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Hot water extraction with in situ wet oxidation: Kinetics of PAHs removal from soil

Ali A. Dadkhah*, Aydin Akgerman✠

Chemical Engineering Department, Texas A&M University, College Station, TX 77843-3122, United States

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Abstract

Finding environmentally friendly and cost-effective methods to remediate soils contaminated with polycyclic aromatic hydrocarbons (PAHs) is currently a major concern of researchers. In this study, a series of small-scale semi-continuous extractions – with and without in situ wet oxidation – were performed on soils polluted with PAHs, using subcritical water (i.e. liquid water at high temperatures and pressures, but below the critical point) as the removal agent. Experiments were performed in a 300 mL reactor using an aged soil sample.

To find the desorption isotherms and oxidation reaction rates, semi-continuous experiments with residence times of 1 and 2 h were performed using aged soil at 250 °C and hydrogen peroxide as oxidizing agent. In all combined extraction and oxidation flow experiments, PAHs in the remaining soil after the experiments were almost undetectable. In combined extraction and oxidation no PAHs could be detected in the liquid phase after the first 30 min of the experiments. Based on these results, extraction with hot water, if combined with oxidation, should reduce the cost of remediation and can be used as a feasible alternative technique for remediating contaminated soils and sediments.

Keywords: Polycyclic aromatic hydrocarbons; Hot water extraction; Wet oxidation; Soil remediation; Kinetics

1. Introduction

A significant group of contamination materials in the soil is polycyclic aromatic hydrocarbons (PAH). Out of 1220 sites on the final NPL (as of August 2002), 592 of them contain PAH contamination. Contaminated media in 501 of these sites are soil and sediments [1]. PAHs are one of the largest classes of carcinogens in the environment [2]. In addition, many PAHs are mutagenic and toxic [3–5]. When dealing with contaminated soils, usually two options are considered. The first is containment and immobilization of the hazardous materials, and the second is treatment of the contaminated soil to clean it to an acceptable level with less risk to public health. In the early days of environment awareness, the first option was more practical and popular among contractors. However, after significant advancement in understanding the scientific foundations of environmental contaminations and knowing that containment methods simply pass the problem to the next generation, remediation is the only option in most all cases. Some remediation methods can be performed by in situ methods eliminating the need to remove the soil. In other methods, soil excavation is needed so it can be treated on site, or moved to another place for treatment or containment.

According to some estimates, bioremediation costs for organic toxic chemical contaminations are in the range of one-quarter to one-half of other remediation techniques [6–8]. However, PAHs are hard to biodegrade and persistent in soil, which rules out the applicability of biodegradation for PAH-polluted soils or at best, biodegradation might be used in cases with very light contamination with low-molecular-weight PAHs [9,10]. Even in such cases, the removal is very low, as reported by Clemente et al. [11], i.e. about 12–69% for low-molecular-weight PAHs like phenanthrene and naphthalene. Hence, one can clearly conclude that for many PAH-contaminated soils, biodegradation is not a feasible solution. Earlier we reviewed other remediation options and advantages of using the hot water as a medium for extracting the PAHs from aged soils as well as wet oxidation technology [12,13].

Regarding the maximum allowed concentration limits of PAHs, there are no universally agreed upon values, either for

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* Corresponding author at: Chemical Engineering Department, Isfahan University of Technology, Isfahan 84156, Iran.
E-mail address: dadkhah@cc.iut.ac.ir (A.A. Dadkhah).

✠ Professor Akgerman passed away during the preparation of this manuscript.

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individual PAHs or for the total concentration. Based on local standards and the risk assessment methods, different values are reported for different countries or even for various sites and applications [14–16]. The concentration limits that are based on risk assessments are more dependent on the preset assumptions, such as life-time exposure duration, exposure frequency, body weight, etc.

Although there were no studies on subcritical wet oxidation of PAHs dissolved in water at the time that this project was started, a few researchers have recently (after or concurrent with this study) started to investigate some sort of combination between hot water extraction and wet oxidation [17,18]. However instead of combining the two steps of extraction and oxidation, they have done these steps in two stages, separating the oxidation process from extraction and performing it under different conditions than the extraction. They have reported two small-scale (0.5 g contaminated soil with additional 2–3 g of clean sand as filler for column) experiments where they extracted the PAHs with hot water in a column and then passed the water through a second heated column for oxidation. In the first report, they performed the oxidation at supercritical conditions in the temperature range of 385–425 °C and used hydrogen peroxide as the oxidizing agent. In the second experiment, they used potassium persulfate as the oxidizing agent and heated the water with extracted PAHs to subcritical temperatures in the range of 100–360 °C. At 300 °C, their best reported conversion for the pressurized hot water oxidation was in the range of 81.8–97.8% for various PAH compounds. It is important to mention that they calculated the conversion or removal efficiency of the PAHs by comparing the amount of the PAHs found in the effluent of second column (oxidation column) with those found in the water effluent of the first column (hot water extraction column). This means that, they did not account for the residual PAHs in the soil when calculating the above conversion numbers.

