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Removal of polycyclic aromatic hydrocarbons from municipal sludge using UV light

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ABSTRACT

This study includes research into using UV light to remove Polycyclic Aromatic Hydrocarbons (PAHs) from municipal sludge. The effectiveness of TiO_2 as a photocatalyst on this UV application was also determined. Sludge samples that were taken from an urban wastewater treatment plant (UWWTP) were exposed to UV-C light in a specially designed setup. The total concentration of Σ_{12} PAH in the sludge, which was 1339 ng g^{-1} of dry matter initially, decreased by 2–77% after 24 h of UV application. The concentrations of some PAH isomers increased after the UV application, which revealed that isomer transformations could emerge due to the effects of temperature and photodegradation. UV light was found to remove 3-ring light compounds more effectively than 4–6-ring heavy compounds. A total PAH decrease of 77% was achieved by adding an amount of TiO_2 equal to 0.5% of the dry weight of the sludge although the removal rate of PAHs from the sludge decreased when the TiO_2 dosage was increased. It is possible that the decreased number of titanium particles caused UV light to scatter and be absorbed in the reaction environment.

Keywords: Municipal sludge; PAH; UV-C; TiO_2; Temperature; Treatment

1. Introduction

The amount of urban wastewater, and thus the sludge volume, increases every year due to increasing populations and rapid urbanization. In 2005, 8 million tons of wastewater treatment sludge was produced in Europe [1], while 27,000 tons of dry matter were produced in Turkey in 2006 [2]. The rapidly increasing amount of sludge causes waste management problems. A possible solution to sludge management problem is its use for agricultural purposes.

There are various semi-volatile organic compounds (SVOC) in urban wastewater treatment sludge, along with pathogens such as bacteria and viruses [3,4]. It is known that Polycyclic Aromatic Hydrocarbons (PAHs), one of the major classes of SVOCs, emerge due to incomplete combustion of organic matters and are introduced to the environment from natural or anthropogenic sources [5]. PAHs reach wastewater treatment plants from soil by infiltration, from surface soils by entering the sewer system, and from the atmosphere by wet and dry deposition [3,4,6]. It is expected that these pollutants will be held within precipitated sludge by binding to the active sludge mass because of their hydrophobic and lipophilic nature [1,7,8]. PAHs in sludge that is applied to soil can have potential mutagenic/carcinogenic effects when they eventually reach the food chain [9]. European Union brought limitations and defined the limit value for the sum of 11 PAH compounds as 6 mg kg^{-1} regarding the agricultural application of sewage sludge [10]. Therefore, these pollutants should be removed from the sludge body [1].

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Various studies on the amount of PAHs in wastewater treatment sludge have been carried out [3,4,11]. However, research on the removal of these pollutants from sludge is limited [11–14]. Cai et al. studied the removal of PAHs from sludge by applying composting technique [12,13]. It is also known that PAH isomers in sludge can be degraded through chemical methods such as the Fenton process [14] and biological methods such as aerobic treatment [1]. Flotron et al. [14] used the Fenton process to degrade PAH isomers in sludge and observed that the use of hydrogen peroxide and ferrous sulfate, without pH adjustment, decreased the PAH concentration in sludge. It is known that persistent organic pollutants (POPs) can be degraded in different matrices with UV technology. It is also known that UV light is absorbed by POPs, including PAHs, polychlorinated biphenyls (PCBs) and pesticides in liquid matrixes, soil and synthetic form [15–18]. After the absorption, molecules are electronically excited and photodegradation occurs after a series of reactions [19]. In the presence of radicals, UV light causes photodegradation by degrading the benzene ring into PAHs [20]. UV light at short wavelengths has the high energy that is required to degrade PAHs [21,22]. It has been reported that PAH isomers in different matrices can be degraded with the use of UV light [22,23]. Several authors have reported that the physical and chemical nature of the matrix in/on which PAHs exist could strongly affect the photodegradation rates [24–26]. Behymer and Hites [26] found that photolytic half-lives of PAHs are highly dependent on the substrate in an experimental study to photolyze eighteen PAH compounds adsorbed on black carbon and coal fly ash samples with varying physical and chemical compositions. Jang and Mcdow [25] suggested that organic composition of the matrix can strongly influence the photodegradation of PAHs as a result of their study, which they investigated benz-(a)-anthracene decay in the presence of known organic constituents of atmospheric particulate matter. Shao et al. [24] reported that the photolysis rate of several PAH compounds were affected from the electron-accepting potential of the solvent molecules and concluded that the constituents of environmental media may influence the photodegradation rates of PAHs. Since PAH removal efficiencies are affected from the composition of the environmental matrix, the complex nature of sludge is highly expected to influence the photodegradation.

