wastewater is done by various methods such as adsorption, separation, membrane adsorption, biological methods, photocatalytic oxidation, Fenton, Electrophenton, Ozonation, etc.[7]. Due to the stability of phenol in aqueous environments and the mentioned processes are inefficient due to their limitations such as high operating costs, low process efficiency, etc. Therefore, the necessity of applying practical and cost-effective processes is required. Catalytic oxidation is the oxidation of compounds using a catalyst, a very effective method for eliminating resistant and complex organic compounds and converting them into valuable and non-harmful compounds[8]. The catalytic oxidation process is carried out in a homogeneous and heterogeneous manner; in the homogeneous form, reactants are in the same phase, and in the heterogeneous form, the reactants are not in the same phases[8, 9]. Due to the better separation of catalyst from the reaction solution and reducing the cost of separation, heterogeneous catalyst oxidation is widely used. Many studies have been performed to eliminate phenol by various methods until now. Shukla et al. were applied Co-ZSM-5 to remove phenol. Shukla et al. were applied Co-ZSM-5 to remove phenol. In this research, the results showed that the catalyst had high activity in removing phenol, but the catalytic activity of Co-ZSM-5 is reducing in the presence of H_2O_2 [10]. Yan et al. had studied the effect of iron-doped ZSM-5 structure on phenol removal by catalytic oxidation in a membrane reactor. Their results showed that the catalyst synthesized with 25% iron had the highest phenol removal activity [11]. Malkotian et al. studied the Fenton process efficiency in removing phenol from wastewater of olive oil factory. The results of their study showed that by using 0.5 molar H_2O_2 at pH 3 and 4, more than 96 % of phenol was removed[12]. Jiang et al. had treated phenolic wastewater by photocatalysis method in the presence of BiOI-ZnO composites. In this study, 99.99% of the initial phenol concentration was decomposed within 2h under simulated solar light irradiation[13]. In the catalytic oxidation method, several parameters depended on the quality of the process. The

chemical properties and crystalline structure of the catalyst are effective parameters used to increase the reaction rate; improve process efficiency and catalyst selectivity. This study aims to remove phenol using a heterogeneous catalytic oxidation process in the presence of heterogeneous catalyst Fe-ZSM-5 and presence of hydrogen peroxide, as well as to investigate operational parameters affecting the efficiency of the process, and the catalyst was characterized by BET, FTIR, XRD, FESEM, and AFM analysis.

MATERIALS AND METHODS

Materials

Phenol and Iron (II) Chloride were supplied from Merck Company (Germany) with a purity of 99%. NH_4 -ZSM-5 zeolite with a Si/Al ratio of 10 was obtained from Alfa Aesar Company (England). H_2O_2 and distillate water were obtained from Mojallai Company (Iran). All the reagents were utilized without further purification.

Nanocatalyst Preparation

The procedure synthesized of Fe-ZSM-5 with various calcination temperatures is shown in Fig. 1. To synthesize of mentioned catalyst, in the first step, 4g NH_4 -ZSM-5 zeolite was added in a 250 ml aqueous solution of $FeCl_2 \cdot 4H_2O$ with a concentration of 0.7M at 25°C and stirred continuously for 6 hrs. Then, the catalyst filtration process was performed, the prepared catalyst was dried in an oven at 110°C for 24 hrs. Finally, the catalyst was calcined at 550, 650, 750, and 850°C for 4 h. Prepared samples calcined at 550, 650, 750, and 850°C were named FZ-1, FZ-2, FZ-3, and FZ-4, respectively.

Nanocatalyst Characterization Techniques

In this research, XRD analysis has been used to determine the crystalline structure. This analyzer (XRD, Siemens D5000) is equipped with a radiation source of Cu - $K\alpha$ ($\lambda=0.154056$ nm) with a scanning speed of 0.02 s⁻¹ (2θ ranging from 5 to 80). In order to determine the porosity and specific surface area of the synthesized catalyst, a ChemBET3000 analyzer was used. Fourier Transform Infrared Spectroscopy analysis was performed to identify functional groups in the synthesized catalyst at 400 to 4000 cm^{-1} wavelength. (TENSOR27 model made by BRUCKER, Germany). In order to determine the porosity and specific surface area of the synthesized catalyst, a ChemBET3000 analyzer was

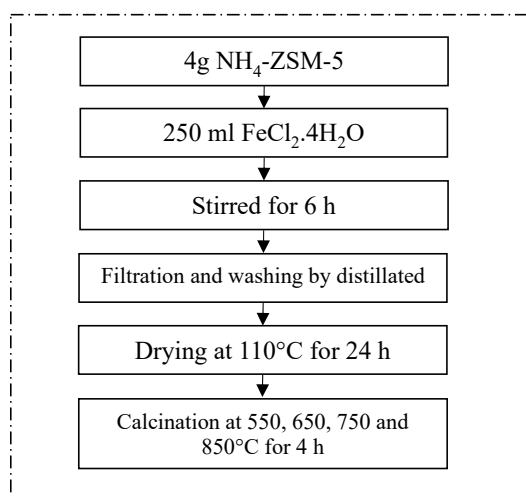


Fig. 1. Schematic flow chart for synthesizing Fe-ZSM-5 samples

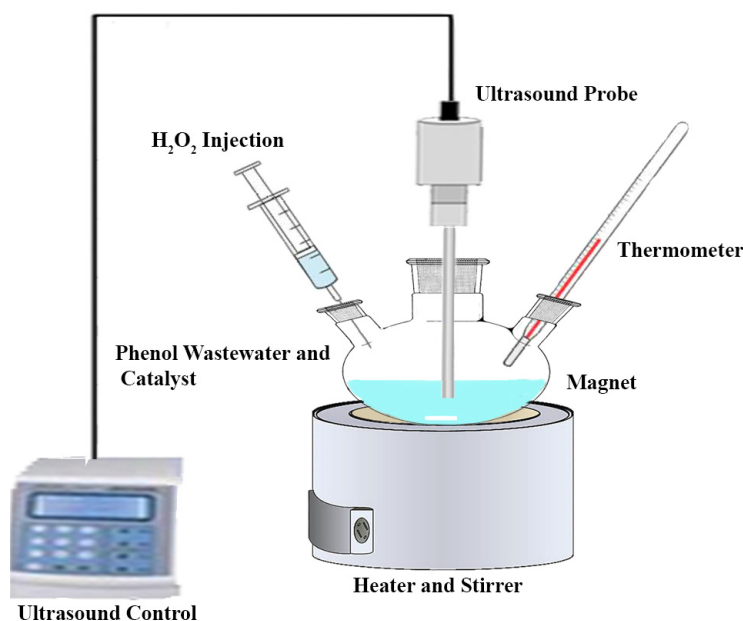


Fig. 2. The Experimental setup for wet catalytic evaluation of Fe-ZSM-5 in the decomposition of phenol

used. The morphological properties of prepared samples were specified by applying a scanning electron microscope equipped with a field emission gun (FESEM, HITACHIS-109 4160).