In this study, we report our findings on a series of semi-continuous experiments on hot water extraction combined with in situ wet oxidation. We performed the experiments at two residence times, using an aged soils sample, double distilled hot water as extracting medium, and hydrogen peroxide as oxidant. From collected data, oxidation rates were calculated and fitted to a kinetic model.

2. Experimental

2.1. Materials

Natural aged soil samples which were polluted with PAHs were used for the experiments. Double-distilled water from the Chemical Engineering Department unit operation lab was used as the extraction medium during the semi-continuous experiments. Dichloromethane (Mallinckrodt UltimAR, 99.9% min) was used as solvent for extracting PAHs from water samples, preparation of samples for gas chromatography, extraction of PAHs from soil with an Accelerated Solvent Extractor (ASE®), dilution of gas chromatograph standards, and cleaning of the equipments and tools. Occasionally acetone (EM Science, 99.99%) was used for some cleaning jobs as well. Nitrogen gas from compressed cylinders was used for the initial pressurization of the extraction vessel, and as oxidizing agent; diluted aqueous solutions of hydrogen peroxide (EM Science, 30% solution) were used.

2.1.1. Soil

An aged soil sample was obtained from a railroad tie plant. This was milled and sieved with a No. 40 mesh (420 μm opening). Then this sample was stored in a glass jar, covered with aluminum foil and stored in the refrigerator for later use. To characterize the PAH contents of the soil, before and after each experiment a representative sample (about 10 g) was taken and extracted by an Accelerated Solvent Extractor (ASE®). Then the extracts were analyzed by using a HP-5890 gas chromatograph. Solvent extracts from this soil were tested against a standard of 16 priority PAHs. Then six substances were selected for follow up, based on the abundance and also to represent a wide range of molecular weights. Table 1 summarizes the PAHs identified in the aged soil together with the ones, marked with an asterisk, which were followed in the extraction/oxidation experiments. The reported concentrations are averages of three separate injections of 1 μL samples to the gas chromatograph and rounded to the nearest integer. Fig. 1 shows the gas chromatogram with the peaks of the organics extracted from untreated soil including those peaks which were not identified.

2.2. Hot water extractions

All experiments were performed in a semi-continuous mode and in a 300 mL stainless steel bolted closure type reactor with a magnetic drive stirrer by Autoclave Engineering. The experimental set-up was moderately modified from previous batch design [12] to allow for continuous flow of the water and the oxidizing agent (hydrogen peroxide). To provide fresh aqueous solution of hydrogen peroxide to the reactor, initial design included two separate containers for the water and hydrogen per-

Table 1
Concentration of PAHs in aged soil, as determined by GC after calibration with a 16 priority PAH standard

PAH	μg/g soil	S.D.
Naphthalene	7	0.42
Acenaphthylene	2	0.46
Acenaphthene[a]	29	1.03
Fluorine	11	0.49
Phenanthrene[a]	46	1.96
Anthracene	21	0.55
Fluoranthene[a]	184	15.39
Pyrene[a]	148	12.28
Benzo(a)anthracene	41	2.48
Chrysene[a]	65	3.54
Benzo(b)fluoranthene	22	3.35
Benzo(k)fluoranthene	32	1.48
Benzo(a)pyrene[a]	25	4.06
Indeno(1,2,3-c,d)pyrene	11	2.25
Dibenz(a,h)anthracene	3	1.36
Benzo(g,h,I)perylene	9	1.66

[a] Selected for treatment studies.

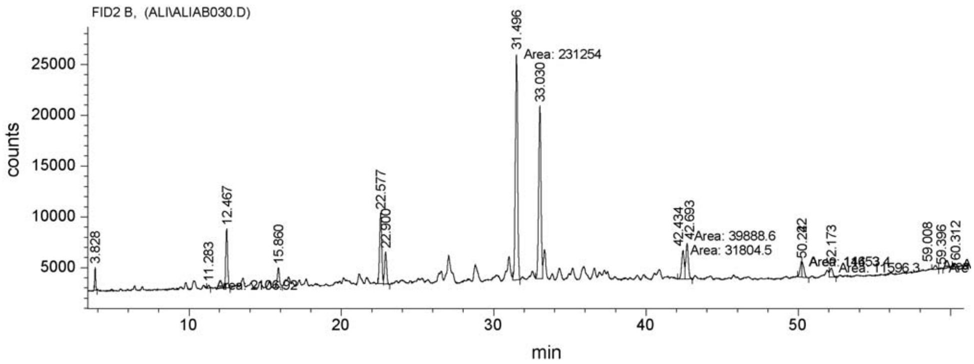

Fig. 1. Gas chromatogram of PAHs extracted by ASE from untreated aged soil.