TiO_2 is one of the most frequently used photocatalysts. It has a large surface area, it is stable in acidic and basic environments, it is easily obtained, and it does not have any toxic effects [27]. It was observed that titanium dioxide facilitates photodegradation of POPs such as PCBs [28–31], PAHs [21,32] and pesticides [33] in solid matrices such as soil. It is also expected that this photocatalyst will accelerate the photodegradation process of PAHs in sludge, which is a solid matrix.

This study involves research on the removal of PAH isomers in urban wastewater treatment sludge with UV light and TiO_2 in a specially designed setup. It aims to add data to the related literature by determining the effects of UV light and the use of photocatalysts on the removal of PAHs.

2. Materials and methods

In the first phase of this study, sludge samples obtained from an urban wastewater treatment plant (UWWTP) were subjected to UV light. The samples were removed from the setup after 24 h and preprocessing for the PAH analysis was performed. In the last phase, PAH concentrations were measured through GC-MS. The details of the experimental studies are presented in Fig. 1. Experimental flow chart was determined by referring the studies in the literature [3,11,34–36].

2.1. Sludge sampling

Sludge samples were taken from the exit of belt filter press of an UWWTP located in Bursa, and UWTTP has a population equivalent of 585,000. The source of 35% of the wastewater that reaches the plant is industrial, and the

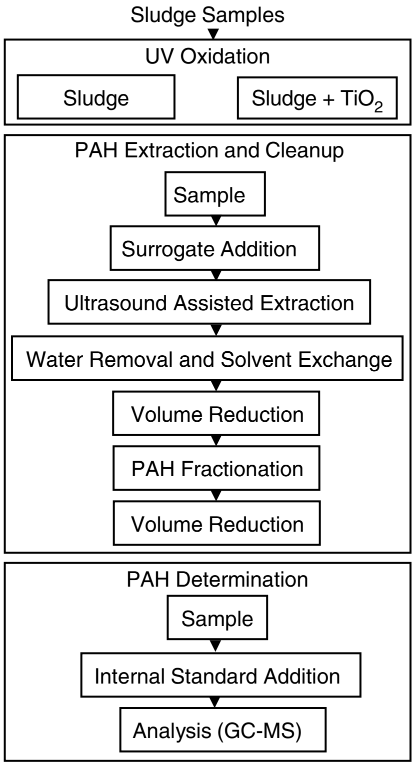

Fig. 1. Flow chart of experimental studies.

other 65% of the wastewater is domestic. The design flow rate of the input wastewater is 87,500 m^3 d^{-1}. The chemical oxygen demand (COD) value of influent is 600–700 mg l^{-1}, and COD value of effluent is 50 mg l^{-1}. The initial concentration of Σ_{12} PAH isomers in the sludge was measured as 1339 ng g^{-1} of dry matter.

Sludge samples taken were brought to the laboratory in glass jars with aluminum lids. UV light was applied on the same day that samples were brought. pH (Method 4500-H^+), dry matter content, and total organic carbon (TOC) (Method 5310B) of the sludge were determined in accordance with Standard Methods [37]. The pH of the sludge was 7.5, its dry matter content was approximately 25%, and TOC value was 35%. TOC measurements were carried out by using SSM-5000 Shimadzu TOC Analyzer TOC-V CPN.

2.2. UV setup and application

The setup designed for the UV experiments is shown in Fig. 2. The setup was made of stainless steel and was designed with the aim of determining the effects of UV-C lights and temperature on PAH isomers. Materials that do not contain organic ingredients were used to prevent their absorption by PAH compounds. Three lamps with 24 W of power at 254 nm UV-C (Philips TUV G8T5) were installed on the roof of the setup at 2 cm intervals. The dimensions of the setup were 45 × 30 × 55 (wide × length × height) cm. A metal fan was installed on the right side to homogenize the air inside the setup. Sludge samples were laid on glass petri dishes with a diameter of 8 cm and then placed onto a shelf designed in a fashion similar to grill shelves. The distance between the shelf and UV source was 18 cm. The indoor ambient temperature was controlled with a heater installed on the exterior surface of the setup. The humidity and temperature inside the setup were measured using a HOBO-S-Thb M002 sensor, and data was collected with an H21-002 HOBO logging microstation.

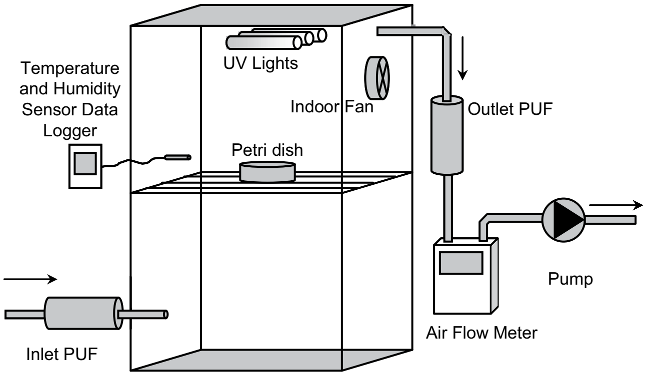

Fig. 2. Experimental setup.

