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Fenton type processes for minimization of organic content in coloured wastewaters. Part II: Combination with zeolites

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Abstract

The addition of solid particles, namely synthetic zeolites NH_4ZSM5 and HY, was investigated in order to enhance the efficiency of AOPs for dye wastewater treatment. Experiments were conducted at the optimal operating parameters for each Fenton type process and studied coloured pollutants established in Part I of this study in order to find the optimal dose of applied zeolites and understand their role in the new combined AOPs. Degradation of the studied dyes, C.I. Reactive Blue 49 and C.I. Reactive Blue 137, was monitored by means of the UV/VIS, TOC and AOX analysis, thus determining decolourization and mineralization extents of model solutions. Organic content adsorbed onto applied zeolites after the treatment was scanned and characterized using FT-IR spectrophotometer. Applied AOPs in combination with zeolites were shown to be very successful in colour removal, >98%, similarly like Fenton type processes reported in Part I of this study, while improvements in the mineralization of the studied dyes depended on the type and the dose of zeolite, as well as on dye structure and the type of applied AOP.

Keywords: Coloured wastewater; Reactive Blue 49; Reactive Blue 137; Fenton process; Fenton “like” process; Zeolite

1. Introduction

Coloured wastewaters from dye production and application industries pose a serious threat for the environment owing to the recalcitrant nature of the dyes. Many conventional wastewater treatment methods are often inappropriate for such pollutants due to their inability to effectively remove and degrade persistent synthetic dyes [1–5]. Wastewater treatment methods based on the OH radical attack to the organic pollutants (AOPs), especially Fenton type processes, seem to offer promise due to their high efficiency for dye degradation [2–9], relatively low cost and the ease of process operation and maintenance [2]. Through the combination of AOPs with traditional wastewater treatment methods, for example adsorption [10,11] or biodegradation [12], the overall process efficiency could be enhanced.

In our previous work, solid particles were used to enhance the efficiency of coloured wastewater treatment by chosen AOPs, including Fenton type processes [13–16]. Synthetic zeolites, the solid particles used in the present study, are three-dimensional, microporous, crystalline solids with well-defined structures that contain aluminium, silica, and oxygen in a regular framework. Zeolites possess void pore space that can host cations, water or other molecules; they have the ability to act as catalysts for chemical reactions that take place within these internal cavities. Furthermore, synthetic zeolites may act as ion exchangers, because the loosely bound nature of the extra-framework metal ions permits the exchange of other types of metals when in aqueous solution. The shape-selective properties of zeolites are also the basis for their use in molecular adsorption [17–19]; in this context, zeolites have been described for use in coloured wastewater treatment, mainly as adsorbents [20–23]. There are examples of the utilization of synthetic zeolites for the degradation of organic compounds in combination with TiO_2, as photocatalyst, in processes involving UV radiation [24–26]. Furthermore, several authors have used Fe-exchanged zeolites in the presence

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of oxidants (i.e. H_2O_2) for organic pollutant degradation including reactive dyes [27–29].

The aim of this work was to improve the efficiency of organic dye degradation by the Fenton type processes investigated in Part I of this study [30], by the addition of solid particles, namely zeolites NH_4ZSM5 and HY. The influence of the zeolites on dye degradation in a model wastewater was monitored in order to find the optimal dosage of zeolite, whereby reaching maximal mineralization extent (i.e. highest process efficiency), and to understand the role of the applied zeolites in new combined AOPs.

2. Experimental

Experiments of model dye wastewater treatment were conducted using the optimal operating parameters established in Part I of this study [30], according to the described procedure for applied Fenton type processes. The two reactive dyes, C.I. Reactive Blue 49 (RB49) and C.I. Reactive Blue 137 (RB137), described earlier [30] were used as model pollutants. The synthetic zeolites, NH_4ZSM5 and HY, were supplied by Zeolyst International [19] and were used as received. Different amounts of zeolites (0.2, 0.4, 0.6, 0.8 and 1.0 $g\,l^{-1}$) were used. A Perkin Elmer Lambda EZ 201 UV/VIS spectrophotometer was used for monitoring decolourization, while the extent of mineralization of RB49 and RB137 was determined on the basis of total organic carbon content (TOC) measurements, performed using a Shimadzu TOC-V_{CPN} 500A Total Organic Carbon analyzer and absorbable organic halides (AOX) were determined using a Dohrmann DX-2000 Organic Halide analyzer. Samples were centrifuged before analysis in order to remove solid particles of zeolites from solution. A Perkin Elmer Spectrum One FT-IR spectrophotometer was used for the scanning the zeolites at the end of the treatment in the range 4000–400 cm^{-1}. Samples of dried zeolites were mixed with KBr in order to prepare pellets according to the standard procedure [31].

