

# The Sonodegradation of a Petrochemical Industry Wastewater

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**Abstract:** In this study, the effects of increasing sonication times (0 min, 60 min, 120 and 150 min), sonication temperatures (25°C, 30°C and 60°C), increasing titanium dioxide (TiO<sub>2</sub>) (0.1 mg/L, 0.5 mg/L, 10 and 20 mg/L), sodium chloride (NaCl) (1 g/L, 2.5 and 15 g/L), ferrous ion (Fe<sup>+2</sup>) (2 mg/L, 8 and 20 mg/L) and ferric ion (Fe<sup>+3</sup>) (10 mg/L, 20 and 50 mg/L) concentrations on the dissolved chemical oxygen demand (COD<sub>dis</sub>), total organic carbon (TOC) and total polycyclic aromatic hydrocarbons (PAH) removal efficiencies were monitored at a sonication frequency of 35 kHz and a sonication power of 640 W for a raw petrochemical industry wastewater (PCI ww). As the sonication time and temperature were increased from 60 to 120 and 150 min, and from 25 °C to 30 °C and to 60 °C, the COD<sub>dis</sub>, total PAH and TOC yields increased from around 52-58% and 69%-72% to 80-87% and 78%-90%. The maximum COD<sub>dis</sub>, total PAH and TOC yields were obtained with 20 mg/l TiO<sub>2</sub>, 15 mg/l NaCl, 20 mg/L Fe<sup>+2</sup> and with 50 mg/L Fe<sup>+3</sup>, particularly after 150 min sonication at 60 °C. However, it is important to note that after 150 min sonication in the samples free of the chemicals mentioned above, in other words, in the samples with only sonication exhibited high yields as is the samples added the chemicals. After sonication with the chemicals, the EC<sub>50</sub> values decreased significantly versus sonication times. The maximum *Daphnia magna* acute toxicity removal yield was 99.91% at NaCl=1 g/L at 60°C after 150 min sonication.

**Keywords:** Sonication, Petrochemical industry, Polycyclic aromatic hydrocarbons (PAHs), Dissolved chemical oxygen demand (COD<sub>dis</sub>), total organic carbon (TOC), Wastewater, *Daphnia magna* acute toxicity assay, Titanium dioxide (TiO<sub>2</sub>), Sodium chloride (NaCl), Ferrous iron (Fe<sup>+2</sup>), Ferric iron (Fe<sup>+3</sup>).

## 1. INTRODUCTION

PAHs are organic compounds, widely distributed in the environment, formed by the incomplete combustion of organic materials during natural or antropogenis processes. They comprise a large group of compounds with two or more fused benzene rings that are less soluble in H<sub>2</sub>O and less volatile with increasing molecular weigths. PAHs are highly hydrophobic, with a low biodegradability in wastewater treatment plants [1-12, 15-17]. PAHs are listed as US-EPA and EU priority pollutants, and their concentrations therefore need to be controlled in treated wastewater effluents [13–14]. Due to their toxic, mutagenic and carcinogenic properties, the US-EPA classifies sixteen PAHs as priority pollutants [13-14].

Some sonochemical transformations that have been observed include degradation of nucleic acid bases and degradation of aqueous carbon tetrachloride, 1,1,1-trichloroethane, methylene chloride, trichloroethylene, chloroaromatics, methylene chloride, alkyl phenol ethoxylate, substituted benzenes and PAHs. These studies indicate that sonochemistry may be a useful tool in degrading aqueous pollutants. Four mechanisms have been proposed to account for sonolytic degradation: (1) oxidation of hydroxyl radicals

(OH<sup>•</sup>), (2) pyrolytic decomposition, (3) super critical water oxidation and (4) combustion [12]. OH<sup>•</sup>, commonly present during sonication of aqueous solutions, were not present in sufficient quantities to account for the degree of PAH degradation. This result, along with the observation of a polar product that appears to be the same as the photochemical product, suggest that pyrolysis and/or combustion-type reactions proceeding via a PAH radical cation may be predominant in the sonolysis of PAHs in aqueous solution [10, 18]. The main initial step of degradation must be the sonochemical formation of some intermediate species, not only molecules, unlike the case of pre-sonolysis, but also short-life species such as radicals. As soon as these species are formed, the rapid photo-catalytical reactions occur successively to lead to the complete oxidation.

David [8] found that naphthalene, phenanthrene, anthracene and pyrene removal efficiencies varied between 93 and 95%, after a sonication time of 90 min in a sonicator having a power of 400 W and a frequency of 20 kHz. Kim *et al.* [19] investigated the sonochemical decomposition of dibenzothiophene, and 72% removal efficiency was found at a sonicator having a power of 600 W and a frequency of 20 kHz after 180 min sonication time. Psillakis *et al.* (2004) [20] found 99% removal efficiency for 0.01 µg/L of acenaphthalene, penanthrene and naphthalene at a power of 300 W and frequency of 24 kHz. Benabdallah *et al.* (2007) [9] found 57% of naphthalene, 40% of

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pyrene and 45% of total COD removal efficiencies at a sonicator having a power of 70 W and frequency of 20 kHz. Taylor *et al.* [10] investigated the sonication of PAHs namely anthracene, phenanthrene and pyrene. 46%, 20% and 50% removal efficiencies were found for anthracene, phenanthrene and pyrene, respectively, at a power of 600 W and a frequency of 20 kHz. Laughrey *et al.* [12] investigated the effects of dissolved oxygen, air and nitrogen gas to the sonication of phenanthrene, pyrene and anthracene.

In İzmir-Turkey, the petrochemical industry wastewaters are treated with conventional activated sludge systems and are released in the receiving bodies since low COD<sub>dis</sub>, TOC and total PAH removal efficiencies were observed. Although some studies were performed to increase the biodegradation of total PAH, COD<sub>dis</sub> and TOC with sonication, the recent literatures [10, 11, 12] shows that the addition of TiO<sub>2</sub>, NaCl, Fe<sup>+2</sup> and Fe<sup>+3</sup> increases the sonication yields of pollutants present in PCI ww. Therefore, in this study, the aim is to investigate the effects of ambient conditions, increasing sonication time (0 min, 60 min, 120 and 150 min), increasing sonication temperatures (25°C, 30°C and 60°C), increasing TiO<sub>2</sub> (0.1 mg/L, 0.5 mg/L, 10 and 20 mg/L), increasing NaCl (1 g/L, 2.5 and 15 g/L), increasing Fe<sup>+2</sup> (2 mg/L, 8 and 20 mg/L) and increasing Fe<sup>+3</sup> (10 mg/L, 20 and 50 mg/L) concentrations on the sonodegradation of seventeen PAHs (total PAH), TOC and COD<sub>dis</sub> in an petrochemical industry wastewater. Furthermore, the acute toxicity test was evaluated with *Daphnia magna*.

## 2. MATERIALS AND METHODS

### 2.1. Operational Conditions

BANDELIN Electronic RK510 H sonicator were used for PCI ww. The sonication frequency and the sonication power were 35 kHz and 650 W, respectively. Raw and sonicated PCI ww were filled up 500 mL to the glass serum bottles and were closed with closers for the measurements of volatile compounds of PCI ww. Sonicated samples were taken from 0, 60th, 120th and 150th min of sonication time and were kept in a refrigerator at 4°C for experimental analysis. The increasing sonication times (0 min, 60 min, 120 and 150 min), increasing sonication temperatures (25°C, 30°C and 60°C), increasing TiO<sub>2</sub> (0.1 mg/L, 0.5 mg/L, 10 and 20 mg/L), increasing NaCl (1 g/L, 2.5 and 15 g/L), increasing Fe<sup>+2</sup> (2 mg/L, 8 and 20 mg/L) and increasing Fe<sup>+3</sup> (10 mg/L, 20 and 50 mg/L) concentrations studied in this study were chosen from the recent literatures [10-14].

### 2.2. Analytical Methods

The following analysis were carried out in the influent and effluent samples;

#### 2.2.1. PAHs Sample Preparation and Analysis

Samples were filtered through a glass fiber filter (47 mm-diameter) to collect particle-phase in series with a resin column (~ 10 g XAD-2) to collect dissolved-phase PBDEs. Resin and H<sub>2</sub>O filters were ultrasonically extracted for 60 min with a mixture of 1/1 Acn/Hxn. Prior to extraction, all samples were spiked with PAH surrogate standards to monitor analytical recovery efficiencies. The volume of extracts was reduced and transferred into Hxn using a rotary evaporator and a high-purity N<sub>2</sub> stream. After volume reduction to 2 mL by a gentle flow of N<sub>2</sub>, the samples were cleaned up on an AL-SA column containing 3 g of SA (3% H<sub>2</sub>O) and 2 g of AL (6% H<sub>2</sub>O). The column was pre-washed with 20 mL of DCM followed by 20 mL of PE. The sample in 2 mL of Hxn was added to the top of the column and PAHs were eluted with 20 mL of DCM. After solvent exchange into Hxn, the final sample volume was adjusted to 1 mL by N<sub>2</sub> blow-down. A gas chromatograph (GC) (Agilent 6890N) equipped with a mass selective detector (Agilent 5973 inert MSD) and a capillary column (HP5-ms, 30 m, 0.25 mm, 0.25 mm) were used to take measurements. The initial oven temperature was 50°C for 1 min and then increased to 200°C at 25°C 1 1/min, and then from 200°C to 300°C at 80°C 1 1/min, which was held for 5.5 min. The injector ion source and quadrupole temperatures were 295°C, 300°C and 180°C, respectively. High purity helium (He) was used as the carrier gas at constant flow mode (1.5 mL/min, 45 cm/s linear velocity). The MSD ran in selected ion-monitoring mode. Compounds were identified on the basis of their retention times, target and qualifier ions. Qualification was based on the Internal Standard Calibration Procedure. Physical and chemical properties of PAHs were measured in this study (Table 1).

#### 2.2.2. pH, T(°C), ORP (mV), COD (mg/L) and TOC (mg/L) Measurements

pH, T(°C), ORP (mV), COD<sub>dis</sub> and TOC were monitored following the Standard Methods 2550, 2580, 5220 D, 5310 [21].

#### 2.2.3. Chemical Oxygen Demand Dissolved (COD<sub>dis</sub>) Measurements

COD<sub>dis</sub> was determined with Close Reflux Method following the Standard Methods 5220 D [21] using an

Table 1: Physical and Chemical Properties of PAHs Measured in this Study

PAHs <sup>**</sup>	Cas-No <sup>a</sup>	Molecular Formula <sup>a</sup>	MW <sup>a</sup> (g/mol)	T <sub>m</sub> <sup>a</sup> (°C)	T <sub>b</sub> <sup>a</sup> (°C)	S <sub>w</sub> <sup>a</sup> (25°C) (mg/L)	VP <sup>a</sup> (25°C) (mm Hg)	H <sup>a</sup> (25°C) (atm m <sup>3</sup> /mol)	log K <sub>OA</sub> <sup>c</sup> (25°C)	log K <sub>OW</sub> <sup>a</sup>
NAP	91-20-3	C <sub>10</sub> H <sub>8</sub>	128	80	218	31	8.50E-02	4.40E-04	-	3.36
ACL	208-96-8	C <sub>12</sub> H <sub>8</sub>	152	93	280	16.1	6.68E-03	1.14E-04	6.34	3.94
ACT	83-32-9	C <sub>12</sub> H <sub>10</sub>	154	93	279	3.9	2.15E-03	1.84E-04	6.52	3.92
FLN	86-73-7	C <sub>13</sub> H <sub>10</sub>	166	115	295	1.69	6.00E-04	9.62E-05	6.9	4.18
PHE	85-01-8	C <sub>14</sub> H <sub>10</sub>	178	99	340	1.15	1.21E-04	3.35E-05 <sup>b</sup>	7.68 <sup>b</sup>	4.46
ANT	120-12-7	C <sub>14</sub> H <sub>10</sub>	178	215	340	0.0434 <sup>†</sup>	2.67E-06 <sup>d</sup>	5.56E-05	7.71	4.45
CRB	86-74-8	C <sub>12</sub> H <sub>9</sub> N	167	246	355	1.8	7.50E-07 <sup>e</sup>	1.16E-07 <sup>b</sup>	8.03 <sup>b</sup>	3.72
FL	206-44-0	C <sub>16</sub> H <sub>10</sub>	202	108	384	0.26	9.22E-06	8.86E-06	8.76	5.16
PY	129-00-0	C <sub>16</sub> H <sub>10</sub>	202	151	404	0.135	4.50E-06	1.19E-05	8.81	4.88
BaA	56-55-3	C <sub>18</sub> H <sub>12</sub>	228	84	438	0.0094	2.10E-07	1.20E-05	10.28	5.76
CHR	218-01-9	C <sub>18</sub> H <sub>12</sub>	228	258	448	0.002	6.23E-09	5.23E-06	10.30	5.81
BbF	205-99-2	C <sub>20</sub> H <sub>12</sub>	252	168	-	0.0015	5.00E-07	6.57E-07	11.34	5.78
BkF	207-08-9	C <sub>20</sub> H <sub>12</sub>	252	217	480	0.0008	9.70E-10 <sup>d</sup>	5.84E-07	11.37	6.11
BaP	50-32-8	C <sub>20</sub> H <sub>12</sub>	252	177	495 <sup>†</sup>	0.00162	5.49E-09 <sup>d</sup>	4.57E-07	11.56	6.13
IcdP	193-39-5	C <sub>22</sub> H <sub>12</sub>	276	164	536	0.00019	1.25E-10	3.48E-07	12.43	6.7
DahA	53-70-3	C <sub>22</sub> H <sub>14</sub>	278	270	524	0.00249	1.00E-10	1.23E-07	12.59	6.75
BghiP	191-24-2	C <sub>22</sub> H <sub>12</sub>	276	278	>500	0.00026	1.00E-10	3.31E-07	12.55	6.63

<sup>\*\*</sup>Naphthalene (NAP), acenaphthylene (ACL), acenaphthene (ACT), fluorene (FLN), phenanthrene (PHE), anthracene (ANT), carbazole (CRB), fluoranthene (FL), pyrene (PY), benz[a]anthracene (BaA), chrysene (CHR), benz[b]fluoranthene (BbF), benz[k]fluoranthene (BkF), benz[a]pyrene (BaP), indeno[1,2,3-cd]pyrene (IcdP), dibenzo[a,h]anthracene (DahA), benzo[ghi,perylene] (BghiP).  
MW: Molecular weight, T<sub>m</sub>: Melting point, T<sub>b</sub>: Boiling point, S<sub>w</sub>: Solubility in water, VP: Vapor pressure, H: Henry's law constant, log K<sub>OW</sub>: Octanol-water coefficient, log K<sub>OA</sub>: Octanol-air coefficient, <sup>†</sup> at 24°C.  
<sup>a b c d e f</sup> [22].

