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PHOTOCATALYTIC EFFICIENCIES OF ALTERNATE HETEROGENEOUS CATALYSTS: IRON MODIFIED MINERALS AND SEMICONDUCTORS FOR REMOVAL OF AN AZO DYE FROM SOLUTIONS

Photocatalytic degradation of reactive dye solutions have been compared using two types of heterogeneous catalysts, i.e., semiconductors and iron modified clays. Decolorization and mineralization efficiencies of the catalysts were performed in a slurry batch reactor with UVA and UVC (365 and 254 nm, respectively) light sources using reactive azo dye solutions. Two natural minerals (zeolites and beidellites) modified with Fe^{3+} , Fe^{2+} and semiconductors (TiO_2 -P25 and ZnO) were used as photocatalysts. Iron modified minerals produced similar results compared to homogeneous photo-Fenton reactions under UVC radiation. Fe^{2+} -beidellite and Fe^{3+} -zeolite showed the best efficiency for dye removal with 98.5% at 75 min and 96.3% at 90 min, respectively, which is higher than the other iron modified minerals under UVA radiation. ZnO and TiO_2 exhibited initial dye removal rates under UVA as 98.9% and 95.5% at 45 min, respectively. Mineralization efficiencies for TiO_2 , ZnO and Fe^{2+} -beidellite, Fe^{3+} -zeolite under UVA were 86.2%, 74.5% and 76.9%, 67.8%, respectively. However mineral catalysts performed 99% dye removal rates within 15 min with respect to semiconductor catalyst values (over 97% within 45min) under UVC radiation. Mineral catalysts and TiO_2 provided higher initial TOC removal rates as 92% in 60 min under UVC radiation.

1. INTRODUCTION

Textile industries produce large amounts of wastewater owing to high consumption of water primarily in the washing, dyeing, and finishing operations [1]. Textile dyes and other industrial dyestuffs constitute one of the widest groups of organic compounds in colored wastewaters. These complex dye effluents create serious environmental pollution problems and they can cause hazardous byproducts through oxidation or other chemical reactions taking place in the receiving media [2].

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In recent studies, advanced treatment systems have been developed other than conventional wastewater treatment processes. These are mainly Fenton and Fenton-like processes, ozonation, photochemical and electrochemical treatment, semiconductor photocatalysis, wet oxidation and various combinations of these methods [3–6]. These processes primarily associate the generation of a highly effective and non-selective oxidizing agents, i.e., hydroxyl (OH^\bullet), superoxide (O_2^\bullet), and hydroperoxyl (HO_2^\bullet) radicals as well as ionized water ($\text{H}_2\text{O}^\bullet$) for the destruction of dangerous and hazardous pollutants found in wastewaters.

Homogeneous photo-Fenton processes have been successfully used in the removal of several types of organic pollutants. Production of eco-friendly end product is a special feature of these processes. However, they produce essential amount of sludge containing Fe ions at the end of wastewater treatment. In order to overcome this drawback and reuse of Fe ion capacity continuously, heterogeneous photo-Fenton or photo-Fenton like processes were introduced by modifying iron ions onto porous solids as a heterogeneous catalyst. After such modification iron remains mainly in the solid phase as either exchanged or adsorbed ions. For these processes, major reactions occur at the solid–liquid interface [7–11].

Heterogeneous photocatalysis using semiconductors is one of the encouraging advanced oxidation processes. Due to its high photocatalytic activity, semiconductor-assisted photocatalysis have been found to be an effective process for the elimination of contaminants in wastewaters [12–14]. Among several semiconductors, TiO_2 and ZnO are known as good photocatalysts for the degradation of several environmental pollutants [15, 16] owing to their high photosensitivity, stability and large band gap. Great number of toxic chemicals such as recalcitrant dyes, phenols, pesticides, persistent organic chemicals can be degraded by this process.