3. Results and discussion

Investigations were directed to enhance efficiency of Fenton and Fenton "like" processes for degradation of RB49 and RB137 by the addition of NH_4ZSM5 and HY zeolites, and to determine their optimal dose. Decolourization of model dye solutions by Fenton type processes in combination with zeolites was very successful, with over 98% being achieved in all cases (Tables 1–3), regardless of dye and zeolite type and dose. It should be emphasized that control experiments with the addition of applied zeolites to RB49 and RB137 solutions without Fenton's reagent, showed no changes in the UV/VIS spectra of the dye solutions after 2 h of treatment, showing that the adsorption of dye molecules onto the zeolites does not play a role in the decolourization process. This was also confirmed by the comparison of the FT-IR spectra of the zeolites before and after treatment, where no changes were observed. Taking into account that the decolourization efficiency of Fenton type processes for RB49 and RB137 model solutions was rather high (>95%) [30] and that the residual dye concentration in the treated water was below the visibility limit even without zeolite addition [32], it can be concluded that applied zeolites do not significantly influence decolourization efficiency.

Table 1
Decolourization of model dye solutions by Fenton processes: RB49, $Fe^{2+}/H_2O_2 = 1{:}20$, $c(Fe^{2+}) = 0.5$ mM at pH 3 and RB137, $Fe^{2+}/H_2O_2 = 1{:}30$, $c(Fe^{2+}) = 0.5$ mM at pH 3

Zeolite dose ($g\,l^{-1}$)		0.2	0.4	0.6	0.8	1.0
RB49						
Colour removal (%)	NH_4ZSM5	100.00	99.73	98.91	98.91	98.56
	HY	99.73	99.65	99.05	99.11	98.78
RB137						
Colour removal (%)	NH_4ZSM5	100.00	99.87	98.98	98.56	99.87
	HY	99.89	99.68	100.00	100.00	99.85

The extent of mineralization of RB49 imparted by the Fenton process with the addition of different amounts of both studied zeolites, expressed as TOC removal, is presented in Fig. 1. It can be seen that the addition of NH_4ZSM5 zeolite positively affected degradation efficiency at lower doses; the addition of 0.2 $g\,l^{-1}$ and 0.4 $g\,l^{-1}$ NH_4ZSM5 to the Fenton process increased TOC removal from 72.1 to 75.3% and 79.1%, respectively. Further increase of the zeolite dosage lowered degradation efficiency in comparison to the Fenton process without the addition of zeolite. Fig. 1 also reveals a negative effect of the HY zeolite on the degradation efficiency of RB 49. Mineralization extents ranged between 29 and 42.4%, which was 30–40% lower compared to that achieved using the Fenton process without zeolite. However, it should be noted that, as in the case of the NH_4ZSM5 zeolite, better results were obtained using a lower HY dosage. In contrast, the addition of both zeolites to the Fenton process in the case of the degradation of RB137 increased the extent of mineralization in the range 3–13%, depending on the type and dose of zeolite (Fig. 2). Best results of 45.4 and 47.7% of TOC removal were obtained by the addition of 0.8 $g\,l^{-1}$ NH_4ZSM5 and 0.4 $g\,l^{-1}$ HY zeolite, respectively; the efficiency of mineralization decreased with further increase of zeolite, but the mineralization of RB137 achieved was still higher than in the case without zeolite addition.

Table 2
Decolourization of model dye solutions by Fenton "like" processes: RB49, $Fe^{3+}/H_2O_2 = 1{:}10$, $c(Fe^{3+}) = 0.5$ mM at pH 3 and RB137, $Fe^{3+}/H_2O_2 = 1{:}40$, $c(Fe^{3+}) = 0.5$ mM at pH 3

Zeolite dose ($g\,l^{-1}$)		0.2	0.4	0.6	0.8	1.0
RB49						
Colour removal (%)	NH_4ZSM5	99.71	98.53	98.71	98.61	98.96
	HY	99.00	99.65	99.00	99.17	98.85
RB137						
Colour removal (%)	NH_4ZSM5	99.07	98.09	98.17	98.11	98.27
	HY	99.59	98.78	99.14	99.00	98.78

Table 3
Decolourization of model dye solutions by Fenton "like" processes: RB49, $Fe^0/H_2O_2 = 1:20$, $c(Fe^0) = 0.5$ mM at pH 3 and RB137, $Fe^0/H_2O_2 = 1:20$, $c(Fe^0) = 1.0$ mM at pH 3

Zeolite dose ($g\,l^{-1}$)		0.2	0.4	0.6	0.8	1.0
RB49						
Colour removal	NH_4ZSM5	100.00	100.00	99.61	99.69	99.96
(%)	HY	100.00	99.95	99.09	98.17	99.87
RB137						
Colour removal	NH_4ZSM5	100.00	99.18	99.11	98.91	98.21
(%)	HY	100.00	99.78	99.14	99.09	98.71