Table 1
Experimental conditions for samples

Sample group no.	Study conditions	Variables		
		UV	Indoor temperature (°C)	TiO_2 dose (%)
1	19°C	–	19	–
2	36°C	–	36	–
3a	UV, 34°C	+	34	–
3b	UV, 34°C	+	34	–
4	UV, 54°C	+	54	–
5	UV, 54°C	+	54	0.5
6	UV, 54°C	+	54	20

1 – UV close, thermostat close, temperature 19°C; 2 – UV close, thermostat open, temperature 36°C; 3 – UV open, thermostat close, temperature 34°C; 4 – UV open, thermostat open, temperature 54°C; 5 – UV open, thermostat open, temperature 54°C, TiO_2: 0.5% by dry sludge weight; 6 – UV open, thermostat open, temperature 54°C, TiO_2: 20% by dry sludge weight.

In the first phase of the study, the time required for the sludge to become 90% dry matter was determined. The performed experiments (3, 6, 12 and 24 h) showed that 90% dry matter was achieved after 24 h. 90% dry matter is the desired value for thermal sludge drying processes.

The variables and experimental conditions tested in this study are presented in Table 1. The UV-C light intensity which the sludge samples exposed to was 0.6 mW cm^{-2}. Light intensity was determined with a UV Radiometer at 254 nm (UVR-1, Topcon Inc., Japan). The light intensity which the samples were exposed was at the same level for all the experimental trials. 20 g of wet sludge were set in each of the petri dishes at a height of 5 mm. All of the experimental studies were carried out 3 times. The dark control samples of triplicate experiments were prepared by putting the samples in the set-up ambient without UV light. Since the temperature of the set-up ambient without UV was different from the ambient of other samples compared, a single trial, where dark controls were also prepared by covering the samples with aluminum foil in order to prevent the contact with UV light as described by Zhang et al. [21], was undertaken. In this single trial the effect of temperature over the removal efficiency was eliminated. Dark controls were used along with the samples in Group 3 to compare the situation with and without UV application.

The surface area of the TiO_2 (Degussa P25) applied to sampling groups 5 and 6 (Table 1) was ≈50 m^2 g^{-1}. The sludge samples were subjected to preprocessing for the PAH analysis after they were exposed to UV light. The relationship between the amount of sludge dry matter and the amount of PAH isomers removed was evaluated statistically as part of the study.

The volatilized PAH compounds during UV application were captured by vacuuming the inlet air with a flow of 0.8 $m^3 h^{-1}$ and collecting the compounds on polyurethane foams (PUFs) with 2 × 5 cm length and 5.5 cm diameter (Fig. 2). Air was taken into the setup after capturing all PAHs and other possible organic pollutants by employing PUFs (Inlet PUFs in Fig. 2). This cleaned air was then carried the evaporated PAHs from the sludge to the PUFs located at the outlet (Outlet PUFs in Fig. 2).

2.3. PAH extraction, cleanup and determination

5 g of raw wet sludge (25% dry matter) from UWWTP were weighed and placed in a glass vial after the addition of 20 ml of dichloromethane/petroleum ether (DCM/PE) (1:1, v/v). Sludge samples that had been in the UV apparatus for about 24 h were extracted and cleaned in the same manner as the raw sludge. All of the chemicals used in the experimental studies were GC grade. Each sample was spiked with 4μg of a surrogate standard mix. Five surrogate standards, naphthalene-d10 (Nap-d10), acenaphthene-d10 (Ace-d10), phenanthrene-d10 (Phe-d10), chrysene-d12 (Chr-d12) and perylene-d10 (Per-d10) were used to monitor the recovery of different PAH compounds. The extraction and cleaning procedure have been described in detail elsewhere [11]. The steps of the procedure can be seen in Fig. 1.

Before their first usage, the PUFs used were extracted with distilled water, MeOH, acetone/hexane (ACE/HEX 1:1), and dichloromethane (DCM) in Soxhlet extractor for 24 h and then dried under 60°C [38]. PUF cartridges were kept in glass jars with Teflon covers until usage [38]. After sampling, the PUF cartridges were extracted for 24 h in the Soxhlet extractor with 1:1 (v/v) acetone/hexane mixture.