Various clay minerals including clinoptilolite from zeolite group and beidellite from smectite group have been used as heterogeneous catalysts in photo-Fenton reactions. Zeolites are naturally occurring hydrated aluminosilicate minerals belonging to the class of minerals called tectosilicates [17]. Clinoptilolite with a simplified formula $(\text{Na},\text{K})_6\text{Si}_{30}\text{Al}_6\text{O}_{72} \cdot n\text{H}_2\text{O}$ is the most abundant natural zeolite characterized by relatively large, intersecting open channels of ten- and eight-membered tetrahedral rings [18]. The net negative charge of zeolite is balanced by the exchangeable cation (e.g., Na^+ , K^+ , Ca^{2+}). Beidellite with a simplified formula $\text{Na}_{0.7}\text{Al}_4(\text{Si}_{7.3}\text{Al}_{0.7})\text{O}_{20}(\text{OH})_4 \cdot x\text{H}_2\text{O}$ is also a clay mineral of the smectite family, which is distinguished by layered structures composed of polymeric sheets of SiO_4 tetrahedra linked to sheets of $(\text{Al}, \text{Mg}, \text{Fe})(\text{O}, \text{OH})_6$ octahedral. Beidellite has more ordered distribution of pillars in the interlayer space making a higher thermal stability and a much stronger acidity [19].

Photoactivation by irradiation is usually used in the near UV range, yielding hole (h^+)/electron (e^-) pairs that react directly with substrate on the catalyst surface or give hydroxyl radicals by reaction with water. In some cases, the attendance of different chemical oxidants (e.g., H_2O_2 , O_3) improves the treatment efficiency [3–6]. UVC emitting

light sources are generally used as a UV radiation source. However, the relative spectral distribution of the solar radiation can be given as follows: 7% UVA, 1.5% UVB and 0.5% UVC, noting that UVC radiation does not reach the Earth surface [20]. Therefore UVA radiation is preferred due to its availability in sunlight and economic evaluation.

Several recent investigations [7–11] have reported successful removal of wide range of organics from aqueous solutions applying heterogeneous photo-Fenton processes. Some researchers [7, 9, 21] have synthesized bentonite and laponite clay-based Fe nanocomposites used as heterogeneous nanocatalysts for the photo-Fenton discoloration and mineralization in the presence of UVC light and H_2O_2 . Leon et al. [8] and Kusic et al. [22] investigated the use of heterogeneous Fenton type catalyst to remove organic pollution under UVC radiation.

Photocatalytic properties of semiconductor nanoparticles are useful in the removal of organic contaminants [4, 5]. Most studies [12–16] focused on large bandgap semiconductor oxides such as TiO_2 and ZnO whose photoexcitation with UV light supplies electron–hole pairs initiating the production of hydroxyl radicals in aqueous solutions. Yassitepe et al. [14] prepared ZnO plates for photocatalytic degradation of textile dyes in aqueous solutions. Konstantinou et al. [6] studied the photocatalytic decolorization and degradation of an azo dye in aqueous solution with TiO_2 -P25 as photocatalyst in slurry form using UVA radiation (365 nm).

Topkaya et al. [16] also successfully investigated photocatalytic degradation of an azo dye, pesticide and antibiotic solutions under UVA and UVC radiation with pure ZnO and composite ZnO/TiO_2 catalyst plates. In this study, photocatalytic degradation (decolorization and mineralization) of reactive dye solutions were investigated using two types of heterogeneous catalysts, i.e. semiconductors (TiO_2 and ZnO) and iron modified clays (zeolite and beidellite). In the first stage, heterogeneous photo-Fenton type reactions were carried out, and in the second stage semiconductor photocatalysts were investigated. The results were used to compare the efficiency of the catalysts under the same reactor conditions using actinic lamps as UVA sources. An evaluation was also performed using UVC radiation source.

2. EXPERIMENTAL

Materials. Reactive azo dye Remazol Brilliant Red F3B (C.I. Reactive Red 180) was provided by the DyStar and used without purification. The structure of this reactive azo dye is presented in Fig. 1. It is one of the mostly used commercial dyestuffs in textile industry. H_2O_2 solution (30 wt. %) was of analytical grade and purchased from Merck. Natural zeolite and beidellite samples were obtained from the Bigadiç and Black Sea regions of Turkey, respectively. TiO_2 -P25 was obtained from the Degussa and ZnO was supplied from the Sigma-Aldrich. The main characteristics of the zeolite [18] and

beidellite [19] have been presented elsewhere. Deionised water was used throughout the experiments. All experiments were carried out at the original pH of dye solutions.

