Degradation of ketoprofen using iron-supported ZSM-5 catalyst via heterogeneous Fenton oxidation

I P I Azusano1,3,4, A R Caparanga1 and B H Chen2

1School of Chemical, Biological, and Materials Engineering and Sciences, Mapúa University, 658 Muralla St., Intramuros, Manila 1002, Philippines
2Department of Chemical Engineering, National Cheng Kung University, 1 University Road, Tainan 70101, Taiwan
3School of Graduate Studies, Mapúa University, 658 Muralla St., Intramuros, Manila 1002, Philippines
4Email: paoloazusano@gmail.com

Abstract. Heterogeneous Fenton oxidation provides an alternative method of degrading ketoprofen from wastewater. The purpose of this study is to investigate the degradation of ketoprofen using iron-supported ZSM5 zeolite catalyst. Iron was impregnated into ZSM5 via the impregnation method, with loading variation of 1wt% and 3.5wt% Fe/ZSM5. Characterization of the catalyst was performed using XRD, SEM, ICP-OES, TGA, BET and TPD. Batch degradation reaction were performed with a working volume of 100 mL ketoprofen solution, mechanically stirred at 900 rpm. Amount of H2O2 used was equivalent to 11 times (in excess) the required stoichiometric amount for ketoprofen mineralization. Catalyst loading was varied between 1 g/L and 4 g/L. HPLC was utilized in determining ketoprofen concentration in the solution during the degradation reaction. Ketoprofen degradation of 100% was observed after 20 minutes using catalyst with 3.5% weight at 4 g/L loading. Iron leaching was also measured using ICP-OES to compare the amount of iron leached between heterogeneous and homogenous Fenton reaction. Percentage of iron leached showed 8.93% and 57.09% for heterogeneous and homogenous Fenton reaction, respectively. The study showed promising results in degrading ketoprofen using an iron-supported ZSM5 via the heterogeneous Fenton reaction with lower iron leaching percentage compared to homogenous Fenton reaction.

1. Introduction
Ketoprofen (2-(3-benzoylphenyl)-propionic acid, KET) is a nonsteroidal anti-inflammatory drug (NSAIDs), a major group of pharmaceuticals used to treat fever, inflammation and pain [1]. Conventional wastewater treatments are inefficient at eliminating NSAIDs from effluents due to the hydrophilic nature and resistance to biological degradation of pharmaceuticals [2] – and since usage of NSAIDs have increased due to the population growth, its residual presence in surface and ground water possess risks toward human health and aquatic environment [3–5]. In previous studies, KET with concentrations ranging from ng L\(^{-1}\) up to µg L\(^{-1}\) monitored in effluents and surface waters showed potential negative effects including oxidative stress and endocrine disrupting effect [6,7]. The Fenton process is a well-known advanced oxidation process (AOP), a technology used in treating trace organic chemicals (TrOC) in wastewater effluents. The Fenton process utilizes ferrous iron as catalyst that reacts with H₂O₂ in an acidic condition to produce hydroxyl (\(^{*}\)OH) radicals through a reaction.
known as the Fenton reaction. However, the usage of ferrous iron as a catalyst increases the overall cost of the wastewater treatment process due to the formation of iron sludge which requires additional downstream treatment. Hence, numerous studies on impregnating iron ions on supports in order to reduce sludge formation and improve the Fenton process has gained attraction over the years. Supports are mostly porous in nature; thus, allowing ferrous and ferric ions to adhere on its surface and prevent the leaching of ferrous ions that results to sludge production. Among various materials considered for iron ion supports, zeolites have been proven to be efficient supports for iron in the heterogeneous Fenton process attributed to its microporous nature, high surface area and high hydrothermal stability [8].

Among various advanced oxidation processes (AOPs), the catalytic AOP (cAOP) such as the Fenton process is a low-cost competitive method since it requires no energy input to activate the \( \text{H}_2\text{O}_2 \), its catalysts are economic and non-toxic, and its sludge production effect can be addressed through iron impregnation on the support by formation of a heterogeneous Fenton catalyst. Whereas, several heterogeneous catalyst has been used for pollutant degradation such iron oxides, soil, and industrial waste, other studies immobilize iron on support materials such as clay, activated carbon, silica, zeolites, etc [8]. As previously mentioned, zeolites as support for iron, owing to its highly porous nature, has shown several advantage over homogeneous Fenton process: (a) catalytically active at near neutral pH, (b) improved degradation rate due to combination of oxidation and adsorption, (c) and allows easy catalyst recycling due to its \( \mu \)m range particle size [9]. Heterogeneous Fenton oxidation of pharmaceutical compounds such as ibuprofen [10] and paracetamol [3], catalyzed by iron loaded ZSM5 zeolites proved to be effective.

