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APPLICATION OF SEVERAL ADVANCED OXIDATION PROCESSES FOR THE DESTRUCTION OF ORGANICS IN EFFLUENTS OF PTA PRODUCTION

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ABSTRACT

In this study, the efficiency of several advanced oxidation processes such as ultrasonic oxidation, heterogeneous Fenton-like oxidation, ultrasound or UV assisted heterogeneous Fenton-like oxidation, heterogeneous sonophotoFenton oxidation and oxidation with ultrasound+UV light combination was tested for COD reduction in effluents of purified terephthalic acid (PTA) production. The highest COD removal was achieved as 18% when UV light assisted heterogeneous Fenton-like oxidation was applied to PTA manufacturing wastewater in the presence of 5 wt% iron containing TiO_2 catalyst. This combined advanced oxidation process seems to be a promising one to enhance the COD removal when it is used after biological treatment.

Keywords: Advanced oxidation processes, Purified terephthalic acid, Degradation

1. INTRODUCTION

The manufacturing process for purified terephthalic acid (PTA) generates liquid effluent streams containing p-toluic acid, 4-carboxybenzaldehyde, terephthalic acid (TPA), benzoic acid, phthalic acid in addition to acetic acid. TPA has a particular interest. Because it is toxic and acts as endrocrine disruptor.

TPA is widely applied as a raw material in making polyester fiber, polyethylene terephthalet bottles, polyester films etc. These five aromatic compounds make up 75% of the chemical oxygen demand (COD) of the waste stream. The pollution potential is generally estimated in terms of COD. For each ton of PTA manufactured, approx. 4-10 kg COD m^{-3} are generated with 3-4 m^3 of wastewater. Both PTA and its manufacturing wastewater show acute, chronic and molecular toxicity to organisms and threat the aquatic life. Therefore, PTA wastewater needs to be treated before discharging.

So far, studies on the destruction PTA manufacturing wastewater were reported by biological treatment using microorganisms or by adsorption. Nevertheless, biodegradation is slow, the activity of the biomass is lost during biodegradation because of the inhibition of microorganisms. On the other hand, adsorption leads to another form of solid waste [1-6]. However, p-toluic acid, 4-carboxybenzaldehyde, benzoic acid, phthalic acid and terephthalic acid show high resistance to biodegradation. The low biodegradation rate increases the cost of treatment significantly. For this reason, development of innovative methods of treating PTA wastewater efficiently and economically is necessary. Physico-chemical method (coagulation-flocculation) has been reported as an option for pretreatment of PTA wastewater to enhance the biodegradation rate [7]. Aluminium sulphate, polyaluminium chloride (PAC), ferrous sulphate and ferric chloride are the well known coagulants in the application of coagulation-flocculation process. In the study done by Karthik et al. [7] PAC in conjunction with lime and polyelectrolyte removed about 63.1% COD from PTA wastewater. Coagulation-flocculation process coupled with aerobic bio-oxidation treatment of PTA wastewater achieved a COD removal of 97.4%. Verma et al. [8] investigated coagulation-flocculation as a pretreatment process for the treatment of purified terephthalic acid (PTA) wastewater. Ferric chloride was found to be the most effective coagulant with COD removal efficiency of 75.5%.

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In recent years, advanced oxidation processes (AOPs) such as photocatalytic oxidation, ozonation, Fenton oxidation and sonication which are based on oxidation by highly reactive hydroxyl radicals attracted great attention for degradation of organic pollutants in petrochemical industry wastewater. The mechanism of the Fenton reaction is based on the electron transfer between H_2O_2 and a transition metal ion (iron is the most common one) acting as a catalyst to produce $OH^{\cdot}$ radicals. However, homogeneous Fenton reactions have some disadvantages such as, limited pH range for the reaction, production of iron containing sludge and difficulty of regeneration of catalyst. The drawbacks of homogeneous Fenton reactions can be overcome by using heterogeneous catalysts. Photo Fenton process is a hybrid technique that use Fenton reagent together with light [9]. Sonication of aqueous solutions provokes the formation and collapse of cavitation bubbles. During the collapse high temperatures and pressures are obtained, leading to the formation of chemical species such as $H^{\cdot}$, $OH^{\cdot}$, $O^{\cdot}$ and H_2O_2. Those high-energy phenomena cause degradation of organic compounds in aqueous solutions. The degradation proceeds oxidation by $OH^{\cdot}$ radicals at the bubble-liquid interface or in bulk solution [10]. The destruction of polycyclic aromatic hydrocarbons (PAHs) was investigated in a real petrochemical industry wastewater by sonication [11]. Destruction of TPA was studied by AOPs of UV-TiO_2, UV-H_2O_2, UV-H_2O_2-Fe, O_3, O_3/Fe, O_3/TiO_2, UV-O_3-H_2O_2-Fe and UV-O_3-H_2O_2-Fe-TiO_2 [12], by ferric chloride in alkalized wastewater [13], by photocatalytic degradation with ZnO catalyst [14], by visible light irradiation with 0.6 mole% $WO_3/BiOCl/Bi_2O_3$ catalyst [15], by ozonation catalyzed with Fe^{2+}, H_2O_2 and UV-light [16]. Destruction of benzoic acid was studied by several AOPs such as sonolysis [17-20], iron-catalyzed homogeneous or heterogeneous photocatalysis [21-25] and heterogeneous (Fe/SBA-15 catalyst) photo-Fenton process [26]. These methods are promising processes as a pre-treatment stage to obtain more easily biodegradable molecules with lower toxicity for the subsequent anaerobic digestion of the wastewater containing TPA.