Experimental Setup for Catalytic Performance Test

Sonodegradation of phenol was accomplished in a 250 ml batch reactor equipped with an ultrasonic probe (Bandelin UW3200), thermometer, and H_2O_2 injector. Fig.2 shows the experimental setup for catalytic evaluation of Fe-ZSM-5 in degradation of phenol. Experiments were carried out with 0.1 g of

prepared Fe-ZSM-5 as a catalyst in 100 ml synthetic phenolic wastewater. The pH and temperature of wastewater were adjusted at 4.25 and 70°C, respectively. In order to provide the ambient heat to perform the reaction of phenol removal at 50°C, 60°C, 70°C, 90°C, an oil bath was used. The ambient temperature was controlled by a thermometer. The ultrasonic source was adjusted in pulse mode and output power of 30 w. The changes in phenol concentration were recorded by using an HPLC (Agilent, 1290 Infinity LC). In order to investigate degradation efficiency, each 15 min sampling of

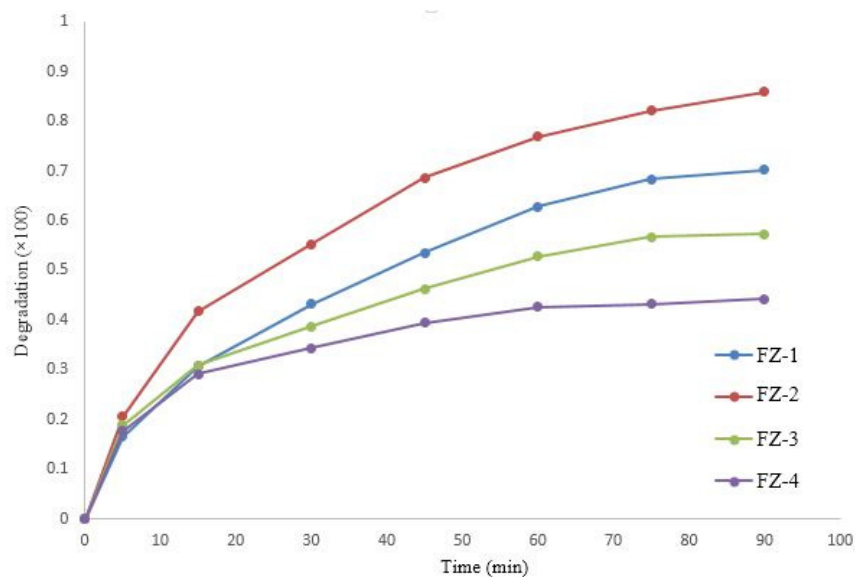


Fig. 3. The catalytic activity of Fe-ZSM-5 samples in phenol degradation

synthetic phenolic wastewater was performed. The removal efficiency of phenol calculated by applying the following equation:

$$\text{Removal efficiency}\% = (1 - C/C_0) \times 100\%$$

Which C_0 and C is the initial and final concentration of phenol in the synthetic phenolic wastewater in specified times. Fig.2 reveals the experimental setup for wet catalytic evaluation of Fe-ZSM-5 in the decomposition of phenol. The parameters such as the phenol concentration, catalyst loadings, H_2O_2 concentration, and the pH value of the solution were investigated.

RESULTS AND DISCUSSIONS

Catalytic Activity of Fe-ZSM-5 Calcined at Different Temperatures

Fig.3 reveals the catalytic activity of Fe-ZSM-5 samples in the sonocatalytic decomposition of phenol. Experiments were carried out using a mixture of 0.1 g of prepared catalyst in 100 ml of synthetic phenolic wastewater at pH 4.25 and the initial phenol concentration of 55 ppm. All experiments were carried out under ultrasound irradiation in a batch reactor equipped with an ultrasound probe, H_2O_2 injector, and thermometer. Results showed that the FZ-2 and FZ-4 samples had the best and the worst catalytic activity in phenol degradation, respectively. According to Fig.3, FZ-2 had removed 85% of the initial phenol concentration while FZ-1, FZ-3, and FZ-4 samples

just degraded 66.12%, 50.36%, and 39.87%, respectively. The samples' catalytic activity can be explained by the number of iron ions in the MFI structure and samples' crystallinity. According to Fig.3, the amount of iron has a significant role in the degradation of phenol. Due to the effect of calcination temperature on the iron crystalline structure, by increasing the calcination temperature over 650°C, the amount of iron in synthesized samples has decreased. Zhu et al. have similar results with our study[14].

XRD Analysis of Fe-ZSM-5 Calcined at Different Temperatures

XRD analysis was applied to study the influences of calcination temperature on the crystalline structure of Fe-ZSM-5. Fig.4 represents XRD patterns of FZ-1, FZ-2, FZ-3, and FZ-4. According to the X-ray diffraction pattern, the peaks at $2\theta = 7.97, 8.88, 20.87, 23.18, 26.88,$ and 36.91 indicate the formation of the ZSM-5 ground state crystal phase[15, 16]. The peaks at the values $2\theta = 36.56, 39.52, 50.17,$ and 59.96 verified the presence of the $\alpha\text{-Fe}_2\text{O}_3$ phase and the doped iron content with the ZSM-5 structure.[17]. According to Fig.4, by increasing the calcination temperature, MFI intensity increased, and $\alpha\text{-Fe}_2\text{O}_3$ intensity decreased. The X-ray diffraction pattern confirmed the excellent form of the synthesized catalyst's crystal phase; all peaks indicate the catalyst sample's MFI structure.