The viable degradation of other NSAIDs such as diclofenac and ibuprofen, utilized AOPs such as photocatalytic ozonation, photocatalytic oxidation and non-thermal dielectric barrier discharge [5,11]. Moreover, heterogeneous Fenton oxidation of ibuprofen using iron loaded ZSM5 zeolite in previous study have also shown to be effective [10]. In previous studies, KET have been degraded by various AOPs such as the sulfate radical advance oxidation process (SRAOP) [6], electrochemical advance oxidation process (eAOP) and electro-Fenton process (EF) [12] exhibited viability of degrading KET. Hence, due to success of iron loaded ZSM5 zeolite in ibuprofen degradation, this study chose ZSM5 as zeolite to be impregnated with iron for KET degradation as catalyst for the heterogeneous Fenton process.

The aim of this paper is to synthesis and characterize a catalyst using ZSM5 as a support for the heterogeneous Fenton process for the degradation of KET. In this work, KET was degraded, for the first time, by the heterogeneous Fenton oxidation using an iron-supported ZSM5 zeolite. Characterization methods include powder X-ray diffraction (XRD), scanning electron microscopy (SEM), temperature-programmed desorption (TPD), thermogravimetric analysis (TGA) and Brunauer-Emmett-Teller surface area (BET). Catalytic activity of the synthesized catalyst for the degradation of KET was also studied by investigating the effect of iron loading and catalyst loading. High performance liquid chromatography was utilized in determining KET concentration after reaction.

2. Experimental

2.1. Chemicals and reagents
For catalyst synthesis of Fe/ZSM5, Iron (III) Chloride Hexahydrate (97-102%) was purchased from Alfa Aesar, 2-Propanol (≥99.8%) was from Honeywell Riedel-de Haen, ZSM5 (CBV 3024E) was from Zeolyst and Ketoprofen (99.9%) was from Hongda Pharmaceuticals Co., Ltd. Sulfuric acid (95%, Extra Pure Grade) was from Duksan Reagents, Acetic acid (Glacial), Acetonitrile (HPLC Grade) and Ferrous Sulfate, 7-Hydrate (Granular) were from J.T Baker™, HYDRANAL® (Methanol Dry) was from Riedel-de Haen, Methyl Alcohol (Anhydrous, 99% HPLC Grade) was from Macron Fine Chemicals™ and Hydrogen Peroxide (30-31%) was from Sigma- Aldrich.

2.2. Synthesis of iron-supported ZSM5 catalyst
The Fe-supported ZSM5 zeolites were prepared via impregnation method. Iron (III) Chloride Hexahydrate (FeCl₃·6H₂O) was dissolved in isopropyl alcohol to form an aqueous iron salt solution. ZSM5 zeolite was then added into the aqueous iron salt solution resulting in a sample containing 1% and 3.5% weight Fe. The suspension was stirred for 30 mins at 900 rpm followed by an ultrasound process at 40 °C for 30 mins to promote iron dispersion on the ZSM5 particles. The suspension was then heated in an oven at 110 °C for 4 hours. Resulting powder was then washed to remove loosely attached iron ions and other impurities. Lastly, the Fe/ZSM5 powder was dried and ground. The obtained samples were named Z1 and Z3.5 corresponding to 1% and 3.5% weight iron, respectively.

2.3. Catalyst characterization

XRD analysis were carried out with a Rigaku Ultima diffractometer with Cu Kα radiation at 40 kV and 40 mA, recordings were in the 2θ range of 5º to 65º and a scan step of 0.01º(2θ). SEM (JEOL JSM-5700F, Japan) was used to observe the morphology of the catalyst. Amount of iron loaded into ZSM5 zeolite and iron leaching was measured using ICP-OES (Ultima 2000, Horiba Jobin Yvon). Characterization of catalyst BET specific surface area was performed with Micrometrics ASAP 2020 using N₂ at 77K as the adsorbate. Temperature-programmed desorption of NH₃ was carried out to measure the acidity of the catalyst.