PAH content was analyzed using an Agilent 7890 model gas chromatography (GC) equipped with an Agilent 5975C inert XL mass selective with triple axis detector (MSD). A capillary column (HP5-MS, 30 m × 50 μm × 0.25 μm) was used. Details of the PAH analysis can be found elsewhere [11]. Sixteen PAH compounds identified by the United States Environmental Protection Agency (USEPA) were targeted: naphthylene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorine (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene, (Fl), pyrene (Pyr), benzo[a]anthracene (BaA), chrysene, (Chr), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene, (BkF), benzo[a]pyrene (BaP), indeno[1,2,3-c,d]pyrene, (InP), dibenzo[a,h]anthracene (DahA), and benzo[g,h,i]-perylene (BghiP).

2.4. Quality assurance/ouality control

10% of the sludge samples were used as field blanks to determine any contamination during sample handling, transportation, and analyses. They were prepared by filling thimbles with 5 g of sodium sulfate. The blanks were extracted and cleaned in the same manner as the samples. All matters were cleaned by DCM and acetone to prevent contamination [36].

To evaluate the extraction efficiency of the target compounds, all samples were spiked with surrogate standards. The concentrations of PAH surrogate standards were calculated to be 4 ng ml^{-1} prior to extraction. Phenanthrene-d10 was used as a surrogate for Phe, Ant, Fl, Pyr and BaA, and its average recovery was 31%. The average recovery for Chrysene-d12, which served as a surrogate for Chr, BbF, BkF and BaP, was 46%. Perylene-d12 served as a surrogate for InP, DahA and BghiP. Its average recovery was 60%. Naphthylene (Nap), acenaphthylene (Acy), acenaphthene (Ace) and fluorine (Flu) were not reported in this study because of the low recovery rate (<5%). 4 ng ml^{-1} Pyrene d-10 was spiked into the samples as an internal standard for volume correction just before quantification of the PAH compounds. The PAH results obtained from GC were corrected according to the recovery of internal standards.

Prior to analysis of the samples, GC-mass spectrometry (MS) was calibrated for seven concentration levels (0.01, 0.1, 0.5, 1.25, 2.5, 5 and 10 μg ml^{-1}) to determine the linearity of the responses. In every case, the r^2 of the calibration curve was ≥0.99. System performance was verified by analysis of the midpoint calibration standard every 24 h during the analysis period. Instrument detection limits (IDLs) were determined using the area of a peak with a signal/noise ratio of 3 at the lowest standard calibration level. The quantifiable PAH amount for a 1-μl injection was 0.1 pg.

The limit of detection (LOD) was defined as the mean blank mass plus three standard deviations [3,32]. The LODs for PAHs ranged from 0.079 μg kg^{-1} for DahA to 14.445 μg kg^{-1} for Phe. Samples quantities exceeding the LOD were quantified and corrected by subtracting the mean blank amount from the sample amount. Experimental results were expressed as ng g^{-1} dry solid (DS). Correlation calculations were performed using the software package SPSS 13.0 for Windows.

3. Results and discussion

3.1. Effect of UV and temperature on PAH removal

The initial levels of Σ_{12} PAH compounds in the sludge taken from the plant and PAH levels remaining in sludge that had been processed under different working conditions in the UV setup for 24 h is shown in Fig. 3.

The temperature was 19°C when both the UV lamps and thermostat were turned off (Group 1). The temperature was 36°C when the UV lamps were turned off and the thermostat was set to 40°C (Group 2). The total amount

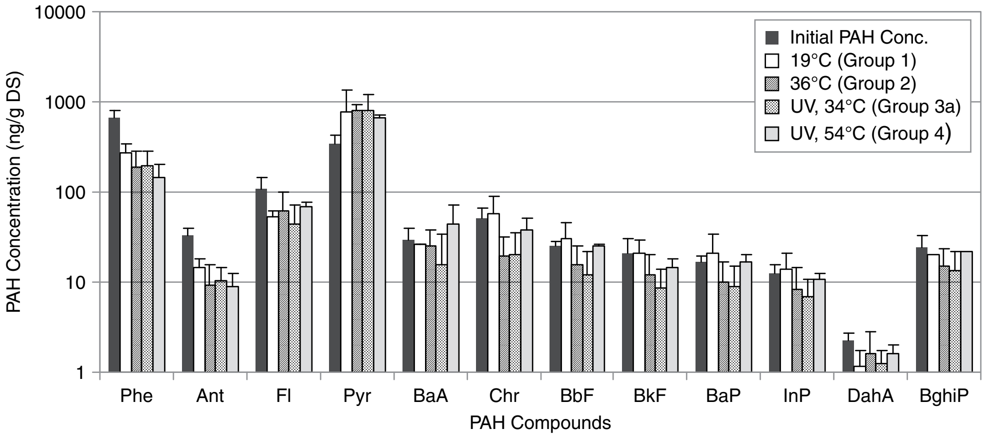

Fig. 3. Changes in the levels of PAH compounds after UV application.

of PAH in the sludge after 24 h in Group 1 decreased 2%, while it decreased 12% in Group 2 (Table 1). It was observed that the percentage of dry matter in the sludge reached 52% at 19°C and 93% at 36°C. The amount of sludge water that evaporated within 24 h was recorded, and it was determined that the samples with higher evaporation rates also had higher amounts of dry matter. It was observed that there was a strong correlation (r^2 = 0,924, $p < 0.01$) between the residual PAH concentration in the sludge and the percentage of dry matter of the sludge. As the amount of dry matter increased, more PAH compounds were removed from the sludge. It was concluded that reaching approximately 90% dry matter in the sludge was beneficial to the removal of PAHs.