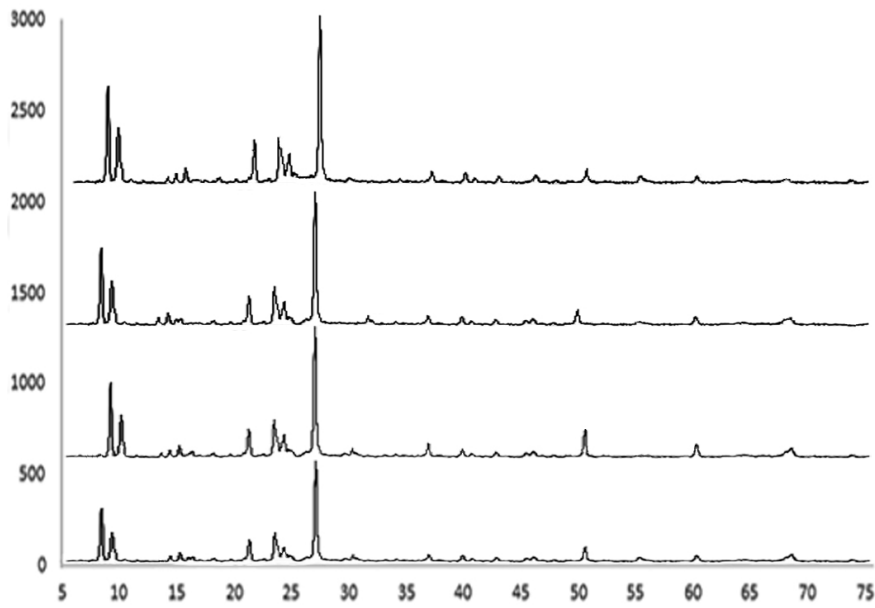


Fig. 4. XRD patterns of Fe-ZSM-5 samples calcined at different temperatures

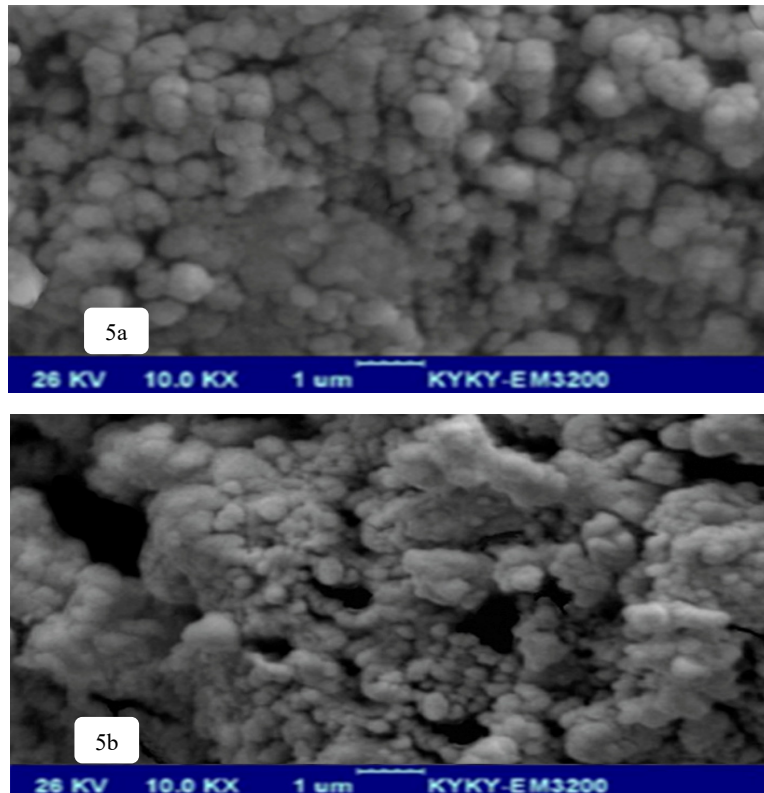


Fig. 5. FESEM images of FZ-2 and FZ-3 samples

FESEM analysis of Fe-ZSM-5 samples Calcined at Different Temperatures

The morphology of the FZ-2 and FZ-4 with the best and the worst catalytic activity was studied by

FESEM analysis. Fig.5 represents the FESEM image of the FZ-2 and FZ-4 samples. FESEM images of the FZ-2 sample revealed that the particles had been formed in spherical shapes without any cracks free

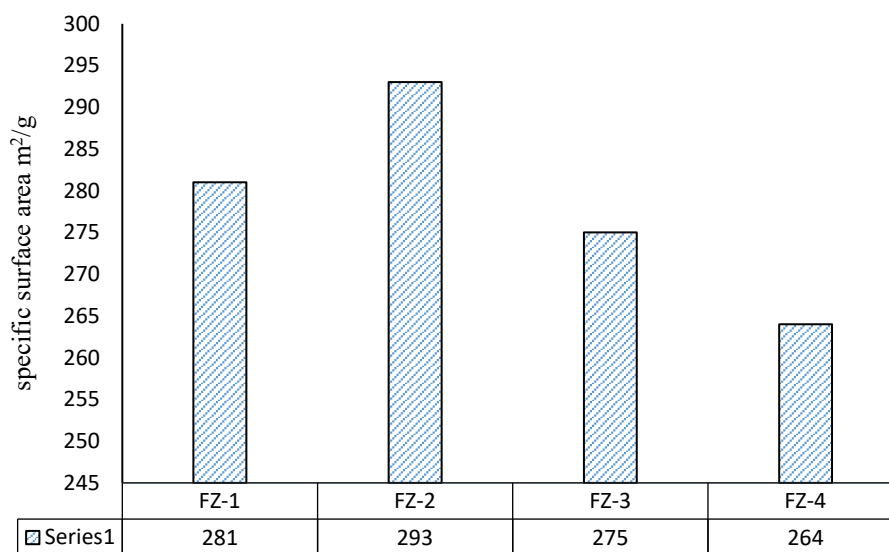


Fig. 6. BET surface area analysis of Fe-ZSM-5 samples calcined at different temperatures

and aggregation of the nanocrystals. According to Fig.5b, with increasing the calcination temperature, cracks, and holes distributed all over the surface of the FZ-4 sample, which led to low contact surface and lower catalytic activity due to the decrease in surface area of the catalyst. Fig.5a confirms the good morphology and homogeneous surface of the FZ-2 sample, and the synthesized catalyst has a suitable particle size distribution. The catalyst's homogeneous surface increases the contact surface between the phenol molecules and the catalyst and eventually increases the surface reaction rate and phenol removal efficiency.