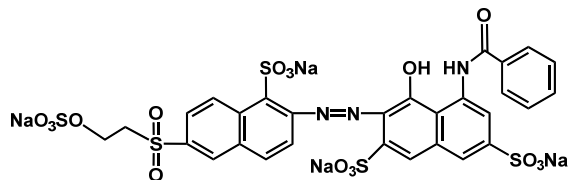


Fig. 1. Chemical structure of the dye

Preparation of mineral catalysts. Natural beidellite and zeolite samples were grounded in a laboratory type ball mill and washed with distilled water in order to remove surface dust. Selected 180–425 μm sized natural clay minerals were modified with Fe^{3+} and Fe^{2+} ion solutions as follows: 10 g of clay and 100 cm^3 of 0.02 mol/dm^3 $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and 0.02 mol/dm^3 $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ solutions were mixed and shaken at 175 rpm for 1 h at 60 °C. The samples were washed with deionised water and dried at room temperature. The experiment was repeated six times to increase the ion exchange capacity. Fe^{3+} and Fe^{2+} modified zeolite and beidellite catalysts were symbolized as $\text{Fe}^{2+}\text{-Z}$; $\text{Fe}^{3+}\text{-Z}$ and $\text{Fe}^{2+}\text{-B}$; $\text{Fe}^{3+}\text{-B}$, respectively.

Iron ion concentration in solutions was measured by the atomic absorption spectroscopy (AAS) method (Perkin Elmer, 1100) and the content of exchanged iron ions adsorbed on clays (q) was calculated using the following equation

$$q = \frac{(C_0 - C)V}{m} \quad (1)$$

where q is the final amount of iron ions adsorbed on clay (mg/g), C_0 and C are the initial and final Fe^{3+} , Fe^{2+} concentrations in solution (mg/dm^3), respectively, m is the weight of clay used (g), V is the volume of solution (dm^3). The results are given in Table 1.

Table 1

Amount of iron exchanged on clays (q)

Loading time [h]	mg Fe^{3+}/g of zeolite	mg Fe^{3+}/g of beidellite	mg Fe^{2+}/g of zeolite	mg Fe^{2+}/g of beidellite
1	7.0	9.6	4.1	9.7
2	15.2	18.8	7.2	18.0
3	22.0	26.8	10.2	26.1
4	28.2	35.0	12.5	33.9
5	32.5	43.2	14.6	42.2
6	37.0	51.4	16.6	50.4

Photochemical reactor. Experimental studies were carried out in a batch 500 cm³ laboratory-scale quartz photoreactor (Fig. 2). The reactor assembly was surrounded by six UVA (Philips Actinic BL 8W) and/or UVC (Philips TUV 8W FAM) type lamps which predominantly emit radiation at 365 and 254 nm, respectively. Light intensity of the lamps was 3.5 and 3.2 mW/cm² for UVA and UVC, respectively. Measurements were carried out by a UV light meter (Lutron UVA-365, UVC-254), as it was described elsewhere [23].

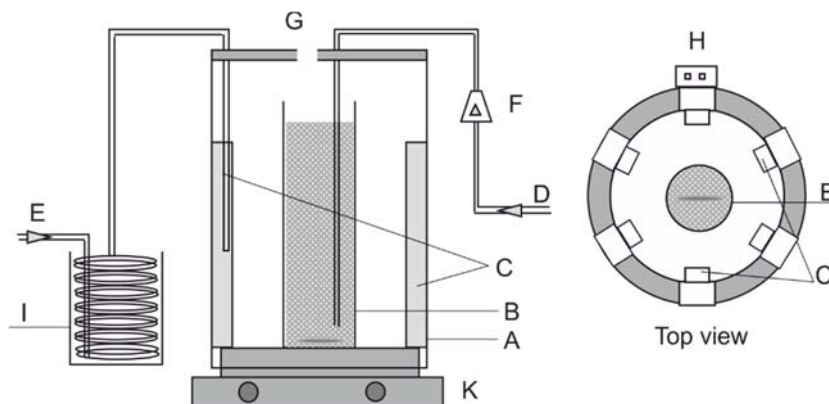


Fig. 2. Reactor used in the experiments: A – lamp assembly, B – quartz batch reactor, C – UV lamps, D and E – air inlet, F – flowmeter, G – sampling point, H – switches for power supply, I – ice bath, K – stirrer

Chemical analyses. Samplings were performed at 15 min intervals and the catalyst particles were removed by centrifuging. The color removal of dye solutions was analyzed by measuring the absorbance with a photometer (Hach-Lange DR 3200) at λ_{\max} of 520 nm. TOC measurements were carried out using a Hach-Lange IL 550 TOC analyzer. All experiments were performed in triplicates.

