

The Potential of Fe-exchanged Y Zeolite as a Heterogeneous Fenton-type Catalyst for Oxidative Degradation of Reactive Dye in Water

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The study aimed to investigate the potential of Fe-exchanged zeolites of Y-type as a catalyst in heterogeneous Fenton-type processes for the degradation of model organic pollutant, reactive azo dye C.I. Reactive Blue 137, in water. The research work was directed to investigate the influence of process variables, such as FeY catalyst dosage, Fenton reagent ratio, and initial operating pH on the efficiency of the treatment process. The performance of the studied heterogeneous process was compared with corresponding homogeneous Fenton-type processes, while the influence of UV light on both heterogeneous and homogeneous processes was investigated as well. The results of FeY catalyst characterization indicate that the iron content is mainly built into the inner zeolite micropores providing the benefit to zeolite stability and activity of the catalyst. Based on the decolorization and the mineralization degree of RB137 model wastewater, the overall process efficiency was estimated. Homogeneous and heterogeneous Fenton processes yielded similar decolorization and mineralization, but the concentration of Fe ions in the bulk after treatment was significantly lower in the latter case. Moreover, the use of the heterogeneous catalyst allowed the UV-assisted process to be operated at milder pH conditions, pH 5, while the most suitable pH for the dark heterogeneous process showed to be pH 3.

Key words:

Heterogeneous catalysis, Fenton-type process, FeY, zeolites, model wastewater, UV irradiation, degradation mechanisms

Introduction

Water resources are globally facing tremendous and ever-increasing pressures. Water bodies have a limited capacity to process the pollutant charges of the effluents from different sources. The elimination of organic pollutants from industrial wastewater is an environmental target of special interest. A noteworthy class of water pollutants is dyes. Synthetic dyes are extensively used in many fields of modern technology, e.g. various branches of textile, leather tanning and paper industries, as well as in food technology, agricultural research, light harvesting arrays and photoelectrochemical cells.¹ Disposal of dyes in water resources must be avoided. The synthetic origin and complex molecular structure of dyes is what makes them stable and difficult to biodegrade, while the weathering of organic dyes through oxidation, hydrolysis, or other chemical reactions occurring in the wastewater can produce metabolites toxic to animals and human health.² Therefore, various treatment technologies for dye wastewater are being applied in order to prevent environmental contamination.^{1–7}

The biological oxidation and physical-chemical methods, and their combinations are the most commonly used for wastewater treatment. However, these processes are quite ineffective in removing color from wastewater since dyestuff are generally biorecalcitrant due to their aromatic structure,^{8,9} while physical-chemical treatments provide only a phase transfer of dyes and often produce large quantities of sludge.^{4,10}

Consequently, a more promising technology based on an advanced oxidation process (AOP) has been studied extensively, through which a broad range of organic dyes can be oxidized quickly and non-selectively. These processes which involve accelerated production of the hydroxyl-free radical are capable of degrading dyes at ambient temperature and pressure.^{1,2,10} Among various AOPs, the homogeneous Fenton process is the most widely used catalytic process for dye decolorization.¹ The main disadvantage of homogeneous catalytic processes such as Fenton's, comes from the requirement of catalyst recovery or separation. In many cases, the separation of the catalyst from the reaction mixture is technically and/or economically unfeasible. As novel AOPs, the heterogeneous catalytic and photocatalytic oxidation processes are

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promising alternative methods for the removal of dyes and other organic pollutants from the water matrix.

Different catalyst supports such as synthetic and natural zeolites, bentonites, pillared clays or resins are applied within heterogeneous Fenton-type processes.^{11–17} Among them, synthetic zeolites are characterized by their unique properties and the ability to selectively adsorb smaller organic compounds.^{18–20}

This study aimed to investigate the degradation of an reactive azo dye as a model pollutant in water matrix by using Fe-exchanged Y-zeolite as catalyst in the heterogeneous Fenton-type processes. The heterogeneous and corresponding homogeneous Fenton-type processes were compared and their efficiency estimated on the basis of decolorization and mineralization degree, concentration of iron ions after treatment in bulk, and final pH value. The influence of UV irradiation on both heterogeneous and homogeneous processes was also studied.

Experimental section

Materials

The chemicals used – $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, p.a.; $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$, p.a.; $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, p.a.; H_2O_2 , 30 %; H_2SO_4 , > 98 %; NaOH , p.a.; $\text{C}_{12}\text{H}_8\text{N}_2 \cdot \text{H}_2\text{O}$, p.a.; KSCN , p.a.; CH_3COOH , 99.5 %; CH_3COONa , p.a.; HCl , 36.5 % were supplied by Kemika, Croatia, and Sigma Aldrich, Germany. Zeolite of Y-type in the protonic form ($\text{H}^+ \text{Y}$) and reactive azo dye, C.I. Reactive Blue 137 (RB137), used as model pollutant in the study were purchased by Zeolyst International, USA and CIBA-Geigy, Switzerland, respectively. FeY-zeolite catalyst was prepared from HY-zeolite by ion-exchange from aqueous solution according to Neamtu *et al.*¹² All solutions were prepared with deionized water with conductivity less than $1 \mu\text{S cm}^{-1}$.

Experimental procedure

The experiments were performed in a glass water-jacketed batch reactor of 0.8 L total volume, while the volume of the treated solution was 0.5 L. The middle of the reactor was occupied with a quartz tube where a mercury lamp (typical intensity on $2 \text{ cm} \approx 4.4 \text{ mW cm}^{-2}$) was vertically placed. The value of incident photon flux by reactor volume unit at $\lambda = 254 \text{ nm}$, $I_0 = 3.68 \cdot 10^{-6} \text{ Einstein s}^{-1}$, was calculated on the basis of hydrogen peroxide actinometry measurements.²¹ In dark Fenton-type processes, the UV lamp was turned off. In all experiments, RB137 dye was used as a model dye pollutant present in water matrix in concentration of

$\gamma = 20 \text{ mg L}^{-1}$. Mixing of the reaction mixture was provided by a magnetic stirring bar, while temperature was maintained at $25 \pm 0.3 \text{ }^\circ\text{C}$ by circulating the water through the jacket around the photoreactor. The experiments were performed in the following manner: firstly, the appropriate catalyst/zeolite dosage was added to the model dye solution, which was followed by adjustment of pH to the desired value, and the addition of the required amount of H_2O_2 . The duration of each experiment was 60 min; samples were taken periodically from the reactor (0, 2, 5, 10, 20, 30, 40, 50, 60 min), centrifuged to remove solid particles (where required) and thereafter immediately analyzed. All experiments were repeated at least three times and averages are reported, while the reproducibility of experiments was within 5 %.

