1. Introduction

Treatment of industrial wastewaters to remove the effluents before their discharge into any water stream is of utmost importance and environmental regulations provide strict guidelines on the quality of the water discharged. These wastewaters contain recalcitrant contaminants including toxic organic compounds and dyes which significantly pollute the environment as well as posing a threat to aquatic life. Conventional treatment methods such as homogenous advanced oxidation treatments using iron based catalysts are used to degrade and decolorize recalcitrant contaminants. In addition to conventional methods, Fenton oxidation, an advanced and efficient oxidation process is used for the treatment of recalcitrant wastewaters. It utilizes H$_2$O$_2$ and iron-based catalysts (eqn (1)), to produce highly oxidative and non-selective species with a redox potential of 2.80 eV which lead to the degradation of recalcitrant organic contaminants.

$$\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{HO}^+ + \text{Fe}^{3+} + \text{HO}^- \quad (1)$$

These methods are demonstrated to be very efficient and fast. However, the high cost associated with the use of oxidizing agent (especially H$_2$O$_2$) as well as the use of stoichiometric amounts of catalysts are the major disadvantages of advanced oxidation processes (AOPs) based water treatment. Besides, these processes tend to release high concentrations of iron, which is consumed during the treatment of wastewater and this causes the formation of secondary metal pollutants in the form of sludge which is not desirable. The European Union limited the concentration of discharged iron ions in treated effluents to 2 ppm.

To overcome these difficulties, heterogeneous processes were considered as viable and attractive alternatives. In heterogeneous Fenton process, generally a porous matrix is used to hold the active catalyst phase. A variety of catalytic materials such as Fe, Cu, MnO$_2$, Ni$_2$O$_3$, ZnO, Pt, and TiO$_2$ supported on pillared clay, zeolites or activated carbons have been used as heterogeneous catalysts. Iron based catalysts supported on zeolites supports have been found more efficient compared to the other supported iron catalysts. Iron oxides supported on the ZSM-5 zeolites have shown high surface area, extraordinary stability, and remarkable porosity. Fine-size iron oxide particles cause to suppress reaction between H$_2$O$_2$ and iron, and the formed Fe$^{3+}$/Fe$^{2+}$ complexes on the support (ZSM-5) surface. Activity of Fe-ZSM-5 catalyst is normally controlled by the concentration and morphology of the iron particles dispersed on the porous support of ZSM-5. Normally, Fe-ZSM-5 catalyst is synthesized...
using hydrothermal process, ion exchange method, incipient wetness impregnation and chemical vapor deposition techniques. Fe-ZSM-5 synthesized through ion-exchange method has shown lesser activity compared to that prepared by hydrothermal process. However, many studies have shown that due to the acidic mediums and high temperature, leaching of metal occurs from the support matrix, which leads to deactivation of Fe-ZSM-5 catalyst.

Metal–organic frameworks (MOFs) consist of iron as a metal in the ligand framework can potentially overcome the aforementioned disadvantages associated with the zeolites supported iron particles. These MOF based catalysts have significantly improved the efficiency, stability and the reusability of catalysts used for the heterogeneous oxidation processes.

The main objective and scope of this work was to extend the application of the newly developed 2-step process for the synthesis of an efficient Fe-ZSM-5 catalyst. In our previous work, MOF based Fe-ZSM-5 catalyst was synthesized using 2-step process, characterized and evaluated for the degradation and decolorization of mixture of dyes. The results were encouraging, and 100% of dye degradation, and 77% of total carbon content (TOC) removal were achieved at optimized conditions. These results had motivated authors to optimize the catalyst yield for larger scale production. Therefore, in this work, influence of the independent process variables such as temperature (°C), time (h) and stirring speed (rpm) were considered and optimized. CCD was used to design the experiments and ANOVA was used to analyse the data to obtain the interaction between the selected process variables. The quality of the predicted model was confirmed through determination coefficient (R²), the model F-value and adequate precision (AP).

In addition to optimized catalyst’s yield, catalytic activity of the catalyst, synthesized at optimized conditions in terms of adsorption and oxidation were needed to be explored further. Therefore, three set of experiments (including adsorption and oxidation) were carried to cover these objectives. In these experiments, three dyes, Acid Blue 113, Methyl Orange and Reactive Black 5, were used individually and in the mixture form.

2. Materials and methodology

2.1. Materials

All the purchased chemicals were used without any additional purification. 2,2'-Bipyridine, iron chloride, ethanol and 2-propanol were purchased from Merck and used for the synthesis of Fe-ZSM-5 catalyst. Commercially available ZSM-5 (SiO₂/Al₂O₃ mole ratio 50) was obtained from Zeolyst International and used as a supporting material for nano-sized iron oxide particles. Acid Blue 113, Methyl Orange, Reactive Black 5, and hydrogen peroxide (30%) were obtained from Merck and were used for the catalytic evaluation of the synthesized catalyst.