Aquamate thermo electron corporation UV visible spectrophotometer (2007). First, the samples were centrifuged for 10 min at 7000 rpm. Secondly, 2.50 mL volume samples were treated with 1.5 mL 10216 mg/L K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> with 33.30 g/L HgSO<sub>4</sub> and 3.5 mL 18 M H<sub>2</sub>SO<sub>4</sub>, which contains 0.55% (w/w) Ag<sub>2</sub>SO<sub>4</sub>. Thirdly, the closed sample tubes were stored in a 148°C heater (thermoreactor, CR 4200 WTW, 2008) for 2 h. Finally, after cooling, the samples were measured at 600 nm with an Aquamate thermo electron corporation UV visible spectrophotometer (2007). The Close Reflux Method COD was used to measure the COD<sub>dis</sub> in PCI ww before and after sonication experiments. 0.45 µm membrane-filtered (Schleicher and Schuell ME 25, Germany) wastewater samples were used to measure the dissolved COD (COD<sub>dis</sub>) in PCI ww prior and after sonication experiments.

#### 2.2.4. Total Organic Carbon (TOC) Measurements

TOC was measured following the Standard Methods 5310 [21] with a Rosemount Dohrmann DC-190 high-temperature total organic carbon (TOC) analyzer (1994).

#### 2.2.5. Measurement of some Conventional Parameters

Total COD, NH<sub>4</sub>-N, NO<sub>3</sub>-N, NO<sub>2</sub>-N, total-P and PO<sub>4</sub>-P were measured with cell test spectroquant kits (Merck) in a spectroquant NOVA 60 (Merck) spectrophotometer (2003). Oil, dissolved oxygen (DO), pH and temperature T (°C) were determined with Standard Methods 5520 B, 3550, 2540 C, 2540 E, 2550, 2580, respectively [21].

#### 2.2.6. Daphnia magna Acute Toxicity Test

Toxicity was tested using 24 h born *Daphnia magna* as described in Std. M [21]. After preparing the test solution, experiments were carried out using 5 or 10 *daphnids* introduced into the test vessel. These vessels were controlled with 100 mL of effective volume at 7-8 pH, providing a minimum Dissolved Oxygen (DO) concentration of 6 mg/L at an ambient T of 20-25°C. Young *Daphnia magna* was used in the test (in first start ≤ 24 h old). A 24 h exposure is generally accepted for a *Daphnia* acute toxicity test. The results were expressed as mortality percentage of the *Daphnids*.

The immobile animals, which were not able to move, were reported as dead *Daphnids*.

### 2.2.7. Statistical Analysis

The regression analysis between  $y$  (dependent) and  $x$  (independent) variables was carried out using Windows Excel data analysis. An ANOVA test was performed in order to determine the statistical significance between  $x$  and  $y$  variables

### 2.2.8. The Removals of PAH, COD<sub>dis</sub> and TOC

The removal efficiency percentages of PAH, COD<sub>dis</sub> and TOC was calculated based on Equation (1)

$$E = \frac{\text{Influent total PAH, COD}_{dis} \text{ and TOC concentration} - \text{Effluent total PAH, COD}_{dis} \text{ and TOC concentration}}{\text{Influent total PAH, COD}_{dis} \text{ and TOC concentration}} \times 100 \quad (\text{Eq.1})$$

E: Removal efficiency (%)

Concentrations were mg/l and ng/mL

## 3. RESULTS AND DISCUSSION

### 3.1. Raw Wastewater

The characterization of raw wastewater were taken from the influent of aeration unit of a PCI ww treatment plant in İzmir, Turkey as shown in Table 2.

**Table 2: Characterization of Petrochemical Industry Wastewater**

Parameters	Values	Concentrations
pH	6.00-7.50	
DO (mg/L)		1.78
ORP (mV)		28.2
TSS (g/L)		31.03
TVSS (g/L)		25.06
BOD <sub>5</sub> (mg/L)		584
COD <sub>total</sub> (mg/L)		1475
COD <sub>dissolved</sub> (mg/L)		1127
Total-N (mg/L)		15.4
NH <sub>4</sub> -N (mg/L)		2.20
NO <sub>3</sub> -N (mg/L)		1.8
NO <sub>2</sub> -N (mg/L)		0.046
Total-P (mg/L)		10.6
PO <sub>4</sub> -P (mg/L)		6.8
Oil (mg/L)		206.5

### 3.2. Sonication Experiments

#### 3.2.1. Effect of Increasing Sonication Times on the PAH, COD<sub>dis</sub> and TOC Removal Efficiencies in Ambient Conditions

PCI ww samples were put to the a sonicator and the sonicator was operated at increasing sonication times(t) at 25°C ambient conditions (0 min, 60 min, 120 and 150 min) 56.05%, 62.30% and 80.16% COD<sub>dis</sub> removal efficiencies were observed at t=60 min, t=120 min and t=150 min, respectively (Figure 1a). 54.92%, 61.33% and 79.65% total PAH removal efficiencies were observed after 60 min, 120 min and 150 min sonication times, respectively (Figure 1b). These results showed that the COD<sub>dis</sub> and total PAH removal efficiencies of PCI ww increased as the sonication times were increased to 150 min. Sonication time has a positive effect of sonodegradation yields of PAHs and COD<sub>dis</sub> pollutants.

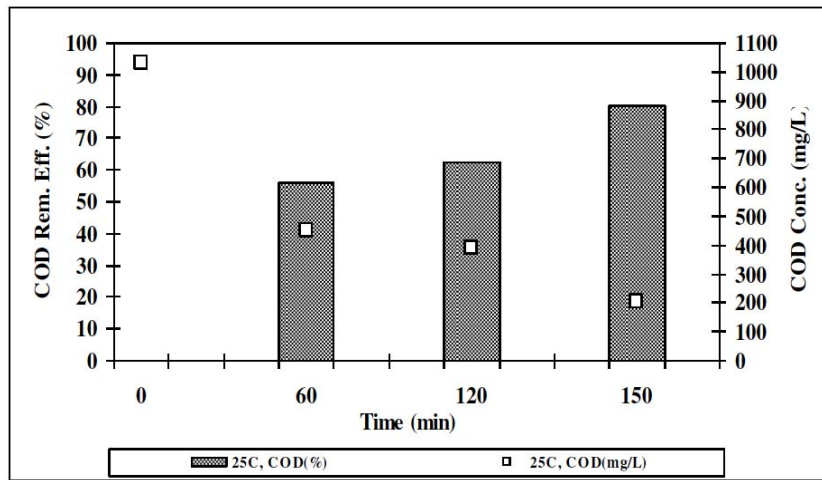
55.39%, 62.74% and 78.37% of TOC removal efficiencies were observed at t=60 min, t=120 min and t=150 min, respectively, at an initial TOC concentration of 620.81 mg/L at 25°C ambient conditions. Total TOC concentrations decreased from 620.81 to 276.94, from 620.81 to 231.33 and from 620.81 to 134.3 mg/L at 60 min, 120 min and 150min (Figure 1c), respectively. Increasing sonication time also increases the TOC yields. The maximum yields for all pollutants was observed at 150 min sonication time. Long contacting times under sonication increased the yields due to the production of high OH radical concentrations ending to high degradation yields.

The ANOVA test statistics showed that a significant linear relationship was found between the COD<sub>dis</sub>, total PAH and TOC yields and increasing sonication times ( $R^2 = 0.96$ ,  $F = 0.67$ ,  $p = 0.001$ ;  $R^2 = 0.98$ ,  $F = 0.45$ ,  $p = 0.001$ ;  $R^2 = 0.97$ ,  $F = 0.39$ ,  $p = 0.001$ ).

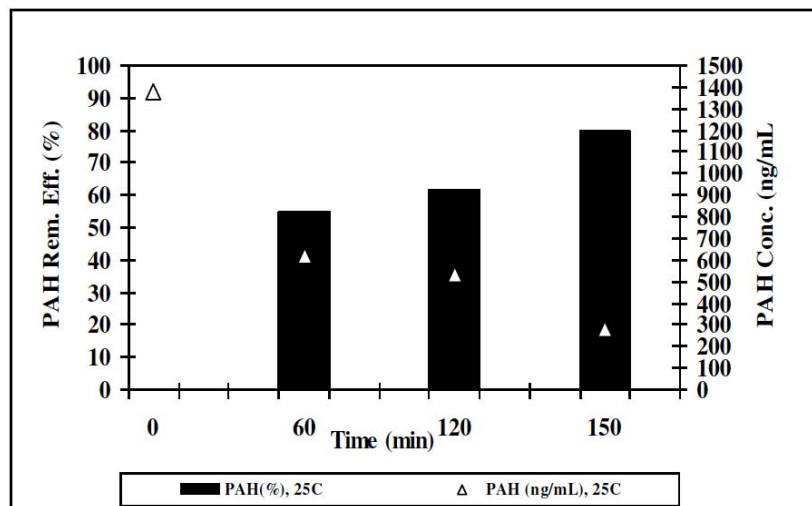
**The other pollutant parameter in PCI wastewater such as COD<sub>total</sub>, Total-N, NH<sub>4</sub>-N, NO<sub>3</sub>-N, NO<sub>2</sub>-N, Total-P, PO<sub>4</sub>-P and oil were removed with yields varying between 78% and 85% after 150 min sonication time at 25°C ambient temperature. As the sonication contact times were increased, the yields of all the pollutants mentioned above increased.**

#### 3.2.2. Effect of Increasing Temperatures on the Removal of PAH, COD<sub>dis</sub> and TOC at increasing Sonication Times

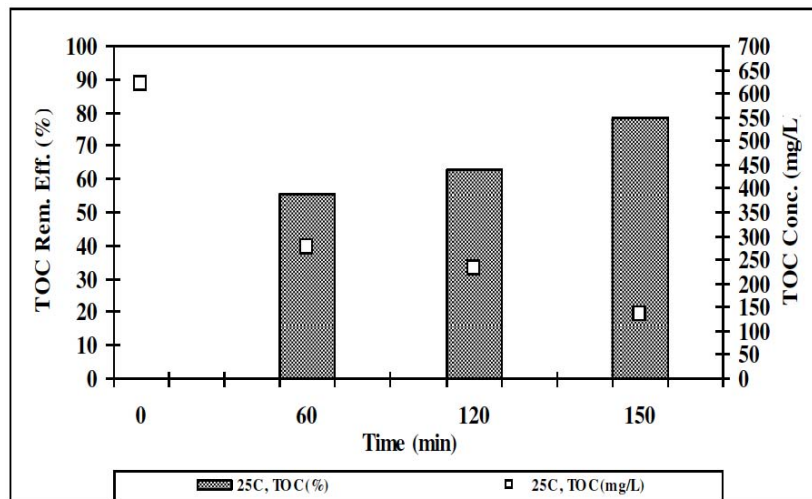
PCI ww samples were operated with sonicator at 25 °C, 30°C and 60°C temperatures during 0 min, 60 min,



a



b

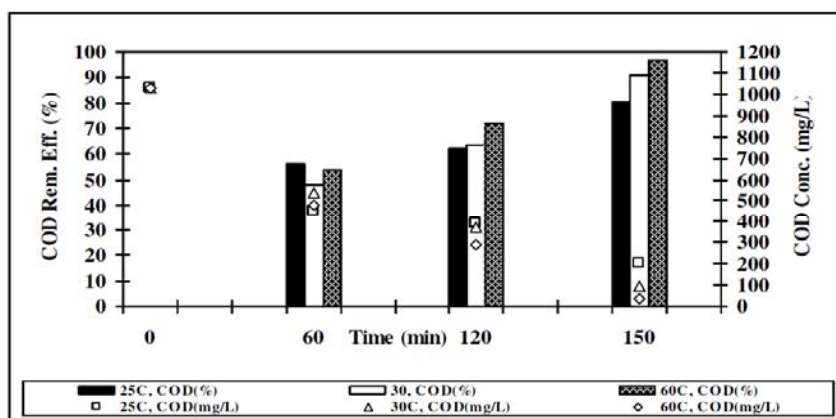


c

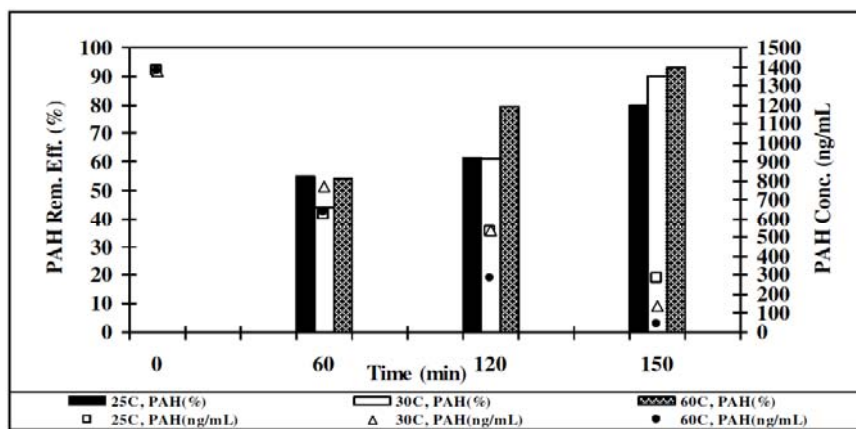
**Figure 1:** Effect of increasing sonication time on the (a)  $COD_{dis}$ , (b) PAH and (c) TOC removal efficiencies in 25°C ambient conditions versus increasing sonication times.