Analysis

The extents of decolorization were established by measuring absorbance in the visible spectra at the characteristic wavelength of the used RB137 dye ($\lambda_{\text{max}} = 610 \text{ nm}$) by UV/VIS spectrophotometer, Lambda EZ 201, Perkin Elmer, USA. The mineralization of RB137 solution was established based on measurements of total organic carbon content (TOC), performed by total organic carbon analyzer; TOC-V_{CPN}, Shimadzu, Japan. Concentrations of iron ions in the bulk were monitored by colorimetric methods using the same UV/VIS spectrophotometer mentioned above. Ferrous ions were identified by the reaction of Fe^{2+} with 1,10-phenanthroline giving an orange-red colored complex ($\lambda_{\text{max}} = 510 \text{ nm}$), while ferric ions were determined by the reaction of Fe^{3+} with thiocyanate forming under acidic conditions a red colored complex ($\lambda_{\text{max}} = 480 \text{ nm}$).²² The consumption of hydrogen peroxide in the bulk during the treatment by applied processes was monitored using modified iodometric titration method.²² Initial and final pH values were measured using Handylab pH/LF portable pH-meter, Schott Instruments GmbH, Germany. Used zeolites, both in non- and Fe-exchanged form, were characterized by Perkin-Elmer Sciex Elan[®] 5000 ICP-MS instrument, USA, Quanta 200 Environmental Scanning Electron Microscope (ESEM), USA and Perkin Elmer Spectrum One FT-IR spectrophotometer, USA.

Results and discussion

Zeolites characterization

The applied Y-zeolite was characterized both in its non-exchanged and Fe-exchanged form using SEM and ICP analysis. SEM images of HY and FeY-zeolite are presented in Fig. 1(a) and (b) re-

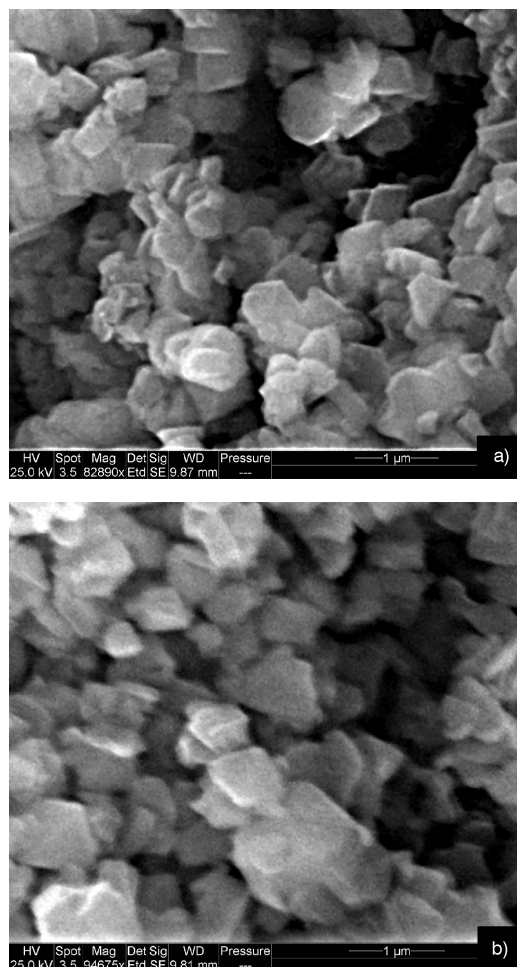


Fig. 1 – SEM images of applied zeolites; (a) HY and (b) FeY

spectively. It can be observed that zeolites appeared as a conglomerate of irregular polyhedra ranging in diameter particle from $d_p = 0.3$ to $1.0 \mu\text{m}$, and no significant differences were noticed in their morphologies. The surface of the Fe-exchanged zeolite seems to be smooth with no obvious deposit of iron species. Such an observation indicates that iron species are mainly built into the zeolite pores benefiting stability and activity of the zeolite catalyst.²³ Quantitative analysis of HY and FeY-zeolites was performed by ICP-MS analysis using the standard method when solid particles are digested transferring the metal constituents into the solution (Table 1).²² It can be seen that even in the non-exchanged zeolite, some iron content, $w = 1.3 \cdot 10^{-4}$ g per gram of zeolite, was detected. Thus, the preliminary experiments using non-exchanged Y zeolite in combination with H_2O_2 were performed, but no color or TOC removal was recorded (results not reported), indicating that the iron content present in trace amounts is either insufficient to catalyze H_2O_2 decomposition throughout the Fenton reaction or that the iron is present in some inactive form for the

Fenton catalytic reaction. On the other hand, the iron content of $w = 1.74 \cdot 10^{-2}$ g per gram of zeolite in Fe-exchanged Y-zeolite is detected and corresponds closely to the theoretical value calculated in this study and literature¹² as well (Table 1). It should be noted that by ICP analysis of zeolites three times lower aluminum content is detected in FeY in comparison to its non-exchanged form, indicating the dealumination of Y-zeolite type during ion-exchanged procedure in the solution proposed in literature.¹² According to Neamtu *et al.*¹³ the increase of $r_{\text{Si/Al}}$ ratio (dealumination) may negatively influence the catalyst stability against leaching due to the weaker interactions of Fe ions with zeolite lattice.

Table 1 – Iron content in applied zeolites according to ICP-MS analysis

Zeolite	$r_{\text{SiO}_2/\text{Al}_2\text{O}_3}$	Fe ($\cdot 10^{-3} \text{ g g}^{-1}$)		
		experimental	theoretical	literature ¹²
HY	60	0.13	0	NA*
FeY	160	17.4	17.1	16.9

*NA – not available

Heterogeneous Fenton type processes using FeY catalyst

In heterogeneous AOPs, the pollutant can be removed from the water matrix by adsorption onto the solid surface thus contributing to overall process efficiency. Therefore, in the first step of the study, HY and FeY zeolites were tested for their adsorption ability under applied experimental conditions. After addition of the zeolites, pH values of the model dye solution were adjusted at 2 to 7 and stirred for 1 hour at $25 \pm 0.3 \text{ }^\circ\text{C}$. The samples were centrifuged and thereafter analyzed by UV/VIS spectrophotometry. The recorded spectra were compared with the spectra of the model dye solution. No changes were observed, indicating that the parent dye molecule RB137 cannot be removed from the model dye solution by adsorption onto the zeolite surface under applied experimental conditions. Thus, in further experiments, color removal by applied heterogeneous AOPs contributed only to the oxidative degradation of the dye molecule to its colorless by-products.