oxide and consequently two pumps to feed them to the extraction vessel. This design would give the opportunity to have enough water in the water container for the duration of the experiment, and refill the hydrogen peroxide container periodically with fresh solution as shown in Fig. 2. Mini pumps No. 1 and 2 were from Thermo Separation and Milton Roy Companies with 46–460 and 16–160 mL/h capacities, respectively. However, in application, this configuration did not produce a satisfactory flow rate. The second pump failed to deliver the desired flow rate due to a small flow rate of hydrogen peroxide solution (even with higher dilution to use higher flow rate), high relative pressure upstream of the check valve, and production of oxygen bubbles in the flow line. To overcome this problem, feed water was mixed with the desired quantity of 30% hydrogen peroxide solution and was pumped by a single pump to the reactor vessel. To prevent formation of oxygen bubbles in the line and to keep the hydrogen peroxide solution fresh before reaching the reactor, a 250 mL plastic bottle was used to hold the feed, which was frequently refilled from a prepared solution, which was kept in a refrigerator. Moreover this plastic bottle was kept in an ice bath to reduce oxygen release to a minimum.

In each run, about 60 g of soil was weighed in a balance. Then about 10 g of this sample was extracted by ASE and quantification by GC analysis. The rest of the sample (about 50 g) was added to the reactor. After taking out the glass jar containing the aged soil from the refrigerator, it was left in the dark

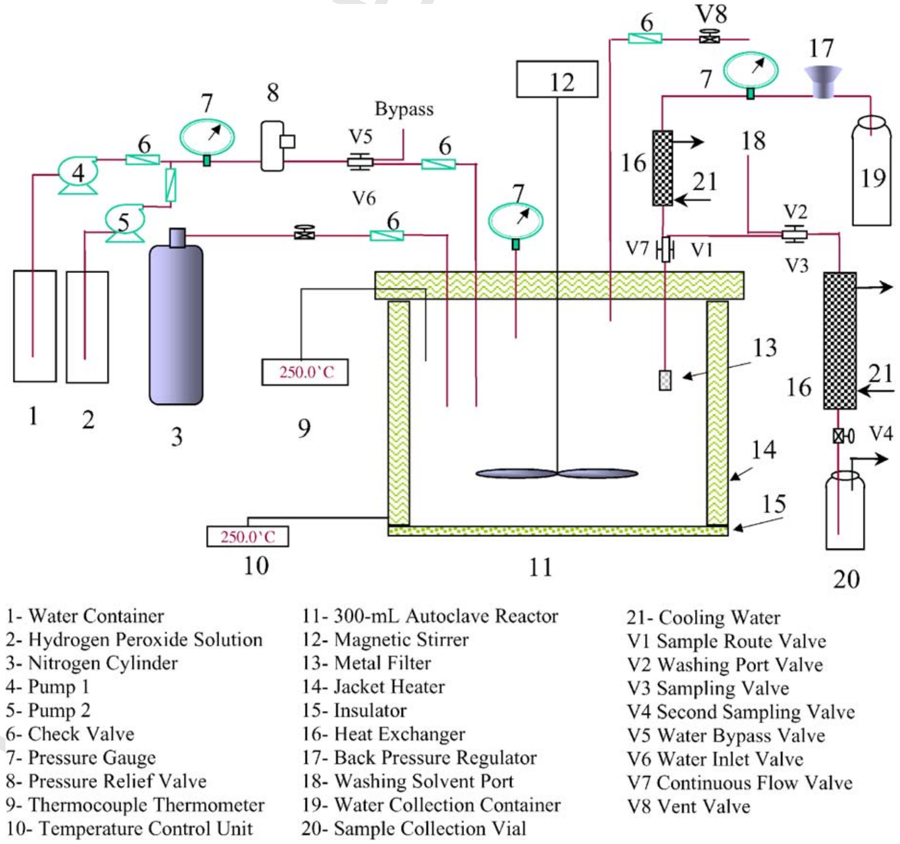

Fig. 2. Initial design for continuous flow experiments.