120 and 150 min of sonication times. In general, as the sonication times were increased from 60 min to 120

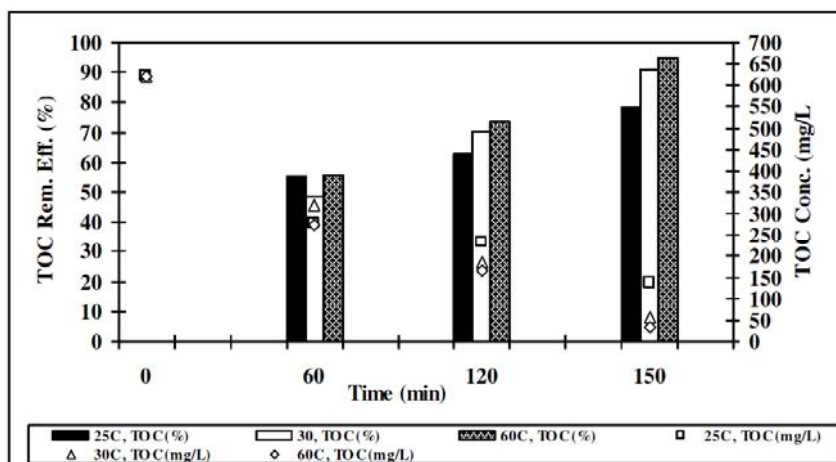
and to 150 min, the  $COD_{dis}$  yields also increased. No significant differences in  $COD_{dis}$  yields were measured



a



b



c

**Figure 2:** Effect of increasing temperature on the (a) COD<sub>dis</sub>, (b) PAH and (c) TOC removal efficiencies versus increasing sonication times.

after 60 min sonication times between 25 °C, 30°C and 60°C temperatures. 90.60% and 96.51% maximum COD<sub>dis</sub> removal efficiencies were observed at 30°C and 60°C, respectively, at an initial COD<sub>dis</sub> concentration of 1027.43 mg/L after 150 min sonication (Figure 2a). As the temperature was increased from 25 °C to 30°C, the COD<sub>dis</sub> removals remained stable at 120 min sonication

time. At this time, the COD<sub>dis</sub> removals were high at 60°C temperature.

The total PAH yields, measured at 25 °C, 30°C and 60°C temperatures were approximately close to each other after 60 min sonication time. The effect of temperature was found to be non-significant in this

sonication time. The total PAH concentrations decreased from 1378.77 to 138.68 ng/mL and from 1378.77 to 42.78 ng/mL at 30°C and 60°C, respectively, after 150 min. (Figure 2b). 89.94% and 96.90% maximum total PAH removal efficiencies were observed at 30°C and 60°C, respectively, after 150 min sonication.

The COD<sub>dis</sub> and total PAH removal efficiencies of PCI ww increased for the increasing sonication temperature (60°C), particularly after 150 min of sonication time. Some recent literatures, relevant to this study, were compared with our study: 78% COD<sub>dis</sub> removal efficiency was observed with sonochemical degradation at 50 µg/L initial PAHs mixture concentration (naphthalene, acenaphthylene and phenanthrene) in H<sub>2</sub>O at sonication times of 30, 60 and 120 min, with 20 and 40°C temperatures, at powers of 45, 75 and 150 W, and at ultrasound frequencies of 24 and 80 kHz [12]. Benabdallah El-Hadj *et al.*, (2007) found 34% - 31% and 50% - 44% PAH removal efficiencies in mesophilic (35°C) and thermophilic (55°C) anaerobic digestions for mixture of naphthalene and pyrene in a sonicator having a frequency of 20 kHz and an ultrasonic power of 70 W, after 20 min sonication time [9]. In our studies, high COD and total PAH yields were observed than the studies mentioned above.

As the sonications times and temperatures were increased from 60 min to 120 and 150 min, and from 25 °C to 30°C and 60°C, the TOC yields increased. 91.01% and 94.93% maximum TOC removal efficiencies were observed at 30°C and 60°C, respectively, at an initial TOC concentration of 620.81 mg/L. The TOC concentrations decreased from 620.81 to 55.8 mg/L and from 620.81 to 31.5 mg/L at 30°C and 60°C, respectively (Figure 2c).

The ANOVA test statistics showed that a significant linear relationship was found between the COD<sub>dis</sub>, total PAH and TOC yields and increasing temperatures ( $R^2 = 0.98$ ,  $F = 0.56$ ,  $p = 0.001$ ;  $R^2 = 0.95$ ,  $F = 0.40$ ,  $p = 0.001$ ;  $R^2 = 0.98$ ,  $F = 0.32$ ,  $p = 0.001$ ).

**The other pollutant parameters in PCI wastewater such as COD<sub>total</sub>, Total-N, NH<sub>4</sub>-N, NO<sub>3</sub>-N, NO<sub>2</sub>-N, Total-P, PO<sub>4</sub>-P and oil were removed with high yields, varying between 93% and 97%, after 150 min of sonication time at 30°C temperature. At 60°C, the removals of the aforementioned pollutant parameters exhibited the same yields with 60°C temperature after 150 min sonication (data not shown).**

Sonochemical reactions are induced by directing sound waves into liquids, thereby producing cavitation bubbles [11, 12]. Ultrasonic action produces radicals such as hydrogen, hydroxyl and hydroperoxyl radicals (H<sup>•</sup>, OH<sup>•</sup>, O<sub>2</sub>H<sup>•</sup>, respectively) and can be classified as an advanced oxidation process (AOP) [12]. The formation of cavitation bubbles and the extent of bubble collapse depend on the sonication frequency, power and sound intensity. In the presence of OH<sup>•</sup>, the number of collapsing cavities is also increased, thus leading to enhanced degradation rates. The collapse of bubbles in the reaction cell occurs more rapidly and the number of cavitation bubbles increases thus producing a higher concentration of OH<sup>•</sup> at optimum ultrasonic intensities. These OH<sup>•</sup> react with the pollutants and enhance their yields [11, 12].

The literature data concerning the sonodegradation of PAHs is scarce and, moreover, results are contradictory. Indeed, some works mentioned that PAHs are (i) oxidized by means of H, H, OH and -OOH (hydrogen, hydroxyl and hydroperoxyl radicals [12, 13], whereas other studies argued that (ii) a pyrolytic process can occur [10] and finally that (iii) both processes are possible [11,12]. The first process was evidenced by the identification of hydroxylated by-products. These radicals can result in the destruction of solutes containing organic pollutants. In the second pathway, the formation of hydroxylated by-products was not observed under ultrasonic irradiation; it is suggested that OH are not important species and PAH removals were performed via high-temperature pyrolysis [11-13].

The operating cost of sonication appear to be less severe than would be required by conventional thermochemical methods (e.g. wet air oxidation), which require high temperatures and pressures [12, 13]. Furthermore, the sonication process does not require the use of extra chemicals (e.g. oxidants and catalysts), commonly employed in several advanced oxidation processes (e.g. ozonation, Fenton's reagent), thus avoiding the respective costs as well as the need to remove the excess of toxic compounds prior to discharge.

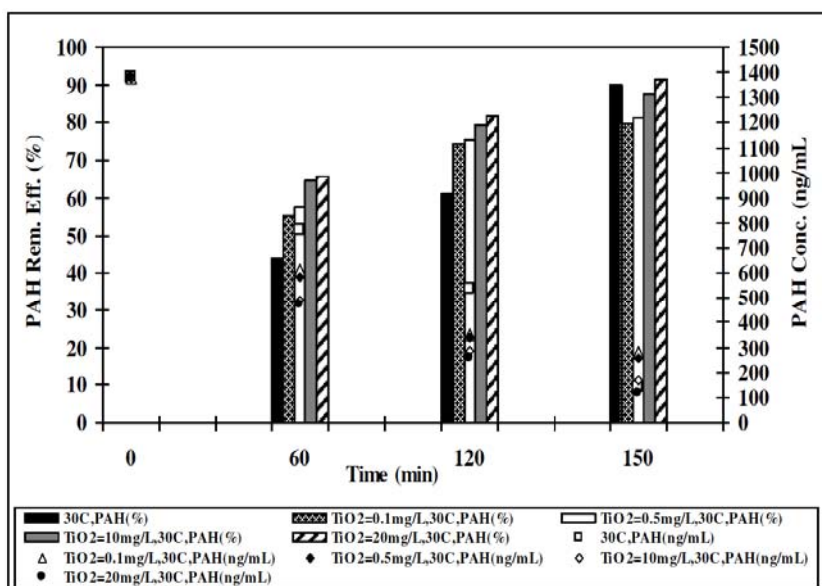
### **3.2.3. Effect of Titanium Dioxide (TiO<sub>2</sub>) Concentration on the PAH, COD<sub>dis</sub> and TOC Removal Efficiencies at increasing Sonication Times and Temperatures**

Increasing the TiO<sub>2</sub> concentrations from 0.1 mg/L to 0.5 mg/L and 10 to 20 mg/L elevated the total PAH yields significantly after 60 and 120 min of sonication at

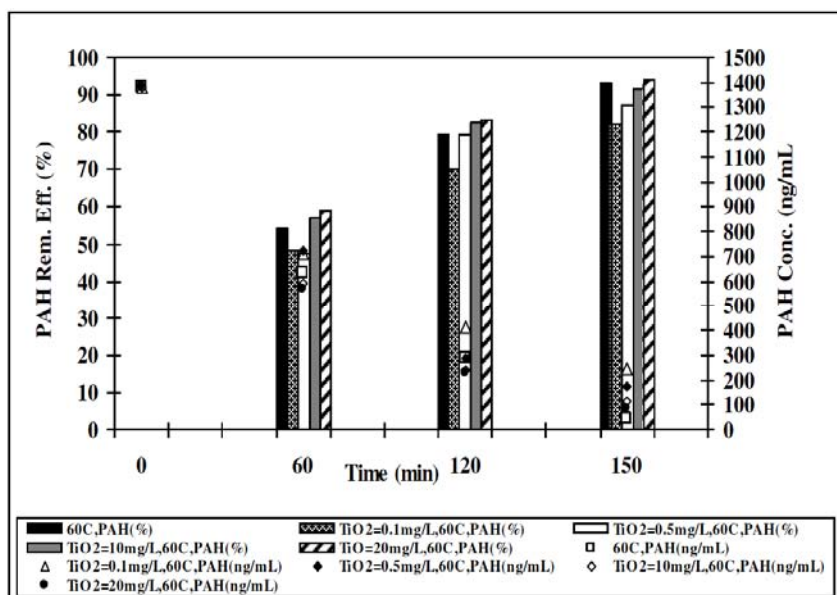
30°C. However, after 150 min of sonication, the total PAH yields at 30° C without TiO<sub>2</sub> exhibited similar results with the samples containing 20 g/l TiO<sub>2</sub>. As the sonication times were increased from 60 min to 120 min, the total PAH yields increased approximately from 79.58% to 81.47%, to 87.59% and to 91.55% at an initial PAH concentration of 1378.77 ng/mL, at increasing TiO<sub>2</sub> concentrations from 0.1 mg/L to 0.5 mg/L, to 10 and to 20 mg/L, respectively, at 30°C. (Figure 3a). It was found that as the TiO<sub>2</sub> concentration was increased from 0, 1 mg/l to 10 and 20 mg/l, the total PAH yields increased, at 30°C, after 60 and 120

min of sonication. After 150 min of sonication, the contribution of increasing TiO<sub>2</sub> was not found to total PAH removals.

At 60°C, although the total PAH yields increased in general versus increasing sonication times, at 60 and 120 min sonication times, the maximum PAH yields observed with 10 and 20 mg/l TiO<sub>2</sub> exhibited similar yields with only sonication, without TiO<sub>2</sub>. The maximum total PAH yields were around 93.88% for TiO<sub>2</sub>=10 mg/l, TiO<sub>2</sub>=20 mg/L, and with only sonication (Figure 3b).



a



b

Figure 3: Effect of increasing TiO<sub>2</sub> concentrations (a) TiO<sub>2</sub>=0.1 mg/L, TiO<sub>2</sub>=0.5 mg/L, TiO<sub>2</sub>=10 and TiO<sub>2</sub>=20 mg/L at 30°C and (b) TiO<sub>2</sub>=0.1 mg/L, TiO<sub>2</sub>=0.5 mg/L, TiO<sub>2</sub>=10 and TiO<sub>2</sub>=20 mg/L at 60°C on the total PAH removal efficiencies in petrochemical industry wastewaters versus increasing sonication times.

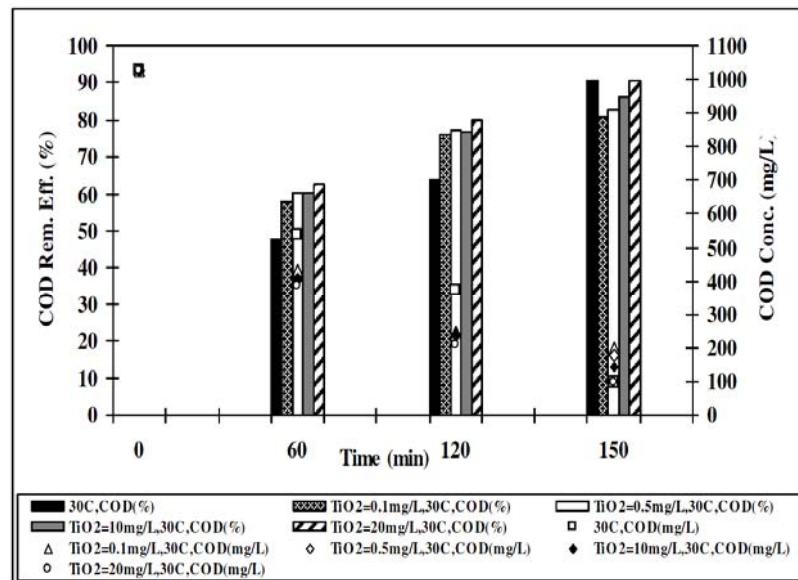


At 30°C, the increasing of TiO<sub>2</sub> concentrations elevated the COD<sub>dis</sub> removals after 60 and 120 min of sonication. The maximum COD<sub>dis</sub> yields were 58% and 81% for the aforementioned sonication times. After 150 min of sonication, the maximum COD<sub>dis</sub> yield was calculated as 93% with 20 mg/l TiO<sub>2</sub> and with only sonication without TiO<sub>2</sub>. At high sonication times, sonication alone provided high COD<sub>dis</sub> removal efficiencies (Figure 4a).