2.2. Catalyst preparation

2.2.1. Synthesis of Fe-monometallic complex. Fe-ZSM-5 catalyst was synthesized using “2-Step” process, which was developed and successfully evaluated for the production of a variety of heterometallic catalysts with improved features. This process involves precipitation, followed by thermal decomposition.

At the start, a mono metallic-organic framework (MOF) was synthesized by reacting 2,2’-bipyridine with iron chloride using 2-propanol as solvent. For this, 3.6 g of FeCl₃·4H₂O and 8.5 g of bipyridine ligand were dissolved in 25 mL of solvent separately and reacted in a lab-scale reactor. The reaction mixture was continuously stirred at 36 °C. Fine crystalline material containing [Fe(bpy)₃]Cl₂ complex was then filtered, and washed with ether solution to eliminate impurities. The yield of the crystalline material was 77%.

2.2.2. Impregnation. In this step, ZSM-5 zeolite and Fe-complex were separately dispersed in the methanol solvent, and then mixed dropwise to impregnate the fine particles of Fe-complex for 2 h. The concentration of Fe-MOF was set to get a 3% Fe on the ZSM-5 (wt/wt). Due to impregnation, color of the crystalline material became reddish-brown. After impregnation, the crystalline material was dried for 2 h (at 100 °C) and in the presence of air, calcined at 650 °C for 7 h. The temperature was increased slowly to eliminate the ligand part of MOF.

2.2.3. Characterization. ZSM-5 support and the synthesized materials were characterized through EDX, STA, FESEM, FTIR, HRTEM and BET techniques. Composition and surface morphology of the ZSM-5, Fe-complex, and Fe-ZSM-5 were studied using Phenom ProX SEM and simultaneous thermal analyzer (STA) having model number “Perkin Elmer (STA-6000)”. About 5 mg of Fe-ZSM-5 catalyst was subjected to STA. The sample was heated from ambient temperature to 800 °C. The temperature was ramped slowly (10 °C min⁻¹), with oxygen flowing at 30 ml min⁻¹.

HRTEM was performed using the instrument having model number “JEOL JEM2100-F”. FTIR analysis was carried out through Perkin Elmer FTIR-spectrum 400 to observe shifts due to coordinate bonding in Fe-complex, and formation of the new chemical structure of Fe-ZSM-5.

Surface area of ZSM matrix and synthesized Fe-ZSM-catalyst were studied using Surface Area and Porosity Analyzer (ASAP 2020). The BET method was used to determine the surface area and pore width. N₂ adsorption–desorption curves were employed to estimate the pore volume. Similarly, the t-plot scheme was used to calculate the micropore volume.

2.3. Process optimization

The developed process involved precipitation of MOF followed by its impregnation with ZSM-5 and calcination. Precipitation of Fe based MOF was the major part of the whole process compared to the impregnation and calcination parts of the catalyst synthesis. Therefore, this work aimed at accessing and optimizing process parameters that play the vital part in synthesising the Fe-complex.

In the first step, suitable conditions for the precipitation and impregnation were determined and the synthesized Fe-ZSM-5 was characterized completely through FTIR, EDX, SEM and BET. In the second step, experiments were conducted for the
synthesis of Fe-complex and the optimized response values were obtained from Response Surface Methodology (RSM). Formations of complex and crystals yields were confirmed through FTIR and weight analysis.

RSM was used to optimise the synthesis of monometallic precipitations. RSM with Central Composite Design (CCD) uses lower-order polynomial and has shown its reliability for the optimization of many chemical processes.\textsuperscript{37–38} In the present study, all experiments that required for Fe-complex precipitation were designed using CCD with the help of Design Expert (Version: 6.0.8). Temperature (\(^\circ\text{C}\)), time (h) and stirring speed (rpm) were chosen as independent process variables, while the yield (\%) of the Fe-complex was the output response. A specified range of the selected parameters is given in Table 1. Details of the experimental design with the actual and predicted values are summarised in Table 2.

2.3.1. Efficiency evaluation of the synthesized Fe-ZSM-5. Experiments were carried out to determine the efficiency of the Fe-ZSM-5 catalyst, synthesized at optimized conditions. Three dyes, Acid Blue 113, Methyl Orange, and Reactive Black 5 and their mixtures were used for this purpose. The efficiency was evaluated based on dye decolorization, degradation and Total Organic Carbon (TOC) removal.