The next step of the study aimed to determine the optimal Fenton reagent ratio in the investigated range using two different FeY dosages of $\gamma = 1.61$ and 3.22 g L^{-1} , according to ICP analysis corresponding to $c = 0.5$ and 1.0 mmol L^{-1} , respectively (Table 1). Experiments were performed at pH 3 (Fig. 2). It can be noticed that the catalyst dosage

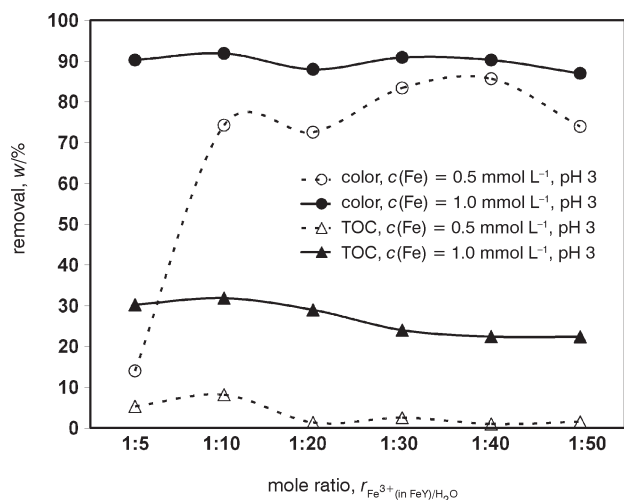
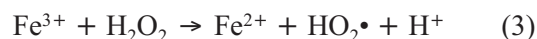
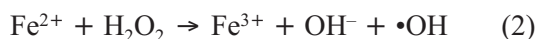


Fig. 2 – Influence of FeY dosage and FeY/H₂O₂ ratio on the decolorization and mineralization of RB137 solution by heterogeneous dark Fenton process, FeY/H₂O₂, at pH 3 (*t* = 60 min)

and Fenton reagent ratio influenced process efficiency. Using lower catalyst dosage, incomplete decolorization and low TOC removal were achieved. On the other hand, higher catalyst dosage yielded rather high decolorization extents, over 90 % throughout all investigated Fenton reagent ratios. Consequently, partial TOC removals were similar throughout the investigated range of Fenton reagent ratios, from 22.4 to 31.9 % of TOC removal. The highest process efficiency was achieved using catalyst dosage of 3.22 g L⁻¹ ([Fe] = 1 mmol L⁻¹) and Fenton reagent ratio 1 : 10 (Fig. 2). An increase in Fenton reagent ratio led to increased efficiency of FeY/H₂O₂ process, reaching the highest value of TOC removal, with Fenton reagent mole ratio 1 : 10, while its further increase beyond that point negatively affected process efficiency (Fig. 2). Such behavior is characteristic for homogeneous Fenton processes.^{24–27} The scavenging nature of H₂O₂ when present in excess can be described by the following eq. (1):



Accordingly, the Fenton mechanism, which can be represented with two main reactions (2) and (3):²⁵



plays a major role in OH radicals generation in dark heterogeneous Fenton processes using FeY catalyst as well. It should be pointed out that in the case of heterogeneous Fenton processes, the above reactions may occur simultaneously at the zeolite surface and in the bulk due to the leached iron ions. The mechanism of OH radical generation in the ze-

olite pores is proposed by Neamtu *et al.*,¹² while the dominance of either surface Fenton reactions or bulk Fenton reactions depends on the portion of leached iron ions from the zeolite catalyst surface, i.e. depends on catalyst stability. The leaching of iron ions from the zeolite surface, i.e. zeolite micropores, depends on $r_{\text{Si/Al}}$ ratio¹³ and the operating pH value, as demonstrated in our previous study where Fe-exchanged zeolite of ZSM5 type was used as a heterogeneous catalyst in the Fenton-type process.²⁸

The next step of the study focused on the applicability of FeY-zeolite catalyst throughout the pH range of 2 to 7 (Fig. 3). This part of the research aimed to provide information on the oxidative potential of used dark heterogeneous Fenton-type process for the degradation of the model organic pollutant and the stability of FeY-catalyst toward leaching influenced by changes in pH environment. To this end, the dark heterogeneous Fenton-type process was performed using FeY catalyst dosage and Fenton reagent ratio established as optimal in the range investigated in the previous step of the study (Fig. 2). From Fig. 3, one can observe that a rather high (91.9 %) decolorization degree was obtained only at pH 3, which is typical for the homogeneous Fenton process. In all other cases, rather low decolorization extents, < 40 %, were achieved. Like homogeneous Fenton processes,²⁶ the dark heterogeneous process using FeY catalyst should be maintained in tight acidic pH range. Thereby, low process efficiency at pH lower than 3 could be contributed to the inability of iron ions to decompose H₂O₂ due to the formation of stable oxonium ion (H₃O₂⁺),²⁹ while the constant decrease in efficiency with an increase of pH over 3 could be due to the formation of iron-hydrocomplexes. Parkhomchuk *et*

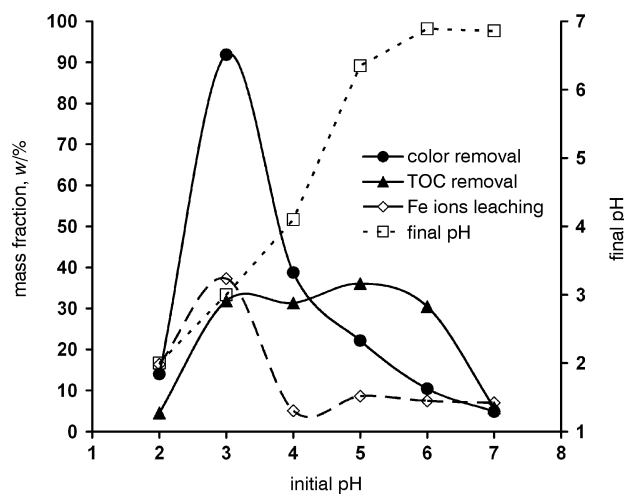


Fig. 3 – Influence of initial operating pH value on the decolorization and mineralization of RB137 solution by heterogeneous dark-Fenton process, FeY/H₂O₂, as well as on the leaching of Fe ions from zeolite support ([Fe] = 1 mmol L⁻¹, [H₂O₂] = 10 mmol L⁻¹, FeY dosage γ = 3.22 g L⁻¹, *t* = 60 min)