BET Analysis of Fe-ZSM-5 samples Calcined at Different Temperatures

The most common method of specific surface area measurement, widely used in catalyst studies, is the BET analysis. This analysis is based on the adsorption of nitrogen on the specific surface area of the catalyst. The analysis was performed using the BET analysis device Chem BET 3000 model. According to the BET analysis results (Fig.6), the specific surface area of the synthesized Fe-ZSM-5 catalysts calcined at 450, 550, 650, and 750°C were 281, 293, 275, and 264 m²/g, respectively. It seems that by increasing the calcination temperature, the crystallinity of MFI and the samples' specific surface area have decreased. According to the results, which obtained from different researches, the addition of metal cations to the ZSM-5 has an

optimal amount, by increasing the number of metal cations more than the optimal amount, reduces the ZSM-5 unique surface[18]. It reveals that the amount of iron added to the ZSM-5 structure in this study is appropriate. Also, the results confirm that by increasing the calcination temperature, the amount of doped iron in the MFI structure and occupied area by iron ions have decreased [11, 17]. The results have good agreement with FTIR and XRD analysis.

FTIR analysis

In order to determine functional groups in the synthesized samples, the FTIR analysis was performed within the range of 400 – 4000 cm⁻¹. The results were shown in Fig.7. The intensity of the bonding in 450 and 500 cm⁻¹ shows the zeolite's crystalline structure[19]. The form of peaks at 548.01cm⁻¹ shows the hybrid vibration intensity of five double bonds in the MFI structure of Fe-ZSM-5 zeolite. The intensive peak formed in the range of 1096 cm⁻¹ is related to the stretching vibration between the Si-O-Si bonds, which is sensitive to the Si/Al ratio, by decreasing the ratio of this peak, it leads to a shift in lower values[20]. The IR spectrum in the 3900–3000 cm⁻¹ region shows the vibration and elasticity of the O-H bonds. Also, the reduction rate observed in 3622 cm⁻¹ implies iron ions in the synthesized catalyst structure. According to Fig.7, by increasing the calcined temperature, the intensity of iron peaks

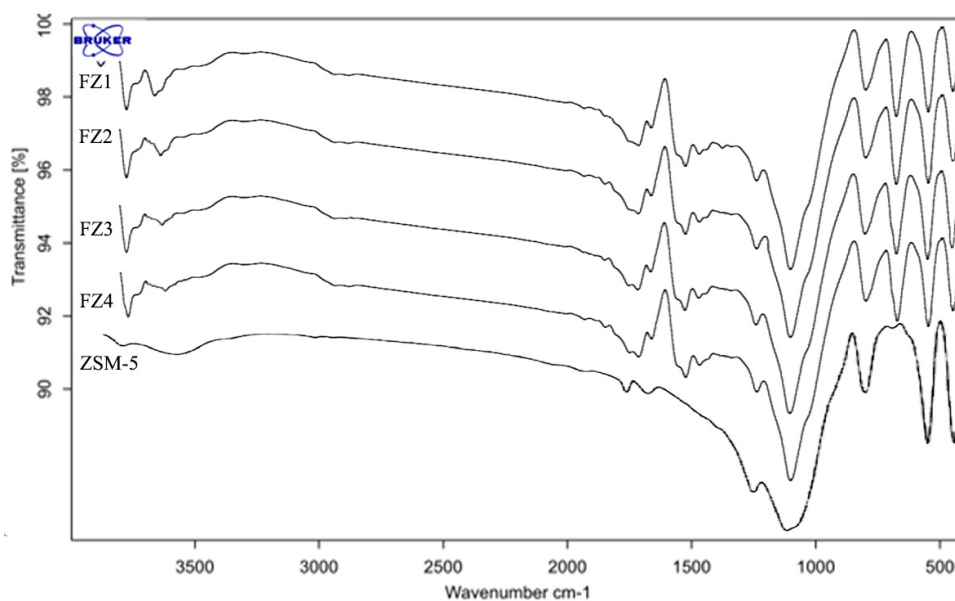


Fig. 7. FTIR analysis of Fe-ZSM-5 samples

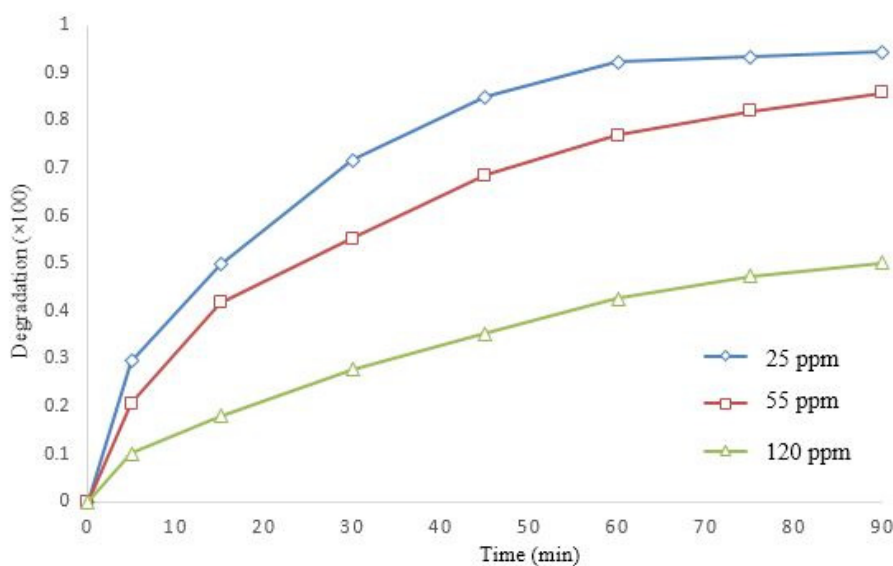


Fig. 8. Effect of Initial Phenol Concentration on Catalytic Degradation of Phenol

has decreased in the FTIR diagram. Iron oxide nanoparticles have successfully penetrated the catalyst structure by forming a bond with oxygen molecules present in the zeolite structure.