In Group 1, the amount of 3-ring PAHs in the sludge decreased by 56% and the amount of 4–6-ring PAHs decreased at different rates ranging from 0% to 49%. The average removal rate of 4–6-ring compounds was 5%. In Group 2, the amount of 3-ring compounds in the sludge decreased by 69% and the amount of 4–6-ring compounds decreased at rates ranging between 0% and 62%. The average removal rate of 4–6-ring compounds was 12%. Increasing the temperature from 19°C to 36°C increased the removal rate of 3-ring compounds (Phe, Ant) from 56% to 69%. The average removal rate of 4–6-ring compounds was increased from 5% to 12%. No chemical admixture was added and there was no difference in UV application between the studies of Group 1 and Group 2. The only variable here was the temperature. Therefore, the decrease in the amount of PAH was due to the temperature increase from 19°C to 36°C, in accordance with the evaporation mechanism.

PAH compounds in the evaporated air were captured by using PUFs (Outlet PUFs) for the samples in Group 3b. PAH compounds and the levels determined in the PUF samples can be seen in Fig. 4. The dominant PAH compounds detected were Phe, Ant and Fl. This leads to consider that these light PAH compounds could have been evaporated.

In Groups 3a and 3b, the temperature was 34°C when the UV lamps were turned on and the thermostat was turned off. In this setup, the total amount of PAHs in the sludge after exposure was 15% lower than its input value. The 3-ring PAH compounds were decreased by 68% with the effect of UV and temperature. In Group 4, the indoor setup temperature increased to 54°C when the UV lamps and thermostat were turned on. The decrease in the total amount of PAHs was 21% under these conditions. It was determined that the total residual PAH amount was lower due to the temperature increase. This may have been caused by the fact that as the temperature increases the light compounds (3-ring) are more efficiently removed. Similarly, studies in the literature show that increasing the temperature from 10°C to 30°C increases the degradation of PAHs [39,40].

As seen in Fig. 3, the amount of 3-ring compounds in the sludge when the UV lamps were turned on at 34°C and 54°C decreased by 68% and 75%, respectively. The average amount of 4–6-ring compounds in the sludge at 34°C and 54°C decreased by 18% and 15%, respectively. Increasing the temperature during UV exposure

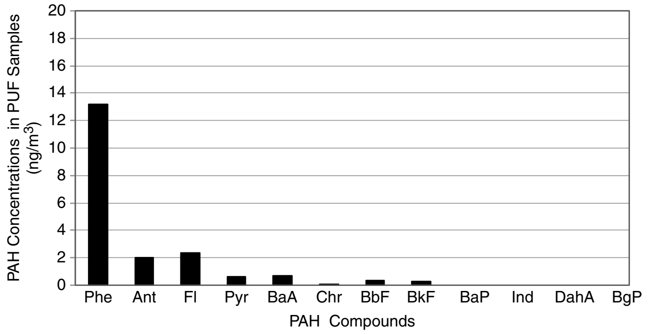

Fig. 4. Evaporated PAH levels after UV application.

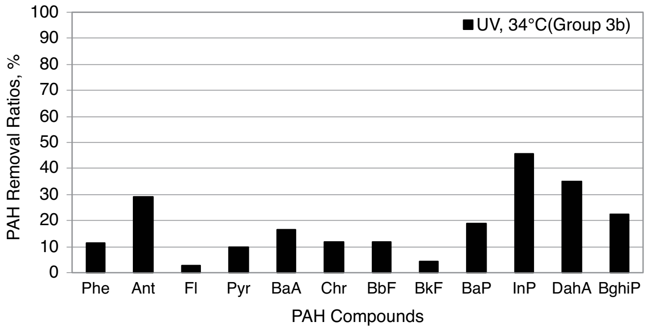

Fig. 5. PAH removal with the effect of photodegradation.