Process parameters. The effects of temperature, initial pH, H₂O₂ dosage, catalyst loading, initial dye concentrations, light intensity and TOC removal with iron modified catalysts were previously investigated using reactive orange 16 dye solutions and the optimum conditions were determined [23]. Reactive Red 180 and Reactive Orange 16 belong to the same class reactive dyes, Reactive Red 180 has a larger molecule and a higher molecular weight. Degradation of the dye solutions in the presence of hydrogen peroxide was performed at optimum conditions as previously reported (i.e. 35 °C, initial dye concentration of 100 mg/dm³, original pH of the dye solution of 5.2, 15 mmol/dm³ H₂O₂ dosage, 1 g/dm³ catalyst loading) The degradation with semiconductors was performed at 25 °C, original pH of the solution, and 1 g/dm³ of the catalyst loading. All experiments were carried out using 500 cm³ of the dye solution of 100 mg/dm³ initial concentration.

3. RESULTS AND DISCUSSION

3.1. THE EFFECT OF MINERAL AND IRON ION TYPE

The best efficiencies for color removal were initially obtained for Fe^{2+} -B after 75 min (98.5%) and Fe^{3+} -Z catalysts after 90 min (96.3%). All catalysts showed similar color removal efficiencies at the end of the reaction time (120 min) (Fig. 3).

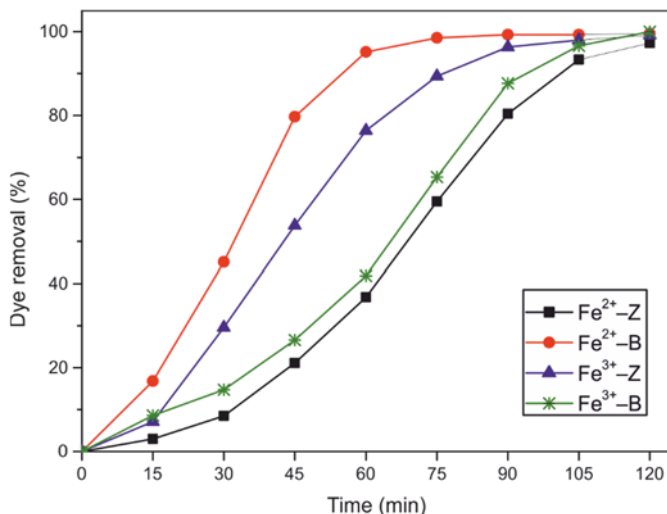


Fig. 3. Dye removal for mineral and iron ion type catalysts; pH 5.2, 35 °C, 1.0 g/dm³ of the catalyst, 15 mmol H₂O₂/dm³, UVA nd 100 mg/dm³ initial dye concentration

Both Fe^{3+} and Fe^{2+} amounts adsorbed on beidellite were approximately 50 mg/g after 6 h (Table 1). Zeolite indicated higher capacity for Fe^{3+} (37.0 mg/g) compared to Fe^{2+} (16.6 mg/g) after 6 h. Therefore, the removal rate was achieved higher for Fe^{3+} -Z than for Fe^{2+} -Z. On the other hand, Fe^{2+} -B catalysts yielded better rates than Fe^{3+} -B, overall beidellite revealed better rates than zeolite. The activation energies and apparent rate constants of Fenton and Fenton like reactions were compared by Garrido-Ramírez et al. [11]. It was found that Fe^{2+} rather than Fe^{3+} effectively initiated the hydroxyl radical formation. However, the photo-reduction of Fe^{3+} to Fe^{2+} through the use of ultraviolet radiation improved the catalytic reaction with the generation of more radicals. Additionally, Fenton-like reactions effectively utilized photo-reduction and generation of more radicals as heterogeneous catalysis [24, 25].