until it reached room temperature and was thoroughly shaken before opening its cap. This step was done to avoid condensation of water on the soil and to homogenize the soil. Then once again, soil was mixed thoroughly with the stainless steel scoop before placing the appropriate amount of soil on the balance. Two hundred to two hundred and twenty (200–220) mL of double distilled water was then added on top of the soil. These steps reduced the dead volume in the reactor to a minimum. The reactor vessel was bolted to the main body, which supported the tubing, temperature sensor, and mixer. All reactor exit valves were closed and it was pressurized with nitrogen to the initial pressure of 400–450 psig. Heating was provided by a cylindrical ceramic heater, which surrounded the reactor body. The temperature controller was connected to the heater thermocouple rather than the thermocouple measuring the inside reactor temperature. Then the heater was turned on, while monitoring the temperature inside the reactor. When the temperature approached 10–20 °C below the set point, the mixer was started at 300–500 rpm. The initial heating period usually took between 45 and 90 min. Also, at the same time the pump was started, the outlet valve for back pressure regulator was opened to establish the desired flow rate. Before starting each series of experiments, the pump was calibrated at room temperature and 1000 psig, which was the operating pressure through all of the continuous flow experiments. The back pressure regulator was set to keep the pressure constant at 1000 psi. A heat exchanger with tap water as cooling medium was used before the back pressure regulator to protect it from damage by hot water. Extraction time then was started when the reactor temperature was at the desired set point within a ±5 °C.

Sampling was in 10 min intervals for the first 2 h and in 30 min intervals after 2 h until the end of the experiment, which normally was 6 h. For some experiments, sampling intervals were slightly different. Sampling was done by opening the Valves V1 and V3 for about 1 min and closing them in order to trap the sample between two sampling valves V3 and V4, where it was cooled by circulating water through the heat exchanger. Then by opening valves V4 and V2 respectively the sample was transferred to a 22 mL vial with 2 mL of methylene chloride in it. The sample trap was washed a few times with methylene chloride through Valve, V3, and using a glass syringe, to collect any PAHs that may have been precipitated out on the walls. Sampling vials then were shaken by hand and the lower portion (methylene chloride with the dissolved PAHs) was separated using disposable glass pipettes. All washes were collected together with the initial sample, the amount of solvent reduced by evaporation, and a sample is injected into the HP-5890 GC for analysis. A Zebron ZB-5 column by phenomenex (Torrance CA) was used in the GC. Column specifications are 30 m long, 0.53 mm ID and 1.50 μm film thickness. Table 2 shows GC conditions and temperature program settings.

At the end of each run, while the reactor was still at the experimental temperature and pressure conditions, the water in the reactor was discharged to a collection vessel through the sampling line and the dry soil was removed from the reactor. Then about 10 g of this treated soil was extracted again by methylene chloride in an ASE 200 extractor as mentioned earlier. Extraction by ASE is fast, accurate and uses much less solvent [19–21]. The difference between the initial and the final soil analysis gives the extent of PAHs removed from the soil. The difference between the total amount of PAHs removed (soil analysis difference before and after extraction) and the amount dissolved in water (water sample analysis) gives the amount of PAHs destroyed by oxidation.

Table 2
Gas chromatograph settings and temperature programs

	Spiked soil experiments	Aged soil experiments
Injection port temperature (°C)	300	300
FID detector temperature (°C)	325	325
Initial temperature (°C)	150	120
Initial time (min)	2	5
Heating rate (°C/min)	20	3
Final temperature (°C)	300	310
Final time (min)	30.5	10
Column head pressure (psi)	10	40
Helium flow rate (mL/min)	15	15

2.3. *Hot water extraction combined with oxidation*

The series of extraction/oxidation experiments were basically similar to the hot water extraction experiments explained above. For combined extraction and oxidation experiments, the vessel was initially charged with the same amount of soil as before. Also instead of distilled water, an equivalent volume of aqueous solution of hydrogen peroxide was added to the vessel. After heating to operating temperature, the same solution was pumped to the vessel.

3. Results and discussion

Eight experiments were performed and numbered from C1 to C8. However some of them were just repeat of runs with problems or to check the reproducibility. For setting the residence time, it was necessary to find the liquid phase volume in the vessel. This was not possible by just subtracting the volume of soil in the reactor from the total volume of the vessel due to the volume of the mixer and also void volume inside the mixer shaft. So the volume of the initial water in the vessel, added to the amount of water needed to be pumped into the vessel, in order to move the pressure gauge indicator was calculated to be 265 mL. So for 1 h residence time, the flow rate was set to 265 mL/min, and for 2 h residence time, it was changed to 132.5 mL/min.