All of the experiments were performed in a laboratory-scale stirred tank reactor (500 mL capacity) equipped with a magnetic stirrer. Two solutions (0.5 M sulfuric acid and 1 M sodium hydroxide) were employed to regulate the initial pH of dye solution. Earliest set of experiments were carried out to evaluate the adsorption rate of the selected dyes. Three stock solutions containing Acid Blue 113, Methyl Orange, and Reactive Black 5 were prepared and treated individually under dark for 4 h. Each solution had starting concentration of 100 mg L\(^{-1}\). Continuous stirring was applied during adsorption experiments. Optimized value of catalyst (Table S1) was used in each experiment. These values were selected based on the finding of our previous work,\textsuperscript{39} which aimed at determining the effects of process factors such as starting concentration of dye and H\(_2\)O\(_2\), starting pH value, catalyst amount, time and temperature for Fenton heterogeneous process. The treated samples were centrifuged, filtered and examined for decolonization.

The next set of experiments was done to examine the degradation of Acid Blue 113 with higher concentrations. In every experiment, 100 ml of solution having known dye concentration was used and the pH of the dye solution was adjusted prior to be transferred into the stirred reactor. A stirring speed of 250 rpm was used for solution mixing and particles distribution. A desired amount of Fe-ZSM-5 and H\(_2\)O\(_2\) (33.3 g L\(^{-1}\)) were introduced into the reactor after stabilizing the reactor’s temperature and the process time monitored after the addition of H\(_2\)O\(_2\). After the reaction, samples were taken from the solution, filtered through syringe filters (0.20 \(\mu\text{m}\) Millipore) and analyzed directly.

The treated samples were examined employing a Merck UV-spectrophotometer (Spectroquant Pharo 300) and the degradation and decolorization of the samples were estimated as follows:

\[
\text{Decolorization (\%) } = \left(1 - \frac{\text{Abs}_t}{\text{Abs}_0}\right) \times 100 \quad (2)
\]

\[
\text{Degradation (\%) } = \left(1 - \frac{C_t}{C_0}\right) \times 100 \quad (3)
\]

where Abs\(_t\) and Abs\(_0\) represent the UV absorption observed at \(\lambda_{\text{max}}\) for the selected dye, at starting and after specified time \(t\). Likewise \(C_0\) and \(C_t\) are the starting and final concentrations.

<p>| Table 1 | Process parameters for Fe monometallic precipitation process |</p>
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<th>Standard order</th>
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<th>Time (h)</th>
<th>Stirring speed (rpm)</th>
<th>Actual value (yield%)</th>
<th>Predicted value (yield%)</th>
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</table>

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Total organic content (TOC) was examined using a TOC Analyzer (Shimadzu-00077). Normally, the TOC value is taken as the difference between the total carbon content (TC) and inorganic carbon content (IC). Eqn (3) illustrates the percentage reduction in TOC values.

\[
\text{TOC} (%) = \left(1 - \frac{\text{TOC}_1}{\text{TOC}_0}\right) \times 100
\] (4)

In addition to UV and TOC analysis, high performance liquid chromatography (HPLC, Agilent technology 1200 series) was used to examine the treated dye solutions. This study has illustrated the clear picture of the degradation products. Separation column, C18 (4.6 mm × 150 mm × 5 μm) had the mobile phase acetonitrile/water (v/v) operated at 60/40 ratio. The flow rate of mobile phase was maintained at 1 mL min⁻¹. To identify different compounds and intermediate moieties generated from the Fenton degradation of selected dyes, the HPLC unit was calibrated using standard analytical reagents namely benzene, phenol, aniline, hydroquinone, catechol, benzoquinone, formic acid, oxalic acid, and malic acids. The compounds produced during Fenton-oxidation were identified through comparing retention times with those of calibrated runs under similar conditions.

In the third set, degradation of Methyl Orange, and Reactive Black 5 individually, and in mixture form with Acid Blue 113 were studied. Table S2† illustrates the different prepared compositions (v/v) of the mixtures containing Acid Blue 113, Methyl Orange, and Reactive Black 5. All of these four mixtures were treated at optimized conditions.

2.3.2. Deactivation of synthesized Fe-ZSM-5. It is common practice that the catalyst's deactivation occurs due to the leaching of metal ions from the support matrix. In this study, leaching was directly measured using ICP. Instrument was calibrated using six standard solutions containing 0, 5, 10, 20, 50, 100 ppm of the iron. Leaching was also indirectly measured through the EDX analysis to support and confirm the ICP study. After the specified reaction time, the solid particles of Fe-ZSM-5 catalyst were filtered, washed with methanol and dried at 200 °C. EDX analysis was used to study the change in the composition. Similarly, the FTIR and SEM studies were used to examine the change in linkage and morphology of Fe-ZSM-5 due to metal leaching or in situ transformation.