Similar to the Fenton process, in the case of the Fenton "like" process, Fe^{3+}/H_2O_2, a negative effect on the degradation efficiency of RB49 model solution was observed (Fig. 3) in the case of the HY zeolite. Without zeolite addition, 45.3% of TOC was removed, whereas in the case of the addition of the HY zeolite, maximal TOC removal was 39.0%. In contrast, in the presence of zeolite, the extent of mineralization was increased; the addition of $0.2\,g\,l^{-1}$ NH_4ZSM5 zeolite increased TOC removal to 76.9%. It should be noted that the effectiveness of the Fenton "like" process, Fe^{3+}/H_2O_2, without zeolite in the case of the degradation of RB49 was significantly lower in comparison to the Fenton process (45.3 and 72.1% TOC removal, respectively), but the addition of NH_4ZSM5 enhanced the extent of mineralization of the model solution to the same level, namely >75% TOC removal. In Fig. 4 a comparison of RB137 mineralization by Fe^{3+}/H_2O_2 process with and without the addition of the NH_4ZSM5 and HY zeolites is presented. Again, a positive effect was observed by the addition of both zeolites on the Fe^{3+}/H_2O_2 process efficiency. Mineralization extents of RB137 model solutions were 5–17% higher than in the case without zeolite addition. Somewhat better results were obtained using the HY zeolite; a maximum of 62.6% TOC removal was obtained for an HY dose of $1.0\,g\,l^{-1}$. From Figs. 1–4, the degradation efficiency for both RB49 and RB137 using the Fe^{2+}/H_2O_2 and Fe^{3+}/H_2O_2 processes with the addition of the NH_4ZSM5 and HY zeolites is presented, some similarity in the behaviour of studied systems could be observed. The utilization of the NH_4ZSM5 zeolite in both Fe^{2+}/H_2O_2 and Fe^{3+}/H_2O_2 processes increased the extent of mineralization of RB49, whilst a negative influence was observed in the case of the HY zeolite. This different behaviour of the two zeolites can be contributed to their different structures. NH_4ZSM5 has a pentasyl structure that is characterized by parallel channels with pore sizes of 5.3–5.6 Å and with crossed channels of pore size 5.1–5.5 Å, whereas the HY zeolite has a basic cubic structure of pore size 7.4 Å [33]. By analogy with the findings of Kawai and Tsutsumi [34] that a phenol molecule, which has a benzene ring of 6.8 Å diameter, was able to be adsorbed within the micropores of the ZSM5 zeolite due to the

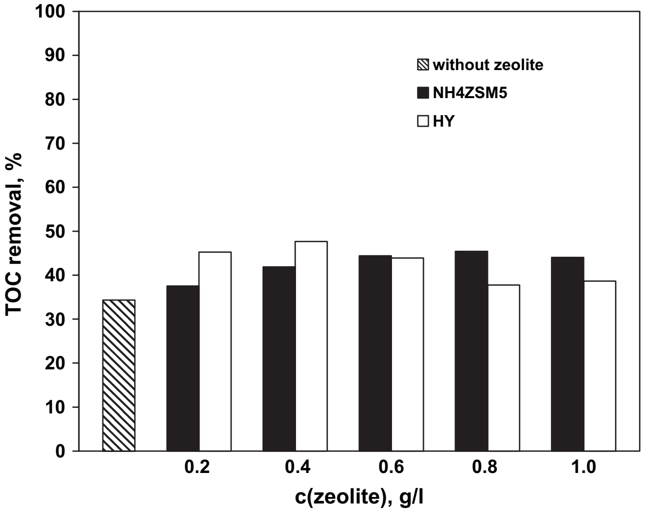

Fig. 2. Influence of type and dose of zeolite on Fenton process, Fe^{2+}/H_2O_2, at optimal operating conditions for the mineralization of RB137.

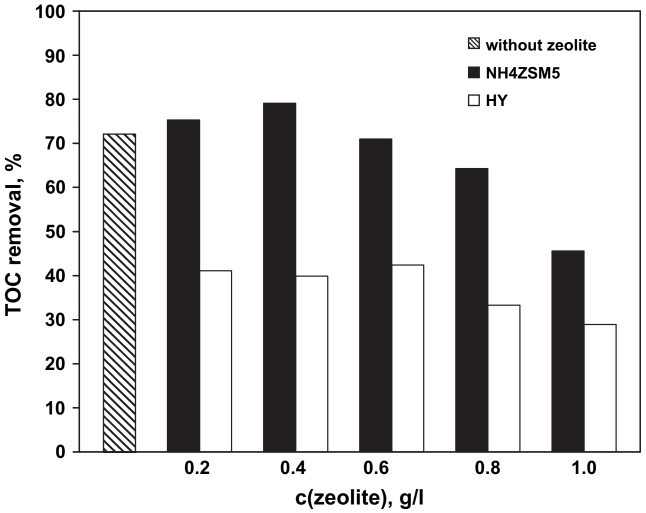

Fig. 1. Influence of type and dose of zeolite on Fenton process, Fe^{2+}/H_2O_2, at optimal operating conditions for the mineralization of RB49.