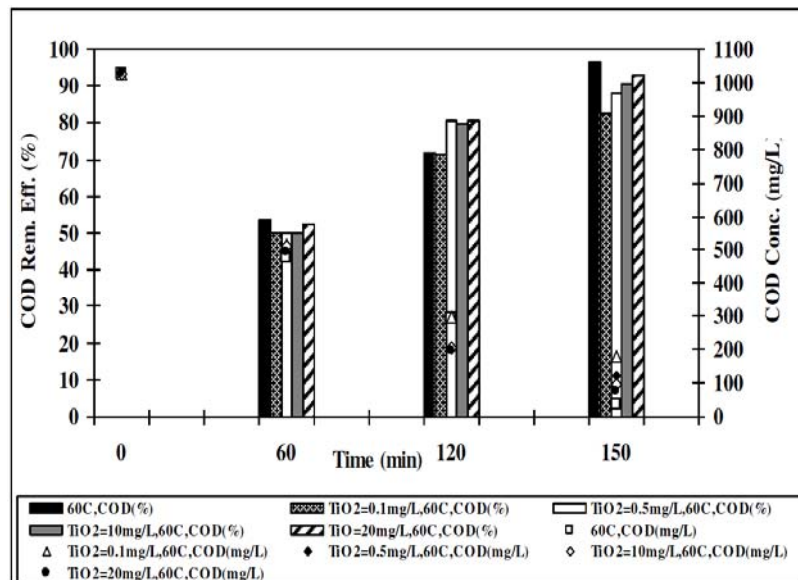
The COD<sub>dis</sub> removal efficiencies were the same at all TiO<sub>2</sub> concentrations and at the samples with only 60

min of sonication (around 52%) at 60°C. The maximum COD<sub>dis</sub> removal efficiencies were measured around 80% with 0, 5 mg/l, 10 and 20 mg/l TiO<sub>2</sub> concentrations. After 150 min of sonication, the sonication alone provided the maximum COD<sub>dis</sub> removal efficiency (99%). At this sonication time, all the TiO<sub>2</sub> concentrations did improve the COD<sub>dis</sub> yields (Figure 4b).

At 30°C, 79.28%, 80.85%, 84.96% and 87.31% of TOC removal efficiencies were measured in 620.81 mg/L of initial TOC concentration for TiO<sub>2</sub>=0.1 mg/L,

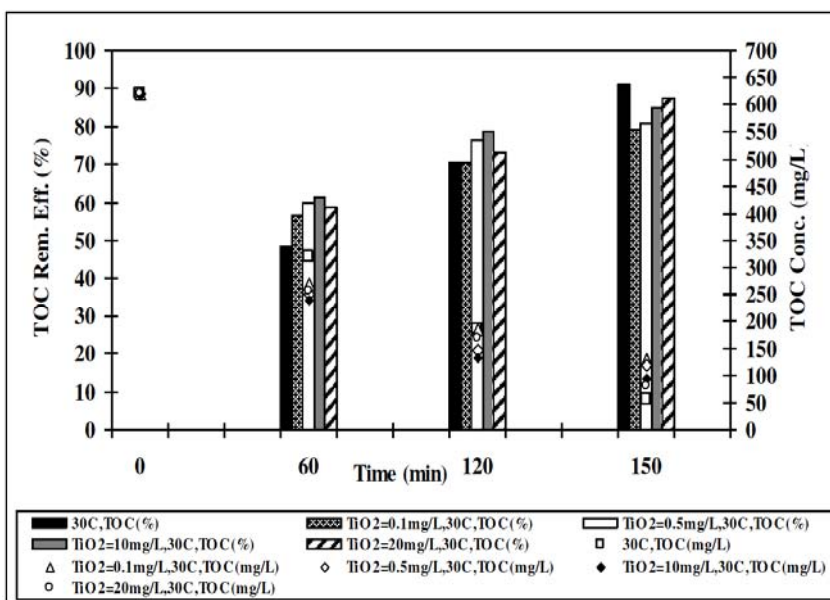


a

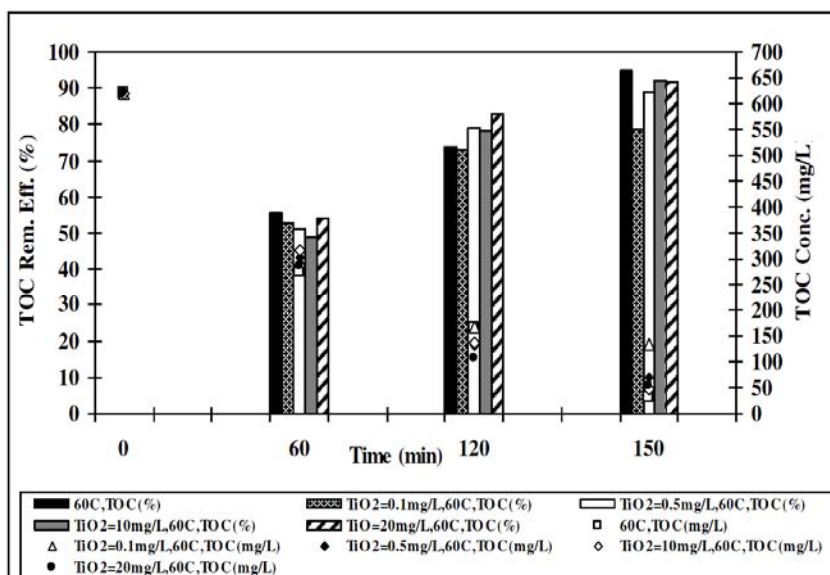


b

**Figure 4:** Effect of increasing TiO<sub>2</sub> concentrations (a) TiO<sub>2</sub>=0.1 mg/L, TiO<sub>2</sub>=0.5 mg/L, TiO<sub>2</sub>=10 and TiO<sub>2</sub>=20 mg/L at 30°C and (b) TiO<sub>2</sub>=0.1 mg/L, TiO<sub>2</sub>=0.5 mg/L, TiO<sub>2</sub>=10 and TiO<sub>2</sub>=20 mg/L at 60°C. on the removals of COD<sub>dis</sub> removal efficiencies in petrochemical industry wastewaters versus sonication times.



a



b

**Figure 5:** Effect of increasing TiO<sub>2</sub> concentrations (a) TiO<sub>2</sub>=0.1 mg/L, TiO<sub>2</sub>=0.5 mg/L, TiO<sub>2</sub>=10 and TiO<sub>2</sub>=20 mg/L at 30°C and (b) TiO<sub>2</sub>=0.1 mg/L, TiO<sub>2</sub>=0.5 mg/L, TiO<sub>2</sub>=10 and TiO<sub>2</sub>=20 mg/L at 60°C. on the TOC removal efficiencies in petrochemical industry wastewaters versus sonication times.

TiO<sub>2</sub>=0.5 mg/L, TiO<sub>2</sub>=10 and TiO<sub>2</sub>=20 mg/L, respectively (Figure 5a). 78.73%, 88.81%, 92.18% and 91.54% of TOC removal efficiencies were observed for TiO<sub>2</sub>=0.1 mg/L, TiO<sub>2</sub>=0.5 mg/L, TiO<sub>2</sub>=10 and TiO<sub>2</sub>=20 mg/L at 60°C, respectively (Figure 5b).

The ANOVA test statistics indicated that a significant linear relationship was found between the COD<sub>dis</sub>, total PAH and TOC yields and increasing TiO<sub>2</sub> ( $R^2 = 0.97, F = 0.32, p = 0.001; R^2 = 0.97, F = 0.34, p = 0.001; R^2 = 0.97, F = 0.29, p = 0.001$ ). However, after 120 and 150 min of sonication, the sonication alone

provided high pollutant yields as in 20 mg/l TiO<sub>2</sub> added samples.

In general, the following two points of view, namely, sonoluminescence and “hot spot”, should be accepted to explain the reaction process of sonocatalytic degradation of organic pollutants in solution in the presence of TiO<sub>2</sub> catalyst. Firstly, it has been well known that the ultrasonic irradiation can result in the formation of light with a comparatively wide wavelength range. Those lights whose wavelengths are < 375nm, beyond all doubt, can excite the TiO<sub>2</sub> particle acting as

a photocatalyst and a great deal of OH with high oxidative activity forming on the surface of the TiO<sub>2</sub> particles. High temperatures sufficiently brings many cavities producing OH<sup>•</sup> on the surface of TiO<sub>2</sub> particles [23, 24]. At long sonication times, the addition of TiO<sub>2</sub> did not positively affect the pollutant yields because at high contact times, the TiO<sub>2</sub> decrease the OH radical productions. Both sonocatalytic and ultrasonic destruction in the presence of TiO<sub>2</sub> decreased gradually along with the increased temperature [25]. In general, for most chemical reactions, the higher the temperature in the reaction system, the quicker the reaction rate since the radical reactions depend strongly on the system temperature. However, acoustic cavitation, which produces holes on the surface of TiO<sub>2</sub> particles or OH<sup>•</sup> radicals in aqueous solution, depends on the change of system temperature. It is well known that both sonocatalytic and ultrasonic degradation of organic pollutants are related to the acoustic cavitation. The acoustic cavitation can give rise to holes with strong oxidability on the surface of TiO<sub>2</sub> particles, which either can directly decompose the organic pollutants adsorbed on the surface of TiO<sub>2</sub> particles or indirectly remove the organic pollutants in the aqueous solution through the OH<sup>•</sup> radicals resulting from hole oxidation of H<sub>2</sub>O molecules. When the temperature in the aqueous solution became high, the vapor or gas bubbles did not escape from the reaction system and thus grew or collapsed the OH radicals and increased the acoustic cavitation. Sometimes, high temperatures act against ultrasonic degradation because the holes on the surface or inside the TiO<sub>2</sub> particles result from acoustic cavitation. In addition, sonocatalytic degradation relates to the adsorbability of TiO<sub>2</sub> particles. In general, appropriate adsorbability is likely to encourage sonocatalytic removal. Suitable quantities of organic pollutants adsorbed on the surface of TiO<sub>2</sub> particles can be directly decomposed by the holes. However, high temperatures generally weaken the adsorbability of TiO<sub>2</sub> particles, permitting large numbers of organic pollutants to freely and rapidly move in the solution and thus avoid degradation.

**The other pollutant parameter in PCI wastewater such as COD<sub>total</sub>, Total-N, NH<sub>4</sub>-N, NO<sub>3</sub>-N, NO<sub>2</sub>-N, Total-P, PO<sub>4</sub>-P and oil** were removed with high yields varying between 90% and 95% after 150 min sonication time at 30°C temperature with 10 mg/l TiO<sub>2</sub>. At 60°C, the removals of the aforementioned pollutant parameters were increased to 93 and 98% with 20 mg/l TiO<sub>2</sub> at 60°C temperature, after 150 min (data not shown).

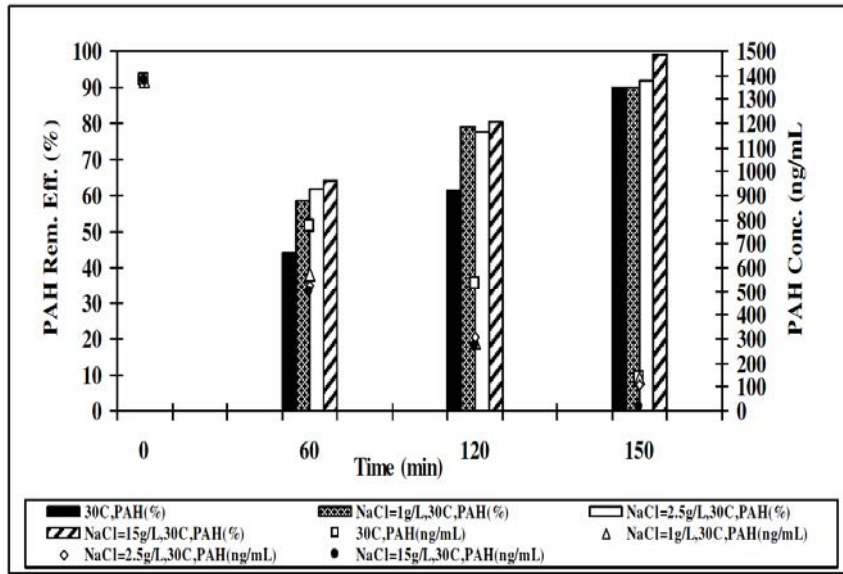
### 3.2.4. Effect of Sodium Chloride (NaCl) Concentration on the PAH, COD<sub>dis</sub> and TOC Removal Efficiencies at increasing Sonication Times and Temperatures

Increasing NaCl concentrations (1 g/L, 2.5 and 15 g/L) were added in PCI ww before the sonication experiment. At 30°C, 90.02%, 92.03% and 99.12% maximum total PAH removal efficiencies were observed at 1 g/L, 2.5 and 15 g/L NaCl concentrations, respectively, at 30°C after 150 min (Figure 6a). After 120 min of sonication, the maximum total PAH yields were found with 2.5 and 15 g/l around 82% after 150 min. The maximum total PAH removal was observed with 15 g/L NaCl after 150 min. At 60 min sonication time, the maximum yields were observed after 150 min sonication time with 15 g/l NaCl as 99.99%. The total PAH yields significantly increased with the addition of NaCl. The total PAH yields increased significantly from 63% to 85% with the addition of 15 g/l NaCl (Figure 6b).

