Removal of polycyclic aromatic hydrocarbons (PAHs) from contaminated sewage sludge using advanced oxidation process (hydrogen peroxide and sodium persulfate)

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Abstract

This study has been carried out with the aim of evaluating the treatability of polycyclic aromatic hydrocarbon compounds of PAHs available in urban and industrial sewage sludge utilizing advanced chemical oxidation methods contingent on free sulfate radicals using hydrogen peroxide and heat activation methods. For this purpose, various parameters including (3, 5, 7, 9, and 10), persulfate’s concentration (2, 10, 5, 15, and 20 mmol), the ratio of peroxide to persulfate (1, 0.5, 0.3, 0.2, and 0.1), sludge temperature (25°C, 35°C, 45°C, and 55°C) and the primary concentration of PAHs were considered at the 20 d reaction periods. Through making use of gas chromatography–mass spectrometry (GC-MS), after 40-min period, the quality and quantity of the compounds available in the samples were determined using a mass detector and the drawn standards curve. After examining the effectiveness of eliminating PAH compounds in various conditions, the chemical oxygen demand test was carried out for the samples related to optimal removal of PAH compounds to determine the real efficiency of the process in eliminating intermediate compounds originated from PAHs oxidation. The results demonstrate that the advanced chemical oxidation method (persulfate-peroxide) can effectively result in the elimination of PAH compounds from the sludge.

Keywords: Sewage sludge; Advanced oxidation; Persulfate; Polycyclic aromatic hydrocarbons

1. Introduction

Business activities and human beings’ biological functions along with the industrialization of societies, urbanization, and population increment and its concentration in special geographic areas have resulted in the emergence and occurrence of numerous environmental problems. One of the most significant environmental areas that are exposed to pollution are available water resources, which due to natural and man-made activities have sometimes become a threat to the health of communities [1,2]. Among all, sewage is considered as one of the major reasons for water resources pollution. In addition to wastewater which may include some problems, another important issue in wastewater treatment plants is the production of sludge; the sludge can have its own composition depending on various factors such as the origin of the wastewater, the purification process, environmental conditions, etc. [3,4]. Among all, a group

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of pollutants that their presence in the sewage and accordingly the sludge has been proven, are organic pollutants, for example, polycyclic aromatic hydrocarbons (PAHs); they enter the sewage through various sources and are absorbed by particles and are separated from sludge along with sewage due to resistance to common treatments, especially biological treatment, and their parasitic feature [5]. PAHs are relatively soluble in water, have high lipophilic properties. PAH compounds can enter to the environment mainly through the discharge of waste from industrial plants such as refineries, wastewater treatment plants, natural sources, and household and municipal uses of some compounds containing PAH and then, in the next stage can enter the sewage by discharge from the mentioned sources and finally concentrate and accumulate in sewage sludge [6]. Most PAHs are absorbed to particles at low vapor pressure in the air. In the case of dispersing in water or being absorbed on a particulate material, they may be decomposed when exposed to ultraviolet light of sunshine. In the atmosphere, PAHs can produce Dyane, nitro, di-nitro-PAHs, and sulfonic acids with pollutants including ozone, nitrogen, and sulfur oxides, respectively. Moreover, PAHs may be decomposed by some microorganisms in the soil [5,7]. Various types of physical, chemical, and biological processes, involving photolysis, hydrolysis, biological decomposition, evaporation, absorption, and simple evolution, are utilized to reduce the concentration of PAHs which are found in the environment [8]. The present study has made use of advanced oxidation based on persulfate as a chemical method for reducing the concentration of PAHs found in the environment. Persulfate \( (S_{2}O_{8}^{2−}) \) is one of the strongest oxidants possessing a higher potential \( (E^\circ = 2.01 \text{ V}) \) in comparison with \( H_{2}O_{2} \) \( (E^\circ = 1.76 \text{ V}) \) [8–10]. In addition, persulfate has other advantages, such as high stability, low relative cost, being solid, easy storage, and transport as well as the ability to break down toxic and resistant compounds with no residues and sludge. These advantages introduce the use of persulfate-based oxidation as an attractive option in the treatment of pollutants in the environment, especially water and wastewater. Establishing and activating the sulfate radicals can be obtained through heat, intermediate, or transition metal catalysts, or UV radiation and then, based on the following relations, it produces sulfate and hydroxyl radicals and enters into chain reactions with the desired pollutant [9–14]:

\[
S_{2}O_{8}^{2−} + \text{initiator} \rightarrow SO_{4}^{−} + (SO_{4}^{−} \text{ or } SO_{3}^{2−})
\]  
(1)

\[
SO_{4}^{−} + H_{2}O \rightarrow H^{+} + SO_{4}^{2−} + HO^−
\]  
(2)

These processes have been investigated in various studies [15–21]. In the present research, the major purpose was the determination of the efficiency of PAHs removal from urban sewage sludge (recipient of industrial sewage) using AOPs \( (H_{2}O_{2} \text{ and sodium persulfate}) \) system.