3. Results and discussions

3.1. Characterization of synthesized Fe-ZSM-5 catalyst

EDX results of the ZSM-5 support and prepared Fe-ZSM-5 are provided in Table 3. Percentage compositions were determined using surface area method. Elemental mapping of Fe-ZSM-5 clearly illustrated the presence of aluminum, silicon, iron, carbon, nitrogen and oxygen atoms inside the solid cluster. The ratios of silicon, oxygen, and carbon were prominent as compared to iron, aluminum, and nitrogen atoms (Fig. S1 & S2†). From the EDX mapping, it is clear that iron oxide particles were uniformly dispersed on ZSM-5 matrix. Further EDX analysis illustrates that the calcination caused the complete removal of the ligand part from the supported monometallic Fe-complex, producing nano oxides on the surface of the support (Table 3).

Fig. 1 illustrates the degradation and removal of ligand material. In the synthesized catalyst, the stoichiometrically removable part was 30.06% which is well supported by the STA and EDX analyses. The degradation of bipyridine ligand occurs below 250 °C. However, as impregnated MOF in ZSM-5, removal of the same was completed up to 500 °C. Above this temperature, no further weight loss was detected.

Fig. 2 illustrates the FESEM and HRTEM images of iron oxides supported catalyst. Surface morphology of the synthesized Fe-complex was significantly transformed after calcination. Initially, the ZSM-5 particles were relatively larger and clear (Fig. 2(b)). However, after impregnation and thermal decomposition of the impregnated Fe-complex, formation of nano-sized particles of iron oxides occurred on the matrix of ZSM-5. FESEM and HRTEM studies (Fig. 2(c)-(e)) well have supported these morphological changes.

The specific surface area of the support and catalyst (in m² g⁻¹) was determined by measuring the volume of N₂ gas, using the BET (Brunauer–Emmett–Teller) method. Table S3† shows the specific surface areas, pore width, and pore volume. Presence of nano sized iron particles reduced the specific surface area of ZSM-5 from 297 to 241 m² g⁻¹. Similarly, the pore volume was also changed from 0.17 to 0.11 cm³ g⁻¹. BET analysis confirmed the filling of iron oxide particles in the pores of ZSM-5 matrix. Synthesized Fe-ZSM-5 had greater pore size.
(2.66 nm) than the parent ZSM-5 (2.45 nm). This may be attributed to multilayer formation of nano sized particles on ZSM-5 support, which can be seen FESEM images (Fig. 2). Changes in the pore size, and surface area were well supported by the literature.

The FTIR spectra (Fig. S3†) of the [Fe(bpy)2]Cl2 complex was studied by using the spectra of 2,2'-bipyridine as a reference to study the shift in the wave number as a result of coordinate bonding. The main ring stretching vibrations $\nu$(C=N), and $\nu$(C=C) were observed at 1553 and 1579 cm$^{-1}$ for the bipyridine ligand. In the Fe-complex (Fig. S3†), a slight shift in vibrational frequency was observed in the range of 1592–1595 and 1561–1563 cm$^{-1}$. In addition, breathing mode of bipyridine was found to be shifted from 991 cm$^{-1}$ to 1012 cm$^{-1}$ when it formed coordination compound with iron. Similarly, in the case of synthesized Fe-ZSM-5, new bands appeared in the range of 2886–2888, and 1094–1136 cm$^{-1}$, which had distinguished it from the FTIR spectra of ZSM-5. These shifts and observations confirmed the formation of a chemical linkage between the iron and ZSM-5 in Fe-ZSM-5.

XRD analysis of the synthesized Fe-complex, Fe-ZSM-5 and the ZSM-5 support is provided in the Fig. 3. No clear evidence of free 2,2'-bipyridine (ref. code 00-015-1119), iron metals atoms and/or salts were observed in Fe-complex diffractogram. It was believed that that the metal salts completely reacted with ligand to form the complex phase and that the unreacted quantities were too small to be detected by XRD. The powder diffraction pattern of synthesized Fe-complex was well matched with C$_{30}$H$_{30}$ClFeN$_{4}$ (ref. code 00-008-0524), characterized by three intense peaks at $2\theta = 10.15$, 21.38 and 22.63 and other less intense peaks at higher $2\theta$ values. Similarly, the synthesized Fe-ZSM-5 catalyst has shown the distinctive diffractograms of the supporting matrix (ZSM-5, $2\theta = 7$–9° and 23–25°) provided in the literature. This analysis revealed that the loading of Fe-MOF in accessible positions insight the zeolite matrix had not damaged the crystallinity of the matrix. However, intensities of characteristic peaks were reduced due to filling of metallic nano oxides into the zeolite matrix of ZSM-5. This indicated that the X-ray absorption was lowered by the presence of Fe nano oxide particles. Several other researchers have reported similar results about filling of oxides in zeolitic matrix.