2.4. Fe/ZSM5 catalytic activity

KET degradation was carried out by batch in 250 mL beaker with a working volume of 100 mL of ketoprofen solution (50 mg/L) at a constant stirring rate of 900 rpm. Catalyst at 100 mg (1 g/L) and 400 mg (4 g/L) loading was added into the solution and allowing a preliminary adsorption step for 30 minutes. Sulfuric acid was used to adjust the pH of the solution to 2.8-3.0. Oxidation step was initiated after 30 minutes by adding excess H₂O₂ at 11 times the stoichiometric amount required for KET mineralization, according to the following equation:

\[ C_{16}H_{14}O_3 + 36H_2O_2 \rightarrow 16CO_2 + 43H_2O \]  \hspace{1cm} (2.1)

Aliquot samples of 1 mL were withdrawn from the beaker at certain time intervals and was quenched with 1 mL of isopropyl alcohol followed by centrifugation at 6000 rpm for 5 minutes. The samples were then filtered onto 0.20 µm pore size disposable filter membrane.

2.5. Analytical measurements

Concentration of KET aliquots during oxidation were measured by HPLC equipped with LC-40D (Shimadzu) pump, fitted with a TSK-Gel ODS-100S C₁₈ column (250x4.6mm i.d. 5 µm particle) maintained at 40 °C, Altima C₁₈ guard column (7.5x4.6 mm i.d. 5 µm particle) and coupled with an SPD-40 (Shimadzu) UV detector set at optimum wavelengths of 260 nm. The mobile phase consisted of a 40:40:19.5:0.5 (v/v/v) methanol/acetonitrile/water/acetic acid mixture at a flow rate of 1 mL min⁻¹. Injection volume for all analysis was 20 µL using injection system Rheodyne 7725i.

3. Results and discussion

3.1. Characterization

3.1.1. Powder x-ray diffraction (XRD). As shown in figure 1, characteristic peaks for ZSM5 in sample Z1 and Z3.5 was retained which indicates a similar ZSM5 zeolite structure after calcination and impregnation. Iron oxide (Fe₂O₃ or Fe₃O₄) peaks in the diffractograms for Z1 and Z3.5 were unidentified, and this result is consistent to previously reported works [13,14] suggesting that iron ions were impregnated in low amounts or highly dispersed in the surface of the zeolite, either which would result to peak overlap by the strong signal of ZSM5 [15]. The decrease in intensity of peaks for Z1 and
Z3.5 can be attributed to the higher X-ray absorption coefficient of Fe compounds added into samples [16,17].

![Figure 1. X-ray Diffractogram of ZSM5 with different iron loading.](image)

3.1.2. Scanning electron microscopy. SEM image of zeolites in figure 2 exhibit similarity to previously reported work [18], wherein this type of ZSM5 is known as ZSM5(III) and has a crystallite shape described as rods with particle size ranging from 1000-1500 nm, as observed.

![Figure 2. SEM images of (a) ZSM5 and (b) Z3.5 (magnification: x30000).](image)

3.1.3. Iron loading. The impregnation method resulted to a final iron loading of 1.015 wt% (Z1) and 3.569 wt% (Z3.5) with an iron lost percentage of 0.744 wt% (Z1) and 0.241 wt% (Z3.5) from the initially loaded iron amount, showing an effective impregnation method.