2. Materials and methods

For evaluating the presence of PAH compounds, samples of municipal wastewater sludge were collected and from five municipal wastewater treatment plants in Tehran and one industrial wastewater treatment plant and then analyzed. Initially, the physical and chemical properties of the used sludge were recorded (Table 1). For evaluating the pH effect on the performance of the system, the pH of the sludge was changed at 3–11 using 3 N sulfuric acid and caustic acid and pH meter (Hach, Agilent Technologies), and its effect was evaluated through keeping constant the other parameters and its optimal amount was determined. Experiments were carried out over a period of 20 d. In the next step of the experiments, the sodium peroxide (at concentrations of 2–20 mM/L) was utilized as an oxidizer in laboratory conditions (temperature approximately 25°C) to determine the optimal concentration of persulfate in the oxidation of PAHs, and the required samples were taken and analyzed. After determining the optimal persulfate concentration, hydrogen peroxide was used as the activator of persulfate ion in molar ratios of 0.1–1 to the persulfate ion; the sampling was done based on the procedure, and its optimal amount was determined.

For examining the performance of the advanced oxidation process (AOPs) based on the sulfate radicals in the removal of PAH compounds from raw sewage sludge, the chemical oxygen demand variable (COD) was also utilized investigate the removal amount of this variable and the performance of the process in oxidation and removal of other organic matter as well as other intermediate compounds generated from possible degradation of PAHs. In this research, the reaction times were 48 h (2 d later), 5, 10, 15, and 20 d. At each of these times, the samples were taken. They were dried after the addition of 100 cc of methanol and then extracted through the Soxhlet method (EPA METHOD 3540C) for 16–24 h. After adsorption of hydrophilic and colored materials by glass adsorbent activated with 9 N hydrochloric acid and evaporation of the solvent and bringing the sample volume to about 1 cc, they were injected by EPA METHOD 8270D method into gas chromatography–mass spectrometry (GC-MS) Agilent Technologies 7890A, and PAH values were measured and read. For evaluating the concentration of PAHs in urban sewage sludge, a GC-MS device (model: Agilent

<table>
<thead>
<tr>
<th>Compound name</th>
<th>Amount (mg/kg DW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naphthalene</td>
<td>4.95</td>
</tr>
<tr>
<td>Anthracene</td>
<td>4.82</td>
</tr>
<tr>
<td>Fluoranthene</td>
<td>3.65</td>
</tr>
<tr>
<td>Pyrene</td>
<td>2.95</td>
</tr>
<tr>
<td>Benzo[a]anthracene</td>
<td>1.1</td>
</tr>
<tr>
<td>Chrysene</td>
<td>2.75</td>
</tr>
<tr>
<td>Benzo[e]acephenanthrylene</td>
<td>ND</td>
</tr>
<tr>
<td>Benzo[k]fluoranthene</td>
<td>2.38</td>
</tr>
<tr>
<td>Benzo[a]pyrene</td>
<td>2.9</td>
</tr>
<tr>
<td>Dibenzo[a,h]anthracene</td>
<td>ND</td>
</tr>
<tr>
<td>Benzo[g,h,i]perylene</td>
<td>1.44</td>
</tr>
<tr>
<td>Indeno[1,2,3,c,d]pyrene</td>
<td>1.36</td>
</tr>
</tbody>
</table>

COD: 9.500 mg/L, TSS: 42.65 g/L, temperature: 24°C, pH: 6.8, and total PAH: 28.3 mg/kg DW
Technologies 7890A equipped with the Agilent J&W column (HP-5 ms, 30 m × 0.32 mm, 0.25 μm) was used. The prepared and condensed samples were injected into the oven of the GC-MS device. The required time for all the PAH compounds removal from the device column was approximately 40 min. For determining the complete removal efficiency of PAHs and the intermediate compounds caused by its degradation in the raw treated urban sewage sludge, the efficiency of COD was also investigated. For this task, the Cecil spectrophotometer apparatus Aquarius model, the COD digestion reactor HACH DRB 200 with the capability of temperature setting, oven, decoder, digital scale, condensed sulfuric acid, potassium dichromate, mercuric sulfate, silver sulfate, and hydrogen phosphate potassium (KHP) were used. It is noteworthy that for each concentration, the test was repeated twice.