In these studies mainly, destruction of organic pollutant into intermediates was followed in the wastewater and the decrease in pollutant concentration was measured. Fewer studies have dealt with the reduction in COD or TOC load of wastewater by treatment. In effluent of PTA production, terephthalic and benzoic acids contribute to the significant COD. This COD load must be dropped to required limitation of max 250 ppm before discharge the PTA manufacturing wastewater in order to protect the receiving environment. No study was reported up to now on COD reduction in real PTA production effluent by using AOPs.

On the other hand, AOPs such as photocatalytic oxidation and sonication were used efficiently for the COD reduction of wastewaters. About 50% of COD reduction was achieved in sonolytic degradation of azodicarbonomide industry wastewater [27]. The effectiveness of the ultrasonic irradiation was also tested for organic compounds in raw rubber mill effluent at different power densities of ultrasound. High COD reduction of about 80% after 2h was achieved [28]. In another study, treatment of dye wastewater having high COD in the range of 12000 to 13000 mg/L was achieved with a COD reduction of 71.75% after 90 min of sonication [29]. Verma and Kumari [30] applied sonication, photocatalytic degradation and sonophotocatalytic AOPs to decrease the COD load of pharmaceutical industry wastewater. High COD reductions of 51%, 94% and 98.5% were obtained after 5 hours of treatment, respectively In the study done by Vassilakis et al. [31], sonication was applied as pretreatment step of aerobic biodegradation of p-coumaric acid and p-hydroxybenzaldeyde which are commonly found in effluents of agricultural origin. It was seen that COD removal was increased for both compound by using sonication as pretreatment step when compared with the biodegradation only (a COD removal of about 10% and 65% for p-coumaric acid for biodegradation only and sonication+biodegradation after 5 hours of treatment). Similar to sonication, photocatalytic degradation is also very efficient for COD reductions of several industries' wastewater. For example a COD reduction of 80% was obtained in photocatalytic degradation of real petroleum refinery wastewater in the presence of nanotitania after 2h of oxidation under the studied conditions [32]. In the photocatalytic degradation of phenol and phenolic derivatives from refinery in the presence of nanoparticles of TiO_2, about 75% of COD reduction was achived after 2h of oxidation under the studied conditions [33]. Also in the solar photo-Fenton degradation of petroleum wastewater at Sohar Oil Refinery a COD reduction of about 40% was obtained.

As seen from the studies given in literature, AOPs are very efficient techniques for the removal of COD from several kinds of wastewaters. So, in this study, it was aimed to investigate the efficiency of several AOPs on COD load of the effluents of PTA production. The processes of sonication, heterogeneous Fenton-like oxidation, ultrasound assisted heterogeneous Fenton-like oxidation, heterogeneous photoFenton oxidation and heterogeneous sonophotoFenton oxidation were tested as advanced oxidation techniques. Iron containing TiO_2 and ZSM-5 zeolite catalysts were used as heterogeneous catalysts.

2. EXPERIMENTAL

2.1. Materials

For the preparation of iron containing ZSM-5 zeolite catalysts, commercial ZSM-5 type zeolite (MFI) with different Si/Al ratio (H-MFI(27), H-Pentasil (45), H-MFI(55) and H-MFI (90)) were provided by Clariant- Süd-Chemie. Commercial Fe-ZSM-5 zeolite catalyst was obtained from Clariant. TiO_2 (P-25) obtained from Sigma-Aldrich was used in the preparation of iron containing TiO_2 catalysts. H_2O_2 solution (in wt% of 35) of analytical grade was purchased from Merck. All aqueous solutions were prepared with distilled water obtained from a Millipore Direct Q purification unit.

2.2. Catalyst Preparation

Iron containing ZSM-5 zeolite catalysts were prepared by ion-exchange method and the methods of Schwidder et al. [34] and Long and Yang [35] were applied with small differences. For instance, Fe-ZSM-5(90) catalyst was prepared as follows: 5 g of H-MFI(90) zeolite, 1.825 g of iron powder (Riedel-de Haen AG) and 0.5 dm^3 of deionized water were added to a double-necked flask equipped with a gas inlet-outlet tube and a magnetic stirrer. Then, nitrogen was passed through the flask for 3 min and 4.1 mL of HCl (in wt% of 37, J.T. Baker) was slowly charged into the mixture. The mixture was stirred under nitrogen atmosphere for 5 days. After waiting for ion exchange for 2 days, the mixture was filtrated and the obtained FeZSM-5(90) sample was washed with deionized water until no Cl^- detected in the washing water. Then the catalyst was dried at room temperature for 4 days and calcined at 873 K for 2h.

1wt% and 5wt% containing TiO_2(P25) catalysts were prepared by incipient wetness impregnation method reported by Arana et al. [36] and catalysts were calcined at 500 ºC. TiO_2(P25) calcined at 500 °C was also tested as catalyst.

2.3. Catalyst Characterization

The prepared iron containing ZSM-5 zeolite catalysts were characterized by using XRD and nitrogen adsorption measurements. Shimadzu XRD-6000 model diffractometer was used with CuKα radiation for the determination of crystalline structure of the catalysts. The surface areas of the samples were measured with Quantachrome Autosorb-1 model static volumetric adsorption instrument. Degassing was performed at 250 °C for 3h. Iron content of the catalysts was determined with fusion dissolution method by Thermo Scientific ICAP 6500 ICP-AES device.