Effect of Initial Phenol Concentration on Catalytic Degradation of Phenol

Initial pollutants concentration is one of the effective parameters of the catalyst oxidation process. For this purpose, different concentrations

of 25, 55, and 120 ppm of phenol were applied. All experiments were carried out with 1g/lit catalyst loading and 10mmol hydrogen peroxide at pH=4.25. The results of the experiments have been shown in Fig.8. As shown in Fig.8, the process efficiency decreases with increasing the phenol concentration, thereby increasing concentration from 55 to 120 ppm; the phenol removal rate is reduced from 85.82 % to 50.10 %. However, the amount of phenol removal with the initial

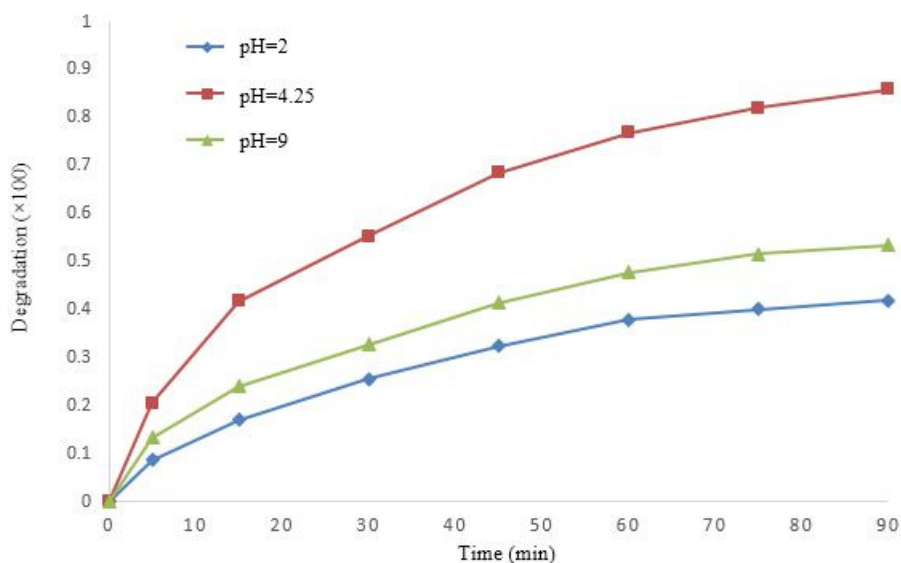


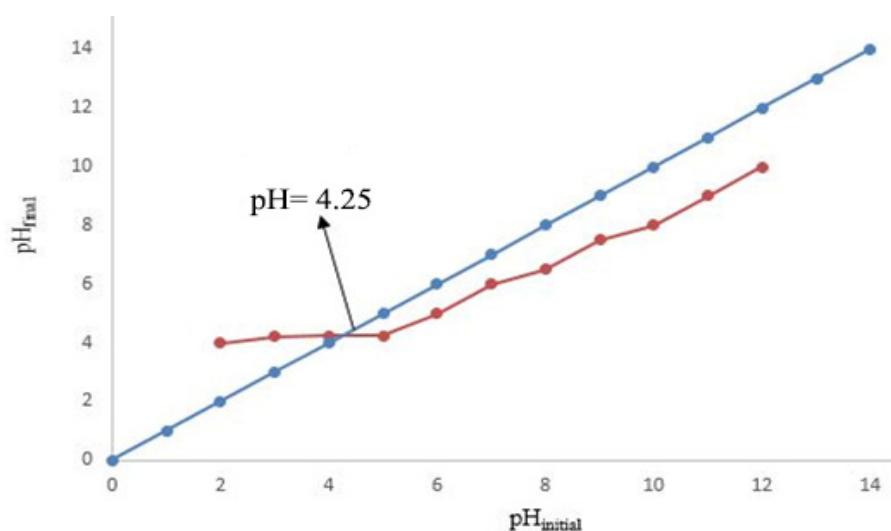
Fig. 9. Effect of Wastewater pH on Catalytic Degradation of Phenol

concentration of 25ppm is 94.36%. The reduction of catalyst activity at high concentrations of phenol can be correlated with the amount of contact and availability of materials with active sites of the catalyst, as well as the number of hydroxyl radicals produced[21]. By increasing the concentration of phenol from 55 to 120 ppm, the concentration of phenol molecules increased at the catalyst surface, thus reducing exposure to the catalyst's active sites. [22]. On the other hand, by increasing the phenol concentration, the number of hydroxyl radicals is reduced compared to the phenol molecules. The two mentioned cases reduce the phenol's catalytic elimination by increasing the concentration from 55 ppm to 120 ppm.

Effect of Wastewater pH on Catalytic Degradation of Phenol

The solution's pH is important and influential in the catalytic oxidation process, which influences the catalyst's electronic properties and surface charge, affecting the interaction between pollutant molecules and catalyst surface. According to the results in Fig.9, the maximum phenol removal with the percentage of 82.82 was found at pH=4.25. However, in lower pHs and higher pHs, the amount of phenol removal decreased. The degradation rate at pH 2 and 9 was 41.98 % and 53.51 %, respectively. The catalytic oxidation of phenol in the presence of H_2O_2 is in the form of a radical reaction between the OH^\cdot , H_2O^\cdot , and ROO^\cdot radicals. Therefore phenol removal reaction strongly depends on the pH

value of the phenol solution[23, 24]. Therefore, it appears that at pH=4.25, H_2O_2 was stable, and thus the amount of phenol removal was maximum. On the other hand, the reduction of phenol removal by changing pH depends on the structural properties of phenol, the reaction of phenol solubility in water as well as changes in surface and electrical properties of the catalyst[25]. According to the dissolution of phenol in water, $(C_6H_5O^-)$ and (H^+) are produced, which the $(C_6H_5O^-)$ is alkaline and (H^+) is acidic[26, 27]. Therefore, by reducing the wastewater solution pH's, the ion concentration (H^+) and positive charge are increased in the solution. By increasing the H^+ in the solution, the H^+ ions act as a separating layer between the phenol molecules and the catalyst surface, which leads to adsorb fewer pollutants on the catalyst surface and finally reducing the catalytic activity[28]. On the other hand, the amount of negative charges increases inside the solution by increasing the wastewater solution's pH. At pH=9 with the existence of anions $(C_6H_5O^-)$ in the solution and injecting of the OH^- ions, the concentration of negative charges is increased inside the solution, which ultimately reduces the percentage of phenol removal by affecting the surface properties of the catalyst and impeding the adsorption of pollutant on the catalyst surface. As regards that the zero points of metal oxides change with pH, the pH changes have caused surface charge variation of the catalyst, therefore inhibiting the adsorption of phenol from the surface of Fe-ZSM-5[29]. To