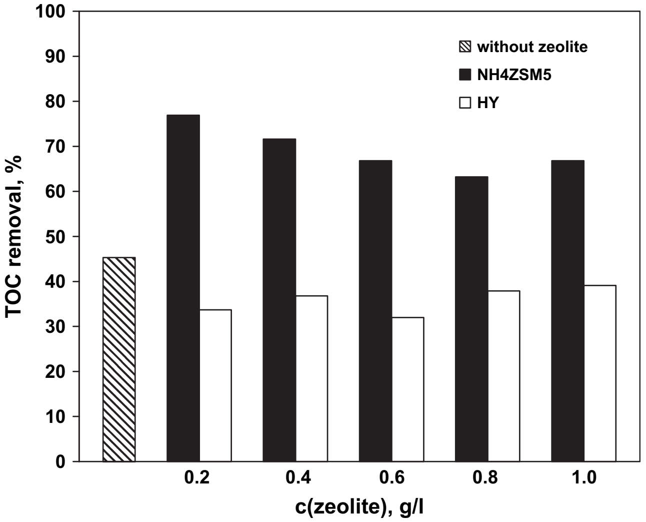

Fig. 3. Influence of type and dose of zeolite on Fenton "like" process, Fe^{3+}/H_2O_2, at optimal operating conditions for the mineralization of RB49.

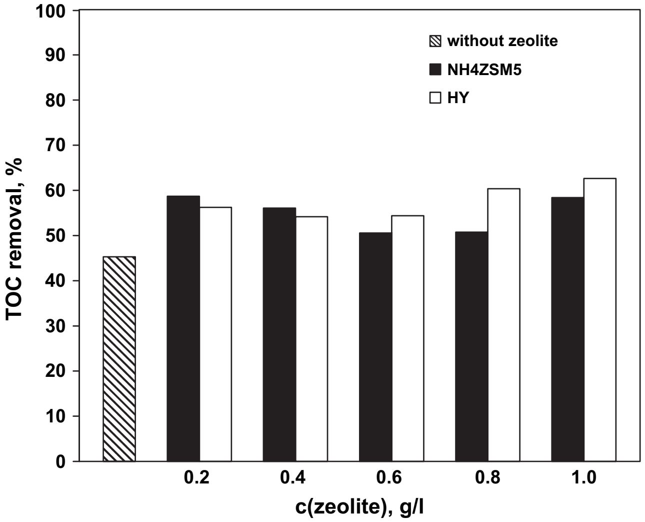

Fig. 4. Influence of type and dose of zeolite on Fenton "like" process, Fe^{3+}/H_2O_2, at optimal operating conditions for the mineralization of RB137.

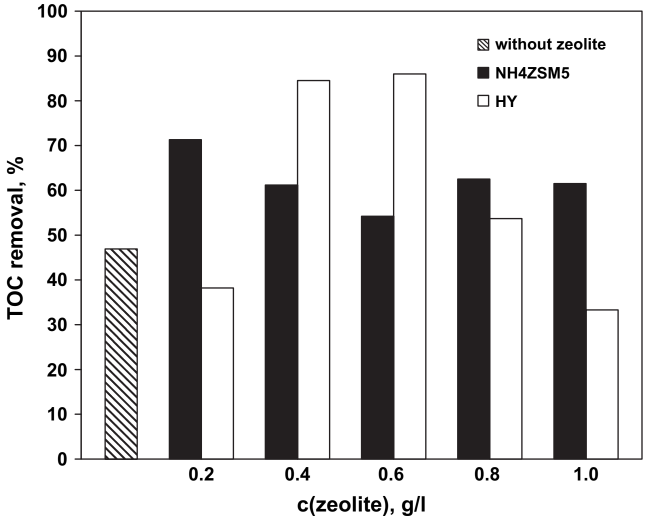

Fig. 5. Influence of type and dose of zeolite on Fenton "like" process, Fe^0/H_2O_2, at optimal operating conditions for the mineralization of RB49.

flexibility of the phenol molecule as well as due to the thermal motion of the pore openings of the zeolite, it can be proposed that some of the oxidation products which were formed during the degradation of RB49 by the Fe^{2+}/H_2O_2 and Fe^{3+}/H_2O_2 processes were small "benzene-ring-based" structures capable of being adsorbed onto the surface of the NH_4ZSM5 zeolite as well as being able to penetrate the NH_4ZSM5 zeolite pores. Although, similar or even better results could be expected in the case of HY zeolite due to its larger pores, its observed lower effectiveness of RB49 degradation suggests that a more complex phenomenon is in operation and that the other mechanisms apart from geometrical constraints prevail. The process efficiency of AOPs for oxidative degradation of organics directly depends on the concentration of the reactive species. Therefore, presumably, a lower concentration of radical species necessary for dye degradation (i.e. quenching radical species) by the zeolite could be a plausible explanation for such an effect [16].