2.4. Degradation Tests of the Effluents of PTA Production

The effluent of PTA production with a COD load between 3000-4000 mg/dm^3 taken from a petrochemical plant was degraded by several individual or combined advanced oxidation processes (AOPs) such as ultrasonic oxidation (sonication), heterogeneous Fenton-like oxidation, Ultrasound (US) assisted Fenton-like oxidation, UV light assisted heterogeneous Fenton-like oxidation, UV light and US assisted heterogeneous Fenton-like oxidation (heterogeneous sonophoto Fenton oxidation) and by combined use of US+UV.

The major pollutants and their concentration levels in the effluent tested were presented roughly in Table 1. The original pH of the wastewater was 3.5 and the wastewater was filtrated before the application of AOPs.

Table 1. Major pollutants in the effluent of PTA production (before water treatment)

Compound	Concentration level, ppm
p-toluic acid	450
4-carboxybenzaldehyde	80
Terephthalic acid	700
Benzoic acid	100
Acetic acid	1000

2.4.1. Ultrasonic oxidation (sonication) runs

An ultrasonic bath with a frequency of 40 kHz (C.E.I.A model CP 102 digit, Italy) and an ultrasonic reactor with a frequency of 850 kHz (Meinhardt, 5/1575) were used with an ultrasonic power of 84 W and 75 W, respectively. In the runs with ultrasonic bath, the glass reactor filled with 0.15 dm^3 of wastewater was immersed into the bath filled with 1700 mL of water as the coupling fluid. Ultrasonic reactor was operated at continuous mode and the temperature of the reaction mixture was kept constant by adjusting the temperature of cooling water in the jacket around the reactor.

2.4.2. Heterogeneous Fenton-like oxidation

These runs were performed under isothermal conditions in a glass batch reactor equipped with a mechanical stirrer. A wastewater volume of 0.15 dm^3 was degraded. After a reaction time of 60 min, the reduction in the chemical oxygen demand (COD) of the solution was determined using a Lovibond (Germany) Checkit Direct COD Vario Device. The activity of the prepared iron-containing ZSM-5 zeolites and commercial FeZSM-5 catalyst were tested in the COD reduction of wastewater.

2.4.3. US assisted heterogeneous Fenton-like oxidation runs

These runs were performed in the ultrasonic bath or in the ultrasonic reactor. The glass reactor containing wastewater, catalyst and H_2O_2 was immersed into the ultrasonic bath and the wastewater solution was sonicated indirectly while sonication was direct in the ultrasonic reactor with powers of 50 or 75 W. Commercial catalyst was tested in these runs.

2.4.4. UV light assisted heterogeneous Fenton-like oxidation runs

These experiments were carried out in the experimental set-up given in the section of "Heterogeneous Fenton-like oxidation Runs" with a UV-C lamp (Philips TUV, 8W) located horizontally at the top of the glass reactor. The system was covered with an aluminum foil to prevent the reaction mixture from the sun-light. Commercial FeZSM-5 zeolite and iron containing TiO_2 catalysts were tested in these runs.

2.4.5. UV light and US assisted heterogeneous Fenton-like oxidation (heterogeneous sonophotoFenton oxidation) Runs

In these runs, the glass batch reactor used in "Heterogeneous Fenton-like oxidation Runs" was immersed into the ultrasonic bath and the UV-C lamp was located horizontally at the top of the reactor. The reaction mixture was protected from the sun light with an aluminum foil cover as in the previous UV light assisted runs. Commercial FeZSM-5 zeolite and iron containing TiO_2 catalysts were used in these runs.