Table 3 shows the flow conditions for the selected experiments. In Experiments C1 and C4, inflow was composed only of pure water. For Experiments C6–C8, double-distilled water and 30% aqueous solution of hydrogen peroxide were mixed first in an external bottle, and then fed to the vessel by the pump. For Experiments C6 and C7, the ratio of 30% hydrogen peroxide to water was 1–10. However, for Experiment C8, the flow rate of hydrogen peroxide was halved keeping the total flow rate of water and hydrogen peroxide mixture as C7 to give 1 h residence time. This was done to reduce the oxidation rate so the isotherm

Table 3
Data for different continuous flow experiments

	Residence time (h)	Water flow (mL/h)	30% H_2O_2 flow (mL/h)	Soil weight (g)
C1	1	265	0	50.00
C4	2	132.5	0	50.40
C6	2	121.24	12.10	49.82
C7	1[a]	242.13	24.21	50.87
C8	1	253.57	12.10	50.95

[a] Residence time is similar to C8, but hydrogen peroxide flow rate was double compared to Experiment C8.

shape could be detected. Even with this reduction in hydrogen peroxide concentration, the oxidation rate was so fast that almost no PAH could be detected in nearly all water samples that were collected during Experiment C8.

3.1. Hot water extraction

Fig. 3 shows the initial and residual concentrations of six PAHs in the un-extracted and extracted aged soil after 4 h. In this experiment, residence time was 1 h. It is clear that, the soil after this experiment is almost clean of the PAH and only small amounts of PAHs remain in the soil. Fig. 4 shows comparable results for Experiment C4 when the residence time was increased to 2 h. However, some degree of discrepancy is seen in the initial PAH concentrations in the soil before extraction. Due to the solid nature of soil and difficulties in getting a true homogenous sample, this can be reasonably justified. However, there is not much difference in the residual PAHs in the extracted soil, and maximum residual concentration of individual PAHs was <1 μg/g soil.

Fig. 5 shows the variation of concentration of different PAHs with time in Experiment C1 with 1 h residence time. Although this is an extraction-only experiment, the final concentration of fluoranthene and pyrene after 4 h of experiment is very low compared to the concentrations in the samples at the first hour of the experiment. For other PAHs, this variation is less apparent.

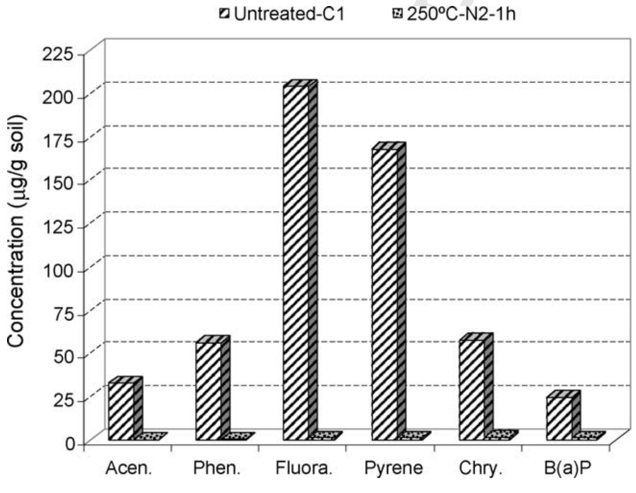

Fig. 3. Concentration of PAHs in the aged soil before and after 4 h extraction with continuous flow of hot water at 250 °C under nitrogen atmosphere, and residence time of 1 h (Experiment C1).

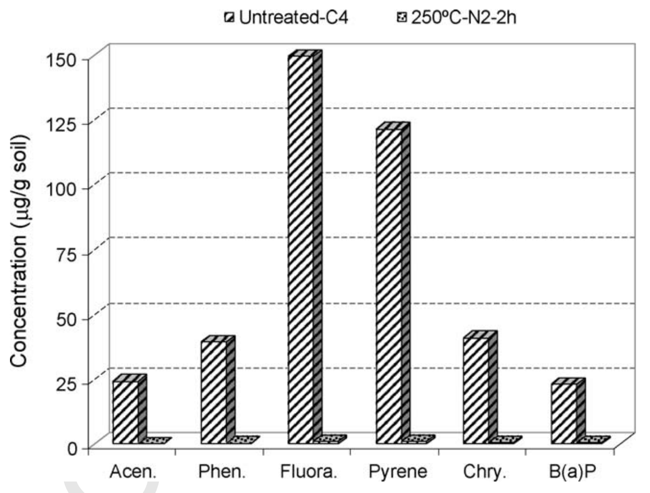

Fig. 4. Concentration of PAHs in the aged soil before and after 4 h extraction with continuous flow of hot water at 250 °C under nitrogen atmosphere, and residence time of 2 h (Experiment C4).

Additionally to check for reproducibility of the results, the 2 h residence time experiment was repeated three times (Experiments C2–C4). Fig. 6 shows the PAH concentration in effluent water samples. Other than some high concentration values for fluoranthene and pyrene in Experiment C2, there is not much difference between the values from experiments C3 and C4.