3.1.4. Brunauer-Emmett-Teller (BET) surface area. Data shown in figure 3 seems to follow adsorption isotherm Type IV and H3. Below P/P₀ = 0.1, predominant adsorption ends, which can be attributed to micropore filling while the hysteresis loop between P/P₀ 0.55 and 1.0, can be associated with capillary condensation and existence of large mesopores [16]. BET surface area of 340.09, 333.22 and 284.21 m²/g were determined for ZSM5, Z1 and Z3.5, respectively. The decreasing trend of the BET specific surface observed after impregnation can be attributed to iron molecules clogging the zeolite pore, inferring to success of iron impregnation on the zeolite.
3.1.5. Temperature-programmed desorption (NH3). Based on figure 4, samples showed major desorption peak at 180.5 ºC (ZSM5) and 168.0 ºC (Z1 and Z3.5), indicating a range associated with weak acid sites, while desorption at 466.8 ºC (ZSM5), 450.5 ºC (Z1) and 439.5 ºC (Z3.5), indicates a strong acid site [19], with values shown in table 1. As the Fe loading increases, between Z1 and Z3.5, a decrease in desorption quantity is observed for the weak acid site while reduction in both quantity and strength is observed for the strong acid site as the peak temperature shifts to a lower value. In previous studies of ZSM5, it has been determined that its Bronsted acid sites of about 96% is located inside the zeolitic channels – possibly causing Fe species to infiltrate and replace the Bronsted acid protons on the surface [17]. This is in line with results shown for the TPD – NH3 profiles, notably between sample Z1 and Z3.5. For ZSM5, peak temperature is higher than Z1 and Z3.5 for both weak and strong acid site – indicating a reduction in acid strength, evidenced by the shift of peak temperature for both iron loaded samples.

Figure 3. N2 adsorption/ desorption isotherms of (a) ZSM5, (b) Z1 and (c) Z3.5.

Figure 4. NH3-TPD profiles of ZSM5, Z1 and Z3.5.
Table 1. Catalyst acidity at peak temperatures measured in TPD – NH$_3$ profiles.

|     | ZSM5 | Z1  | Z3.5 |
|-----|------|-----|------|
|     | Temperature (ºC) | NH$_3$ (cm$^3$/g cat STP) | Temperature (ºC) | NH$_3$ (cm$^3$/g cat STP) | Temperature (ºC) | NH$_3$ (cm$^3$/g cat STP) |
| 180.5 | 0.52989 | 168.1 | 0.64449 | 168.0 | 0.60309 |
| 466.8 | 0.14505 | 450.5 | 9.382 x 10$^{-2}$ | 439.5 | 1.497 x 10$^{-2}$ |
| Total | 0.67494 | 0.73831 | 0.61806 |

3.2. KET degradation

Heterogeneous Fenton reaction mechanism includes three possible mechanism as previously reported: (a) surface free radical mechanism (b) non radical mechanism involving high valent iron species on catalyst surface and (c) homogenous pathway by leached iron in solution [10].

3.2.1. Control Experiments. To observe KET degradation by hydroxyl radicals only, figure 5 shows the reaction with Z1, Z3.5 and ZSM5 at 4 g/L without H$_2$O$_2$ and H$_2$O$_2$ only without catalyst. The reaction concentration of Z1, Z3.5 and ZSM5 was measured 30 minutes after zeolite was added to the solution, to allow adsorption. A relative decrease in concentration of Z1, Z3.5 and ZSM5 was observed in the beginning (77.21%, 80.24% and 73.08%, respectively) and showed an insignificant change after an hour (78.84%, 79.56% and 72.20%, respectively). Decrease in concentration for Z1, Z3.5 and ZSM5 (at 4 g/L) without H$_2$O$_2$ shows possible adsorption activity for KET while also highlighting that ZSM5 had the most decrease in adsorbed concentration compared to Z1 and Z3.5; and this may have been due to ZSM5 having larger BET surface area compared to the iron loaded Z1 and Z3.5. Previous study using Fe/ZSM5 for ibuprofen degradation also showed 25% adsorbed concentration at 4.8 g/L catalyst loading [10]. Meanwhile, no change was observed in KET concentration for reaction with H$_2$O$_2$ only.

![Figure 5](image)

Figure 5. Control experiment degradation profile. [KET]$_0$ = 50 mg/L, ambient temperature, ZSM5, Z1 and Z3.5 was measured 30 minutes after zeolite was added (time = 0) to the solution.