Fig. 10. pH_{Hpzc} Determination of Fe-ZSM-5

properly understand the change of the surface charge of the catalyst from the zero points of charge, which is a concept related to the phenomenon of attraction in physical chemistry, it is used to determine the adsorption between the zero-point value of colliding particles or substrate with the pH of the electrolyte. According to the above concept, the zero points of charge (pzc¹) describe the conditions that the surface is zero in terms of electric charge[30]. At this point, the catalyst surface loads are zero. The point of pH where the surface loads are equal to zero is also called the isoelectric point. It is important to specify this point to determine the properties of the catalyst surfaces[31]. Thus, in pH higher than pH_{pzc}, the catalyst's surface has a negative load, and at pH lower than pH_{pzc}, the surface of the catalyst has an approving load. Thus, the ions with an opposite load are easily adsorbed onto the catalyst surface. As shown in Fig.10, the given pH_{pzc} for the sample Fe-ZSM-5 is 4.25. Therefore, the Fe-ZSM-5 catalyst has the best performance when the solution's pH is equal to pH_{pzc} or near the pH. On the other hand, the nature of pollutant materials and their dissolution in water is essential. According to the scientific references[32, 33]. The phenol's pH in water is in the acidic range and the range of 5-6, which justifies pH_{pzc} analysis. Hence, choosing the optimum pH to remove the maximum phenol should be done according to the two critical factors, pH_{pzc}, and pH of the phenol solution's pH. It shows that it was stable at pH= 4.25, and on the

other hand, due to its nature, the density of positive and negative charges is balanced; thus, the surface charge of the catalyst is neutral.

Effect of Initial Catalyst Concentration on Catalytic Degradation of Phenol

The amount of catalyst loading is one of the most critical parameters in the catalytic oxidation process. Different amounts of 0, 0.5, 1, 1.5, and 2 g/L of the Fe-ZS-5 catalyst were used to investigate the effect of catalyst concentration on phenol degradation. The results of the experiments are shown in Fig.11. According to the results, by increasing the amount of zeolite up to 1 g/l, phenol removal increased to 85.82%, so that with increasing the catalyst loading to 1.5 and 2, phenol removal decreased to 67.64 % and 55.73 %, respectively. The reduction of catalyst efficiency with increasing the catalyst amount is related to the catalyst particles' uniform dispersion and agglomeration. Increasing the catalyst concentration in the wastewater causes the agglomeration of nanoparticles, decreasing active sites, and consequently, process efficiency. On the other hand, the removal rate decreased due to the catalyst particles' poor dispersion and insufficient active sites to attract pollutant molecules onto the catalyst surface. In the study carried out by Shukla et al. by increasing catalyst concentration up to 0.6 g/l, the phenol removal efficiency increased[10]. The dispersion of the catalyst particles in the wastewater has an essential role in the catalytic oxidation process.

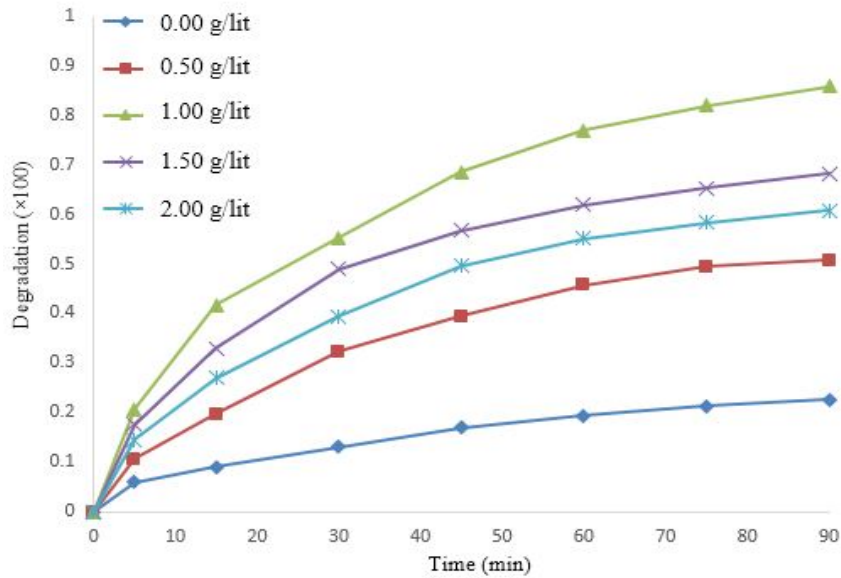


Fig. 11. Effect of Initial Catalyst Concentration on Catalytic Degradation of Phenol