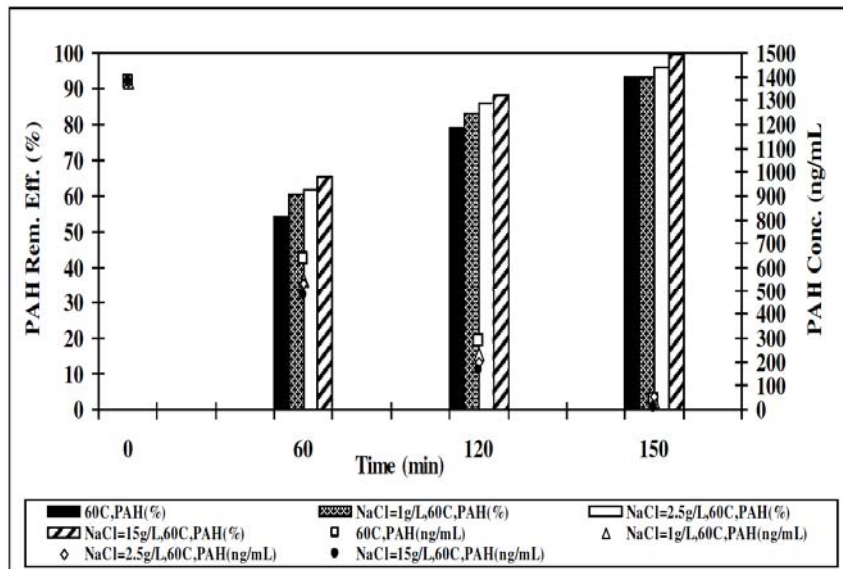
Psillakis *et al.* [20] investigated the sonodegradation of 150 µg/L initial total PAH mixture (naphthalene, acenaphthylene and phenanthrene) in aqueous solution. 84.4% naphthalene, 96.6% of acenaphthylene and 83% of phenanthrene removal efficiencies were found by ultrasonic irradiation with 100 g/L of NaCl (10%, w:v) solution at a sonicator having a power of 150 W at an ultrasound frequency of 24 kHz, and at a sonication temperature of 20°C, after 60 min irradiation time [20]. Our results are extremely higher and the NaCl dosage used is times less as compared to the dosage mentioned in their study.

Figure 7a exhibited the COD<sub>dis</sub> removals versus increasing NaCl concentrations at 30°C. 90.14%, 92.07% and 99.11% COD<sub>dis</sub> removal efficiencies were observed for NaCl=1 g/L, NaCl=2.5 and NaCl=15 g/L, respectively, at 30°C after 150 min of sonication, at an initial COD<sub>dis</sub> concentration of 1027.43 mg/L (Figure 7a). For a short sonication time of 60 min, the maximum COD<sub>dis</sub> yields were obtained with 2.5 and 15 mg/l NaCl (around 62%) at 30°C. The COD<sub>dis</sub> removals were around 74% with 1 g/l and 15 g/l NaCl after 120 min of sonication. The maximum COD<sub>dis</sub> removal was obtained with 15 g/l NaCl after 150 min of sonication, i.e., 99,90% (Figure 7a).

At 60°C, 93.17%, 95.61% and 99.94% of COD<sub>dis</sub> removal efficiencies were measured for NaCl=1 g/L, NaCl=2.5 and NaCl=15 g/L, respectively, after 150 min of sonication (Figure 7b). The maximum yield was detected with 15 g/l NaCl. After 60 min sonication time,



a



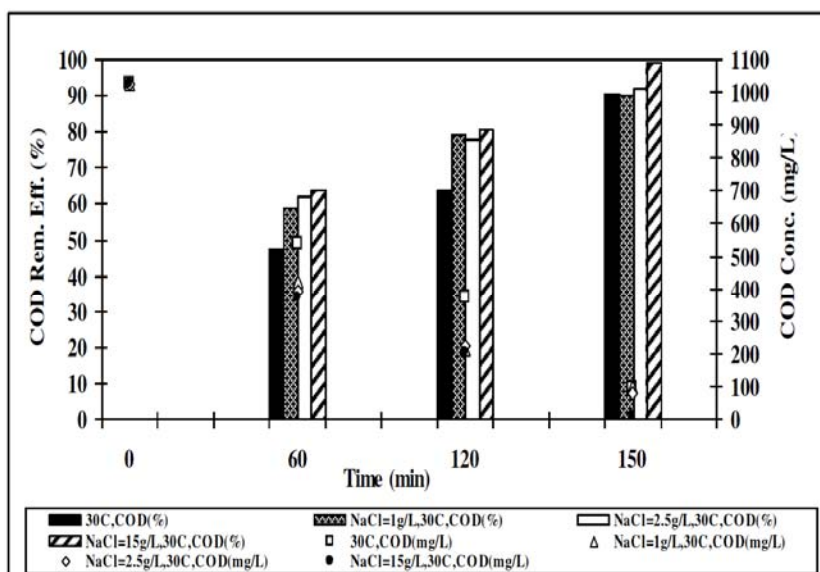
b

**Figure 6:** Effect of increasing NaCl concentrations (a) NaCl=1 g/L, NaCl=2.5 and NaCl=15 g/L at 30°C and (b) NaCl=1 g/L, NaCl=2.5 and NaCl=15 g/L at 60°C on the removal of total PAH removal efficiencies in petrochemical industry wastewaters versus sonication times.

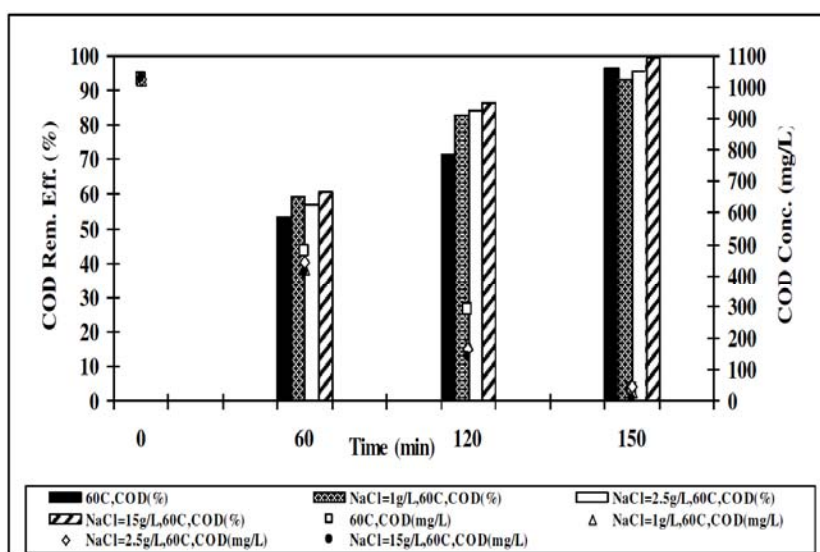
the maximum yields were around 62% with 15 g/l NaCl (Figure 7b). The maximum COD<sub>dis</sub> removal efficiencies were approximately 82% with 15 g/l NaCl.

As shown in Figure 8a, 88.60%, 88.87% and 96.70% of TOC removal efficiencies were observed for NaCl=1g/L, NaCl=2g/L and NaCl=15g/L, respectively, at 30°C after 150 min of sonication, at an initial TOC concentration of 620.81 mg/L. The maximum TOC yield was observed with 15 g/l NaCl, after 150 min at 30°C. The maximum TOC yield was detected at 2.5 g/l NaCl as 58%. The maximum TOC yield was around 76% after 120min sonication with 2.5 g/l NaCl. At 60°C,

82.96%, 90.79% and 99.08% TOC removal efficiencies were detected for NaCl=1 g/L, NaCl=2.5 and NaCl=15 g/L, respectively, after 150 min of sonication (Figure 8b). At a short sonication time of 60 min, similar TOC removals were detected at all NaCl levels and in the sample with only sonication (54%). The maximum TOC removals were 82% and 99.08 % after 120 and 150 min of sonications at NaCl concentrations of 2.5 g/l and 15 g/l NaCl, respectively, at 60°C. The samples with only sonication exhibited high TOC yields (97%) after 150 min of sonication at the aforementioned temperature.



a



b

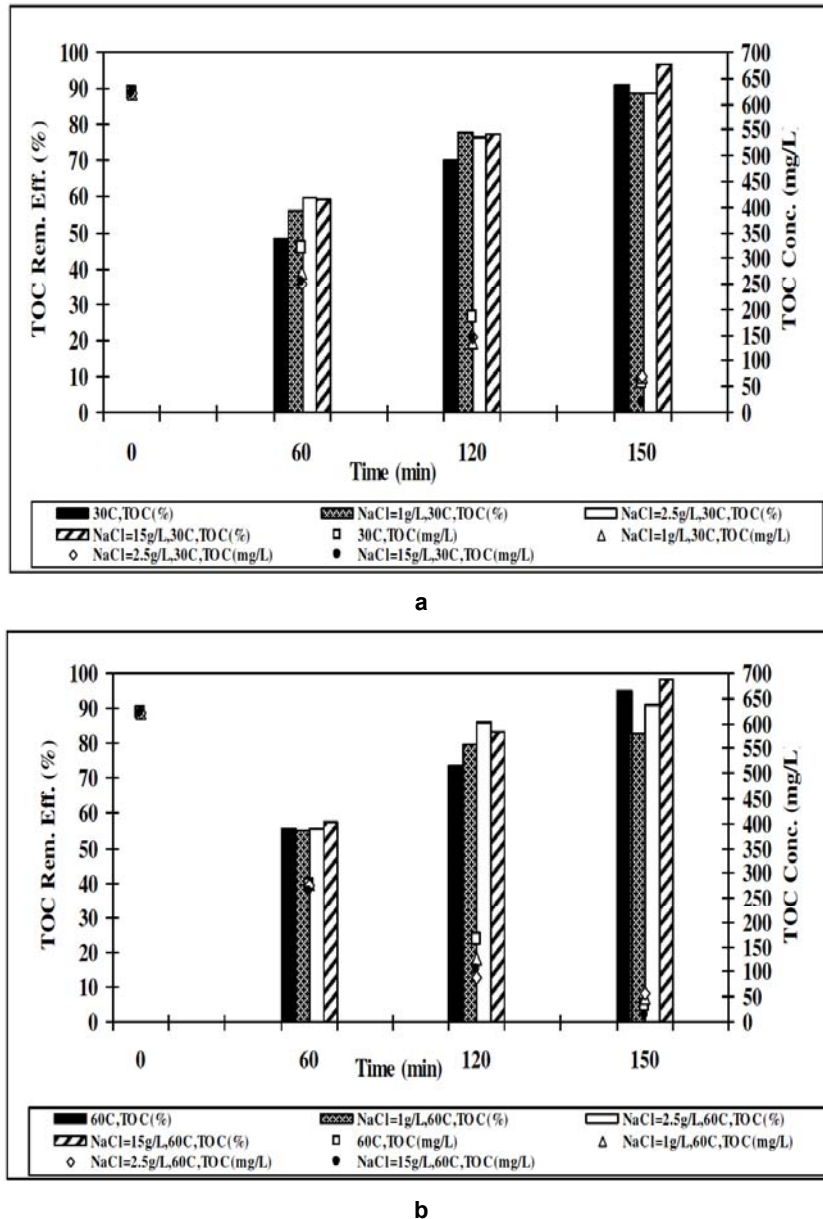
**Figure 7:** Effect of increasing NaCl concentrations (a) NaCl=1 g/L, NaCl=2.5 and NaCl=15 g/L at 30°C and (b) NaCl=1 g/L, NaCl=2.5 and NaCl=15 g/L at 60°C on the removals of COD<sub>dis</sub> efficiencies in f petrochemical industry wastewaters versus sonication time.

The ANOVA test statistics showed that that a significant linear relationship was found between the COD<sub>dis</sub>, total PAH and TOC yields and increasing NaCl concentrations ( $R^2 = 0.98$ ,  $F = 0.30$ ,  $p = 0.001$ ;  $R^2 = 0.97$ ,  $F = 0.31$ ,  $p = 0.001$ ;  $R^2 = 0.96$ ,  $F = 0.26$ ,  $p = 0.001$ ). However, after 150 min of sonication, the sonication alone provided high pollutant yields as seen in 15 g/l NaCl added samples.

**The other pollutant parameter in PCI wastewater such as COD<sub>total</sub>, Total-N, NH<sub>4</sub>-N, NO<sub>3</sub>-N, NO<sub>2</sub>-N, Total-P, PO<sub>4</sub>-P and oil were removed with high yields varying between 88% and 91% after 150 min of sonication at 60°C temperature (data not shown).**

Depending on the nature of the contaminants, addition of salt (NaCl) to the solution can decrease their solubility; consequently, it can increase their hydrophobicity due to the salting-out effect. This is expected to enhance the diffusion of solutes from the bulk solution to the bubble–liquid interface, thus leading to increased degradation rates. A possible explanation would be that adding salt to the reaction mixture results in reduced vapour P and increased surface tension, both of which tend to reduce the number of bubbles formed [20].

The higher NaCl concentrations (10–15 g/l) resulted in high removals. This can be explained by the fact that



**Figure 8:** Effect of NaCl concentrations (a) NaCl=1 g/L, NaCl=2.5 and NaCl=15 g/L at 30°C and (b) NaCl=1 g/L, NaCl=2.5 and NaCl=15 g/L at 60°C on the TOC removal efficiencies in petrochemical industry wastewaters versus sonication time.

a higher amount of NaCl will create more salting out effect than the lower amount, and thus increase the interfacial concentration of the PAHs. All of these factors help to collapse the bubbles more violently, causing high PAH degradation. Since the Na<sup>+</sup> and Cl<sup>-</sup> concentrations in the sonicator were measured as 1.1 and 1.9 mg/l, respectively, after sonication, it can be concluded that a large part of 15 g/l NaCl reached a non-equilibrium adsorption level at the bubble/solution interface under the sonication conditions used. On the basis of this conclusion, it can be mentioned that the non-equilibrium surface excess values for solutes do not fully equilibrate with the bubble/solution interface during sonication. For hydrophobic compounds, in the

presence of excess NaCl, an acoustic bubble in a multibubble field has a finite lifetime, and that lifetime increases. This results in the adsorption of excess salt to the bubble/solution interface during sonication as reported by Sunartio *et al.* [26]. Therefore, the NaCl remaining from the sonication did not cause serious pollution.