3.2. HOMOGENOUS AND HETEROGENEOUS REACTIONS OF THE FENTON CATALYSTS

Despite using 1 g/dm³ of Fe exchanged catalyst, the same amount of Fe ions (Table 1), as $\text{Fe}(\text{NO}_3)_3$ or FeSO_4 was added into the solution to perform homogenous Fenton reactions under similar conditions (35 °C, pH 5.2, 15 mmol H₂O₂/dm³). Homogeneous and

heterogeneous photo-Fenton oxidation efficiencies were compared with respect to the dye removal rates with two best catalyst performances (Fig. 4).

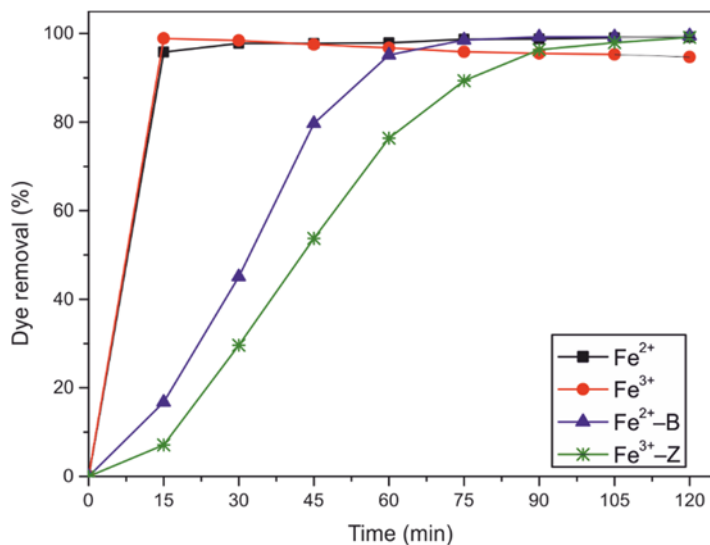


Fig. 4. Efficiencies of homogeneous and heterogeneous photo-Fenton oxidation: pH 5.2, 35 °C, 1.0 g/dm³ of the catalyst, 15 mmol H₂O₂/dm³, UVA and 100 mg/dm³ initial dye concentration

The reason for high removal rates after 15 min for homogeneous reactions were mainly freely available Fe ions in the solution. However, heterogeneous reactions reached that performance after 90 min. The results show that the catalyst pore structure and interface reactions mainly occur at the catalyst surface [23, 26]. On the other hand, remaining iron ions in the solutions causing color interference with the dye absorbance was negligible. The sludge containing Fe ions has been reported to be a substantial problem for such processes [2, 8, 10, 26].

3.3. MINERAL AND SEMICONDUCTOR CATALYST EFFICIENCIES

Performances of two mineral catalysts were compared with those of ZnO and TiO₂ semiconductor catalysts [4, 5, 12, 13] under UVA radiation. The results indicated that dye removal was efficiently achieved for all type of catalysts after 90 min (Fig. 5). ZnO and TiO₂ showed similar tendency and dye removal efficiencies were 98.9% and 95.5% after 45 min, respectively. Fe²⁺-B presented better dye removal efficiency than Fe³⁺-Z at the initial stages. For Fe²⁺-B, 95.2% removal efficiency was obtained after 60 min whereas for Fe³⁺-Z 96.3% removal efficiency was noted after 90 min. All semiconductor catalysts displayed faster dye removal reactions in comparison with other mineral catalysts.

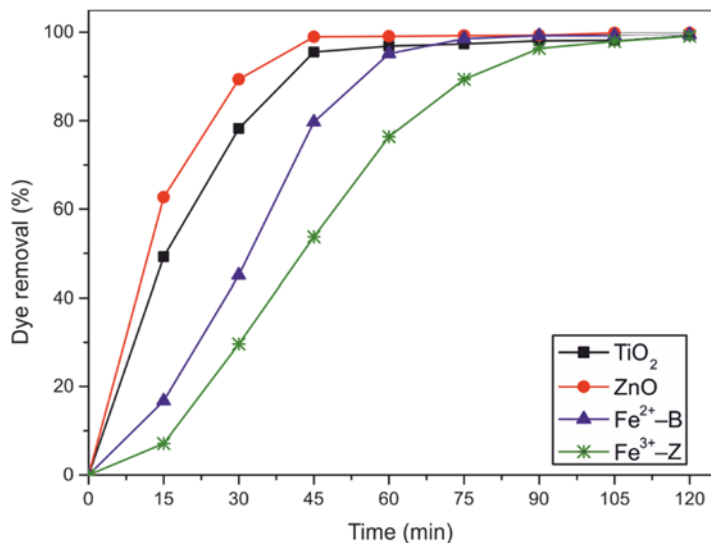


Fig. 5. Efficiencies of mineral and semiconductor photocatalytic oxidation: pH 5.2, 35 °C, 1.0 g/dm³ of the catalyst, and 100 mg/dm³ initial dye concentration