2.4.6. UV light assisted sonication runs

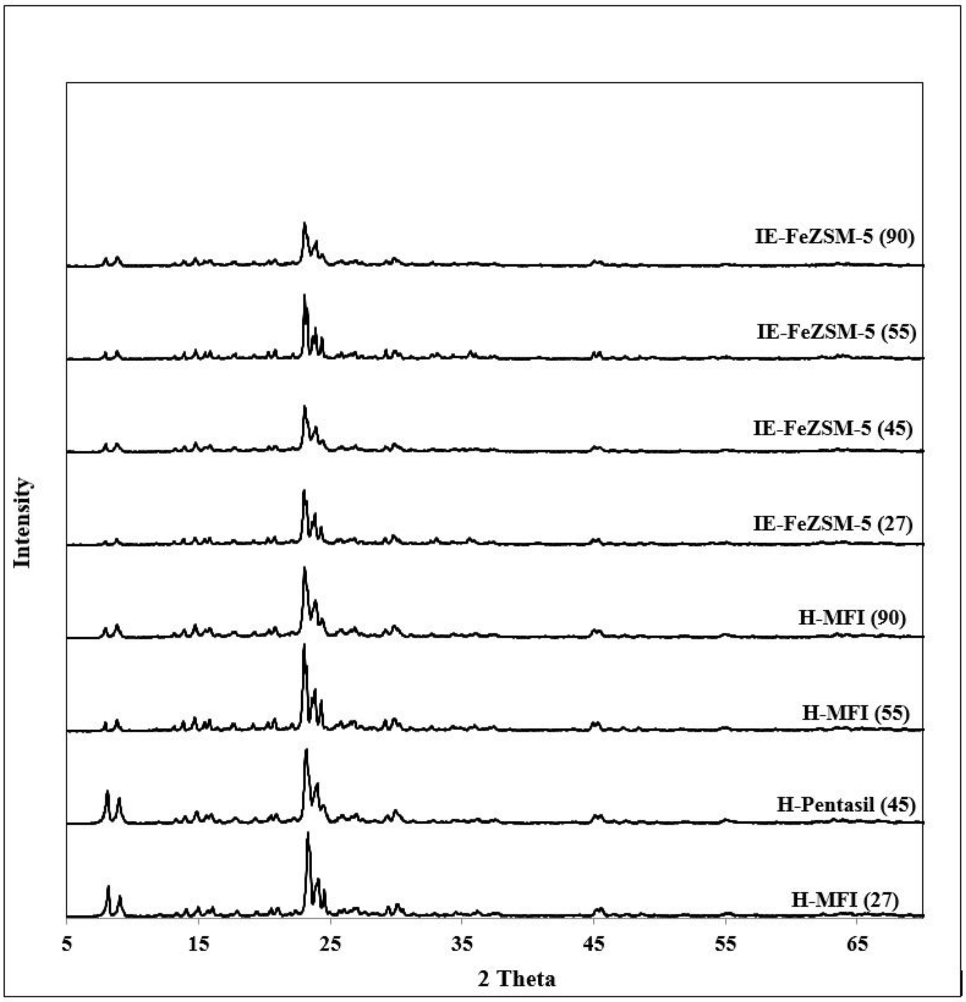
These runs were performed in the glass reactor mentioned above. Reactor containing wastewater and H_2O_2 was immersed into the ultrasonic bath. The effect of UV light power was investigated in these runs. For this purpose, a UV-C lamp with a power of 8W or 2 UV-C lamp with 8W+8W power was located horizontally at the top of the reactor.

3. RESULTS AND DISCUSSIONS

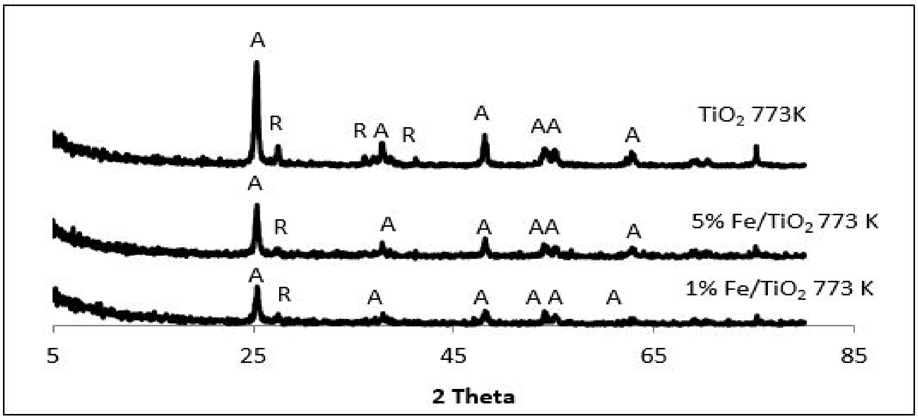
3.1. Characterization Studies

Figure 1a shows the XRD patterns of the FeZSM-5 catalysts prepared together with the parent zeolites for comparison. All the catalysts exhibited the typical diffractograms of the ZSM-5 zeolite (MFI framework) in the 2θ range of 7-9° and 23-25° given in the literature [37-40]. High dispersion of iron ions in compensating positions inside zeolite did not damage the crystallinity of the zeolite. Addition of iron into the zeolite structure decreased the characteristic peak intensities of ZSM-5. This can be attributed to the enhanced absorption of X-ray due to iron cations and the reduction in crystal size of zeolite as a result of acid treatment. The preparation method of the catalyst is so significant in terms of formation of crystalline iron oxides [41, 42]. There is no evidence for the formation of α-Fe_2O_3, γ-Fe_2O_3 (major reflections at 2θ= 33.2° and 35.7°) and any other iron oxide in XRD diffractograms of prepared catalyst samples, even in the IE-FeZSM-5 (90) sample having 8.5 wt % of Fe, probably due to the fine crystallites formed. Figure 1b presents XRD patterns of Fe/TiO_2 catalysts. The peaks at 2θ=25.4°, 37.9°, 48.1°, 53.9°, 55.2° and 62.9° are attributed to the diffractions of the anatase phase and the peaks at 2θ= 27.5°, 36.0° and 41.2° to rutile phase. Peak intensities are weakened by the incorporation of iron into the TiO_2 [43-46].

Table 2 presents BET surface area, external surface area, total pore volume, and average pore diameter of the prepared catalysts and parent zeolites. Table 2 includes iron content of the samples, as well. Commercial FeZSM-5 catalyst has a BET surface area of 391 m^2/g with an Fe_2O_3 amount of 4.4%.



a)



b)

Figure 1. X-ray diffraction patterns of the **a)** Fe/ZSM-5 catalysts and parent ZSM-5 zeolites **b)** Fe/TiO_2 catalysts

Table 2. Nitrogen adsorption and ICP-AES measurements of the catalysts prepared and parent zeolites