3.2. Process optimization and ANOVA analysis

The Fe-complex precipitations were carried out according to the design described in Table 1 with ‘yield’ as the response factor. On the basis of the experimental results, an empirical model (eqn (5)) was developed. This was a second order polynomial (in

![Image](https://via.placeholder.com/150)

**Fig. 3** XRD analysis of Fe-ZSM-5, ZSM-5, and Fe(bpy)-complex (c).
terms of coded factors), showing the interactions among the independent variables to achieve the precipitation yield.

Yield of Fe-complex = 77.61 + 1.59A + 25.46B + 2.83C − 1.44A² − 15.82B² − 1.32C² + 1.83AB + 9.46AC + 0.59BC

This empirical model showed the interaction among independent variables and their influence on the response yield. The predicted and experimental values were summarized and compared in Table 2. The experimental values of the Fe-complexes varied between 10 and 82%, which were in good agreement with the predicted values. ANOVA, an integral and reliable approach, was further employed to confirm the suitability and significance of a model.28 Table 4 illustrates the ANOVA results for the processed values.

\( F \)-Value indicates the reliability and suitability of a model. A variable with prob. > \( F \) of less than 0.05 is considered to have significant effects on the response. The greater the \( F \) value for a particular variable, the more significant the effect of that particular variable on the specific response.29 In the present work, \( F \)-values of 4639 indicated that the precipitation model for the Fe-complexes was suitable. The quality of fit of both models was also confirmed through determination coefficient (\( R^2 \)). The \( R^2 \) value was 0.9998, which was in good agreement with the adjusted \( R^2 \). Adequate precision (AP) is usually used to get the signal to noise (S/N) ratio to confirm the validity of a model and a ratio greater than 4 is recommended. In the present case, an AP value of 179.38 indicated that there was adequate signal to noise (S/N) ratio to confirm the validity of the model. These values confirmed that the model was suitable and could be used to optimize the design space.

3.2.1. Effect of process variables on yield. The perturbation plots (Fig. 4(a)) compares the combined effects of all the three variables. The slope of the curve showed the influence of a variable and the steepest curve was the main focus of attention.30 It was observed that process time (factor B) was the most influencing factor on the yield. Process temperature (factor A) was the second most influencing factor while stirring speed (factor C) was the least influencing. Increasing the process time and impeller speed increased the suspension of crystals which led to maximum exposure of the available surface area to the solution for mass transfer.31 However, at high temperature, increasing stirring caused dissolution of the crystalline material.

Fig. 4(b) illustrates the comparison between the experimental and predicted values. From the plot, it is clear that the experimental values were in a linear relationship with the predicted values, indicating that the predicted values were close to the experimental values. The 2D and 3D contour plots (Fig. S4 & S5†) present a clear and understandable analysis of the process.

The optimization of the results obtained through experiments was carried out using Response Surface Methodology (RSM). Responses were kept within the desired ranges while the maximum yield was targeted. The suggested optimized values of temperature (33 °C), time (4 h) and stirrer speed (245 rpm) were validated through the experiment. The approximate yield of the Fe-complexes was 81.5%. There was a good agreement between the predicted and experimental results under optimized environment.

Furthermore, in the impregnation step, 82–84% yield of Fe-ZSM-5 was observed. The yield can be further increased up to 90% with an efficient filtration system.

3.2.2. Efficiency and stability evaluation of the Fe-ZSM-5 catalyst. Experiments exhibiting Fenton oxidation were carried out to degrade and decolorize three selected dyes. In order to examine the adsorption, the preliminary study was conducted with 100 mg L\(^{-1}\) of dye concentration. After four hours, percentage of adsorbed Acid Blue 113, Methyl Orange, and Reactive Black 5 were 78%, 71%, and 63%, respectively. All the obtained results imply that the adsorption equilibrium was achieved and no further change was detected. The synthesized Fe-ZSM-5 illustrated more adsorption performance for Acid Blue 113 than Methyl Orange, and Reactive Black 5. Difference in adsorption rate may be due to the dissimilar organic structures, which had made difficulties to approach surface of the catalyst. The other reason may be the different binding affinities with the surface of Fe-ZSM-5. Normally, binding affinities are affected by different functional group such as –NH\(_2\), SO\(_3\)\(^-\), –OH.32,33 Similarly the Methyl Orange molecules were more

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<th>Source</th>
<th>Sum of squares</th>
<th>Degree of freedom</th>
<th>Mean square</th>
<th>( F ) value</th>
<th>Prob. &gt; ( F )</th>
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<td>( R_{adj}^2 = 0.9994 )</td>
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</table>
easily adsorbed than Reactive Black 5, which can be related to smaller molecule size of the Methyl Orange.\(^5^2\)