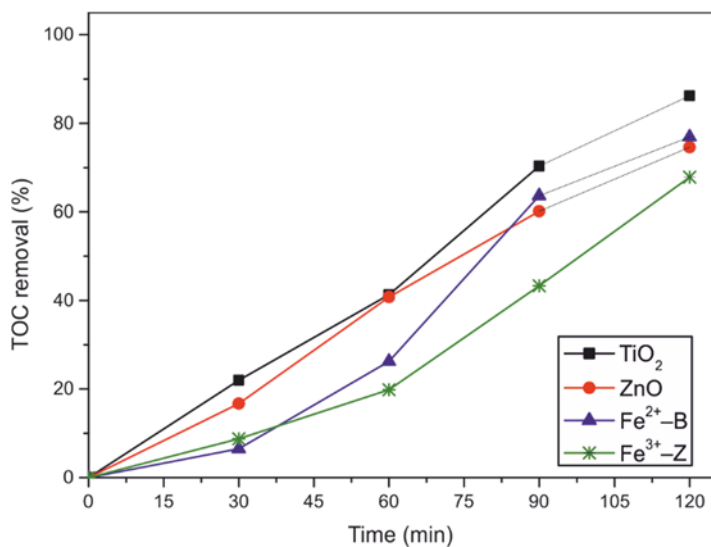


Fig. 6. Mineralization efficiencies of semiconductor and mineral catalysts under UVA radiation: pH 5.2, 35 °C, 1.0 g/dm³ of the catalyst, and 100 mg/dm³ initial dye concentration

In Figure 6, mineralization efficiency as TOC values for mineral and semiconductor photocatalytic oxidation were compared. Similarly as for the dye removal reaction times, higher initial rates were noted when semiconductor catalysts were used. TiO₂

showed better mineralization efficiency than ZnO. Mineralization efficiencies for TiO₂, ZnO and Fe²⁺-B, Fe³⁺-Z were 86.2%, 74.5% and 76.9%, 67.8%, respectively.

Similar trends for TiO₂ and ZnO efficiencies were also obtained by other authors [13, 15, 27]. ZnO showed higher color removal efficiency but TiO₂ performed better mineralization efficiency for dye solutions. It seemed that the adsorption capacity of TiO₂ was higher than for ZnO [15]. In addition, mineralization efficiency of Fe²⁺-B was higher than that of ZnO. The photo-Fenton process of Fe²⁺-B catalyst was more effective than that of ZnO photocatalysis under UVA (Fig. 6).

Mineralization efficiencies are slower than dye degradation. When initial degradation stages of the dye molecules, the azo dye structure is broken and the color disappears. However TOC values indicate the available carbon content in the solution and the removal of TOC progresses at the final stage of the reaction as mineralization and it takes longer time.

3.4. EFFECT OF LIGHT WAVELENGTH

Effects of the light wavelength on the catalysts were also evaluated using UVC and UVA radiation type lamps. Initially, as shown in Fig. 4, homogeneous and heterogeneous photo-Fenton dye removal efficiencies with the use of mineral catalysts were performed using UVA lamps. Dye removal with the mineral catalysts instantaneously occurred as homogenous reactions under UVC radiation (Table 2). Contrary to UVA irradiation, homogeneous and heterogeneous reaction efficiencies showed similar behavior. This finding complies with the results of other authors that higher energy of UVC radiation was more effective than that of UVA radiation [7–9, 21, 22]. Small differences in the results of homogenous catalysis can be attributed to color interference of iron ions in the solutions at the dye absorption wavelength which can be regarded as one of the disadvantages of the method.