Catalyst	BET surface Area, m^2/g	External Surface Area, m^2/g	Iron, wt%	Total pore volume, cm^3/g	Average pore diameter (median pore diameter), nm
H-MFI (27)	368.34	119.57	-	0.1508	0.87*
H-Pentasil (45)	378.53	243.88	-	0.1507	0.98*
H-MFI (55)	334.51	117.85	-	0.1414	0.56*
H-MFI (90)	308.02	170.01	-	0.1256	0.65*
FeZSM-5 (27)	336.59	96.56	6.6	0.1498	0.92*
FeZSM-5 (45)	368.93	205.27	7.6	0.1256	0.59*
FeZSM-5 (55)	302.56	105.13	8.1	0.1079	0.60*
FeZSM-5 (90)	358.24	219.46	8.5	0.1259	0.55*
TiO_2 (P25)	54.1	45.89	-	0.0140	5.91**
1% Fe/TiO_2	55.5	53.73	0.93	0.0150	8.64**
5% Fe/TiO_2	50.5	47.32	4.46	0.0139	8.85**

*by Horvath-Kawazoe method
**by BJH method

3.2. Degradation of the Effluents of PTA Production

3.2.1. Degradation of the effluents of PTA production using ultrasonic oxidation (sonication)

Ultrasonic degradation of effluents of PTA production was investigated using two types of ultrasonic equipment such as ultrasonic bath (indirect sonication) and ultrasonic reactor (direct sonication). The results are shown in Table 3 with the reaction conditions for the effluent pH of 3.5 after a degradation of 1h. The volume of the effluent in ultrasonic reactor was 0.35 dm^3, whereas it was 0.15 dm^3 in ultrasonic bath due to safety limitation of ultrasonic reactor which could not be performed at the volume less than 0.35 dm^3. It was seen that, very little COD removal could be achieved by ultrasound waves. Types of sonication (direct or indirect), ultrasonic power and ultrasonic frequency did not affect the degradation of the effluent.

Table 3. Ultrasonic oxidation (sonication) runs

No of Run	Applied Process	Reaction Conditions	Initial COD, mg/dm^3	COD removal, %
1	Ultrasonic reactor	850 kHz, 75 W, 0.35 dm^3 of wastewater, pH=3.5	4038	1.4
2	Ultrasonic bath	40 kHz, 84 W, 0.15 dm^3 of wastewater, pH=3.5	3900	1.3

3.2.2. Degradation of the effluents of PTA production using heterogeneous Fenton-like oxidation

In this part of the study, type of catalyst was investigated on the heterogeneous Fenton-like oxidation of effluent by keeping the effluent volume, catalyst amount and H_2O_2 amount, temperature, pH of the effluent constant at 0.15 dm^3, 1 g/dm^3, 3 mM, 30 °C, and pH=3.5, respectively. The prepared zeolite catalysts of FeZSM-5(27), FeZSM-5(45), FeZSM-5(55), FeZSM-5(90) and commercial FeZSM-5 were used in the runs for 1h of oxidation, Table 4.

Table 4. Heterogeneous Fenton-like oxidation Runs

No of Run	Applied Process	Reaction Conditions	Initial COD, mg/dm^3	COD removal, %
3	Heterogeneous Fenton-like oxidation	0.15 dm^3 of wastewater, 0.15 g of FeZSM-5(27) catalyst, 3 mM H_2O_2, pH=3.5	4260	0.9
4	Heterogeneous Fenton-like oxidation	0.15 dm^3 of wastewater, 0.15 g of FeZSM-5(45) catalyst, 3 mM H_2O_2, pH=3.5	4150	1.5
5	Heterogeneous Fenton-like oxidation	0.15 dm^3 of wastewater, 0.15 g of FeZSM-5(55) catalyst, 3 mM H_2O_2, pH=3.5	4340	1.4
6	Heterogeneous Fenton-like oxidation	0.15 dm^3 of wastewater, 0.15 g of FeZSM-5(90) catalyst, 3 mM H_2O_2, pH=3.5	4150	4.8
7	Heterogeneous Fenton-like oxidation	0.15 dm^3 of wastewater, 0.15 g commercial FeZSM-5, 3 mM H_2O_2, pH=3.5	4150	6.0

The highest COD removal (4.8%) was obtained with 8.5wt% iron containing FeZSM-5 catalyst (FeZSM-5(90)) in the heterogeneous Fenton-like oxidation of the effluent over the catalysts prepared. This catalyst has the highest external surface area of 219.5 m^2/g among the prepared catalysts, Table 2, and the heterogeneous Fenton-like oxidation of large molecules can easily proceed at the external surface of the catalyst. The amount of catalyst was 1g/dm^3 in the runs. This amount of catalyst was selected according to literature for dye degradation [9, 47-50]. In these studies, different kinds of textile dyes, Rhodamine 6G, Orange II and Reactive Red 141, were successfully degraded by heterogeneous Fenton-like oxidation over Fe and/or Cu containing zeolite catalysts. The increase in iron content of the catalyst (Table 2) enhanced the COD removal. It may be attributed to the increase in $OH^{\cdot}$ radicals formed by the increase in iron content of the catalyst. A COD removal of 6% was achieved with the commercial catalyst. This is a higher efficiency than those of the prepared catalysts.

Temperature was 30 °C at the runs with heterogeneous Fenton-like oxidation. Temperatures higher than 30 °C was not tested in these runs for the sake of heating cost saving even though temperature is the key factor to accelerate the catalytic oxidation.