*al.*³⁰ showed that iron ions incorporated in the zeolite framework are able to form either organic or inorganic complexes. Therefore, it can be assumed that the significant drop in process efficiency, i.e. color removal, occurred at pH values higher than 3 (Fig. 3), was caused by the deactivation of FeY catalyst due to the formation of stable iron-hydro-complexes involving iron ions placed in the zeolite framework. Although our results of SEM analysis indicate that iron ions are incorporated in the zeolite framework, and despite the fact stated by some authors^{12,14} that interactions of positively charged iron ions with the negatively charged zeolite framework could prevent or postpone the formation of stable hydro-complexes, it seems that was not the case in our study using FeY-zeolite catalyst. The plausible explanation could be found in the strong dealumination during preparation of the catalyst, which caused an increase in $r_{\text{Si/Al}}$ ratio, allowing the formation of hydrocomplexes within the zeolite pores. Compared to the FeY/H₂O₂ process operated at pH 3, significantly lower decolorization, but similar TOC removals were obtained in the pH range from 4 to 6. One can assume that the process operated at pH 3 has the highest oxidizing power due to the highest color removal. It should be noted that the contribution of the adsorption of the parent dye molecule onto the FeY zeolite is excluded based on preliminary experiments. Accordingly, it is most likely that TOC removed in the same process is mainly due to the mineralization of organic matter. On the other hand, when processes were performed at elevated pHs above 3, the contribution of adsorption of colorless organics (dye degradation by-products) in the zeolite micropores should be considered as well. In our previous study using the Fenton process and non-exchanged Y-type zeolite,³¹ the obtained results indicated the ability of Y-type zeolite to adsorb the organic compounds of suitable size such as some products of partial dye degradation. The very small or even negligible changes in final pH values obtained when processes were operated at initial pH values above 3, speak in favor of the dominance of dye by-products adsorption over their mineralization in overall TOC removal obtained. As the dye molecule degradation progresses, the formation of aliphatic acids and a consequent decrease in pH value can be expected.^{32,33} Since such pH changes were not observed during the treatment of the model dye wastewater by FeY/H₂O₂ process (Fig. 3) it seems that the step in degradation mechanism of organic dyes including the formation of acidic by-products was not even reached. It can be concluded that the optimal operating pH for the process using FeY-zeolite as heterogeneous Fenton catalyst is 3 (Fig. 3), the same as in the homogeneous Fenton process. Furthermore, the rather high

concentration of iron in the solution after treatment (0.37 mmol L⁻¹) indicates that a significant portion of the Fenton reactions took place in the bulk as well. Although it seems that these results are in contrast with the results obtained by Neamtu *et al.*¹² where the complete color removal was reached at pH 5 and low amount of iron ions in the bulk, it should be pointed out that they operated dark heterogeneous Fenton type process using FeY catalyst at an elevated temperature (50 °C), characteristic for wet peroxide oxidation. The reason for such a high amount of iron ions leached from the zeolite surface at pH 3 (Fig. 3) could be due to the dealumination observed in catalyst preparation. As stated above, dealumination may negatively influence the catalyst stability against leaching.¹³ On the other hand, it seems that the stable hydrocomplexes, presumably formed in the zeolite framework at higher pHs, besides negative influence on the overall oxidation power of FeY/H₂O₂ process, could also inhibit the leaching of iron ions. The recorded lower leaching of iron ions at weak acid and neutral pHs than at acidic (Fig. 3) is in accordance with literature findings.¹¹

The comparison of the efficiency of heterogeneous process using FeY catalyst with corresponding homogeneous Fenton processes with and without the addition of non-exchanged Y zeolite is summarized in Table 2. All processes were operated at same conditions: [Fe] = 1 mmol L⁻¹, [H₂O₂] = 10 mmol L⁻¹, pH 3 and with catalyst or zeolite dosage of 3.22 g L⁻¹. Despite somewhat lower color removal, the highest mineralization, i.e. TOC removal, was achieved by FeY/H₂O₂ process. It can be observed that in the cases of homogeneous Fe²⁺/H₂O₂ and Fe³⁺/H₂O₂ processes, the addition of non-exchanged Y-zeolite negatively influenced TOC removal. Knowing that the adsorption is pH dependent^{34,35} and taking into account the results

Table 2 – Comparison of heterogeneous and corresponding homogeneous dark-Fenton processes with and without addition of non-exchanged Y zeolite ([Fe] = 1 mmol L⁻¹, [H₂O₂] = 10 mmol L⁻¹, zeolite dosage γ = 3.22 g L⁻¹, t = 60 min)

Process	Initial pH	Color removal/%	TOC removal/%	Fe ions bulk concentration/ mmol L ⁻¹
FeY/H ₂ O ₂	3	91.9	31.9	0.37
Fe ²⁺ /H ₂ O ₂	3	98.4	25.6	1.0
Fe ³⁺ /H ₂ O ₂	3	96.9	20.5	1.0
Fe ²⁺ /H ₂ O ₂ /HY	3	98.7	18.9	1.0
Fe ³⁺ /H ₂ O ₂ /HY	3	100	14.3	1.0

presented in Fig. 3 indicating that the adsorption of by-products of partial dye degradation is favored at pHs > 3, it can be concluded that the overall TOC removal achieved by all processes operated at pH 3 (Table 2) is mainly due to the mineralization of organic matter. Another advantage of the FeY/H₂O₂ process over corresponding homogeneous processes is the almost three times lower concentration of iron ions in the bulk after treatment (Table 2), and the avoidance of unnecessary loading of treated water with additional anions like in the cases when Fe²⁺ or Fe³⁺ salts are used.

It is known that UV light improves significantly the efficiency of homogeneous Fenton type processes.^{24,25,27} The influence of UV light on heterogeneous process using FeY zeolite catalyst is investigated within the pH range from 3 to 7 (Fig. 4). As expected, higher decolorization and mineralization extents were obtained in all observed cases. However, it should be noted that similar decolorization and mineralization extents, ranging from 97.4 to 99.7 % and from 72.6 to 75.4 % respectively, were obtained in the pH range from 3 to 5, while increasing the pH to 6 and 7 yielded lower overall process efficiency. Such behavior of dye-UV/FeY/H₂O₂ system is similar to that of dye-UV/Fe²⁺/H₂O₂ reported in our previous work³⁶ where final mineralization extents decreased with increased initial pH from 3 to 7. Quite opposite system behavior was observed in the case when FeZSM5 zeolite was applied as heterogeneous Fenton catalyst; final mineralization extents increased by increasing initial pH from 3 to 7.²⁸ The highest decolorization and mineralization extents, 99.7 and 75.4 % respectively, as well as the far lowest concentration of iron ions in the bulk, only

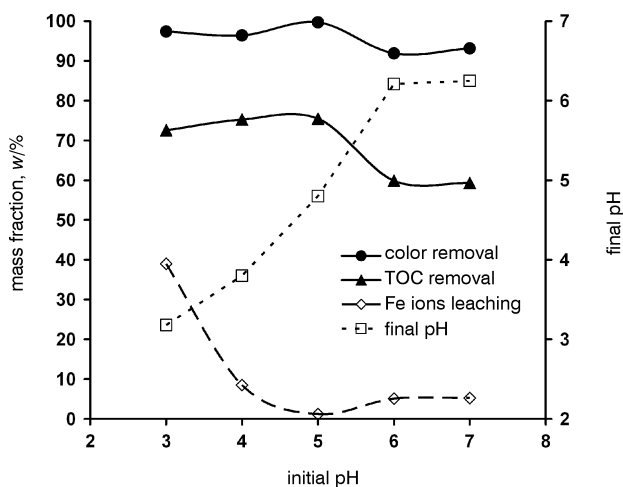


Fig. 4 – Influence of initial operating pH value on the decolorization and mineralization of RB137 solution by heterogeneous photo-Fenton process, UV/FeY/H₂O₂, as well as on the leaching of Fe ions from zeolite support ([Fe] = 1 mmol L⁻¹, [H₂O₂] = 10 mmol L⁻¹, FeY dosage γ = 3.22 g L⁻¹, t = 60 min)

1.86 % of overall added within zeolite catalyst, recorded after one-hour treatment, speaks in favor of pH 5 as the most suitable to operate UV/FeY/H₂O₂ process.