Table 2

Efficiencies [%] of homogeneous and heterogeneous photo-Fenton oxidation for dye removal under UVC irradiation

Time [min]	Fe ³⁺ -Z	Fe ²⁺ -B	Fe ²⁺	Fe ³⁺
15	98.9	99.7	93.3	97.0
30	98.9	99.9	98.0	95.9

Before comparing the efficiencies of mineral and semiconductor catalysis under UVC radiation, semiconductor powder catalysts were tested and assessed with different radiation sources (Fig. 7). The results indicate that semiconductor catalysts produced similar results with respect to dye removal efficiencies. However, it should be pointed

out that TiO_2 showed better performance under UVC radiation in TOC removal (Fig. 7b), as reported by Akyol et al. [15].

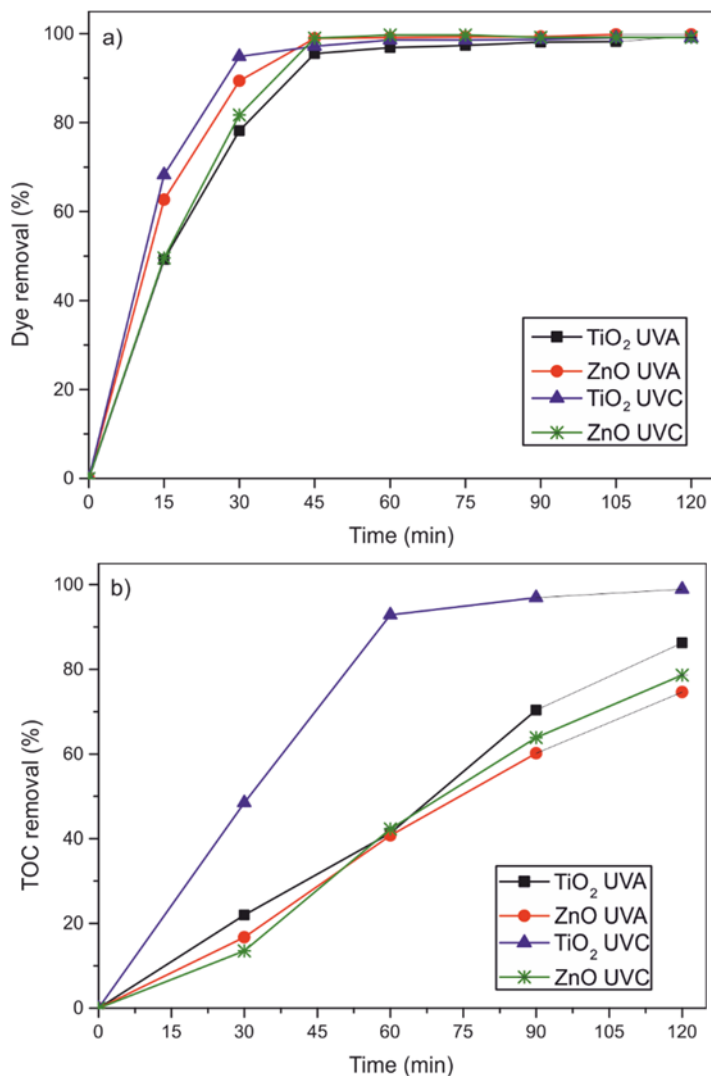


Fig. 7. Dye (a) and TOC (b) removal efficiencies of semiconductor catalysts with various light sources: pH 5.2, 25 °C, 1.0 g/dm³ of the catalyst, 100 mg/dm³ initial dye concentration

Under UVC radiation (Fig. 8a), mineral catalysts produced higher dye removal rates in to comparison to those under UVA radiation. Mineral catalysts showed similar trend and dye removal was accomplished after 15 min for Fe^{2+} -B (99.7%) and Fe^{3+} -Z (98.9%).