3.2.3. Degradation of the effluents of PTA production using US assisted heterogeneous Fenton-like oxidation

The effect of ultrasound was investigated on the heterogeneous Fenton-like oxidation of effluents of PTA production in the presence of commercial FeZSM-5 catalyst using ultrasonic reactor at an effluent volume of 0.35 dm^3, at a temperature of 30 °C, at an effluent pH of 3.5 for the oxidation run of 1h. Commercial FeZSM-5 was used in these experiments because of its high performance. The effects of ultrasonic power, amounts of catalyst and H_2O_2 were investigated keeping all the other parameters constant. When the runs were performed using ultrasonic bath under the same pH value, the volume of the effluent, power of ultrasound, and amount of catalyst were kept constant at 0.15 dm^3, 84W and 1 g/dm^3, respectively. Only the effect of H_2O_2 amount was investigated in indirect sonication of effluent using ultrasonic bath. Table 5 shows the results with reaction conditions.

Table 5. US assisted Heterogeneous Fenton-like oxidation runs

No of Run	Applied Process	Reaction Conditions	Initial COD, mg/dm^3	COD removal, %
8	US assisted Heterogeneous Fenton-like oxidation	0.35 dm^3 of wastewater, ultrasonic reactor, US power=50W, 0.35 g of commercial FeZSM-5, 3 mM H_2O_2, pH=3.5	4200	No removal
9	US assisted Heterogeneous Fenton-like oxidation	0.35 dm^3 of wastewater, ultrasonic reactor, US power=50W, 0.35 g of commercial FeZSM-5, 4.5 mM H_2O_2, pH=3.5	4290	4.2
10	US assisted Heterogeneous Fenton-like oxidation	0.35 dm^3 of wastewater, ultrasonic reactor, US power=50W, 0.7 g of commercial FeZSM-5, 4.5 mM H_2O_2, pH=3.5	4120	3.4
11	US assisted Heterogeneous Fenton-like oxidation	0.35 dm^3 of wastewater, ultrasonic reactor, US power=75W, 0.35 g of commercial FeZSM-5, 6 mM H_2O_2, pH=3.5	4290	7.2
12	US assisted Heterogeneous Fenton-like oxidation	0.35 dm^3 of wastewater, ultrasonic reactor, US power=75W, 0.35 g of commercial FeZSM-5, 9 mM H_2O_2, pH=3.5	4110	3.9
13	US assisted Heterogeneous Fenton-like oxidation	0.35 dm^3 of wastewater, ultrasonic reactor, US power=75W, 0.35 g of commercial FeZSM-5, 12 mM H_2O_2, pH=3.5	4155	5.2
14	US assisted Heterogeneous Fenton-like oxidation	0.15 dm^3 of wastewater, ultrasonic bath, US power=84W, 0.15 g of commercial FeZSM-5, 9 mM H_2O_2, pH=3.5	3925	7.0
15	US assisted Heterogeneous Fenton-like oxidation	0.15 dm^3 of wastewater, ultrasonic bath, US power=84W, 0.15 g of commercial FeZSM-5, 12 mM H_2O_2, pH=3.5	4085	13.3

However, ultrasound (US) affected negatively the COD removal when heterogeneous Fenton-like oxidation was applied in the presence of US (Run 8) at the reaction conditions of 0.35 dm^3 of wastewater, at a US power of 50W, with commercial FeZSM-5 catalyst and H_2O_2 amounts of 1 g/dm^3 and 3 mM. No COD removal could be obtained. It may be attributed to the behavior of solid catalyst particles as a barrier for the propagation of sound waves thereby decreasing the energy transmitted into the system [51].

The increase of H_2O_2 amount from 3 mM to 4.5 mM by keeping the ultrasonic power and amount of catalyst constant, enhanced the COD removal from zero to 4.2% in US assisted heterogeneous Fenton-like oxidation of the PTA production effluent due to the enhanced amount of $OH^·$ radicals formed (Comparison of Runs 8 and 9). Doubling the catalyst amount from 0.35 g to 0.7 g in the presence of H_2O_2 amount of 4.5 mM had no positive contribution to COD removal (Comparison of Runs 9 and 10). When H_2O_2 amount was increased from 4.5 mM (Run 9) to 6 mM (Run 11) as well as ultrasonic power from 50 W to 75 W keeping the catalyst amount constant at 0.35 g, COD removal could be changed from 4.2% to 7.2%. This enhancement in COD removal may arise from the increase in $OH^·$ radicals formed in the presence of high H_2O_2 amount and high ultrasonic power. On the other hand, high US power decreases the catalyst particle size resulting in a larger surface area which improves the mass transfer rate [43, 52]. Nevertheless, a further increase of the H_2O_2 amount to 9 mM (Run 12) keeping the catalyst amount and US power constant did not improve the COD removal due to the hydroxyl radical scavenging effect of H_2O_2 through the reactions below:

$H_2O_2 + OH^{\cdot} \longrightarrow HO_2. + H_2O$ (1)
$HO_2^{\cdot} + OH^{\cdot} \longrightarrow H_2O + O_2$ (2)
$OH^{\cdot} + OH^{\cdot} \longrightarrow H_2O_2$ (3)

$HO_2^{\cdot}$ Radicals are less reactive than $OH^{\cdot}$ radicals. A COD removal of 3.9% could only be achieved.

A further increase of H_2O_2 amount to 12 mM (Run 13) could enhance the COD removal to 5.2% because of the dominant effect of $OH^{\cdot}$ radical formation, eq. 4, rather than the scavenging effect of H_2O_2:

$x\text{-}Fe^{2+} + H_2O_2 \longrightarrow x\text{-}Fe^{3+} + OH^{\cdot} + OH^-$ (4)
where x represents the surface of catalyst.