The different findings in this work for the different zeolites and their interaction with organic compounds agree with previous work reported in the literature. In a study of the catalytic nitration of toluene with zeolite catalysts, Smith [35] obtained a very low yield using the ZSM5 zeolite, suggesting that little of the reaction occurred inside the pores, while the HY zeolite produced a yield of over 99%; this indicated that *ortho* and *para*-substituted benzenes have the ability to diffuse inside the HY zeolite. In contrast, Kusic et al. [36], reported that the ZSM5 zeolite has the ability to adsorb smaller organic molecules of similar structure such as phenol, with an efficiency of 33%, whereas the HY zeolite displayed only 7% efficiency to adsorb the same organic pollutant.

For the RB137 model solution treated using the Fe^{2+}/H_2O_2 and Fe^{3+}/H_2O_2 processes with zeolite addition, similar behaviour was observed for both types of zeolites. Both zeolites positively affected the degradation efficiency of this azo reactive dye, enhancing the extent of mineralization by approximately 10–40%, in the cases of both the Fe^{2+}/H_2O_2 and Fe^{3+}/H_2O_2 processes. Feng et al. [37] proposed degradation mechanism for an azo dye with a structure similar to RB137 that included the formation of mono- and di-substituted benzenes and naphthols. Therefore, it can be assumed that similar byproducts formed during degradation of RB137 by both the Fe^{2+}/H_2O_2 and Fe^{3+}/H_2O_2 processes and that these had the ability to diffuse inside the pores of both types of zeolites. However, the different effects of the same type of zeolite in the cases of RB49 and RB137 could be attributed to the different molecular structure of the two dyes; namely, different byproducts being formed during degradation by hydroxyl radicals due to different degradation process for the two dyes [37,38].

In Fig. 5 the influence of both the type and dosage of the zeolites on RB49 mineralization extents obtained using the Fe^0/H_2O_2 process is presented. By the utilization of the NH_4ZSM5 zeolite, RB49 degradation efficiency was improved

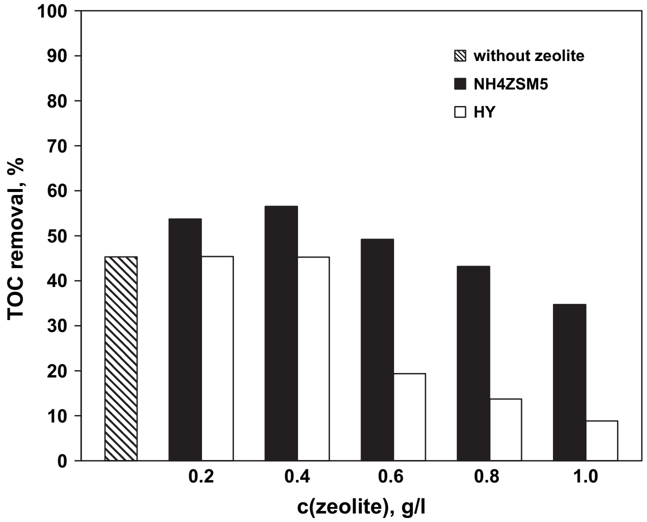

Fig. 6. Influence of type and dose of zeolite on Fenton "like" process, Fe^0/H_2O_2, at optimal operating conditions for the mineralization of RB137.

over the complete investigated range of zeolite dosage. Mineralization of RB49 using the $Fe^0/H_2O_2/NH_4ZSM5$ system was in the range of 54.2–71.3% depending on the amount of added zeolite NH_4ZSM5. By the addition of the HY zeolite to the Fenton "like" process with iron powder notably higher mineralization of RB49 was achieved. The initial TOC for RB49 decreased to 86.0% for the $Fe^0/H_2O_2/HY$ system ($\gamma(HY) = 0.6\ g\,l^{-1}$), which is an improvement over TOC removal results reported in the literature [39,40] for Fenton type processes for the degradation of organic pollutants from coloured wastewater. Hsueh et al. [39] investigated the mineralization of one acid and two reactive azo dyes and reported that TOC removal obtained after 2 h of treatment by a Fenton process ranged between 11 and 22%. The highest TOC removal obtained by Ferrero [40] in a study of the oxidative degradation of dyes and surfactant was approximately 50% after 90 min of treatment by a Fenton process. As previously reported in Part I of this study [30], the presence of solid particles can promote the oxidative degradation of organic compounds by AOPs. Taking into account the results obtained for the degradation of RB49 by the $Fe^{2+}/H_2O_2/HY$ and $Fe^{3+}/H_2O_2/HY$ processes, where a negative influence of HY was observed, it can be concluded that the degradation mechanism of RB49 by the Fenton type process, which utilizes iron powder, takes different pathways and, consequently different degradation products are produced, presumably due to the reactions on the iron powder surface. Therefore, the distinctly high mineralization extent achieved for RB49 using the $Fe^0/H_2O_2/HY$ process in comparison to all other systems can be attributed to the synergistic effect of the two different types of solid particles, iron powder and HY zeolite.