3.2. Hot water extraction combined with oxidation

Hydrogen peroxide was the only oxidizing agent used in these experiments. Three experiments with different flow rate or hydrogen peroxide concentrations were performed (Experiments C6–C8). For the first experiment, the residence time was 2 h, whereas for the next two experiments it was 1 h. However, quantity of hydrogen peroxide that was used in Experiment C8, was about the half of the quantity used in Experiment C7. This means after 2 h of running Experiment C8, the quantity of hydro-

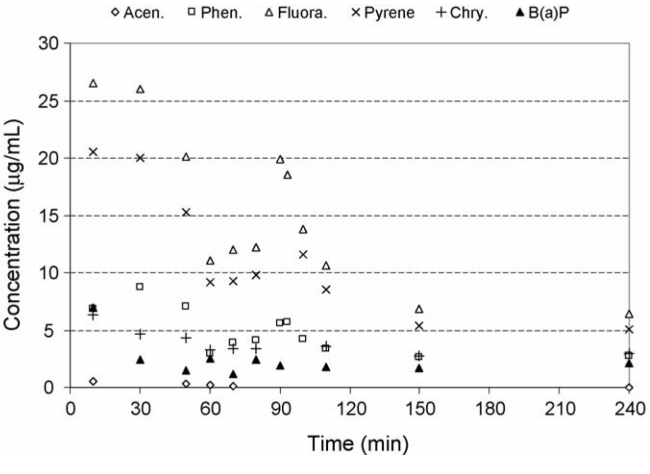

Fig. 5. Variation of PAHs concentrations in the effluent water with time in the extraction-only experiment using hot water and residence time of 1 h (Experiment C1).

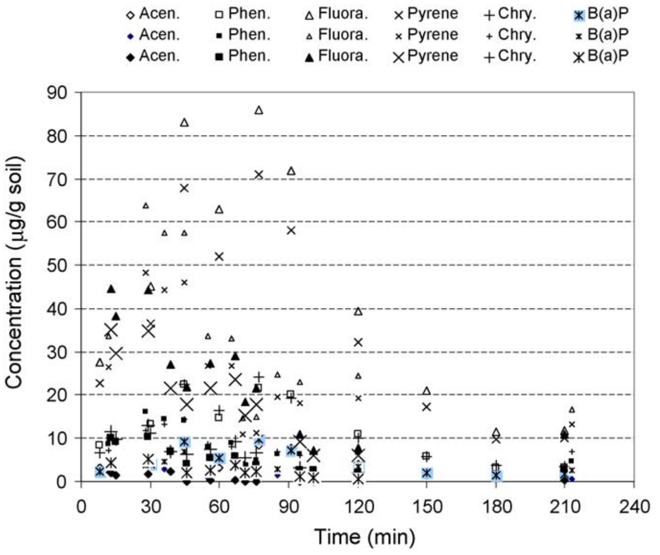

Fig. 6. Concentration of PAHs in water effluent as was obtained by three experiments at 250 °C and 2 h residence time. Three lines of legends are for experiment numbers C2–C4, respectively.

gen peroxide that was used was equal to the quantity that was used during 1 h operation in Experiment C7.

Fig. 7 shows the PAH content of soil before and after the combined extraction and oxidation with 2 h residence time. The residual PAHs in the soil are either non-detectable, or very small and on the edge of the detection limit, which is due to the nature of FID detector in gas chromatograph. It is not clear whether this is the normal noise signal that happened to overlap with the one or more PAH retention time, or a real signal. In any case, these are very small and even were below detection limits in the next two experiments (Figs. 8 and 9). These two last figures show the PAH concentrations in the soil before and after Experiments C7 and C8 with 2 h residence time.

Fig. 10 depicts the variation of PAHs concentrations in the effluent water for Experiment C8 in which 12.1 mL/h 30% aqueous solution of hydrogen peroxide feed was mixed with distilled water to produce total flow rate equivalent to 1 h residence time.

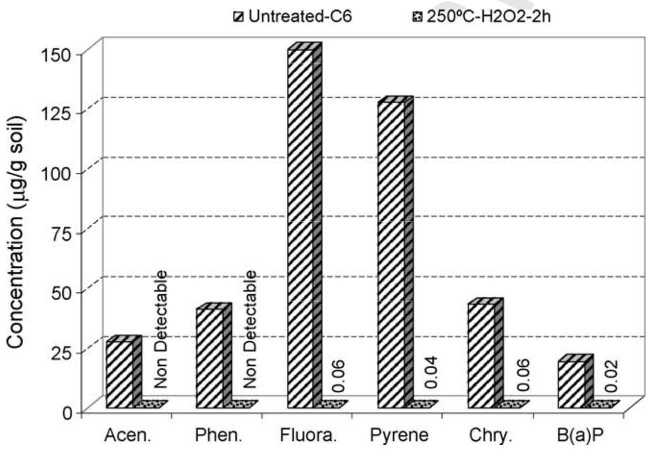

Fig. 7. Concentration of PAHs in the aged soil before and after 6 h extraction with continuous flow of hot solution of water and hydrogen peroxide at 250 °C. Residence time = 2 h (Experiment C6).