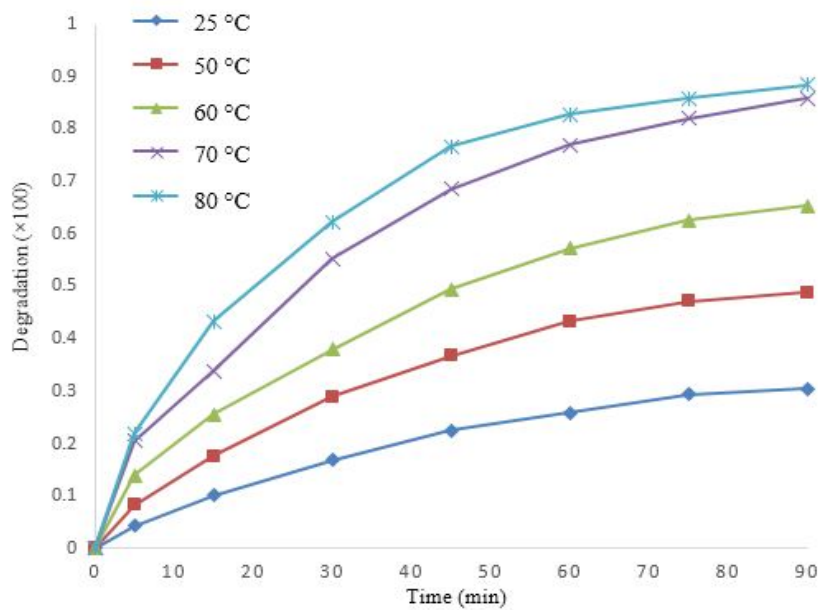


Fig. 12. Effect of Temperature on Catalytic Degradation of Phenol

Effect of Temperature on Catalytic Degradation of Phenol

One of the main parameters which affect the reaction rate of phenol removal is temperature. To study the effect of temperature on the phenol degradation efficiency, the tests were carried out at temperatures of 25°C, 50°C, 60°C, 70°C, and 90°C (Fig.12). The results showed that the temperature

increasing had two different effects on the process. If the temperature rises to 70°C, the reaction rate increases significantly, but the temperature rises from 70°C to 90°C, the reaction rate does not change considerably. According to the Arrhenius equation, the reaction rate was directly dependent on the reaction temperature. According to the mentioned equation, with each increase of 10°C, the

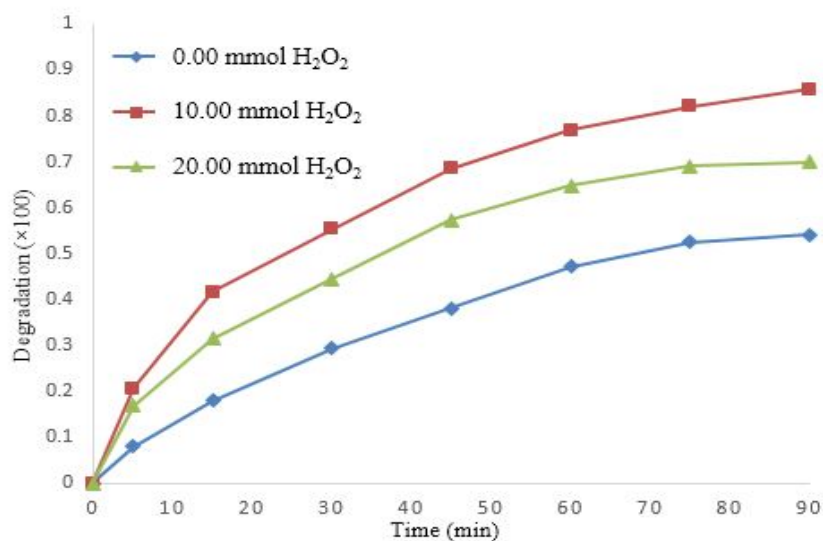


Fig. 13. Effect of H₂O₂ on Catalytic Degradation of Phenol

reaction speed doubles. Therefore, the temperature increasing of the reactor on the industrial scale and its control requires well-equipped equipment. Most of the time gain the temperature is not economical on industrial scales. Increasing reaction temperature leads to the decomposition of H₂O₂ into O₂ and H₂O and reduces the activation energy, which causes better oxidation of phenol[21]. Zazo et al. have observed similar results that by increasing the catalytic oxidation process temperature, the rate of phenol degradation increased [34].

Effect of H₂O₂ on Catalytic Degradation of Phenol

In order to study the effect of H₂O₂ on the efficiency of phenol decomposition, various H₂O₂ concentrations were applied. The results have presented in Fig.13. According to Fig.13, phenol degradation in the absence of H₂O₂ requires more time, so that in this experiment, the removal rate was 58.63% in 90 min. While the hydrogen peroxide concentration increased to 10 mmol, the phenol removal rate increased to 85.82 % in 90 min. Increasing the removal of phenol in the presence of H₂O₂ is due to the production of hydroxyl radicals from the decomposition of hydrogen peroxide into the solution. Therefore, hydroxyl radicals generated in the solution attack the molecules of phenol and decomposed their structure. The presence of hydrogen peroxide reduces the time required for phenol degradation[35]. Rey et al. have the same results in their research. They have studied the catalytic oxidation of phenol by using Fe doped on

active carbon[36]. On the other hand, increasing the hydrogen peroxide concentration does not cause an increase in pollutant removal, so that the hydrogen peroxide results in a certain amount of inhibitors, according to Fig.13. Therefore, the hydrogen peroxide concentration in the reactor environment has an optimum amount that increases it from this amount leading to fewer hydroxyl radicals; in many studies, similar results have been achieved.

Effect of Ultrasound Irradiation Power on Catalytic Degradation of Phenol

In the last decade, ultrasonic waves were used to synthesize nanoparticles for better distribution of nanoparticles and the removal of organic. Ultrasonic waves are used in chemical processes to improve the efficiency of the process and catalyst performance[28]. In order to investigate the effect of ultrasonic waves on the efficiency of the catalytic elimination process of phenol from the BANDELIN ultrasonic device was used in pulse mode with a frequency of 30 kHz and 30W power. The results of the experiments are shown in Fig. 14. It indicates that applying ultrasonic waves without the Fe-ZSM-5 and H₂O₂ has minimal effect on phenol degradation. Therefore, only 4.68 % of the phenol is removed. The results showed that by applying ultrasound waves, the phenol removal increasing in 90 min to 93.27% so that in 60 minutes, more than 86 % of phenol has been removed from wastewater. It seems that by applying ultrasonic, a high-energy bubble is formed inside the solution, which breaks