Table 3 compares the efficiency results of the heterogeneous photo-Fenton processes using FeY-exchanged zeolite operated at pH 3, typical for homogeneous processes, and pH 5, found as optimal for this system, as well as corresponding homogeneous processes with and without addition of non-exchanged zeolite. It can be observed that in all cases, regardless of different initial pH values, decolorization extents ≥ 94 % were achieved. For all applied processes operated at pH 5, similar mineralization results were obtained, regardless of the catalyst type and presence/absence of Y-zeolite (Table 3). The plausible explanation can be found in the fact that both the Fenton mechanism and the photolysis of H₂O₂ contribute to OH radicals generation in UV-assisted Fenton type processes.^{24–27,36} On the other hand, at pH 3, where influence of the Fenton mechanism dominates,²⁷ the results differ according to catalyst type and zeolite presence. The comparison of investigated photo-Fenton type processes based on the results presented in Table 3, demonstrated that the UV/FeY/H₂O₂ was as successful as most of the other corresponding processes considering color and TOC removal. However, due to the small amounts of leached iron from the solid structure (only 1.86 % of the total iron content), the use of FeY as a heterogeneous catalyst in photo Fenton-type process operated at pH 5, minimizes the possible secondary pollution of Fe-containing sludge.

Table 3 – Comparison of heterogeneous and corresponding homogeneous photo-Fenton processes with and without addition of non-exchanged Y zeolite ([Fe] = 1 mmol L⁻¹, [H₂O₂] = 10 mmol L⁻¹, zeolite dosage γ = 3.22 g L⁻¹, t = 60 min)

Process	Initial pH	Color removal/%	TOC removal/%	Fe ions bulk concentration/mmol L ⁻¹
UV/FeY/H ₂ O ₂	3	97.4	72.6	0.39
	5	99.7	75.4	0.02
UV/Fe ²⁺ /H ₂ O ₂	3	100	59.1	1.0
	5	98.0	75.5	1.0
UV/Fe ³⁺ /H ₂ O ₂	3	97.5	59.4	1.0
	5	98.0	74.2	1.0
UV/Fe ²⁺ /H ₂ O ₂ /HY	3	94.8	82.3	1.0
	5	98.4	69.7	1.0
UV/Fe ³⁺ /H ₂ O ₂ /HY	3	99.7	75.4	1.0
	5	93.8	72.7	1.0

Decolorization and mineralization kinetics of the UV/FeY/H₂O₂ process operated at pH 5 using catalyst dosage of 3.22 g L⁻¹ and Fenton reagent ratio 1 : 10 was compared with the following processes: UV, UV/Fe³⁺, UV/FeY, UV/H₂O₂ and FeY/H₂O₂ operated at the same conditions (Fig. 5(a) and (b)). Generally, the organic pollutants with the UV/FeY/H₂O₂ process could be degraded by two main mechanisms: by OH radicals and by direct photolysis. There are also several mechanisms for generation of OH radicals in UV/FeY/H₂O₂ process: by Fenton reactions (eqs. (2) and (3)), both at the catalyst surface and in the bulk, by the photolysis of H₂O₂ (eq. (4))²⁵ and by the photolysis of Fe(OH)²⁺ (eq. (5))^{25,26} formed both at the catalyst surface and in the bulk.



A further benefit of UV-assisted processes is the ability to degrade complexes of ferric ions and organic by-products of dye degradation (Fe-OC), proven to be formed in dark Fenton-type processes and usually related with the formation of carboxylic acids.^{24,25,37} Such complexes, stable in the dark, can be degraded by assistance of UV light thus allowing the Fenton catalytic cycle to be continued.^{24,27,37} According to the findings of Parkhmonchuk *et al.*³⁰ such complexes could be formed even when Fe ions are incorporated into the zeolite framework. The findings of our previous study³¹ involving the investigation of FeZSM5 zeolite catalyst in both dark- and photo-Fenton processes, indicated that Fe-OC could be destroyed allowing the further participation of ferric ions in the Fenton catalytic cycle. It should be pointed out that such considerations involve Fe-OC formed either in the bulk or at the outer zeolite surface where they can be illuminated by UV.

The following comparison of processes presented in Fig. 5, should provide information related to the degradation mechanisms and their involvement in the degradation of organic pollutants by targeted UV/FeY/H₂O₂ process. From Fig. 5(a) it can be seen that the fastest decolorization of RB137 solution occurred by UV/H₂O₂ processes. From the calculated “pseudo”-first order decolorization rates for the first 20 min of treatment (Table 4) it can be