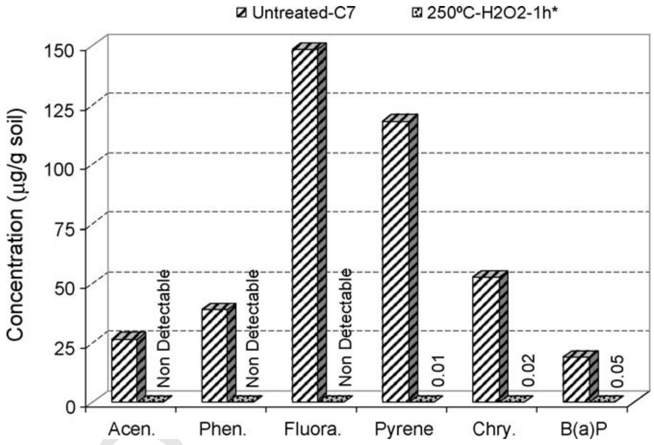

Fig. 8. Concentration of PAHs in the aged soil before and after 6 h extraction with continuous flow of hot solution of water and hydrogen peroxide at 250 °C. Residence time = 1 h, flow rate of 30% hydrogen peroxide = 24.21 mL/h (Experiment C7).

From the chart, it can be seen that the PAH concentration in the effluent water after the first hour of experiment is either zero and undetectable, or very small and negligible. Furthermore, the color of the effluent water changed from dark brown to almost clear and no color after two or three residence times. Moreover, this confirmed the results of the other two experiments C6 and C7. Because the concentrations were very small, they are shown on a logarithmic scale, causing zero values to be dropped off the chart. Depending on the type of local or governmental requirements, it is quite possible to consider this as clean water, or at most one can increase the rate of oxygen input to the reactor to totally nullify the post treatment of the effluent water.

Concentrations of PAHs in soil before and after various experiments have been shown in Figs. 3, 4 and 7–9. But due to large variation in concentration of each PAH in the untreated soil, and to normalize the residue PAHs in the soil to a unified basis, the percent residual concentrations were calculated for all continuous flow experiments (Fig. 11). This graph shows that for extraction-only experiments, residues are much less than those

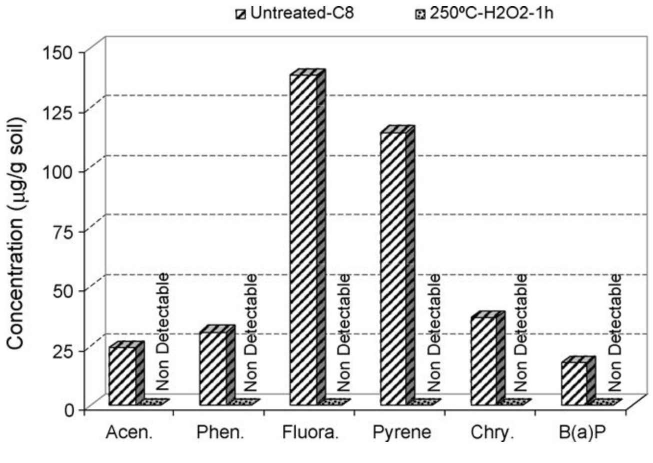

Fig. 9. Concentration of PAHs in the aged soil before and after 6 h extraction with continuous flow of hot solution of water and hydrogen peroxide at 250 °C. Residence time = 1 h, flow rate of 30% hydrogen peroxide = 12.10 mL/h (Experiment C8).

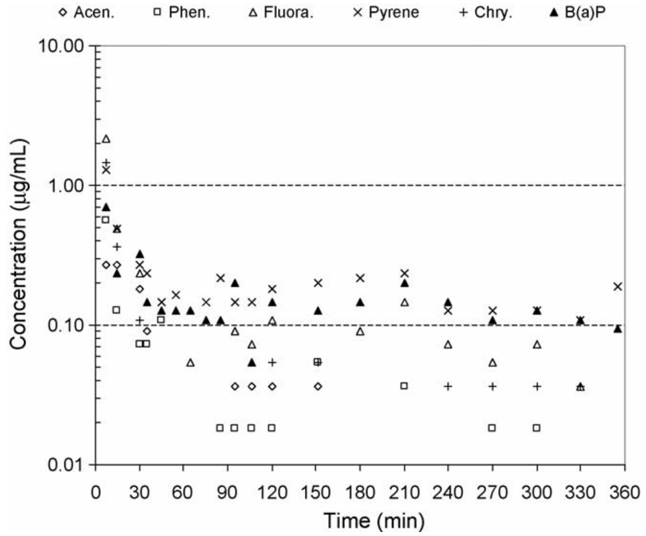

Fig. 10. Variation of PAHs concentrations in the effluent water with time in the combined extraction and in situ oxidation experiment using continuous flow of hot solution of water and hydrogen peroxide at 250 °C. Residence time = 1 h, flow rate of 30% hydrogen peroxide = 12.10 mL/h (Experiment C8).