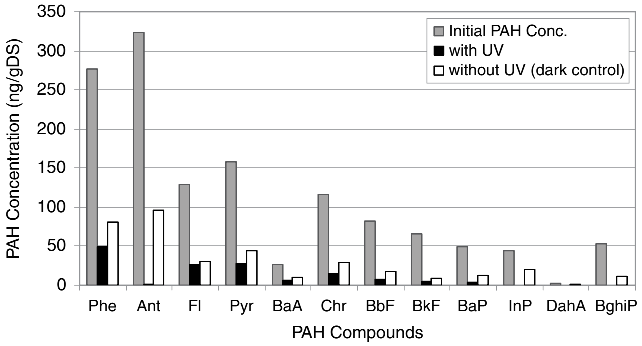

Fig. 6. PAH levels remained in the sludge after UV application.

complicated the removal of the PAH isomers from the sludge. The decrease in the removal rate of heavy compounds when both the UV lamps and thermostat were turned on (Group 1) may have been because of a hard crust that appeared on the top of the sludge at 54°C. It is known that this crust hinders evaporation and therefore poses a problem in sludge drying applications [41]. The crust may act as a layer that limits the movement of PAHs from the sludge to the atmosphere and obstructs the removal of 4–6-ring compounds from solid matrices. Light compounds (3-ring) may be able to evaporate due to their high volatility before the crust forms.

The thermostat was turned on and the UV lamps were turned off in the study of Group 2. However, the thermostat was turned off while the UV lamps were turned on in the study of Group 3. The total PAH concentration in the sludge in Group 2 decreased by 12%, and there was a 15% decrease in Group 3 (Table 1). It was determined that the total residual PAH amount in the sludge decreased by 3% due to UV application when these two studies were compared. The rest of the decrease (12%) is assumed to have been caused by the temperature. Fig. 5 shows the removal ratios of each PAH compound with the effect of UV alone. The amounts removed by evaporation mechanism were subtracted from the overall removal rates to reflect the effect of photodegradation in Fig. 5. The removal rates of heavier compounds such as InP, DahA, BghiP were higher than the light compounds, with the effect of UV light.

The sludge used in the study was taken from the plant after it had been processed in a conditioning procedure and subjected to UV exposure. Dursun and Dentel [42] reported that sludge takes a gel form after the conditioning procedure applied to wastewater treatment sludge. The gel model requires a new approach to conditioning and dewatering of sludge [43]. The gel model can also be used to explain the movement of pollutants in sludge. UV light may not be as successful in the removal of PAHs from sludge as in synthetic PAH degradation studies or the removal of PAH in other matrices (water, soil) because of the gel form of the sludge and the form established by coagulants and flocculants used for conditioning and dewatering. In addition to this, increasing the applied UV intensity may facilitate the removal of PAHs from the sludge. Studies in the literature show that increasing the light intensity increases the degradation of PAHs [32,44,45]. It has been reported that applying 1 mW cm^{-2} of UV intensity on soil from a distance of 15 cm, which is a more clean matrix than sludge, successfully degraded PAHs [21].

Fig. 6 shows the PAH levels remained at the sludge (Group 3b) after being exposed to the UV application. The dark-control samples represent the PAH compounds and their levels remained in the sludge after being exposed to only volatilization mechanism. It can be seen from the figure that all PAH compounds were decreased by a certain level with both mechanisms (photodegradation and evaporation). As would be expected, the PAH levels remained after the UV application at 34°C were found to be lower than the levels at the dark control samples.

It was observed that the amount of PAH isomers in the sludge decreased at rates from 40% to 70% with the application of UV (Fig. 3) but the decrease in the total PAH amount did not exceed 15% because the pyrene and benzo(a)anthracene concentrations did not decrease much, possibly due to transformations among isomers. Guieysse et al. suggested possible isomer transformation during photodegradation [22]. Guieysse et al. reported that BaA and Pyr concentration increased during UV application to the soil extracts and inferred transformation of Bap into BaA and Pyr. Similarly, Ireland et al. suggested possible transformation of high molecular weight PAHs into Phe, a 3-ring PAH compound, in polluted soils [43].

The average removal rates of 3-ring light compounds were 71% and 70%, in Group 2 and Group 3, respectively. The average removal rates of 5–6-ring compounds were 42% and 50%, respectively. Three-ring compounds may have evaporated as temperature increased, and UV light was more effective on heavy compounds in the solid matrix as the percentage of dry matter in the sludge increased. Some researchers [21,22] stated that