**3.2.5. Effect of Ferrous (Fe<sup>+2</sup>) Ions Concentration on the Removal of PAH, COD<sub>dis</sub> and TOC at Increasing Sonication Times and Temperatures**

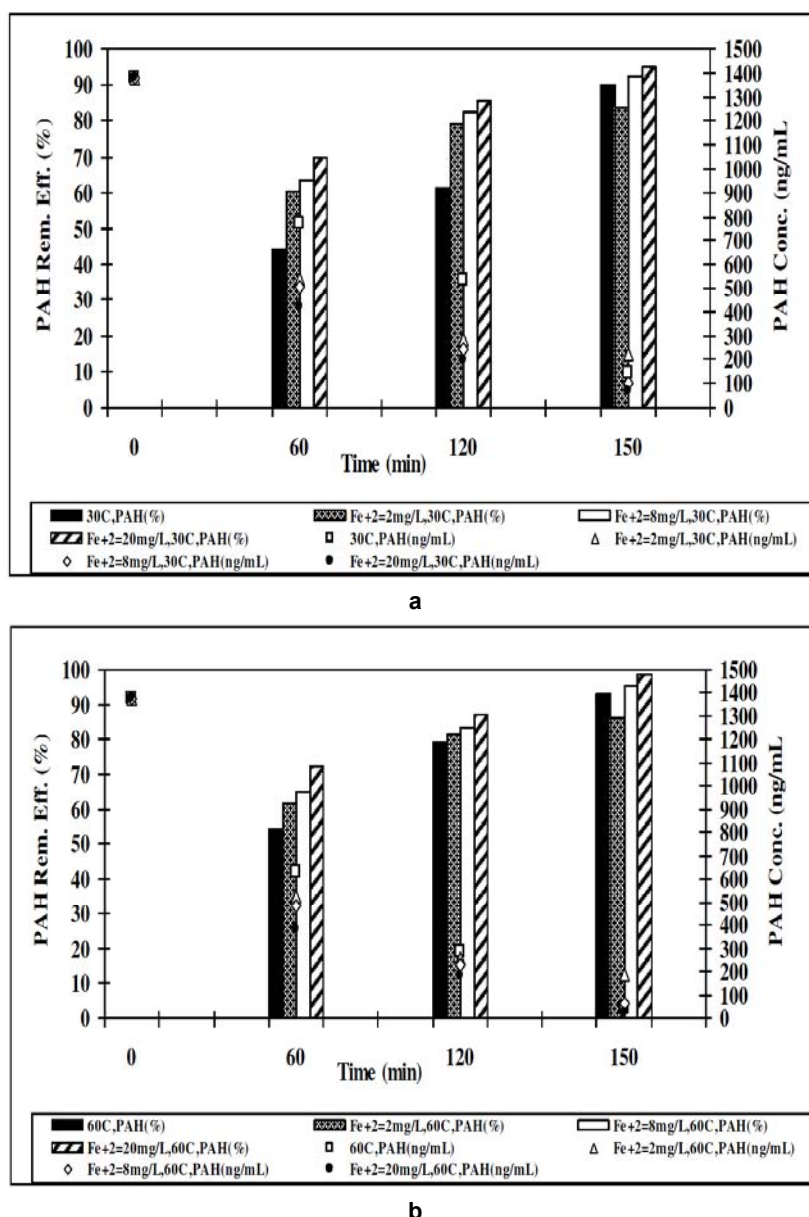
Increasing Ferrous (Fe<sup>+2</sup>) ions concentrations (2 mg/L, 8 and 20 mg/L) were added in PCI ww before sonication process. In this study, it was found that Fe<sup>+2</sup>

addition significantly increased the total PAH removals as compared to the sonication times. At long sonication times, high total PAH yields were obtained at high  $\text{Fe}^{+2}$  concentrations (20 mg/l). At 30°C, 83.97%, 92.51% and 95.05% of total PAH removal efficiencies were measured at  $\text{Fe}^{+2}=2$  mg/L,  $\text{Fe}^{+2}=8$  and  $\text{Fe}^{+2}=20$  mg/L, respectively, at an initial total PAH concentration of 378.77 ng/mL after 150 min of sonication (Figure 9a). At 60 min sonication time, the maximum total PAH yield was 67% with 20 mg/l  $\text{Fe}^{+2}$  at 30°C. The maximum total PAH removals were 95.05% with 20 mg/l  $\text{Fe}^{+2}$  after 150 min.

In Figure 9b, 86.28%, 95.27% and 98.56% of total PAH removal efficiencies were observed for  $\text{Fe}^{+2}=2$

mg/L,  $\text{Fe}^{+2}=8$  and  $\text{Fe}^{+2}=20$  mg/L, respectively, at 60°C after 150 min. The maximum total PAH removals were 72 % with 20 mg/l  $\text{Fe}^{+2}$  after 60 min while the total PAH yields were measured as 98% with 20 mg/l  $\text{Fe}^{+2}$  at 60°C. The samples without  $\text{Fe}^{+2}$  also exhibited high PAH yields (96%) after 150 min of sonication at 60°C.

Psillakis *et al.* [20] studied the sonodegradation of 150  $\mu\text{g/l}$  naphthalene, acenaphthylene and phenanthrene mixtures in aqueous solution. 91.2% naphthalene, 93% f acenaphthylene and 89.8% of phenanthrene removal efficiencies were found with  $\text{Fe}^{+2}=14$  mg/L at a sonicator having a power of 150 W, a frequency of 80 kHz, and a sonication temperature of 20°C, after 260 min irradiation [20]. In our study, high



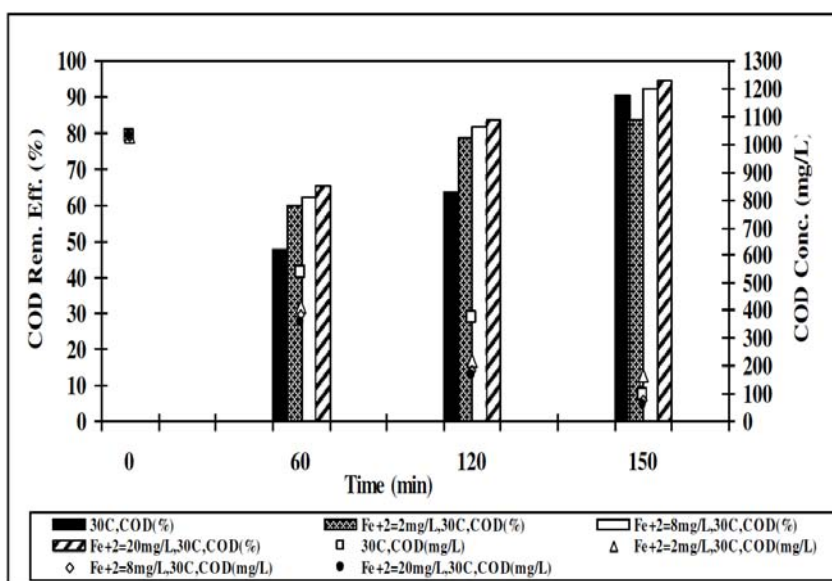
**Figure 9:** Effect of (a)  $\text{Fe}^{+2}=2$  mg/L,  $\text{Fe}^{+2}=8$  and  $\text{Fe}^{+2}=20$  mg/L at 30°C and (b)  $\text{Fe}^{+2}=2$  mg/L,  $\text{Fe}^{+2}=8$  and  $\text{Fe}^{+2}=20$  mg/L at 60°C on the total PAH removal efficiencies in petrochemical industry wastewaters versus sonication times.

PAH yields were detected than the aforementioned study although it was studied at short sonication times.

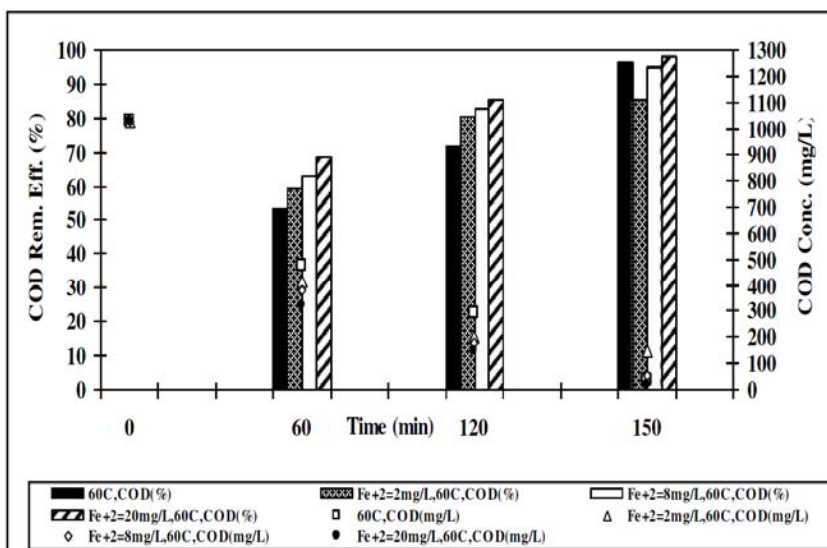
83.72%, 92.31% and 94.37% COD<sub>dis</sub> removal efficiencies were measured at Fe<sup>+2</sup>=2 mg/L, Fe<sup>+2</sup>=8 and Fe<sup>+2</sup>=20 mg/L, respectively, at 30°C after 150 min sonication (Figure 10a). The maximum yields were detected with 20mg/l Fe<sup>+2</sup> at all sonication times. After 60 min of sonication, the COD<sub>dis</sub> efficiencies were around 64% with the same Fe+2 concentration. After 120 and 150 min sonication times, the maximum COD<sub>dis</sub> removals were 81% and 93% with 20 mg/l Fe<sup>+2</sup> at 30°C. It is important to note that the samples without Fe<sup>+2</sup> exhibited 90% COD<sub>dis</sub> yields after 150min at 60°C.

At 60°C, 85.39%, 95.04% and 98.35% of COD<sub>dis</sub> removal efficiencies were observed for Fe<sup>+2</sup>=2 mg/L, Fe<sup>+2</sup>=8 and Fe<sup>+2</sup>=20 mg/L, respectively, after 150min (Figure 10b). The COD<sub>dis</sub> yields were 59% and 79% after 120 and 150 min sonication times with 20mg/l Fe<sup>+2</sup>. Although the COD<sub>dis</sub> yields increased as the Fe<sup>+2</sup> concentration was increased, the samples without Fe<sup>+2</sup> exhibited 90% COD<sub>dis</sub> yields after 150min at 60°C.

Fe<sup>+2</sup>, as a source of OH<sup>·</sup> production for the degradation of organic compounds under sonication, caused destructing of the organic compounds rapidly [20, 24].



a



b

Figure 10: Effect of (a) Fe<sup>+2</sup>=2 mg/L, Fe<sup>+2</sup>=8 and Fe<sup>+2</sup>=20 mg/L at 30°C and (b) Fe<sup>+2</sup>=2 mg/L, Fe<sup>+2</sup>=8 and Fe<sup>+2</sup>=20 mg/L at 60°C on COD<sub>dis</sub> removal efficiencies in petrochemical industry wastewaters versus sonication times.

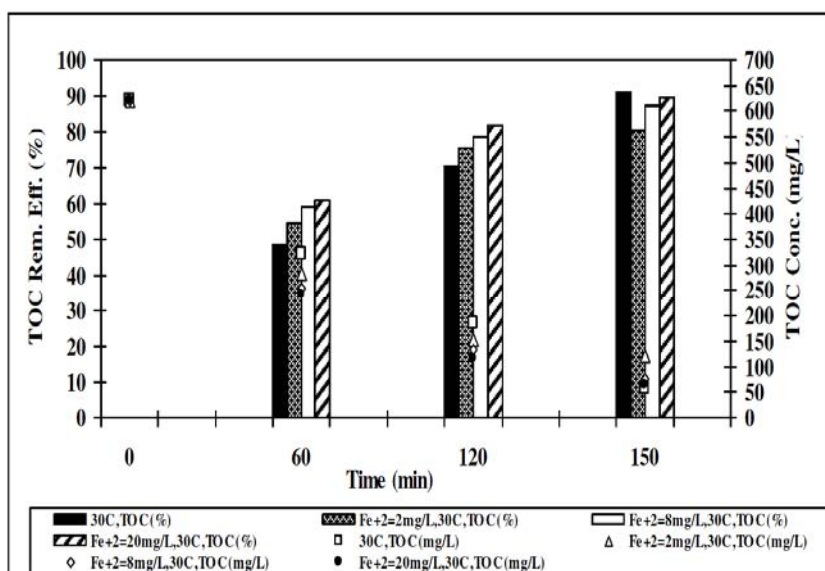


80.45%, 87.45% and 89.57% of TOC removal efficiencies were measured at  $\text{Fe}^{+2}=2$  mg/L,  $\text{Fe}^{+2}=8$  and  $\text{Fe}^{+2}=20$  mg/L, respectively, after 150 min sonication at 30°C. The maximum TOC yields was found to be 92% in the samples without  $\text{Fe}^{+2}$  for the aforementioned temperature and sonication time (Figure 11a). The yields at 60 and 120 min of sonication were 59% and 81%, respectively, with 20 mg/l  $\text{Fe}^{+2}$  at 30°C. At 60°C, 80.66%, 87.02% and 91.14% TOC removal efficiencies were observed for  $\text{Fe}^{+2}=2$  mg/L,  $\text{Fe}^{+2}=8$  and  $\text{Fe}^{+2}=20$  mg/L, respectively, after 150 min sonication (Figure 11b). The sample with only sonication exhibited 95% TOC yields for the same

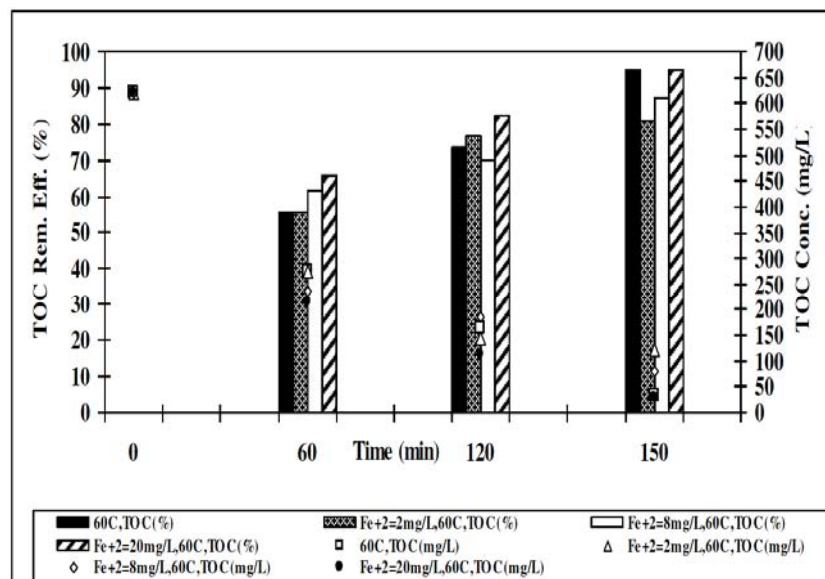
operational conditions. The yields for 60 min and 120 min sonication were 67% and 87% with 20 mg/l  $\text{Fe}^{+2}$ .