The influence of the zeolite on the Fe^0/H_2O_2 process for the degradation of RB137 is presented in Fig. 6. A slight enhancement of mineralization was observed for the addition of small doses of the NH_4ZSM5 zeolite to the Fe^0/H_2O_2 process; maximal TOC removal, 56.5%, was achieved using $0.4\ g\,l^{-1}$ of NH_4ZSM5 which was 11.2% higher than in the case without zeolite. On the other hand, the addition of the HY zeolite had little effect or even a negative effect on the extent of mineralization obtained for the Fe^0/H_2O_2 process. However, in both cases, after the maximum removal was achieved, further addition of zeolite led to a decrease in degradation efficiency. The observed negative influence of larger dose of zeolite on the mineralization of RB137 can be attributed to the capture of radical species in the zeolite pores [16]. Furthermore, the observed decrease in mineralization efficiency by an increase in the dose of added zeolite can be explained by the selective adsorption of only certain byproducts as well as radical species of appropriate size and geometrical structure for diffusion in the zeolite pores. Again, different behaviour of the zeolites and type of reactive dye was observed. In the case of the degradation of RB49, zeolite HY was more suitable, while NH_4ZSM5 improved the degradation of RB137 by the Fe^0/H_2O_2 process. These results indicate different degradation mechanism for the two types of reactive dyes, anthraquinone and azo, which will produce byproducts of different geometrical constraints regarding the investigated type of zeolite, thus supporting the earlier observations that the chemical structure

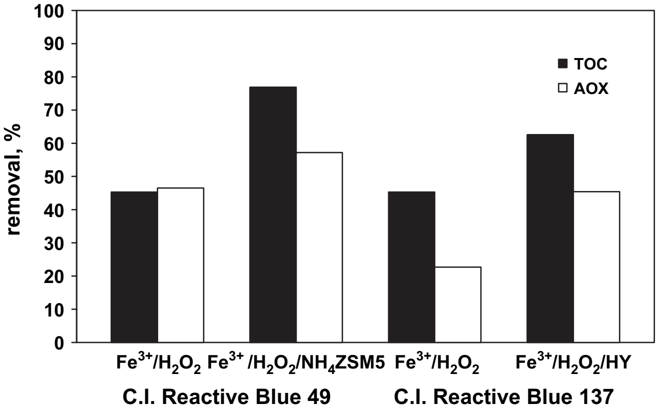

Fig. 8. Comparison of efficiency of Fenton "like" process, Fe^{3+}/H_2O_2, at the optimal operating parameters with and without the addition of zeolites for RB49 and RB137 degradation according to TOC and AOX removal.

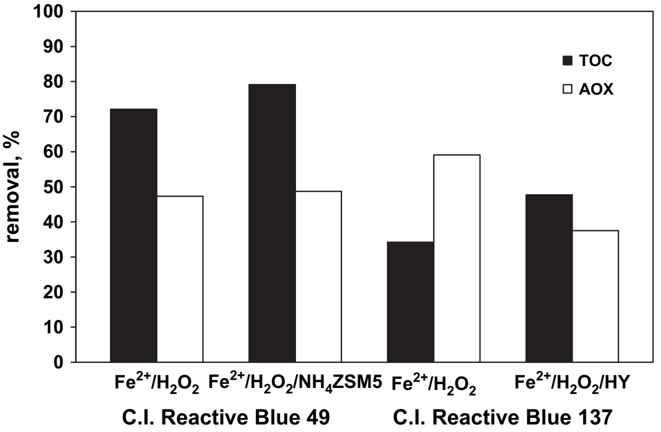

Fig. 7. Comparison of efficiency of Fenton process, Fe^{2+}/H_2O_2, at the optimal operating parameters with and without the addition of zeolites for RB49 and RB137 degradation according to TOC and AOX removal.