Indirect sonication in ultrasonic bath with a US power of 84W caused a positive contribution in COD removal when heterogeneous Fenton-like oxidation and US were applied together (Run 14). The increase of H_2O_2 amount from 9 mM to 12 mM caused an enhancement in COD removal from 7.0% to 13.3%, (Runs14 and 15). The ratio of catalyst amount/solution volume was kept constant as 1 g/dm^3 in the runs performed using ultrasonic bath and ultrasonic reactor except in the runs with the investigation of the amount of catalyst (Run 10).

3.2.4. Degradation of the effluents of PTA production using UV light assisted heterogeneous Fenton-like oxidation

The UV light assisted heterogeneous Fenton-like oxidation of wastewater of PTA production was performed at a volume of 0.15 dm^3, with a catalyst amount of 1 g/dm^3, in the presence of 8W UV-C light. The effects of catalyst type, H_2O_2 amount, reaction temperature and pH of the effluent was investigated on the degradation keeping all the other parameters constant. 1 wt% Fe/TiO_2 (P25), 5 wt% Fe/TiO_2 (P25), bare TiO_2 (P25) and commercial FeZSM-5 were used as catalyst. Table 6 gives the results.

COD removal could not be achieved when the combination of UV-C light and heterogeneous Fenton-like oxidation was used in the degradation of PTA production effluent over 1 wt% Fe/TiO_2 catalyst (Run 16). A little COD removal (1%) could be obtained when this combination was applied to the effluent in the presence of 5% Fe/TiO_2 or commercial FeZSM-5 zeolite with a H_2O_2 amount of 6 mM (Runs 17 and 18). However, under the same conditions except the solution pH, a COD removal of 18.2% could be reached over 5% Fe/TiO_2 catalyst in the UV light assisted heterogeneous Fenton-like oxidation of wastewater (comparison of runs 17 and 19). It was clear that near neutral pH was favorable for the degradation in the presence of 5% Fe/TiO_2 catalyst.

COD removal decreased from 18.2% to 13.9% with the increase in reaction temperature from 30 °C to 45 °C (Runs 19 and 20) in the presence of 1 g/dm^3 of 5 wt% Fe/TiO_2 (P25) catalyst and 6 mM of H_2O_2. This result may be explained by the fact that 5% Fe/TiO_2 is a photocatalyst rather than a Fenton catalyst. It is known that photocatalytic activity is independent of temperature [51].

On the other hand, bare TiO_2 (P25) is not an efficient catalyst in UV light assisted heterogeneous Fenton-like oxidation of the effluent. A COD removal of only 1.3% could be provided by this catalyst (Run 21).

Table 6. UV light assisted Heterogeneous Fenton-like oxidation runs

No of Run	Applied Process	Reaction Conditions	Initial COD, mg/dm^3	COD removal, %
16	UV-light assisted Heterogeneous Fenton-like oxidation	0.15 dm^3 of wastewater, 0.15 g of 1 wt% Fe/TiO$_2$ (P25) catalyst , 9 mM H$_2$O$_2$, UV-lamp=8W, pH=3.5	3604	No removal
17	UV-light assisted Heterogeneous Fenton-like oxidation	0.15 dm^3 of wastewater, 0.15 g of 5 wt% Fe/TiO$_2$ (P25) catalyst , 6 mM H$_2$O$_2$, UV-lamp=8W, pH=3.5	3936	1.0
18	UV-light assisted Heterogeneous Fenton-like oxidation	0.15 dm^3 of wastewater, 0.15 g of commercial FeZSM-5 catalyst , 6 mM H$_2$O$_2$, UV-lamp=8W, pH= 6.61	3300	1.2
19	UV-light assisted Heterogeneous Fenton-like oxidation	0.15 dm^3 of wastewater, 0.15 g of 5 wt% Fe/TiO$_2$ (P25) catalyst , 6 mM H$_2$O$_2$, UV-lamp=8W, pH=6.94	3848	18.2
20	UV-light assisted Heterogeneous Fenton-like oxidation	0.15 dm^3 of wastewater, 0.15 g of 5 wt% Fe/TiO$_2$ (P25) catalyst , 6 mM H$_2$O$_2$, UV-lamp=8W, pH=6.61, T=45 °C	3873	13.9
21	UV-light assisted Heterogeneous Fenton-like oxidation	0.15 dm^3 of wastewater, 0.15 g of TiO$_2$ (P25) catalyst , 6 mM H$_2$O$_2$, UV-lamp=8W, pH=7.12, T=45 °C	3864	1.3

3.2.5. Degradation of the effluents of PTA production using UV light and US assisted heterogeneous Fenton-like oxidation (Heterogeneous sonophotoFenton oxidation)

It was also tried to degrade the PTA production effluent by using the sonophotoFenton hybrid process. For this purpose, runs of 22-26 were carried out by changing the type and amount of the catalyst, the amount of H$_2$O$_2$, the volume of wastewater, and the solution pH (from 3.5 to near neutral pH). Unfortunately, no drastic increase in COD removal was observed in all the reaction conditions, it remained in the range of 0-8%. The results are given in Table 7.