The adopted optimized values for the second set of experiments are provided in Table S1.\(^6^\) These values are based on our previous results in which effects of initial dye concentration, dye/catalyst (wt/wt), catalyst/H\(_2\)O\(_2\) (wt/wt), reaction time, pH, and temperature were considered and optimized.\(^6^\) The finding of previous work includes that the pH had significant effect on the treatment efficiency. At pH 3, the degradation rate of dye was found maximum as compared to pH 5 and pH 9. Effects of other parameters were also significant as described below:

\[
pH > \text{initial dye conc.} > \text{time} > \text{dye/Fe}^{2+} > \text{H}_2\text{O}_2/\text{Fe}^{2+} > \text{temperature}
\]

The efficiency was evaluated based on Acid Blue 113 decolorization, degradation and TOC removal (Table 5). For 100 mg L\(^{-1}\) of initial dye concentration, 99.7% of degradation, 99.8% of decolorization and 77% of TOC removal were achieved. However, the TOC removal was reduced to 69% when the dye concentrations increased to 200 mg L\(^{-1}\). It indicated that less amount of the catalyst was available to interact with H\(_2\)O\(_2\) or the residual H\(_2\)O\(_2\) scavenged hydroxyl radicals.\(^5^4\) These results reflected and supported the findings of our previous work. However, at higher concentrations, the degradation efficiency slightly increased (Table 5).

Treated samples were examined by HPLC. Traces of carboxylic acid, aniline, and benzoquinone were sensed corresponding to the calibrated peaks at ca. 1.92 min, 5.97 min, and 2.420 min, respectively. Formation of aniline may be attributed to the oxidative splitting of the dye amino benzene moiety forming a ‘NH-C\(_6\)H\(_5\) radical which has potential to abstract an amino hydrogen atom from dye molecules.\(^6,5^5\)

\[
\text{C–NH–C}_6\text{H}_5 + \text{‘NH–C}_6\text{H}_5 \rightarrow \text{C–N’–C}_6\text{H}_5 + \text{NH}_2\text{C}_6\text{H}_5 \quad (6)
\]

The other detected moiety was benzoquinone. This compound is frequently detected in the degradation of phenol and benzene.\(^4^6,5^5,5^6\) Further oxidation has caused the splitting of benzoquinone ring into maleic and formic acids.\(^4^6\) These results also reflected the findings of our previous work.\(^6^\)

Table 5  Efficiency of the synthesized catalyst at optimized conditions

<table>
<thead>
<tr>
<th>Dye (mg L(^{-1}))</th>
<th>Dye/catalyst (wt/wt)</th>
<th>H(_2)O(_2)/catalyst (wt/wt)</th>
<th>pH</th>
<th>Time (h)</th>
<th>Temperature (°C)</th>
<th>Decolorization%</th>
<th>Dye removal%</th>
<th>TOC%</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>0.75</td>
<td>2.5</td>
<td>3</td>
<td>4</td>
<td>30</td>
<td>99.7</td>
<td>99.8</td>
<td>77</td>
</tr>
<tr>
<td>200</td>
<td>0.75</td>
<td>2.5</td>
<td>3</td>
<td>4</td>
<td>30</td>
<td>99.6</td>
<td>99.7</td>
<td>69</td>
</tr>
<tr>
<td>300</td>
<td>0.75</td>
<td>2.5</td>
<td>3</td>
<td>4</td>
<td>30</td>
<td>99.3</td>
<td>99.2</td>
<td>69.5</td>
</tr>
<tr>
<td>600</td>
<td>0.75</td>
<td>2.5</td>
<td>3</td>
<td>4</td>
<td>30</td>
<td>99.2</td>
<td>99.3</td>
<td>70</td>
</tr>
<tr>
<td>900</td>
<td>0.75</td>
<td>2.5</td>
<td>3</td>
<td>4</td>
<td>30</td>
<td>99.1</td>
<td>99.1</td>
<td>71.5</td>
</tr>
</tbody>
</table>
3.2.3. Efficiency of the synthesized Fe-ZSM-5 for other dyes and mixture of dyes. In the third set, degradation of Methyl Orange, and Reactive Black 5 individually and in mixture forms were studied. Fig. 5 illustrates the comparison of these experiments. In all cases, color was completely removed in less than an hour. However, the noted TOC removal values were 68% and 71% for Reactive Black 5, and Methyl Orange, respectively. A decrease of 6-8% in the TOC removal indicates that the degradation rate depends on the structures of organic molecules.\textsuperscript{53} Beside this, some study also reveals that degradation of Methyl Orange type azo dye is favored by alkaline medium.\textsuperscript{57}

Table S2\textsuperscript{†} illustrates the composition of mixtures, their percentage degradation and TOC removal. In all cases, color was completely removed in the less than an hour. However, mineralization efficiency for mixtures 1–4 was 70%, 73%, 69%, and 72%. Due to the presence of Acid Blue 113, in mixture 2 and 4, mineralization efficiency was remained maximum. The catalyst has shown relatively less mineralization efficiency for mixture 3 containing Methyl Orange and Reactive Black 5 (Fig. 5). It can be attributed to different structures of dye molecules, or different functional group such as =NH\textsubscript{3}, SO\textsubscript{3}–, -OH.\textsuperscript{52,53} Overall the efficiency of the catalyst against different dyes and their mixture was remained excellent.