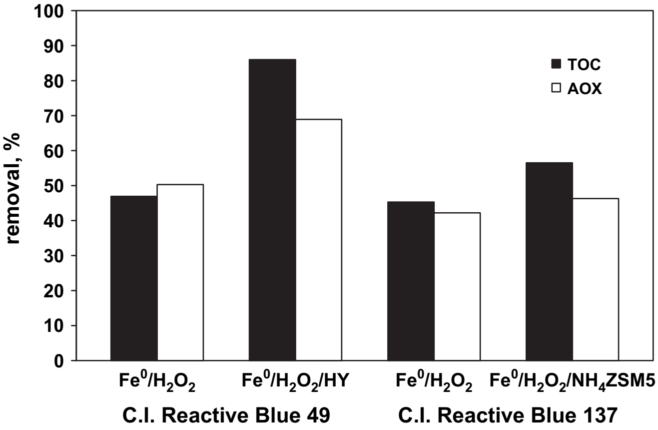

Fig. 9. Comparison of efficiency of Fenton "like" process, Fe^0/H_2O_2, at the optimal operating parameters with and without the addition of zeolites for RB49 and RB137 degradation according to TOC and AOX removal.

of the organic pollutant plays an important role in AOP system behaviour.

In Fig. 7 a comparison of highest mineralization extents, expressed as TOC and AOX removal, of RB49 and RB137 achieved using the Fenton process with and without the addition of zeolites is presented. The overall organic carbon is expressed by the TOC value, while degradation of the reactive anchor (the triazine ring) in the dye molecule can be measured by a decrease of AOX (i.e. concentration of adsorbable organic halide). It can be seen that in the case of RB49, degradation by the Fenton process in the presence of added zeolite NH_4ZSM5 effected only the TOC removal, while the AOX removal stayed the same as in the case with no added zeolite. On the other hand, the addition of the HY zeolite to the Fenton process for RB137 degradation increased TOC removal but at the same time AOX removal was reduced. These results indicate that the presence of HY zeolite leads to the formation of RB137 degradation byproducts that are significantly more susceptible to OH radicals attack than the triazine ring, and presumably are able to diffuse into the zeolite pores, thus suppressing degradation of the reactive part of the dye molecule. The comparison of maximum mineralization for RB49 and RB137 obtained using the Fenton "like" processes, Fe^{3+}/H_2O_2 and Fe^0/H_2O_2 with those obtained by zeolite addition are summarized in Figs. 8 and 9, respectively. For both dyes, improvements in TOC as well as in AOX removal were observed in the case of zeolite addition, leading to the conclusion that in such cases, oxidative degradation of the dyes progresses evenly in the chromophoric and in the reactive part of dye molecule.

Of all the systems studied, best results for degradation of RB49 and RB137 were obtained using Fe^0/H_2O_2/HY and Fe^{3+}/H_2O_2/HY, respectively. In Fig. 10 the IR spectrograms of the two dyes, RB49 (a) and RB137 (b), are presented, whereas the comparison of the IR spectrograms of the untreated HY zeolite and the same zeolite after the treatment of RB49 using the Fe^0/H_2O_2/HY system (a) and RB137 using the Fe^{3+}/H_2O_2/HY system (b) is summarized in Fig. 11. On the basis of the IR spectrograms, the identities of the adsorbed organic compounds cannot be determined with 100% certainty, but the appearance of new characteristic bands indicates the role of HY zeolite in the degradation of RB49 and RB137 using the Fe^0/H_2O_2/HY (a) and Fe^{3+}/H_2O_2/HY (b) systems, respectively. The FT-IR absorption spectra of RB49 and RB137 (Fig. 10(a) and (b)), reveal that the observed TOC and AOX decreases were not caused by dye molecule adsorption. The HY zeolite is characterized by Si–OH vibrations at 3444 cm^{-1}, vibrations of HY acid centres at 1637 cm^{-1} and T–O–T (T = Al, Si) asymmetric stretching vibrations at 1000–1100 cm^{-1}. The presence of symmetric T–O–T (T = Al, Si) stretching vibrations at 600–791 cm^{-1} is also evident; the range from 500 cm^{-1} is characteristic of the silica ring. In the FT-IR absorption spectra of zeolite HY after the treatment of RB49 and RB137 by the Fe^0/H_2O_2/HY (a) and Fe^{3+}/H_2O_2/HY (b) systems, respectively (Fig. 11), the presence of new absorption bands as a consequence of dye degradation can be observed. The characteristic absorption for isocyanurates at 1709 cm^{-1} can be attributed to byproducts formed by degradation of the triazine ring in the reactive dye. Absorbance appearance at 1365–1368 cm^{-1} is characteristic for several organic molecules such as imines, imides, iminocarbonates and sulphoamides [41,42]; these structures are also the possible degradation intermediates of both RB49 and RB137 [37,38].