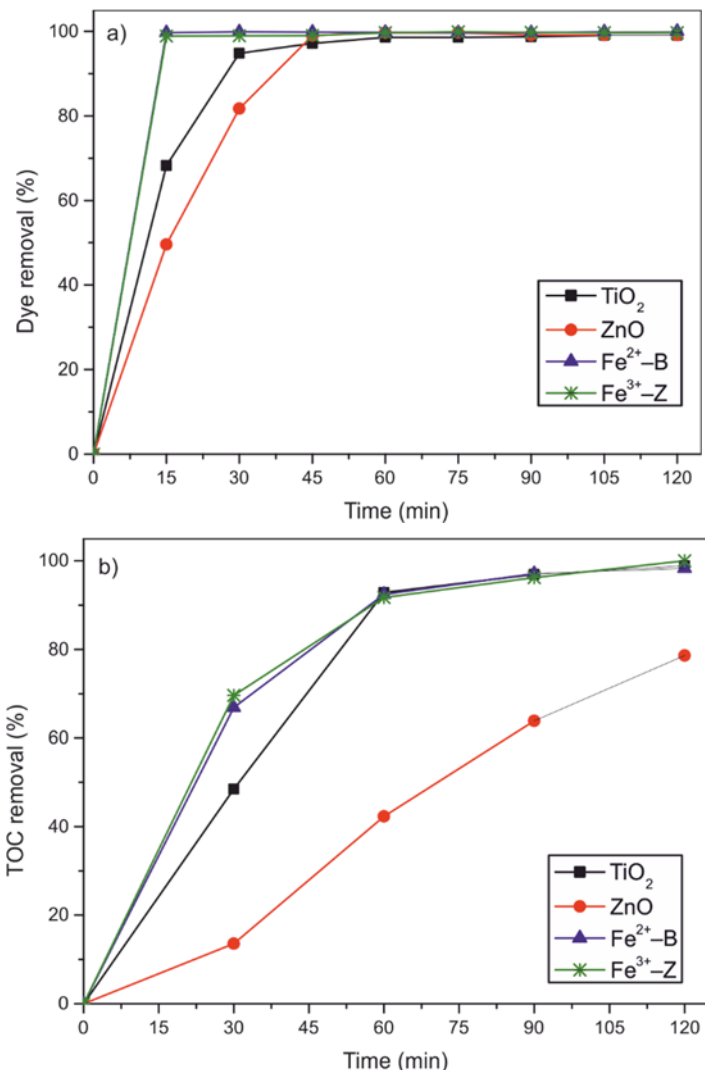


Fig. 8. Dye (a) and TOC (b) removal efficiencies of semiconductor and mineral catalysts under UVC radiation: pH 5.2, 1.0 g/dm^3 of the catalyst, and 100 mg/dm^3 initial dye concentration

On the other hand, the rates of semiconductor catalysis were lower at initial stages and during the reaction, 97.2% and 98.9% dye removal after 45 min was achieved for TiO_2 and ZnO , respectively. The TOC results (Fig. 8b) indicated that mineral catalysts gave shorter removal times under UVC than under UVA. Mineral catalysts performed

the same behavior and reached approximately 92% mineralization after 60 min. similarly TiO₂ followed the same trend with mineral catalysts in contrast to ZnO under UVC radiation.

4. CONCLUSIONS

Zeolite (Z) and beidellite (B) were modified with Fe²⁺ and Fe³⁺ ions and evaluated in terms of catalyst efficiency for heterogeneous photo-Fenton oxidation. Fe²⁺-B and Fe³⁺-Z produced higher dye removal initial rates (98.5% with Fe²⁺-B after 75 min and 96.3% with Fe³⁺-Z after 90 min) than Fe³⁺-B and Fe²⁺-Z under UVA radiation. In comparison to homogenous photo-Fenton reactions, mineral catalysts were found similarly effective under UVA radiation. Heterogeneous mineral catalysts displayed lower initial dye removal rates under UVA radiation.

ZnO and TiO₂ catalysts resulted in 98.9% and 95.5% dye removal rates after 45 min and TOC 86.2%, 74.5% removal rates as after 90 min, respectively, under UVA radiation. Mineralization efficiencies for Fe²⁺-B and Fe³⁺-Z under UVA were 76.9% and 67.8%, respectively. Semiconductor catalysts displayed higher dye and TOC removal rates than mineral catalysts under UVA radiation. TiO₂ and ZnO produced similar dye removal rates under UVC radiation, but TiO₂ was initially faster than ZnO. Mineralization efficiency of TiO₂ was 92% like mineral catalysts, but 80% for ZnO under UVC radiation. In other words, semiconductor catalysts produced similar dye removal rates under either UVA or UVC radiation, but TiO₂ gave a significantly higher TOC removal rate than ZnO under UVC radiation. On the other hand, mineral catalysts performed much better under UVC radiation in both dye and TOC removal rates, and TiO₂ followed the same trend in TOC results.

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