The ANOVA test statistics showed that that a significant linear relationship was found between the  $\text{COD}_{\text{dis}}$ , total PAH and TOC yields and increasing  $\text{Fe}^{+2}$  concentrations ( $R^2 = 0.98$ ,  $F = 0.31$ ,  $p = 0.001$ ;  $R^2 = 0.95$ ,  $F = 0.27$ ,  $p = 0.001$ ;  $R^2 = 0.95$ ,  $F = 0.22$ ,  $p = 0.001$ ). However, after 150 min sonication time, the sonication alone provided high pollutant yields as seen in the 15 mg/l  $\text{Fe}^{+2}$  added samples.

**The  $\text{COD}_{\text{total}}$ , Total-N,  $\text{NH}_4\text{-N}$ ,  $\text{NO}_3\text{-N}$ ,  $\text{NO}_2\text{-N}$ , Total-P,  $\text{PO}_4\text{-P}$  and oil were removed with high yields varying**



a



b

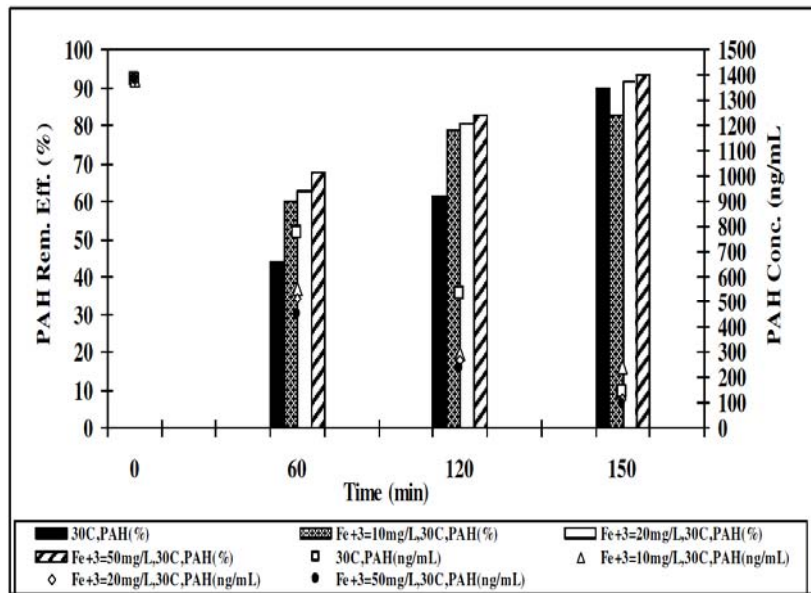
**Figure 11:** Effect of (a)  $\text{Fe}^{+2}=2$  mg/L,  $\text{Fe}^{+2}=8$  and  $\text{Fe}^{+2}=20$  mg/L at 30°C and (b)  $\text{Fe}^{+2}=2$  mg/L,  $\text{Fe}^{+2}=8$  and  $\text{Fe}^{+2}=20$  mg/L at 60°C on TOC removal efficiencies in petrochemical industry wastewaters versus sonication times.

between 79% and 89% after 150 min of sonication time at 60°C temperature (data not shown).

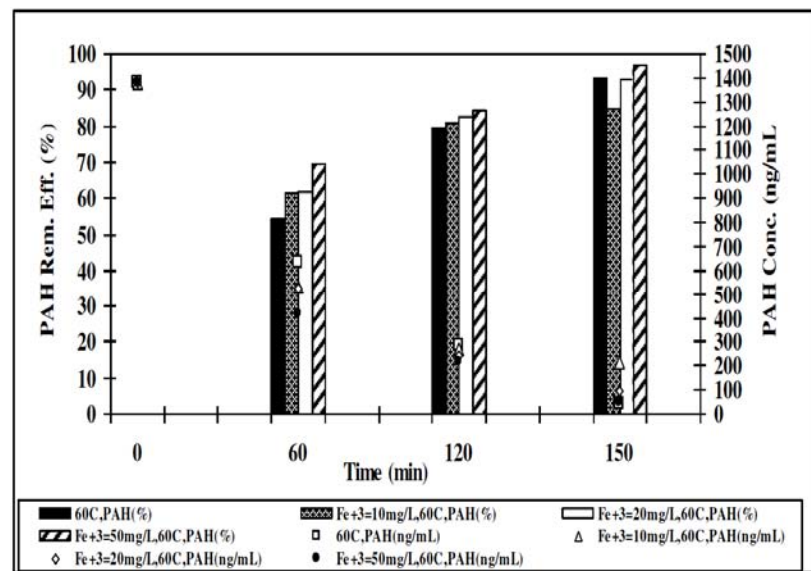
The productions of H<sub>2</sub>O<sub>2</sub> to form HO<sup>•</sup> in the presence of Fe<sup>+2</sup> leads to destruction the benzene rings of hydrophobic and hydrophilic PAHs. Some recent studies showed that there is a highly significant relationship between the average removal percentages and the hydrophobicity of PAHs, indicated by the octanol water partition coefficient in the presence of Fe<sup>+2</sup> [27, 28]. The COD<sub>dis</sub>, total PAH and TOC exhibited higher removals than expected due to their log K<sub>ow</sub>, at 60°C after 150 min sonication time without Fe<sup>+2</sup> addition.

**3.2.6. Effect of Ferric (Fe<sup>+3</sup>) Ions Concentration on the PAH, COD<sub>dis</sub> and TOC Removal Efficiencies at Increasing Sonication Times and Temperatures**

10 mg/L, 20 mg/L and 50 mg/L Ferric (Fe<sup>+3</sup>) ions were added in PCI ww before sonication process. At 30°C, 82.81%, 91.61% and 93.47% total PAH removal efficiencies were measured at Fe<sup>+3</sup>=10 mg/L, Fe<sup>+3</sup>=20 and Fe<sup>+3</sup>=50 mg/L, respectively, at an initial total PAH concentration of 1378.77 ng/ml at 30°C, after 150 min sonication (Figure 12a). The maximum total PAH removal (93,47%) was obtained with 50 mg/l Fe<sup>+3</sup> at 30°C, after 150 min. The samples without Fe<sup>+3</sup> and the samples containing 20 mg/l Fe<sup>+3</sup> exhibited high total



a



b

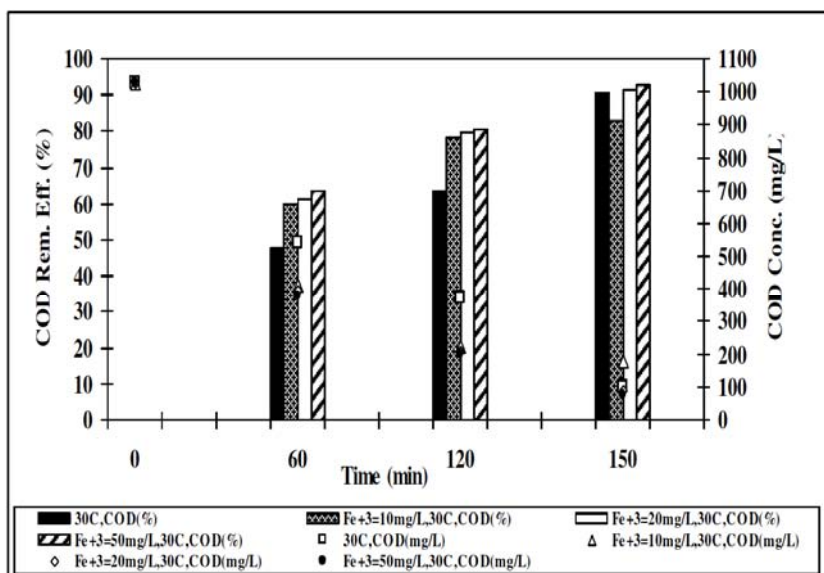
**Figure 12:** Effect of (a) Fe<sup>+3</sup>=10 mg/L, Fe<sup>+3</sup>=20 and Fe<sup>+3</sup>=50 mg/L at 30°C and (b) Fe<sup>+3</sup>=10 mg/L, Fe<sup>+3</sup>=20 and Fe<sup>+3</sup>=50 mg/L at 60°C on the total PAH removal efficiencies in petrochemical industry wastewaters versus sonication times.

PAH yields (around 90%) for the aforementioned operational conditions. The maximum total PAH removals were 70% and 82% with the addition of 50 mg/l  $\text{Fe}^{+3}$  after 60 and 120 min of sonications, respectively, at 30°C. It is important to note that after 120 min, the total PAH was removed with a high removal efficiency (79%) with only sonication.

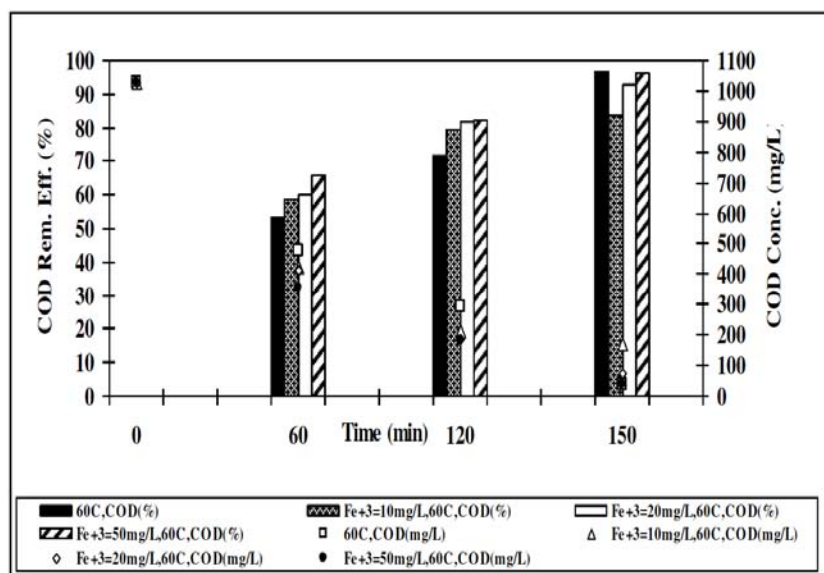
Figure 12b exhibited the total PAH yields at 60°C. 84.61%, 93.00% and 96.76% of total PAH removal efficiencies were found for  $\text{Fe}^{+3}$ =10 mg/L,  $\text{Fe}^{+3}$ =20 and  $\text{Fe}^{+3}$ =50 mg/L, respectively, at 60°C after 150 min of sonication. The maximum total PAH yields were detected with 50 mg/l  $\text{Fe}^{+3}$  at the aforementioned

operational conditions. The maximum yields after 60 and 120 min of sonications were 70% and 89%, respectively, and these removals were found with this  $\text{Fe}^{+3}$  concentration.

At 30°C, 82.71%, 91.33% and 92.66% of  $\text{COD}_{\text{dis}}$  removal efficiencies were found with  $\text{Fe}^{+3}$ =10 mg/L,  $\text{Fe}^{+3}$ =20 and  $\text{Fe}^{+3}$ =50 mg/L, respectively, after 150 min (Figure 13a). At short sonication times (60 and 120min), the maximum  $\text{COD}_{\text{dis}}$  yields were 61% and 78% using 50 mg/l  $\text{Fe}^{+3}$  at 30°C. As the sonication times were increased to 150 min, the effect of  $\text{Fe}^{+3}$  slows down while 97%  $\text{COD}_{\text{dis}}$  removal was detected



a



b

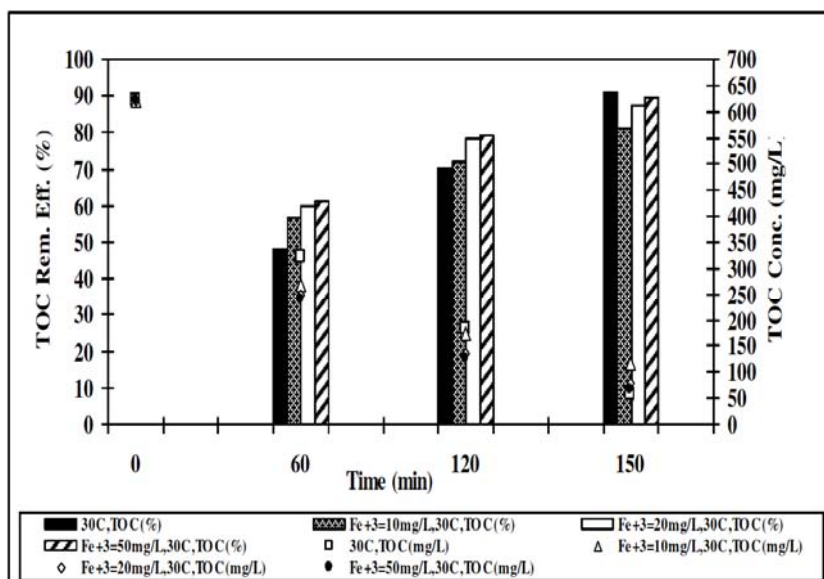
**Figure 13:** Effect of increasing  $\text{Fe}^{+3}$  concentrations (10 mg/L, 20 and 50 mg/L) at 30°C (a) and (b)  $\text{Fe}^{+3}$ =10 mg/L,  $\text{Fe}^{+3}$ =20 and  $\text{Fe}^{+3}$ =50 mg/L at 60°C on the  $\text{COD}_{\text{dis}}$  removal efficiencies in petrochemical industry wastewaters versus sonication times.

with only sonication, 83.62%, 92.68% and 96.33% of COD<sub>dis</sub> removal efficiencies were obtained for Fe<sup>+3</sup>=10 mg/L, Fe<sup>+3</sup>=20 and Fe<sup>+3</sup>=50 mg/L, respectively, at 60°C after 150 min (Figure 13b). At this sonication time, 99% yield was detected in sonication alone samples, without Fe<sup>+3</sup>.