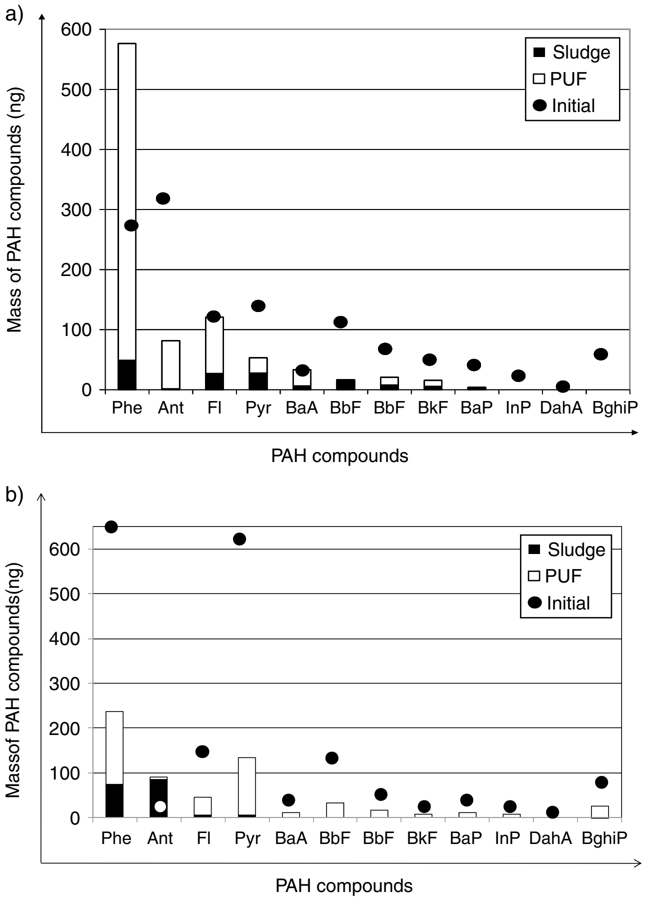

Fig. 7. Mass transfer of PAH compounds after (a) UV application and (b) UV-TiO_2 application.

photodegradation of heavy PAH isomers (5–6 ring) was easier than light isomers since heavy isomers absorb UV light more efficiently. In this study, the removal rate of 5–6-ring compounds from sludge due to UV illumination increased from 42% to 50%, in compliance with the literature.

Figs. 7a and b show the masses of the PAH compounds volatilized and remained in the sludge after UV and UV-TiO_2 application. The figure is based on the calculated amounts using the volume of air vacuumed and mass of the sludge sampled considering the dry matter content. Fig. 7a showed that the Phe content of the sludge is higher than the initial mass. Fig. 7b showed that Ant content of the sludge is higher than the initial mass. This reveals that isomer transformations could have been emerged due to the effects of temperature and photodegradation.

After the sludge had been subjected to the UV in the set-up for 24 h, it was seen that the PAH compounds rather than Phe, Fl and BaA were below their initial mass. Heavy compounds might have been transformed into lighter compounds. Additionally, it can also be suggested that PAHs might have condensed in the inner surfaces of set-up (cover cap, side walls, and ceiling). The increase of Phe up to approximately twice of its initial mass suggests that several PAH isomers could have photo-degraded again in the sludge or gas phase within the setup.

3.2. *Effect of the photocatalyst (TiO_2) on PAH removal*

The changes in PAH concentrations in sludge that was exposed to UV with the use of TiO_2 as a photocatalyst are shown in Fig. 8. In this study, it was observed that using TiO_2 reduces the total PAH amounts by 63%–77%. When titanium dioxide absorbs light with wavelengths shorter than 385 nm, a paired negatively charged electron and positively charged holes [electron (e^-) and cell (h^+)] emerges [46]. The positive hole degrades water molecules, transforming them into hydrogen gas and a hydroxyl radical ($OH^\cdot$) [32,47]. Hydroxyl radicals degrade organic compounds [32]. The humidity of the urban sludge used in this study was 75%. Water molecules in the sludge might have been oxidized by photogenerated holes, as the effect of UV light and the presence of TiO_2 created $OH^\cdot$ radicals [32]. Moreover, O_2^- might have been created from the reactions between O_2 absorbed from the atmosphere on the sludge surface and

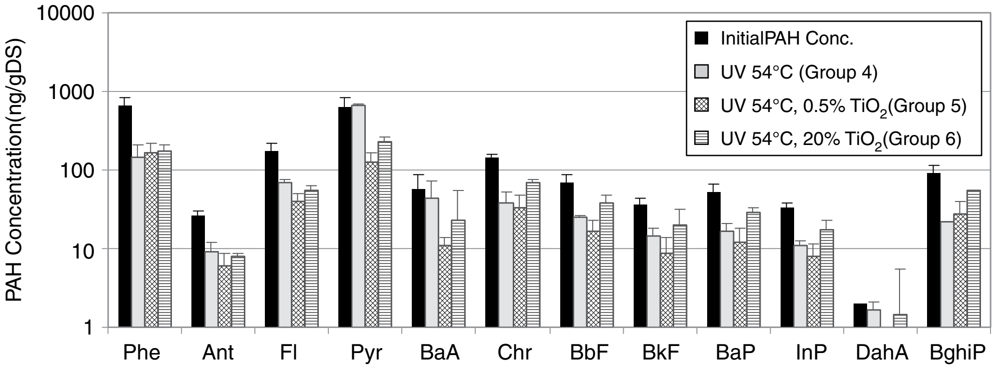

Fig. 8. Changes in the levels of PAH compounds after the application of UV and TiO_2.

electrons in the environment [32]. These radicals, which have a high inclination to react, might have degraded PAH compounds with lipophilic features while degrading organic compounds in the sludge.