Table 7. UV light and US assisted heterogeneous Fenton-like oxidation (Heterogeneous sonophotoFenton oxidation) Runs

No of Run	Applied Process	Reaction Conditions	Initial COD, mg/dm^3	COD removal, %
22	UV-light and US assisted Heterogeneous Fenton-like oxidation	0.15 dm^3 of wastewater, 0.3 g of 5 wt% Fe/TiO$_2$ (P25) catalyst , 6 mM H$_2$O$_2$, UV-lamp=8W, pH= 7.23, T=34 °C, US bath with power of 84 W	2742	3.8
23	UV-light and US assisted Heterogeneous Fenton-like oxidation	0.15 dm^3 of wastewater, 0.15 g of commercial Fe/ZSM-5 catalyst , 12 mM H$_2$O$_2$, UV-lamp=8W, T= 35 °C, US bath with power of 84 W, pH=3.5	2778	4.8
24	UV-light and US assisted Heterogeneous Fenton-like oxidation	0.15 dm^3 of wastewater, 0.3 g of commercial Fe/ZSM-5 catalyst , 12 mM H$_2$O$_2$, UV-lamp=8W, T= 35 ^{0}C, US bath with power of 84 W, pH=3.5	2757	4.5
25	UV-light and US assisted Heterogeneous Fenton-like oxidation	0.075 dm^3 of wastewater, 0.3 g of 5%Fe/TiO$_2$ catalyst , 12 mM H$_2$O$_2$, UV-lamp=8W, T= 34 °C, US bath with power of 84 W, pH=3.5	2970	No removal
26	UV-light and US assisted Heterogeneous Fenton-like oxidation	0.075 dm^3 of wastewater, 0.3 g of 5%Fe/TiO$_2$ catalyst , 12 mM H$_2$O$_2$, UV-lamp=8W, T= 34 °C, US bath with power of 84 W, pH=6.93	2793	8.0

3.2.6. Degradation of the effluents of PTA production using UV light assisted sonication

The oxidation of wastewater of PTA production was also investigated using UV light assisted sonication in ultrasonic bath at an effluent volume of 0.075 dm^3, in the presence of 12 mM H_2O_2, at a temperature of 34 °C keeping the ultrasonic power constant at 84 W but changing the power of UV light from 8W to 16 W. Table 8 gives these results.

Table 8. UV light assisted sonication runs

No of Run	Applied Process	Reaction Conditions	Initial COD, mg/dm^3	COD removal, %
27	UV-light assisted Sonication	0.075 dm^3 of wastewater, 12 mM H_2O_2, UV-lamp=8W, T= 34 °C, US bath with power of 84 W, pH=3.5	2814	5.1
28	UV-light assisted Sonication	0.075 dm^3 of wastewater, 12 mM H_2O_2, UV-lamp=8W+8W, T= 34 °C, US bath with power of 84 W, pH=3.5	2814	3.5

As seen from Table 8, a COD removal of 5.1% could be measured in ultrasonic bath with a power of 84W in the presence of one UV-C lamp. Doubling the power of UV light to 16 W did not affect positively the COD removal, as well.

These results indicate that individual or combined use of AOPs has little effect in the degradation of PTA production effluent. The highest COD removal could be achieved as 18.2% when UV light assisted heterogeneous Fenton-like oxidation in the presence of 5% Fe/TiO_2 catalyst was used. Selection of the catalyst is very important in AOPs. As known well, TiO_2 has been extensively studied as a semiconductor photocatalyst because of its relatively high photocatalytic activity, chemical stability, low cost, and environmental friendliness. When TiO_2 is radiated with light energy greater than its band gap energy (3.2 eV) electrons and holes are generated. The holes react with OH^- or water to produce $OH^•$ radicals (Heterogeneous photo catalysis). But recombination of electrons and holes must be prevented which is a drawback of photo catalytic efficiency. It can be reduced by addition of transition metals such as iron as dopant and photocatalytic efficiency can be improved [36, 43, 53-60]. The presence of the Fe^{3+} in the catalyst also acts as a Fenton like catalyst and helps the production of more hydroxyl radicals via reactions 5- 8 [61].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + •OH + OH^- \quad (5)$$

Iron (III) can then react with hydrogen peroxide in the so-called Fenton-like reaction (equations 6 and 8)

$$Fe^{3+} + H_2O_2 \rightarrow FeOOH^{2+} + H^+ \quad (6)$$

$$FeOOH^{2+} \rightleftarrows HO_2• + Fe(II) \quad (7)$$

$$Fe(III) + HO_2• \rightarrow Fe(II) + O_2 + H^+ \quad (8)$$

Moreover, in the presence of UV-light (at 254 nm) H_2O_2 is decomposed into hydroxyl radicals which react with the effluent of PTA production, Eq.9 [62].

$$H_2O_2 \overset{hv}{\rightarrow} 2OH^{\cdot} \quad (9)$$

All these factors create a synergetic effect that increases the degradation of wastewater from PTA production.

4. CONCLUSIONS

In this study, it was tried to reduce the COD load of the wastewater in PTA production by using several advanced oxidation processes such as heterogeneous Fenton-like oxidation, sonication, heterogeneous Fenton-like oxidation assisted with US or UV or with combination of US and UV together or combined use of US+UV. The preliminary results showed that it could not be possible to achieve a COD removal greater than 18%. However, a more efficient COD removal can be provided by the application of advanced oxidation techniques such as UV light assisted heterogeneous Fenton-like oxidation after the biological treatment of PTA wastewater pretreated by coagulation-flocculation method. For this purpose, further studies are required.

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