3.2.4. Comparison of the Fe-ZSM-5 with existing catalysts. Apart from catalytic activity, efforts were made to compare the performance of the synthesized Fe-ZSM-5 with other frequently used catalysts for the degradation of textile dyes. However, it was revealed that no one had used the Fe-ZSM-5 for the degradation of Acid Blue 113 and Reactive Black 5 (up to authors' knowledge). Therefore, it was an additional novelty of this work. Beside this, for third selected dyes “Methyl Orange”, limited degradation data was available with Fe-ZSM-5. The existing data for the degradation of Methyl Orange, was based on the utilization of UV to enhance the degradation rate,\textsuperscript{72} which significantly increased the process cost. It was found that the degradation of several other textile dyes were also carried out using Fe-ZSM-5 catalysts, synthesized from different ion exchange and hydrothermal methods. However, each researcher had used different process conditions, and reactor type. Therefore, it was not possible to repeat all the experiments for efficiency comparison. To overcome this issue, an alternate option was considered by setting one liter of dye solution as basis and assessing different factors (e.g. dye initial concentration, catalyst used, H\textsubscript{2}O\textsubscript{2} required), efficiencies of catalysts synthesized through different methods were compared (Table 6). Comparative study has given an understandable picture of color and TOC removals from dye solutions.

Table 6 illustrates that Fe-ZSM-5 synthesized using ion exchanged techniques are suitable for the degradation of azo dyes.\textsuperscript{22,56,59} Queiros \textit{et al.}\textsuperscript{22} consumed smaller quantity of their synthesized catalyst as compared to this study. Similarly, Queiros \textit{et al.}\textsuperscript{22} Bolova \textit{et al.}\textsuperscript{28} Unnu \textit{et al.},\textsuperscript{60} and Gric et \textit{al.}\textsuperscript{61} used lower initial concentrations of the selected dye (50 mg L\textsuperscript{-1} and 35 mg L\textsuperscript{-1}) to assess the activities of Fe-ZSM-5 catalysts. It is common practice that with smaller dye concentration, degradation rate increases due to more available hydroxyl radicals and their interaction with organic molecules.\textsuperscript{28} However, even with smaller initial concentrations, the obtained results of TOC reduction were considerably lesser than this work (Table 6). Chen \textit{et al.}\textsuperscript{64} used high catalyst concentration (4000 mg L\textsuperscript{-1}) to decolorize KN-R dye and maximum 90% of decolorization was achieved. Zhou \textit{et al.}\textsuperscript{52} synthesized different types of Fe-ZSM-5 catalysts and evaluated against Methyl Orange. Using UV-visible irradiation, TOC reduction was noted in the range of 8–64%. With excess amount of catalyst and H\textsubscript{2}O\textsubscript{2}, and comparatively increased temperature (333 K), Yaman \textit{et al.}\textsuperscript{59} achieved 81% of COD reduction for the selected dye, Reactive Red 141. However, when researchers used ambient conditions for dye treatment, the degradation rate was significantly reduced (even up to 0% of COD reduction). Similarly, lowering the catalyst amount (1.0 g L\textsuperscript{-1}) also caused the decrease in the COD reduction (32%).

In addition to these, Prihod'ko \textit{et al.}\textsuperscript{64} synthesized Fe-ZSM-5 (improved) and evaluated against Rhodamine G dye. Significant TOC reduction (80%) was reported in a comparatively shorter time (2.5 h). High concentration of H\textsubscript{2}O\textsubscript{2} (5.44–6.8 g L\textsuperscript{-1}) was used in those experiments, which is nearly two time of this work. Beside higher amounts of H\textsubscript{2}O\textsubscript{2}, catalyst synthesis process for improved Fe-exchanged zeolites is complicated and requires longer time (3–4 days) as compared to currently used process.\textsuperscript{26}

On the basis of this comparative study, it is clear that newly developed two-step process can be used to synthesize, efficient and economical Fe-ZSM-5 catalysts for advance oxidation processes to achieve the treatment targets. Apart from the optimization and catalytic activity, stability of the catalyst is also a key factor in oxidation processes. It is a common practice that leaching of metal ions from supporting matrix causes deactivation of the catalyst.\textsuperscript{28} A catalyst showing a minimal amount of leaching is considered as a stable catalyst.