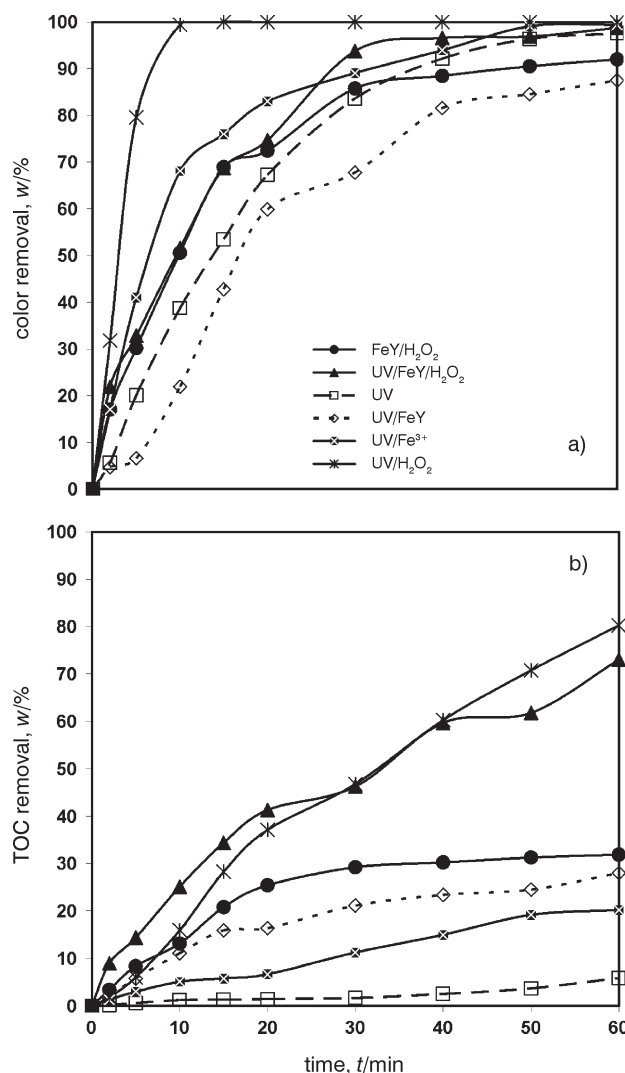


Fig. 5 – Comparison of the kinetics of decolorization (a) and mineralization (b) obtained by studied processes: FeY/H₂O₂, UV/FeY/H₂O₂, UV/FeY, UV/Fe³⁺, UV/H₂O₂, UV ([Fe] = 1 mmol L⁻¹, [H₂O₂] = 10 mmol L⁻¹, FeY dosage γ = 3.22 g L⁻¹, pH 3 for dark process, pH 5 for all processes with UV light)

observed that the decolorization rates followed an increasing order: UV/FeY < UV < FeY/H₂O₂ \approx UV/FeY/H₂O₂ < UV/Fe³⁺ < UV/H₂O₂. With the exception of direct photolysis, heterogeneous processes provide slower decolorization of RB137 model wastewater, presumably due to the diminished transparency of the reaction solution. Accordingly, similar “pseudo”-first order decolorization rates 1.16 and 1.21 · 10⁻³ s⁻¹ were observed for

Table 4 – Calculated “pseudo”-first order decolorization rates ([Fe] = 1 mmol L⁻¹, [H₂O₂] = 10 mmol L⁻¹, γ (catalyst/zeolite) = 3.22 g L⁻¹, pH 3 for dark process, pH 5 for all UV-assisted processes)

Process	FeY/H ₂ O ₂	UV/FeY/H ₂ O ₂	UV/FeY	UV/Fe ³⁺	UV/H ₂ O ₂	UV
$k_{\text{obs}} (\cdot 10^{-3} \text{ s}^{-1})$	1.16	1.21	0.65	1.58	5.00	0.88
r^2	0.980	0.984	0.951	0.978	0.960	0.990

FeY/H₂O₂ and UV/FeY/H₂O₂ processes, respectively (Table 4). For the same reason, the UV/FeY process yielded a lower decolorization rate in comparison to the UV process despite the presence of ferric ions as photocatalysts for organic pollutant degradation,³⁸ incorporated in the zeolite framework. Comparing UV/Fe³⁺ and UV/FeY processes, where the same amount of iron was introduced in the system, a three times higher value of “pseudo”-first order decolorization rate coefficient was observed in the case of the UV/Fe³⁺ process (Table 4). Since ferric iron (Fe(OH)²⁺) acts as photocatalyst,³⁸ the observed behavior speaks in favor of the previous statement made on the basis of SEM analysis (Fig. 1) that most of the Fe³⁺ ions incorporated in the zeolite framework are located in the inner zeolite micropores, and thus cannot be activated by UV light. Similar system behavior was observed in our previous study on FeZSM5 zeolite as a catalyst for Fenton-type processes.²⁸ It can be concluded that the major role in the decolorization of the RB137 model wastewater by UV/FeY/H₂O₂ process has Fenton mechanism generating OH radicals at the interphase involving surface iron ions and H₂O₂ which diffuse in the zeolite pores.

From all above, it can be concluded that UV light does not significantly influence the decolorization of RB137 model wastewater by FeY/H₂O₂ process. However, the results presented in Fig. 5(b) indicate that UV light positively contributes to the mineralization of model wastewater by heterogeneous Fenton-type process. The overall mineralization extent achieved after 60 min of treatment by UV/FeY/H₂O₂, 72.6 % of TOC removal, was more than twice higher than that achieved by FeY/H₂O₂, 31.9 % of TOC removal. The trend of the curves time vs. TOC removal for these two processes (Fig. 5(b)), indicate that the mineralization of RB137 model wastewater by the UV/FeY/H₂O₂ process is somewhat faster and proceeds continuously during the observed treatment period. On the other hand, the curve presenting the mineralization of model wastewater by the FeY/H₂O₂ process, indicates a significant leveling off after 20 min of treatment.

Similar system behavior was observed in the dark homogeneous Fenton process in our previous study;²⁷ due to Fe-OC formed by ferric ions and aliphatic by-products of dye degradation in the solution.³⁷ According to the findings of Parkhomchuk *et al.*³⁰ and results presented in Fig. 5(b), the significant leveling off in the mineralization curve of FeY/H₂O₂ process can be attributed to the formation of Fe-OC, including both leached and surface ferric ions. Since Fe-OC are not resistant to UV illumination and by their destruction the Fenton catalytic cycle is retrieved, the UV/FeY/H₂O₂ process yielded significantly higher mineralization in the

same time points compared to the corresponding dark process (Fig. 5(b)). Besides degradation over the above-mentioned mechanisms, the contribution of adsorption of organic compounds of suitable size should be considered in overall TOC removal. According to our previous findings²⁰ as well as other authors,¹⁹ Y-type zeolite has the ability to adsorb benzene-based structured compounds, i.e. benzene ring substituted with one or more small functional groups. Therefore, it can be assumed that compounds of such structure formed as by-products of RB137 degradation could be adsorbed into FeY zeolite micropores. This is confirmed by the results of TOC removal by the UV/FeY process (Fig. 5(b)). On the basis of the decolorization results (Fig. 5(a) and Table 4), it can be expected that UV/FeY would yield the lowest TOC removal. However, TOC removals achieved during the entire observed period of 60 min were significantly higher than those obtained by UV/Fe³⁺ and UV processes, presumably due to the significant contribution of adsorption mechanism, yielding TOC removal values 28.0 %, 20.2 % and 5.9 % at the end of the treatment in the cases of UV/FeY, UV/Fe³⁺ and UV processes respectively. On the other hand, according to the theory of OH radical generation in the processes using Fe-exchanged zeolites in the presence of H₂O₂,¹³ the minor role of the adsorption in overall TOC removal by UV/FeY/H₂O₂ process is expected. Thus, OH radicals are generated at the zeolite surface where Fe ions are incorporated, and if any organic compounds are adsorbed, its immediate degradation by nearby generated OH radicals is assumed. Similar IR spectra recorded for FeY catalyst before and after treatment by UV/FeY/H₂O₂ (Fig. 6) corrobo-