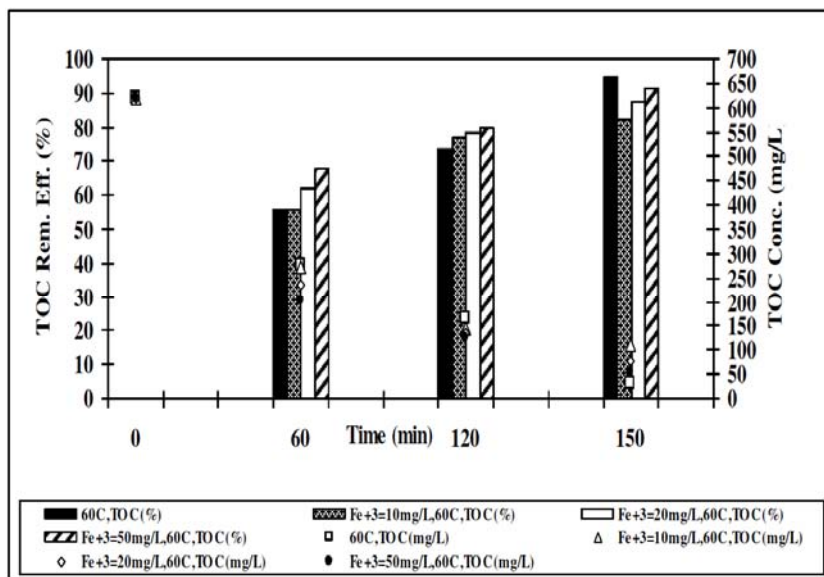
A large fraction of Fe<sup>+3</sup> was formed from the reaction of Fe<sup>+2</sup> with H<sub>2</sub>O<sub>2</sub> and it mainly exists in the form of Fe<sup>+3</sup>-HO<sub>2</sub> or -OH complexes. It was found that the Fe<sup>+3</sup>/US system under O<sub>2</sub> is more effective for mineralization than the Fe<sup>+2</sup>/US system and US only. For Fe<sup>+3</sup>, the overall degradation of organic compounds

by oxidation is slower, but the mineralization process is successfully achieved [24].

At 30°C, 81.22%, 87.37% and 89.49% of TOC removal efficiencies were measured with Fe<sup>+3</sup>=10 mg/L, Fe<sup>+3</sup>=20 and Fe<sup>+3</sup>=50 mg/L, respectively, after 150 min (Figure 14a). 82.12%, 87.70% and 91.53% of TOC removal efficiencies were obtained for Fe<sup>+3</sup>=10 mg/L, Fe<sup>+3</sup>=20 and Fe<sup>+3</sup>=50 mg/L, respectively, at 60°C after 150 min (Figure 14b). As the sonication times were increased from 60 min to 120 min, the addition of Fe<sup>+3</sup> doses elevated all the TOC yields while at long sonication times, sonication alone provided high TOC yields than the Fe<sup>+3</sup> added samples.



a



b

Figure 14: Effect of increasing Fe<sup>+3</sup> concentrations (10 mg/L, 20 and 50 mg/L) at 30°C (a) and (b) Fe<sup>+3</sup>=10 mg/L, Fe<sup>+3</sup>=20 and Fe<sup>+3</sup>=50 mg/L at 60°C on the TOC removal efficiencies in petrochemical industry wastewaters versus sonication times.

The ANOVA test statistics exhibited that a significant linear relationship was found between the  $COD_{dis}$ , total PAH and TOC yields and increasing  $Fe^{+3}$  concentrations ( $R^2 = 0.96$ ,  $F = 0.26$ ,  $p = 0.001$ ;  $R^2 = 0.98$ ,  $F = 0.21$ ,  $p = 0.001$ ;  $R^2 = 0.97$ ,  $F = 0.20$ ,  $p = 0.001$ ). However, after 150 min sonication time, the sonication alone provided high pollutant yields as is in 50 mg/l  $Fe^{+3}$  added samples.

In the presence of  $Fe^{+3}$ , the sonolytic degradation of less hydrophobic PAHs was enhanced by the increase in  $OH^\bullet$  induced from the decomposition of the recombined  $H_2O_2$  [24]. Under these conditions, it can be expected that  $Fe-OOH^{+2}$  might have been produced as an intermediate from the reaction of  $Fe^{+3}$  with  $H_2O_2$  and it may be partitioned as  $Fe^{+2}$  and  $OOH^\bullet$  by the ultrasonic irradiation [24]. The regenerated  $Fe^{+2}$  also catalyzes the decomposition of  $H_2O_2$ . These results suggest that in the presence of  $Fe^{+3}$ , the sonolytic degradation of less hydrophobic PAHs was enhanced by the increase in  $OH^\bullet$ .

### 3.2.7. The Effect of Sonication Process on the Toxicity Removal Efficiencies of Petrochemical Industry Wastewater at Increasing Sonication Times and Temperatures

After sonication experiment, toxicity measurements were applied to the samples using *Daphnia magna* toxicity assays. Results of toxicity values [Effective Concentrations,  $EC_{50}$  (mg/L)] of PCI ww were

calculated based on COD (mg/L) concentrations (Table 3). The effective COD concentration (EC) decreasing the *Daphnia magna* numbers was defined as EC. The acute toxicity value decreased from  $EC_{50}=342.56$  mg/L to  $EC_{32}= 9.82$  mg/L, at  $TiO_2=10$  mg/L and at  $60^\circ C$  after 150 min of sonication (Table 3). This is the maximum decrease of EC value. The maximum *Daphnia magna* acute toxicity removal yield was 97.13% in PCI ww at  $TiO_2=10$  mg/L, and at  $60^\circ C$  after 150 min of sonication (Table 3). The maximum *Daphnia magna* acute toxicity decreases the  $EC_{50}$  value from 342.56 mg/L to  $EC_2= 0.30$  mg/L, at  $NaCl=1$  g/L, and at  $60^\circ C$  after 150 min sonication (Table 3). The maximum *Daphnia magna* acute toxicity removal yield was 99.91% in PCI ww at  $NaCl=1$  g/L, and at  $60^\circ C$  after 150 min sonication (Table 3). The maximum *Daphnia magna* acute toxicity decrease level is the reduction of  $EC_{50}$  value of 42.56 mg/L to  $EC_{20}= 1.70$  mg/L, at  $Fe^{+2}=20$  mg/L and at  $60^\circ C$  after 150 min sonication (Table 3). The maximum *Daphnia magna* acute toxicity removal yield was 99.50% in PCI ww at  $Fe^{+2}=20$  mg/L, and at  $60^\circ C$  after 150 min sonication (Table 3). The maximum *Daphnia magna* decrease value is the decreasing of  $EC_{50}=342.56$  mg/L to  $EC_{15}= 5.34$  mg/L, at  $Fe^{+3}=20$  mg/L and at  $30^\circ C$  after 150 min sonication (Table 3). The maximum *Daphnia magna* acute toxicity removal yield was 98.44% in PCI ww at  $Fe^{+3}=20$  mg/L and at  $30^\circ C$  after 150 min sonication (Table 3). As a result, the maximum *Daphnia magna* acute toxicity removal yield (99.91%)

**Table 3: Toxicity Values [ $EC_{50}$  (mg/L)] of Petrochemical Industry Wastewater after Sonication**

Conditions	EC (mg/L) Values							
	30 (°C)				60 (°C)			
	0. min	60. min.	120.min	150. min	0. min	60. min.	120. min	150. min
	$EC_{50}$				$EC_{50}$			
Raw wastewater, Control	342.56	$EC_{45} = 53.76$	$EC_{28} = 67.08$	$EC_{13} = 11.60$	342.56	$EC_{46} = 71.51$	$EC_{29} = 14.54$	$EC_4 = 5.38$
$TiO_2=0.1$ mg/L	342.56	$EC_{23} = 43.18$	$EC_{10} = 46.95$	$EC_4 = 9.88$	342.56	$EC_{23} = 77.06$	$EC_{16} = 64.94$	$EC_{10} = 53.50$
$TiO_2=0.5$ mg/L	342.56	$EC_{45} = 101.85$	$EC_{32} = 30.74$	$EC_{20} = 21.36$	342.56	$EC_{45} = 127.94$	$EC_{40} = 36.27$	$EC_{30} = 18.46$
$TiO_2=10$ mg/L	342.56	$EC_{50} = 49.01$	$EC_{48} = 35.73$	$EC_{22} = 17.17$	342.56	$EC_{48} = 92.12$	$EC_{45} = 51.68$	$EC_{32} = 9.82$
$TiO_2=20$ mg/L	342.56	$EC_{50} = 30.80$	$EC_{42} = 20.81$	$EC_{40} = 13.35$	342.56	$EC_{50} = 49.12$	$EC_{48} = 31.68$	$EC_{50} = 10.96$
$NaCl = 1$ g/L	342.56	$EC_{34} = 75.76$	$EC_{22} = 29.74$	$EC_{10} = 3.04$	342.56	$EC_{20} = 42.07$	$EC_{10} = 26.66$	$EC_2 = 0.30$
$NaCl = 2.5$ g/L	342.56	$EC_{40} = 43.06$	$EC_{33} = 29.44$	$EC_{19} = 3.26$	342.56	$EC_{40} = 53.00$	$EC_{30} = 24.60$	$EC_{20} = 4.51$
$NaCl = 15$ g/L	342.56	$EC_{35} = 55.86$	$EC_{20} = 30.30$	$EC_2 = 1.37$	342.56	$EC_{38} = 81.20$	$EC_{30} = 16.81$	$EC_{17} = 1.11$
$Fe^{+2}=2$ mg/L	342.56	$EC_{30} = 74.08$	$EC_{15} = 60.82$	$EC_4 = 3.35$	342.56	$EC_{20} = 92.00$	$EC_{14} = 77.40$	$EC_5 = 6.00$
$Fe^{+2}=8$ mg/L	342.56	$EC_{33} = 58.05$	$EC_{20} = 40.90$	$EC_{12} = 3.95$	342.56	$EC_{25} = 83.21$	$EC_{17} = 56.56$	$EC_9 = 16.31$
$Fe^{+2}=20$ mg/L	342.56	$EC_{50} = 46.20$	$EC_{30} = 23.54$	$EC_{20} = 5.21$	342.56	$EC_{50} = 42.02$	$EC_{30} = 22.61$	$EC_{20} = 1.70$
$Fe^{+3}=10$ mg/L	342.56	$EC_{23} = 49.60$	$EC_{12} = 44.42$	$EC_4 = 39.08$	342.56	$EC_{18} = 190.67$	$EC_{10} = 61.67$	$EC_4 = 8.42$
$Fe^{+3}=20$ mg/L	342.56	$EC_{42} = 39.74$	$EC_{15} = 24.90$	$EC_{15} = 5.34$	342.56	$EC_{40} = 82.05$	$EC_{16} = 55.95$	$EC_7 = 18.80$
$Fe^{+3}=50$ mg/L	342.56	$EC_{50} = 112.51$	$EC_{40} = 21.80$	$EC_{10} = 7.54$	342.56	$EC_{50} = 70.55$	$EC_{40} = 18.17$	$EC_{50} = 13.18$

in PCI ww was obtained with NaCl=1 g/L at 60°C after 150 min sonication (Table 3).

#### 4. CONCLUSIONS

- Low frequency (35 kHz) sonication proved to be a viable tool for the effective degradation of TOC, COD<sub>dis</sub> and total PAH in PCI ww.
- The degradation of PAHs, TOC and COD<sub>dis</sub> were a function of sonication time, frequency, T (°C), TiO<sub>2</sub>, NaCl, Fe<sup>+2</sup> and Fe<sup>+3</sup> concentrations.
- As the temperature increased from 25 to 30 and 60°C, the total PAHs and COD<sub>dis</sub> removals increased.
- The maximum TOC, COD<sub>dis</sub> and total PAHs yields were detected after 150 min sonication times with 20 mg/l TiO<sub>2</sub>, 15 mg/l NaCl, 20 mg/l Fe+2 and 20-50 mg/l Fe+3 concentrations after 150 min sonication at 60°C. However, sonication alone without chemical provided high pollutant yields at long sonication time.
- The maximum *Daphnia magna* acute toxicity removal yield was 99.91% in PCI ww at NaCl=1 g/L and at 60°C after 150 min of sonication.
- Sonication technology can provide an effective alternative for destroying and detoxifying the pollutants present in PCI ww. It could be used as a direct treatment at step to treat the pollutants in PCI ww instead of biological treatment plants in Izmir (Turkey).

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