3.2.2. Effect of iron loading. Iron loading directly affects hydroxyl radical generation thus controlling the degradation rate of KET. Based on figure 6, 100% degradation of KET was achieve at 20 minutes for Z3.5 and 35 minutes for Z1. However, it is observed that degradation at 20 mins (100% for Z.35 and 98.35% for Z1) only had a difference of 1.65%, showing almost no significant improvement.
between Z1 and Z3.5 at 4 g/L. Evidently, increasing the iron loading will not be an efficient way of improving catalytic activity. Published work of KET degradation by electro-Fenton [12] process showed similar output with regards to change of iron concentration where lower efficiency is observed upon increasing the iron concentration, and in the same paper complete KET degradation was achieved ([KET]₀ = 50.35 mg/L, [Fe]²⁺ = 0.1 mM, platinum anodes) after 30 minutes – showing comparable result to this work, with complete degradation at 20 and 35 minutes (Z3.5 and Z1, respectively). Moreover, no significant change in the reaction of ZSM5 with H₂O₂, except for concentration change due to adsorption, thus showing the catalytic activity of the iron loaded (Z1 and Z3) catalyst.

3.2.3. Effect of catalyst loading. In figure 7, reaction for Z3.5 between 1 g/L and 4 g/L was conducted to compare the effect of catalyst loading in KET degradation. Complete degradation for Z3.5 was achieved at 20 (4 g/L) and 60 minutes (1 g/L). Meanwhile for Z1, as shown in figure 8, complete degradation was achieved at 35 minutes (4 g/L) and only 95.21% degradation at 60 minutes for 1 g/L. For both Z3.5 and Z1, increase in catalyst loading significantly improved KET degradation; where a difference of 36.33% is observed for Z3.5 at 20 minutes complete degradation for 4 g/L, while a difference of 28.52% is observed for Z1 at 35 minutes complete degradation for 4 g/L. This result is consistent with previous works [20,21] for acetone and MTBE degradation using Fe/ZSM5 catalyst, where oxidation is significantly improved even at high loadings of 25 g/L and 75 g/L respectively. The significant improvement in KET degradation can be attributed to having more active sites available for H₂O₂ decomposition at higher catalyst loading.
Z3.5 at different catalyst loading. \([\text{KET}]_0 = 50 \text{ mg/L}, \) ambient temperature, \(\text{H}_2\text{O}_2\) was introduced 30 minutes after catalyst was added (time = 0) to the solution.

Z1 at different catalyst loading. \([\text{KET}]_0 = 50 \text{ mg/L}, \) ambient temperature, \(\text{H}_2\text{O}_2\) was introduced 30 minutes after catalyst was added (time = 0) to the solution.

3.2.4. Iron leaching. Following European directives, the iron concentration limit for effluents is at 2 mg/L. As shown in table 2, maximum iron leaching was measured from reactions of Z1, Z3.5 and \(\text{FeSO}_4\) at catalyst loading of 4 g/L and 2.5 g/L. Loading at 4 g/L for Z1 and Z3.5 showed iron leaching with values below 2 mg/L. A homogenous Fenton reaction, with similar iron loading as Z3.5 at 4 g/L, was also carried out to compare the amount of iron leaching wherein results show a significant difference in iron leaching percentage with 8.93% and 57.09% for Z3.5 and \(\text{FeSO}_4\) respectively. Moreover, amount of iron leached during the homogenous Fenton reaction at 4 g/L was more than the European directives regulation of 2 mg/L, and such result will be evident at large iron loading. For a relative comparison, iron leaching percentage was measured for reaction at lower similar iron loading with Z1 and \(\text{FeSO}_4\) at 2.5 g/L. As observed, leached iron for both reaction were below 2 mg/L, however percentage of iron leached were approximately close at different iron loading, with Z1 at 12.77% (4 g/L) and 14.85% (2.5 g/L) while \(\text{FeSO}_4\) with 57.09% (4 g/L) and 51.63% (2.5 g/L). The significant difference of iron leaching percentage between heterogeneous and homogenous Fenton reaction is an important factor to consider, as an additional treatment process will be required to remove formed iron sludge and attain the iron limit standards for effluents, thus consuming more resources.

With respect to a real wastewater matrix, it is expected that heterogeneous Fenton oxidation of KET using Fe/ZSM5 zeolite will be lower due to natural water matrices affecting the heterogeneous reaction. Particularly, real wastewater matrix will have natural buffers resulting to a higher pH condition, and since it is known that the Fenton reaction is optimal at lower pH, reaction rate is expected to decrease [6]. Moreover, literature also shows presence of organic and inorganic compounds that could foul and poison catalyst active sites as well as scavenge hydroxyl radical – thus effectively reducing catalytic activity [10].