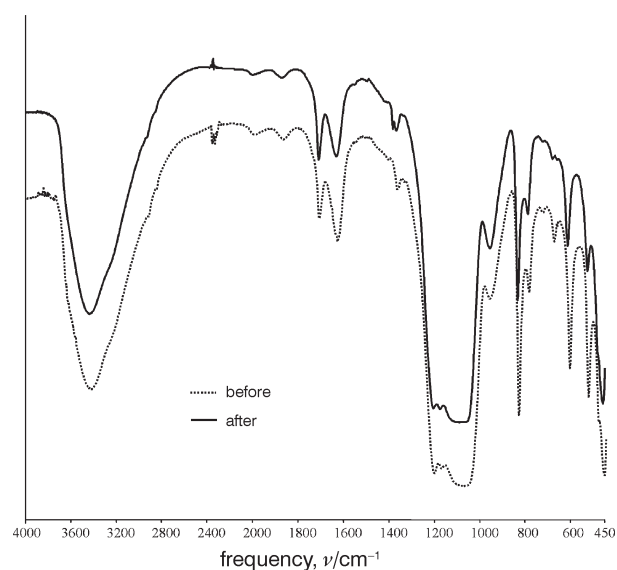


Fig. 6 – IR spectrograms of applied heterogeneous Fenton catalyst FeY before and after treatment of RB137 model wastewater by UV/FeY/H₂O₂ process ([Fe] = 1 mmol L⁻¹, [H₂O₂] = 10 mmol L⁻¹, FeY dosage γ = 3.22 g L⁻¹, pH 6, t = 60 min)

rate this assumption since the adsorbed organics would result with the appearance of new spectral bands. Therefore, TOC removal obtained by the UV/FeY/H₂O₂ process is attributed only or at least predominantly to the mineralization of the organic content of RB137 model wastewater. According to the results presented in Fig. 5 indicating that direct photolysis of RB137 plays a minor role in the presence of FeY catalyst in used amount, it can be assumed that mineralization of organics occurred only through OH radical-based mechanism. In the UV/FeY/H₂O₂ process OH radicals are generated by (i) Fenton reactions, and to some extent by the photolysis of (ii) H₂O₂ and (iii) Fe(OH)²⁺. However, it seems that mechanisms (ii) and (iii) play a minor role due to the diminished transparency of the solution, and the low amount of Fe ions placed at outer zeolite surface. It can be concluded that in the studied UV/FeY/H₂O₂ system, the Fenton mechanism strongly dominates. In the first stage of treatment all Fe ions incorporated in the zeolite framework can be involved, while in the later stage of the process only ferric ions recovered from those captured in Fe-OC can participate in OH radical generation.

The results in Fig. 7, presenting the profiles of H₂O₂ consumption during the treatment of model wastewater by heterogeneous dark- and photo-Fenton type processes, support the above conclusion. It can be noticed that, although leveling off in the mineralization process occurred in the dark due to the inhibition of Fenton catalytic cycle by formed Fe-OC, H₂O₂ was consumed throughout treatment time. A plausible explanation can be found in the side reactions typical for AOPs^{24,26} involving reactions be-

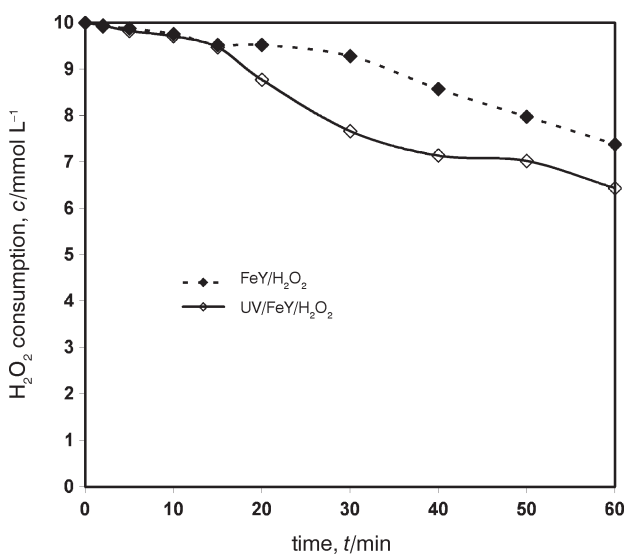


Fig. 7 – Profiles of H₂O₂ consumption during treatment of RB137 solution by FeY/H₂O₂ and UV/FeY/H₂O₂ ([Fe] = 1 mmol L⁻¹, [H₂O₂] = 10 mmol L⁻¹, FeY dosage γ = 3.22 g L⁻¹, pH 3 for dark-process and pH 5 for photo-process)

tween H₂O₂ and other radical and ionic species formed in the system. The same side reactions can be considered in the photo Fenton type process as well, while the consumption of H₂O₂ in the photo-process is still significantly higher than in the dark-process. This difference in H₂O₂ consumed could be mostly due to its involvement in the Fenton reactions with ferric ions recovered from Fe-OC as well as due to its continual photolysis, eq. (4).

To evaluate the stability of the catalyst, recycling experiments of UV/FeY/H₂O₂ process were carried out and the results presented in Fig. 8. For each new cycle, the catalyst was removed from the reaction solution by filtration, extensively washed with deionized water, dried at 50 °C overnight, and re-used under the same experimental conditions. No decrease in decolorization efficiency was observed during four one-hour cycles. From the results presented in Fig. 8, the decrease in activity of reused FeY catalyst in terms of TOC removal can be observed within 40 min of the UV/FeY/H₂O₂ process. However, as treatment progressed, similar mineralization extents were obtained by the end of each cycle: 1st cycle 75.4 %, 2nd cycle 73.2 %, 3rd cycle 72.5 % and 4th cycle 72.4 %. Relatively small iron loss, ranging from 0.01 to 0.0186 mmol L⁻¹, was observed in subsequent catalytic cycles corresponding to 5.5 % of total iron lost in 4 h. The retained activity in consecutive runs and a relatively low iron loss indicate the stability of FeY under experimental studied conditions. It can be concluded that Fe-exchanged zeolite has good potential to be applied as a heterogeneous catalyst in both dark- and photo-Fenton type processes. However, the results presented in Fig. 5 indicate similar or somewhat