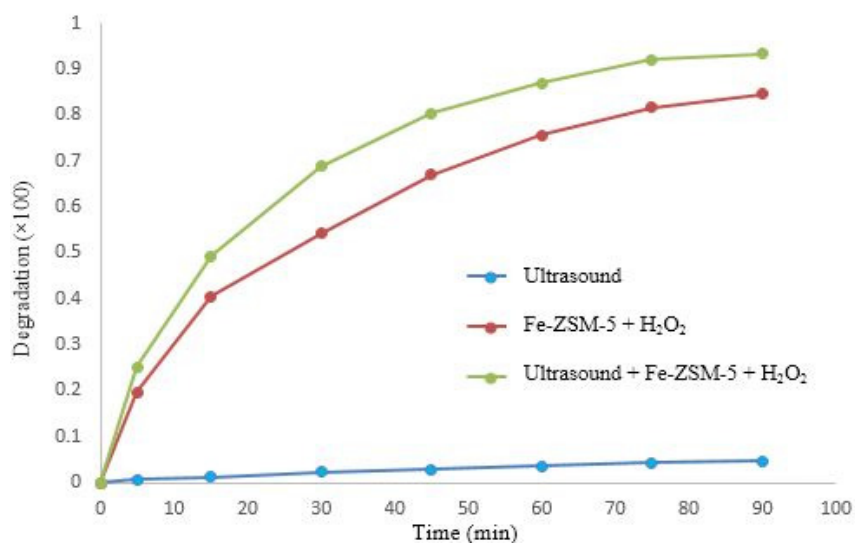


Fig. 14. Effect of Ultrasound Irradiation Power on Catalytic Degradation of Phenol

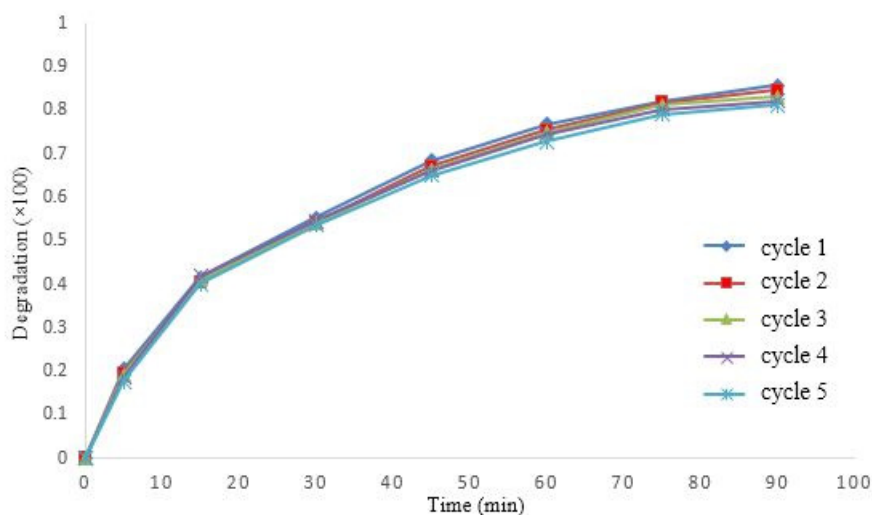


Fig. 15. Reusability Test of FZ-2 Samples

the structure of phenol as well as causes accelerating decomposition of H₂O₂ and production of OH[•] radicals[28, 37]. Ultrasound waves increase the mass transfer between catalyst particles and pollutant molecules increases by reducing the internal mass transfer resistances of the catalyst surface[38]. Ultrasound waves improve the contact between the catalyst particles and the pollutant molecules, improving the catalyst performance in eliminating phenol. On the other hand, in the presence of H₂O₂ in the effluent, [OH[•]] radicals are produced, which have oxidizing properties, breaking the pollutant molecules and weaken their

bonding. Therefore, the simultaneous presence of ultrasound waves and H₂O₂ in the phenol removal process due to reducing mass transfer resistances and production of [OH[•]] radicals improves process efficiency.

Reusability of Fe-ZSM-5 Catalyst

The reusability of the catalysts in the wastewater treatment process is an important factor for their long-term use in the industry. Therefore, the catalysts must have high stability against corrosion as well as high catalytic activity[39]. In order to carry out the stability test of the catalyst, the

catalyst performance in five consecutive periods was investigated in removing phenol in the batch reactor at 70°C and pH = 4.25 with injection flow of 10mmol H₂O₂. After each cycle, the catalyst activity was recorded. At the end of the stability test, the catalytic activity and the catalyst activity reduction rate were compared. The results of the catalyst stability in phenol degradation are shown in Fig.15. According to Fig.15, the catalyst had a high catalytic activity after five consecutive cycles of phenol elimination, so that the comparison of the first cycle and the last cycle of the reusability test showed the catalyst activity only decreased 4.61%.

CONCLUSIONS

In this study, the effect of calcination temperature was investigated in Fe-ZSM-5 catalyst. According to XRD analysis, increasing calcination temperature over 650 °C revealed a decreasing amount of iron in synthesized samples. On the other hand, doped iron in ZSM-5 deformed in samples calcined at 650 °C and 750 °C, caused decreasing in the catalytic performance of mentioned samples. FESEM and BET analysis showed, by increasing the calcination temperature, cracks and holes distributed all over the surface of the FZ-4 sample led to a decrease in the surface area of the catalyst. The present study showed that the Fe-ZSM-5 catalyst has considerable catalytic activity in treating wastewater polluted with phenol. The investigation of effective parameters showed that parameters such as temperature, pH of wastewater solution, catalyst amount, phenol concentration, and H₂O₂ concentration significantly affect the phenol removal process's efficiency. The results showed that the phenol's best catalytic oxidation was performed at pH = 4.25 and T= 70 °C.

On the other hand, the initial concentration of pollutants was effective on phenol removal. However, increasing the phenol concentration from 55 mg/L to 120 mg/L causes to reduction of the phenol removal from 85.82 % to 50.10 %. On the other hand, the presence of H₂O₂ accelerated the phenol removal process. Increasing H₂O₂ up to optimal value reduces process efficiency. The results also showed that the use of ultrasonic waves increases the efficiency of the phenol removal process. In order to study the effect of catalyst concentration on phenol removal, different catalyst concentrations were used. The results showed that the process efficiency decreases with increasing

the catalyst concentration due to the catalyst's agglomeration increase inside the effluent solution.

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CONFLICTS OF INTEREST

The authors declare there are no conflicts of interest.

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