Table 2. Amount of Iron leached for Z1, Z3.5 and \(\text{FeSO}_4\).

| Sample    | Amount Iron Loaded (mg) | Amount Iron leached (mg) | Percentage of Iron leached (%) |
|-----------|-------------------------|--------------------------|-------------------------------|
| Z1, 4 g/L | 4.11                    | 0.52                     | 12.77                         |
| Z3.5, 4 g/L | 14.38                 | 1.28                     | 8.93                          |
| \(\text{FeSO}_4\), 4 g/L | 14.27                 | 8.15                     | 57.09                         |
| Z1, 2.5 g/L | 2.58                    | 0.38                     | 14.85                         |
| \(\text{FeSO}_4\), 2.5 g/L | 2.55                  | 1.32                     | 51.63                         |

4. Conclusion
Iron supported ZSM5 zeolite catalyst was successfully synthesized by impregnation method. Morphology of the catalyst was viewed using SEM where crystallite was observed with shape described as rods associated to having particle size ranging from 1000-1500 nm. Target iron loading of 1% and 3.5% wt iron was achieved by impregnation method, with iron loss of only 0.744% and 0.241% wt for Z1 and Z3.5, respectively, as evidenced by the ICP-OES analysis. BET specific surface area value showed a decreasing trend as the iron loading was increased, possibly indicating the presence of iron clogging the zeolite pores. Analysis of catalyst acid site by TPD showed that most of the site were composed of weak acid and very few strong acid sites, with a decreasing trend of acidity as the iron loading increases. Adsorption was observed in the reaction of catalyst without \(\text{H}_2\text{O}_2\). Complete degradation of ketoprofen using iron supported ZSM5 (Fe/ZSM5) catalyst was achieved fastest at 20 minutes using 3.5 wt% Fe at 4 g/L loading. Effect of varying the iron loading was
observed with complete degradation at 20 minutes for Z3.5 and at 35 minutes for Z1, showing an increased degradation time with respect to iron loading. Effect of catalyst loading variation showed a similar increase in degradation time with respect to catalyst loading of 4 g/L, where complete degradation was achieved at 20 minutes for Z3.5 and at 60 minutes for Z1. Evidently, variation in catalyst loading showed a more significant result in improving the degradation amount by 36.5% (Z3.5 from 1 g/L to 4 g/L) as compared to iron loading variation with only 1.65% (4 g/L from Z1 to Z3.5) increase in degradation amount. This suggests that varying the catalyst load will be more efficient in achieving a higher catalytic activity. Iron leaching for all heterogeneous catalyst loading resulted to a value lower than 2 mg (EU discharge limit) and percentage of iron leached showed significant difference between heterogeneous and homogenous Fenton reaction, 8.93% and 57.09% for Z3.5 and FeSO₄ at 4 g/L catalyst loading, respectively.

Acknowledgement
I would like to extend my gratitude to the DOST-ERDT (Philippines) scholarship for the financial support. Special thanks to Mr. Bai-Yi Lin, Ms. Yan-Ru Chen, Mr. Cheng-Yan Lin, Mr. John Mark L. Osias and Mr. Zhen-Zhe Huang for the support offered during the conduct of this study.