In our previous study, stability of Fe-ZSM-5 was analyzed through EDX, SEM and FTIR and it was confirmed that the leaching was below 2 ppm. In the present case, leaching was measured by ICP techniques. Leaching of iron was observed below 2 ppm for all dyes at higher pH values. However, at pH 3, the measured values of leaching were 2.7, 2.1, 4.1, and 2.8 for mixture 1 to 4. This indicates that catalysis mainly occurred on the active sites, although a slight traces of iron was available in the solution phase. For the mixture 3, the leaching rate (1.4 ppm) was relatively higher as compared to other mixtures. In the present case, fresh and spent samples were also analyzed by EDX to confirm the ICP results. Samples of the used catalysts were obtained from the treated solutions, washed with methanol and heated upto 200 °C prior to EDX analysis. Difference in iron content was used estimate the iron ions leached into the treated water. From comparison, it was revealed that ICP values are little higher side than the EDX results. Similarly the mostly ICP values are in the range of 2–3 ppm, which are slightly increased from the permissible limit (<2 ppm). However the present leaching results are better than most of the reported values.\textsuperscript{7,21,61,62} This has confirmed the stability of the catalyst as reported in previous work.\textsuperscript{6}
Fig. 5  Degradation of individual dye (a), in mixture form (b), and TOC reduction for Reactive Black 5, Methyl Orange, mixture 1, mixture 2, mixture 3, and mixture 4 (c).
Table 6  Comparative study of the synthesized catalyst with other available catalysts

<table>
<thead>
<tr>
<th>Dye</th>
<th>Dye Conc. (mg L⁻¹)</th>
<th>FeZSM-5 wt (mg L⁻¹)</th>
<th>H₂O₂ wt (mg L⁻¹)</th>
<th>pH</th>
<th>Time (h)</th>
<th>Decolorization%</th>
<th>TOC/COD removal%</th>
<th>Reference</th>
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</thead>
<tbody>
<tr>
<td>AB113</td>
<td>100</td>
<td>1330</td>
<td>3333</td>
<td>3</td>
<td>4</td>
<td>99.7</td>
<td>77 (TOC)</td>
<td>Present study</td>
</tr>
<tr>
<td>RB-5</td>
<td>100</td>
<td>1330</td>
<td>3333</td>
<td>3</td>
<td>4</td>
<td>99.1</td>
<td>68 (TOC)</td>
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</tr>
<tr>
<td>MO</td>
<td>100</td>
<td>1330</td>
<td>3333</td>
<td>3</td>
<td>4</td>
<td>99.3</td>
<td>71 (TOC)</td>
<td></td>
</tr>
<tr>
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<td>100</td>
<td>1000</td>
<td>5440</td>
<td>4</td>
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<td>99.0</td>
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<td>35</td>
<td>333</td>
<td>680</td>
<td>3</td>
<td>3</td>
<td>91.0</td>
<td>36 (TOC)</td>
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<td>200</td>
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<td>100</td>
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<td>RR141</td>
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<td>1000</td>
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<td>2</td>
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<td>90</td>
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<td>3.5</td>
<td>2</td>
<td>98</td>
<td>53 (COD)</td>
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</tr>
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<td>567</td>
<td>3</td>
<td>0.5</td>
<td>84</td>
<td>Not available</td>
<td></td>
</tr>
</tbody>
</table>

a AB113 (Acid Blue 113), OII (Orange II), RG (Rhodamine G), MO (Methyl Orange), RR141 (Reactive Red 141), KN-R (Reactive Brilliant Blue KN-R), CV (Crystal Violet), and ATZ (Atrazine).

4. Conclusions

In this study, synthesis, optimization and activity evaluation of Fe-ZSM-5 in advanced oxidation process were conducted. The present study proved that MOF derived Fe-ZSM-5 can be used as a preferred catalyst in Fenton oxidation process for the industrial wastewater treatments containing recalcitrant contaminants.

Catalyst was synthesized using a 2-step process and characterized by EDX, SEM, HRTEM, FTIR and BET. CCD method was used to optimize the yield and interactions among the process variables (temperature, time and stirrer speed). The quality of fit of the polynomial models were confirmed through determination coefficient ($R^2$), the model F-value, probability value (prob. > F), and adequate precision (AP).

Process time was seen as the most influencing variable in catalyst preparation. Effects of temperature and stirrer speed on the yield were also significant. The optimized experimental yield was 81.5%, which was in good agreement with the CCD predicted value. Furthermore, the efficiency of the catalyst, produced at optimized environment was also evaluated against three dyes and their mixtures. Total Organic Carbon (TOC) removal was achieved up to 77%, 71% and 68% for Acid Blue 113, Methyl Orange, and Reactive Black 5, respectively. For the mixtures, TOC removal was observed in the range 69–72%, which possesses an excellent mineralization efficiency range. Besides, it was observed that leaching of iron metal was below 2 ppm.

Acknowledgements

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References