3. Results and discussion

3.1. Effect of pH

The effect of various pH values of the sludge (3, 5, 7, 9, and 11) on the degradation of PAHs compounds by sodium peroxide was examined. The regulation of pH in the mentioned range was done using sulfuric acid and caustic soda. Through selecting the constant concentration of sodium peroxide and under laboratory temperature, pH revealed various effects on acidic, neutral, and alkaline amounts; so that the minimum removal efficiency was observed in neutral conditions, and the maximum efficiency was observed in alkaline conditions. A comparison of the system efficiency at various pHs is demonstrated in Fig. 1. The primary concentration of PAHs compounds in the investigated sludge, based on Table 1, was 28.3 mg/kg dw. However, its value in the system studied using the sodium peroxide concentration of 2,000 mg/L (as an oxidant) and employing various pH values (3, 5, 7, 9, and 11) in laboratory conditions reached 20.1, 17.1, 23.2, 22.2, and 16.4 mg/kg dw after 20 d of the reaction time; the obtained values in the mentioned pH values represent the removal efficiencies of 28.98%, 39.58%, 18.02%, 21.55%, and 42.05%, respectively. The speed of chemical reactions relies on the pH of the environment, and pH directly or indirectly affects the oxidation of chemical materials. According to the obtained results, the effect of pH is almost as mentioned above; so that in both acidic and alkaline pH, the removal rate of pollutants is higher than the neutral conditions, and the relative higher efficiency in alkaline conditions can be

![Graph](image1)

Fig. 1. (a) Effect of pH on the efficiency of PAH compounds degradation and (b) residuals of PAH compounds affected by different pH in AOP's process ($C_{persulfate} = 10$ mM/L, $C_{PAHs} = 28.3$ mg/kg dw, and $T = 25^\circ C$).
referred to the elimination of hydrophobic conditions of PAH compounds. Alkali hydrolysis of sludge at higher pH values has another advantage that can be referred to as stabilization of sludge and expanding sludge dewatering characteristics [22].

3.2. Effect of sodium persulfate concentration

At this stage, the effect of various concentrations of sodium persulfate (2–20 mmol/L) on the degradation efficiency of PAH compounds was investigated (Fig. 2). The results demonstrated that the higher the concentration of sodium persulfate in the urban sewage sludge contaminated with PAHs leads to the higher the removal efficiency of the mentioned compounds. In the AOPs, the type and concentration of the oxidant material are the effective factors in the removal of organic compounds [23]. Persulfate anion is one of the two-electron oxidation agents that can compete with ozone and hydroxyl radicals, by producing sulfate radicals with high oxidation and reduction power [24].

Through increasing the concentration of persulfate to an excessively optimal level, the radicals of persulfate themselves can act as a scavenger and can be a factor for the conversion of radical sulfate to persulfate. On the other hand, radical sulfate can react with persulfate and produce anion sulfate, which in both states results in the loss of radical sulfate and decrement of the removal efficiency [25,26]. The action of radical scavengers can be expressed using the following relations [27,28]:

\[ \text{SO}_4^{2-} + \text{SO}_4^{2-} \rightarrow \text{S}_2\text{O}_8^{2-} \]  
\[ \text{SO}_4^{2-} + \text{HO}^- \rightarrow \text{SO}_4^{2-} + \text{OH}^- \]  

3.3. Effect of peroxide ion ratio on persulfate ion

After recognizing the concentration of persulfate and pH in optimal values of 15 and 9 mmol/L, in the last stages, the effect of the ratio of peroxide ion to the concentration of persulfate ion (1–1.0) was investigated and studied in this stage (Fig. 3). The results showed that by increasing the ratio of hydrogen peroxide to sodium persulfate in urban sewage sludge having PAHs, the removal efficiency of the above compounds increased as shown in Fig. 3. Moreover, it was observed that increasing the ratio of peroxide to sulfate does not possess a linear trend; accordingly, the slope of the curve was positive. Fig. 3 is also an indicator of the remaining PAH compounds affected by various ratios of hydrogen peroxide to sodium persulfate. Considering Fig. 3, it can be understood that an increase in this ratio has merely resulted in the boost of removal efficiency of these compounds in comparison with persulfate.

3.4. Effect of reaction temperature

After recognizing optimal values of pH (9), the concentration of persulfate (15 mmol/L), and the ratio of hydrogen peroxide to persulfate (0.3) at the previous stages, the effect of the reaction temperature was examined and studied in the temperature range of 25°C–55°C. The results showed that with increasing reaction temperature in urban sewage sludge containing PAHs, the removal efficiency of the above compounds has increased as shown in Fig. 4. Increasing the reaction temperature was led to diminishing the PAHs concentration from the primary value of 28.3 mg/kg dw to about 2.7 mg/kg dw; it is indicative of approximately 90% removal efficiency at temperature 55°C. The removal efficiencies in other temperatures, that is, 45°C, 35°C, and 25°C were observed to be 87%, 80%, and 74%, respectively. According to Fig. 4, it is observed that in this stage, the compounds with lesser molar mass and fewer aromatic rings (2 and 3 rings) had lower residual compared to heavier compounds containing more rings (4 rings and more), which is consistent with the results of the study by Karaca and Tasdemir [29].