The total PAH concentration in the sludge decreased by 77% when an amount of TiO_2 equal to 0.5% of the dry weight of the sludge was used (Group 5). The amount of total PAH removed from the sludge decreased to 63% when the TiO_2 dosage was increased from 0.5% to 20% (Group 6). 3–6-ring compounds were removed from the sludge at rates from 70% to 81% with the use of 0.5% TiO_2, however these rates decreased to 41%–73% when the TiO_2 dosage was increased to 20%. This decrease might have resulted from excessive part of the titanium particles causing the UV light to scatter, decreasing the absorption of light in the reaction environment [21].

The studies of Group 4 and Group 5, which used 0% and 0.5% TiO_2, showed that the average concentration of 3-ring compounds in the sludge decreased by 75% and 72%, respectively. In other words, the removal rates of these compounds from sludge increased with the limited use of TiO_2. The degradation rate of 4–6-ring compounds increased to 58% with the use of 0.5% TiO_2. Considering the fact that photodegradation of heavy isomers is easier than that of light compounds in solid matrices [21,22], it was observed that limited use of TiO_2 facilitated the removal of the compounds in this group especially well.

The catalyst surface area required for the degradation of organic compounds is an important matter in UV applications [21]. The removal of PAHs with the use of 0.5% TiO_2 [21] and the removal of 70% of pesticides with the use of 1% TiO_2 [32,33] were realized in UV applications carried out on soil samples. The surface area required for degradation could have been provided with the use of 0.5% TiO_2 by weight in this study. TiO_2, with a surface area of 50 $m^2\ g^{-1}$, transforms luminous energy into chemical energy and provides rapid degradation of organics with the $OH^{\cdot}$ radicals it produces [48].

High specific surface area of TiO_2 implies high amount of active centers at the surface of catalyst and high level of catalyst activity [49]. Zhang et al. [21] who used Degussa P25 TiO_2 as fotocatalyst similar to this study, have reported that increasing the amount of TiO_2 may cause a scattering effect by catalyst particles attenuating the light absorption inside the set up. One possible explanation to the decrease in the PAH removal rates when the amount of TiO_2 increased from 0.5% to 20% is that low loading of TiO_2 has provided enough catalyst surface area and the rest could have caused a scattering effect. Additionally, the reaction products formed on the surface of the catalyst could have competed with the reactant and diffused in the capillary holes of the catalyst decreasing the efficiency as in the surface poisoning phenomena [49].

4. Conclusions

The total amount of PAHs of sludge samples kept at temperatures of 19°C and 36°C without applying UV decreased by 2% and 12%, respectively. In this case, the removal of PAHs was realized through evaporation, as temperature was the only variable. The total amount of PAHs decreased by 21% after UV was applied. Removal efficiencies of heavier compounds such as InP, DahA, BghiP were found to be higher than the light compounds, with the effect of UV light. As the temperature increased during UV application, the PAH removal from the sludge increased. This increase resulted from the removal of light isomers due to the temperature rather than the UV. The dominant compounds detected in the air within the system were Phe, Ant and Fl. The Phe content of the sludge was found to be higher than the initial mass after the UV application. This leaded to consider that heavier PAH compounds could have been transformed into these compounds with the effect of UV and evaporation. However, the removal rate of 4–6-ring compounds from the sludge decreased when the temperature was increased from 34°C to 54°C. A hard crust that formed on the sludge after dewatering may have inhibited the transmission of these compounds into the atmosphere.

The use of TiO_2 during UV exposure improved PAH removal from the sludge. When 0.5% and 20% (of the solid weight of the sludge) TiO_2 photocatalyst were added, the total PAH concentration in the sludge decreased by 77% and 63%, respectively. However, the removal rate of PAHs from the sludge decreased when the TiO_2 dosage was increased. This decrease might have resulted from titanium particles causing the UV light to scatter, decreasing the absorption of light in the reaction environment. In an evaluation of the alternatives for removing PAH isomers, it was determined that the highest PAH removal rate could be obtained by applying UV light at 54°C with TiO_2 as a catalyst.

It should be noted that the thickness of the sludge that UV and TiO_2 applied is an important variable in the removal efficiency obtained. It is possible that UV light can not transfer inside the solid with higher sludge thicknesses.

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