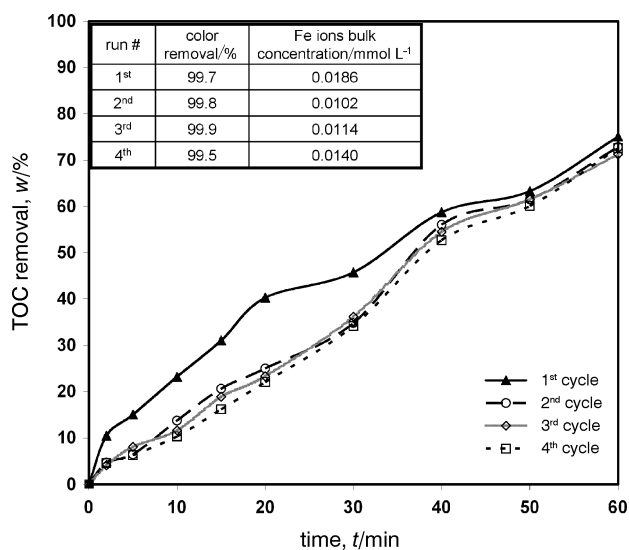


Fig. 8 – Effect of consecutive experiments with the FeY catalyst on the degradation of RB137 model wastewater solution by UV/FeY/H₂O₂ process (γ (RB137) = 20 mg L⁻¹, [Fe] = 1 mmol L⁻¹, [H₂O₂] = 10 mmol L⁻¹, FeY dosage 3.22 g L⁻¹)

lower efficiency of UV/FeY/H₂O₂ in comparison to UV/H₂O₂ process. It seems that the presence of suspended solid particles negatively influenced the overall process efficiency, presumably due to the decreased transparency of the solution, and prevailed over expected catalytic benefit of FeY under applied experimental conditions. When UV-assisted processes for dye wastewater treatment are considered, initial dye concentration may be a crucial factor limiting the process efficiency. Dyes are characterized by high molar extinction coefficients. A rise in initial dye mass concentration induces an inert filter effect so the solution becomes increasingly impermeable to UV irradiation.³⁹ As a consequence, in the UV/H₂O₂ process, hydrogen peroxide can then only be irradiated by smaller portions of UV light. As the rate of photolysis of H₂O₂ directly depends on the fraction of incident light absorbed by H₂O₂ molecules, the HO• formation rate slows down. Consequently, decolorization and mineralization rates of dye should decrease, too. We assumed that the combined UV/FeY/H₂O₂ process would be less sensitive to the changes of initial dye mass concentration, providing an advantage over the UV/H₂O₂ process. In order to verify this assumption, the UV/H₂O₂ and UV/FeY/H₂O₂ processes were applied for treatment of model wastewater containing 200 mg L⁻¹ of RB137, which is 10 times higher than it was in the previous experiments (Fig. 5). The results are presented in Fig. 9. It can be seen that UV/FeY/H₂O₂ is almost twice as efficient than the UV/H₂O₂ process in terms of decolorization extents achieved after 60 min of treatment; 72.52 % > 40.02 %. Even a greater difference was obtained in terms of TOC removals: 8.94 % > 1.18 % (Fig. 9), presumably due to the suppressed

photolysis of H₂O₂ at high initial dye concentration and the catalytic activity of FeY. In the case of the UV/FeY/H₂O₂ process, calculated pseudo-first order decolorization and mineralization rate coefficients are 2.34 and 7.86 times higher, respectively, than in the case of the UV/H₂O₂ process. These results clearly speak in favor of the advantage of UV/FeY/H₂O₂ process application over UV/H₂O₂ process, especially when treatment of dye wastewaters with variable loading is considered. It can be assumed that the problem of decreased transparency due to the usage of catalyst in suspension can be overcome by using immobilized FeY catalyst which should be a subject of future study.

Conclusion

This study aimed to investigate the potential of Fe-exchanged zeolites of Y-type as a catalyst in heterogeneous Fenton-type processes for the degradation of model organic pollutant, reactive azo-dye C.I. Reactive Blue 137, in water. The influence of various process variables, such as FeY catalyst dosage, Fenton reagent ratio and initial operating pH, on the efficiency of the treatment process was evaluated. The performance of the studied heterogeneous process was compared with corresponding homogeneous Fenton-type processes, and the influence of UV light on both heterogeneous and homogeneous processes was investigated as well.

The results of FeY catalyst characterization indicate that the iron content is mainly built into the inner zeolite micropores providing the benefit to zeolite stability and activity of the catalyst. Overall process efficiency was estimated based on the decolorization and mineralization degree of RB137 model wastewater. From the obtained results, it was concluded that Fe-exchanged zeolite has potential for successful application as a catalyst in both dark- and photo-Fenton type processes. Although homogeneous and heterogeneous Fenton processes yielded similar decolorization and mineralization, the concentration of Fe ions in the bulk after treatment was significantly lower in the latter case. That is particularly pronounced in the UV/FeY/H₂O₂ process where only 1.86 % of the total iron content added was recorded in the bulk after treatment. In such a manner, the possible secondary pollution with Fe-containing sludge was minimized, as well the unnecessary loading of treated wastewater by counter ions like in the case when using Fe-salts is avoided. The usage of heterogeneous catalyst allowed the UV-assisted Fenton process to be operated at milder pH conditions, pH 5, while for the dark heterogeneous process the most suitable pH proved to be pH 3. The stability test performed

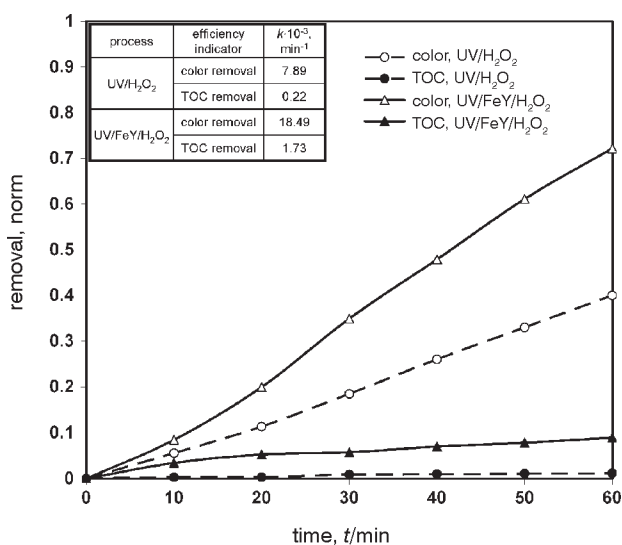


Fig. 9 – Head-to-head comparison of UV/FeY/H₂O₂ and UV/H₂O₂ processes for the treatment of model dye solution containing 200 mg L⁻¹ of RB137 ([Fe] = 1 mmol L⁻¹, [H₂O₂] = 10 mmol L⁻¹, FeY dosage γ = 3.22 g L⁻¹)

throughout several consecutive UV/FeY/H₂O₂ runs indicated rather good stability of the FeY catalyst.

Although the results of the study indicate to some extent that the UV/FeY/H₂O₂ is less or equally efficient as the UV/H₂O₂ process, we have shown that this could be valid only when treating wastewater containing lower dye concentrations where the decreased solution transparency, due to the suspended catalyst, present a disadvantage for the UV/FeY/H₂O₂ process. In the case of higher dye concentration in wastewater where photolysis of H₂O₂ is suppressed, the catalytic effect of FeY clearly speaks in favor of applying the UV/FeY/H₂O₂ process. Additionally, we strongly believe that the problem of decreased transparency due to the use of catalyst in suspension can be overcome by using immobilized FeY catalyst which should be a subject of future study.

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