References
[1] Covinich L G, Bengoechea D I, Fenoglio R J and Area M C 2014 Advanced Oxidation Processes for Wastewater Treatment in the Pulp and Paper Industry: A Review Am. J. Environ. Eng. 4 56-70
[2] Nikolou A, Meric S and Fatta D 2007 Occurrence patterns of pharmaceuticals in water and wastewater environments Anal. Bioanal. Chem. 387 1225-34
[3] Qiao Z, Wang Z, Zhang C, Yuan S, Zhu Y and Wang J 2012 PVAm–PPIP/PS composite membrane with high performance for CO₂/N₂ separation AIChE J. 59 215–28
[4] Crane M, Watts C and Boucard T 2006 Chronic aquatic environmental risks from exposure to human pharmaceuticals Sci. Total Environ. 367 23-41
[5] Hama A K H, Miessner H, Mueller S, Kalass D, Moeller D, Khorshid I and Rashid M A M 2017 Degradation of pharmaceutical diclofenac and ibuprofen in aqueous solution, a direct comparison of ozonation, photocatalysis, and non-thermal plasma Chem. Eng. J. 313 1033–41
[6] Feng Y, Song Q, Ly W and Liu G 2017 Degradation of ketoprofen by sulfate radical-based oxidation processes: Kinetics, mechanisms, and effects of natural water matrices Chemosphere 189 643-51
[7] Diniz M S, Salgado R, Pereira V J, Carvalho G, Oehmen A, Reis M A M and Noronha J P 2015 Ecotoxicity of ketoprofen, diclofenac, atenolol and their photolysis byproducts in zebrafish (Danio rerio) Sci. Total Environ. 505 282-9
[8] Nidheesh P V 2015 Heterogeneous Fenton catalysts for the abatement of organic pollutants from aqueous solution: A review RSC Adv. 5 40552-77
[9] Gonzalez-Olmos R, Martin M J, Georgi A, Kopinke F-D, Oller I and Malato S 2012 Fe-zeolites as heterogeneous catalysts in solar Fenton-like reactions at neutral pH Appl. Catal. B Environ. 125 51-8
[10] Adityosulindro S, Julcour C and Barthe L 2018 Heterogeneous Fenton oxidation using Fe-ZSM5 catalyst for removal of ibuprofen in wastewater J. Environ. Chem. Eng. 6 5920-8
[11] Hama A K H, Omer K M, Mahyar A, Miessner H, Mueller S and Moeller D 2019 Application of Photocatalytic Falling Film Reactor to Elucidate the Degradation Pathways of Pharmaceutical Diclofenac and Ibuprofen in Aqueous Solutions Coatings 9 465
[12] Feng L, Oturan N, van Hullebusch E D, Esposito G and Oturan M A 2014 Degradation of anti-inflammatory drug ketoprofen by electro-oxidation: Comparison of electro-Fenton and anodic oxidation processes Environ. Sci. Pollut. Res. 21 8406-16
[13] Osias J M L, Chen Y C, Lin D Y, Shih Y C, Caparanga A R and Chen B H 2019 Degradation of methylene blue utilizing cobalt-impregnated zeolite beta via sulfate radical-based advanced
oxidation process IOP Conf. Ser. Earth Environ. Sci. 344 12041
[14] Oliveira J S de, Mazutti M A, Urquieta-González E A, Foletto E L, Jahn S L, Oliveira J S de, Mazutti M A, Urquieta-González E A, Foletto E L and Jahn S L 2016 Preparation of Mesoporous Fe2O3-Supported ZSM-5 Zeolites by Carbon-Templating and their Evaluation as Photo-Fenton Catalysts to Degrade Organic Pollutant Mater. Res. 19 1399-406
[15] Wang Y, Xie Y, Yin S, Xu R and Lau R 2016 Municipal solid waste incineration bottom ash supported cobalt oxide catalysts for dye degradation using sulfate radical J. Taiwan Inst. Chem. Eng. 68 246-53
[16] Ouyang C, Li Y and Li J 2019 The ZSM-5-catalyzed oxidation of benzene to phenol with N2O: Effect of lewis acid sites Catalysts 9 44
[17] Wang L C, Zhang Y, Xu J, Diao W, Karakalos S, Liu B, Song X, Wu W, He T and Ding D 2019 Non-oxidative dehydrogenation of ethane to ethylene over ZSM-5 zeolite supported iron catalysts Appl. Catal. B Environ. 256 117816
[18] Jang H G, Min H K, Lee J K, Hong S B and Seo G 2012 SAPO-34 and ZSM-5 nanocrystals’ size effects on their catalysis of methanol-to-olefin reactions Appl. Catal. A Gen. 437-438 120-30
[19] Weitkamp J and Hunger M 2007 Chapter 22 Acid and base catalysis on zeolites Stud. Surf. Sci. Catal. - Stud. Surf. Sci. Catal. 168 787-835
[20] Makhotkina O A, Kuznetsova E V and Preis S V 2006 Catalytic detoxification of 1,1-dimethylhydrazine aqueous solutions in heterogeneous Fenton system Appl. Catal. B Environ. 68 85-91
[21] Gonzalez-Olmos R, Roland U, Toufar H, Kopinke F-D and Georgi A 2009 Fe-zeolites as catalysts for chemical oxidation of MTBE in water with H2O2 Appl. Catal. B Environ. 89 356-64