4. Conclusions

The influence of the type and dose of added zeolites on the efficiency of the Fenton and Fenton type processes for dye degradation was studied and evaluated on the basis of TOC measurements. The optimal dose and type of zeolite for each process were established. Decolourization of both

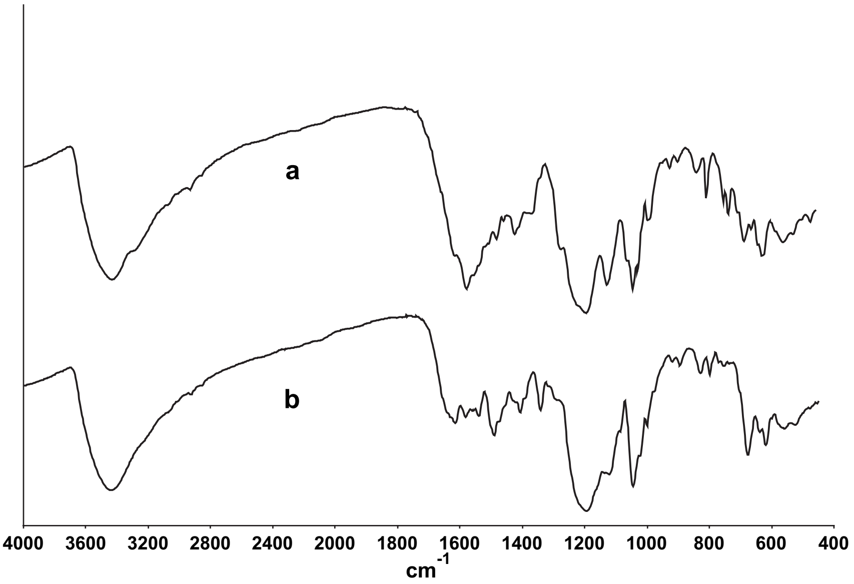

Fig. 10. FT-IR absorption spectra of RB49 (a) and RB137 (b) dyes.

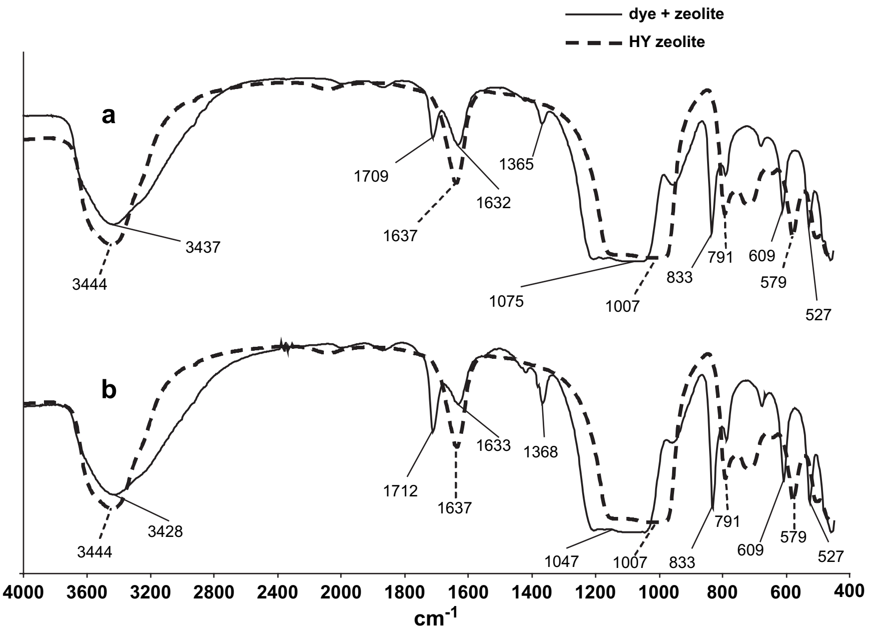

Fig. 11. FT-IR absorption spectra of RB49 (a) and RB137 (b) dyes after the treatment by $Fe^0/H_2O_2/HY$ and $Fe^{3+}/H_2O_2/HY$ systems, respectively.

RB49 and RB137 model solutions was rapid and high, even without zeolite addition, and this parameter was not changed by zeolite addition, with almost complete bleaching (>98%) being obtained after a few minutes. Again, only partial mineralization of RB49 and RB137 was obtained. The enhancement of mineralization of both dyes by the Fenton type process with the addition of zeolites depended on the type and dose of the added zeolites. Maximum mineralization of RB49 (86.0% of TOC removal) was achieved using the $Fe^0/H_2O_2/HY$ system, while AOX removal was enhanced from 50.3 to 68.9%. The highest TOC removal for RB137 (62.6%) was obtained using the $Fe^{3+}/H_2O_2/HY$ system, this being an enhancement of 38.0% in comparison to the same case without zeolites; AOX removal was improved from 22.7 to 45.4%. FT-IR analysis of the zeolites after treatment showed the appearance of new peaks that the generation of organic molecules formed by degradation of the parent dye molecule. These results indicate that the molecular structure of the dyes plays a significant role in the oxidation mechanism of the Fenton type processes.

Acknowledgments

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