Temperature is one of the effective factors regarding the speed of chemical reactions. In some reactions, with a few centigrade increase, the reaction speed might be multiplied. Each constant of the reaction speed is dependent on temperature, which is expressed by Arrhenius’s relationship. For a certain reaction, the constant velocity ratio at a higher temperature to the constant velocity at lower temperatures is regarded as the temperature coefficient (Q) of the reaction. Q is normally determined as the ratio of velocity constants at temperatures in the range of 10°C [30].

3.5. Degradability of PAH compounds in the control sample

PAHs available in sludge were degraded during the purification stage and subsequent sludge treatment as well
Fig. 2. (a) Effect of concentration of sodium persulfate on degradation efficiency of PAH compounds and (b) residuals of PAH compounds affected by primary concentration of persulfate in AOPs process ($C_{PAH} = 28.3$ mg/kg dw, $T = 25^\circ$C, and pH = 11).

Fig. 3. (a) Effect of the ratio of peroxide to persulfate on PAH compounds degradation efficiency and (b) residuals of PAH compounds affected by various ratios of peroxide to persulfate in AOPs process ($C_{persulfate} = 15$ mmol/L, $C_{PAH} = 28.3$ mg/kg dw, $T = 25^\circ$C, and pH = 11).
as during the stabilization stage with various processes, such as aerobic and anaerobic. With regard to Fig. 5, PAH compounds available in the sludge were decreased after the reaction period; so that, their amount was decreased to 11% after the 20 d period. The maximum reduction (about 51%) was related to the naphthalene compound, which is a two-ring compound, followed by anthracene, phenanthrene, pyrene, etc.

3.6. Effect of the primary concentration of PAH compounds in the sewage sludge

After determining the optimum values of pH, concentration of sodium persulfate, ratio of hydrogen peroxide to persulfate, and reaction temperature, the effect of changing the concentration of PAHs on the AOPs system performance were investigated. The results of this investigation are shown in Table 2 and Fig. 6. As can be seen in Table 2 and Fig. 6, increasing the PAHs concentrations and the type of raw sewage sludge are effective on the removal efficiency has led to reducing the removal efficiency under using optimal conditions obtained in the previous stages. Accordingly, for increasing the optimum and achieving standard sludge output, applying some changes in process conditions is crucial that it has been revealed that higher hydrogen peroxide ratios have higher efficiencies for urban sewage sludge. Two ratios of 0.5 and 1 hydrogen peroxide to persulfate were used, which improved the system efficiency; so that, at the end of the process with a ratio of 1, practically the remaining amount of PAH compounds in sludge has reached the below standard sludge output. In general, the half-life of radicals is very short, in the microsecond range. But the important point is performing chain reactions and their reproduction during the process by activators in the reaction medium. Therefore, if there are necessary conditions such as ambient temperature, the presence of peroxide, etc., there will always be the possibility of radical production and reaction [29,31].

COD analysis in the new optimal conditions obtained from these conditions indicates the overall procedure similar to COD elimination efficiency with the major pollutant, that is, PAH compounds, and possesses an incremental procedure over time. Based on the obtained results which are presented in Table 2, primary COD for industrial wastewater sludge was 11,500 mg/L. It can be found out that COD elimination efficiency is less compared to the main pollutant and it is approximately 47%; this is indicative of the conversion of the main pollutant and other organic materials available in sludge to the other intermediate compounds (Table 2).

4. Conclusions

Different parameters including pH (3, 5, 7, 9, and 10), persulfate concentration (20, 15, 10, 5, and 2 mmol), the ratio of peroxide to persulfate (1, 0.5, 0.3, 0.2, and 0.1), sludge
temperature (55°C, 45°C, 35°C, and 25°C), and primary concentration of PAH compounds at 20 d reaction period were used. The results demonstrated that the AOP (persulfate-peroxide) can effectively result in the removal of PAH compounds from sludge. Of course, the results of the COD test showed that although the efficiency of removing PAH compounds in optimal conditions was achieved 90%, the COD removal efficiency was approximately equal to 50% and 47% for urban and industrial sewage sludge, respectively. Accordingly, it can be concluded that through PAH compounds oxidation, some intermediate organic compounds have been produced, the removal rate of which is almost independent of the PAH compounds removal.

Finally, it can be indicated that the AOP (persulfate-hydrogen peroxide) can result in a significant reduction of PAH compounds in various environments, particularly sewage sludge.

References