of batch experiments, but for combined extraction and oxidation experiments, residue results of continuous and batch modes are almost similar. Interestingly here again for oxidation experiments, phenanthrene residue is slightly higher than the next PAH residue which is fluoranthene.

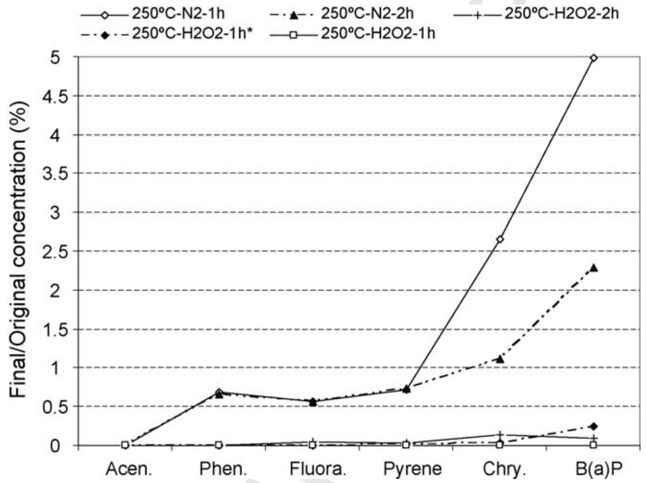

Fig. 11. Percentage of each PAH over the original concentration, remaining in the aged soil at the end of each continuous flow experiment at 250 °C. Hollow diamonds and black traingles show the results for extraction-only experiment with residence time of 1 and 2 h. Black diamonds and hollow squares show the results for combined extraction and oxidation with residence time of 1 h with the double hydrogen peroxide concentration for the former one. Plus marks show the results for the extraction and oxidation experiment with 2 h residence time.

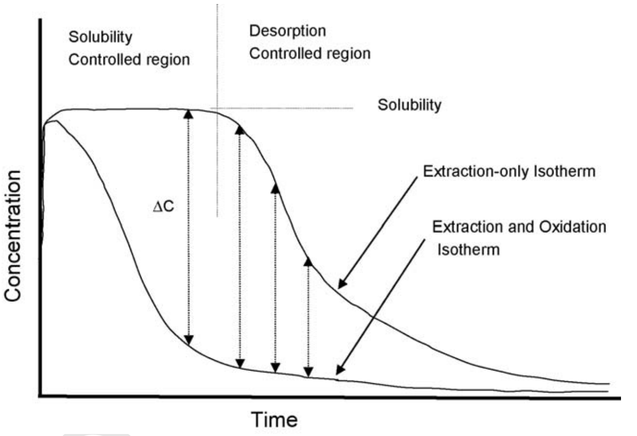

Fig. 12. Schematic of contaminants breakthrough in the effluent in extraction and combined extraction and oxidation.

3.3. *Rate calculations*

PAHs have to be available in the liquid phase to be destroyed by oxidation. In any extraction process, two different mechanisms can control the rate. If the amount of contaminant in the soil is high, then the rate of extraction will be controlled by the solubility of the contaminant in hot water. On the other hand, if the concentration of the contaminants in soil is low, the extraction in fact is desorption and is controlled by the partitioning of the contaminant between soil and water phases, i.e. the desorption isotherm. All extraction processes will be controlled by desorption as the concentration goes down due to extraction. Fig. 12 shows a schematic diagram of breakthrough profiles in extraction-only and combined extraction and oxidation. In the case of extraction with no oxidation, the breakthrough shows the amount of each PAH that is dissolved by hot water or desorbed from the soil. However in the case of combined extraction and oxidation, the concentration of PAHs in the effluent water shows the amount of PAHs that have been left unreacted. Consequently the reaction rate cannot be found just simply based on the concentration data from experiments with oxidation. Hence, the instantaneous amount of each PAH that is being destroyed by oxidation is the difference in the two profiles as is shown by vertical arrows in Fig. 12. This can be expressed as Eq. (1):

$$-n_{\mathrm{C}} + (r_{\mathrm{ds}} - r_{rxn})V = \frac{\mathrm{d}N_{\mathrm{C}}}{\mathrm{d}t} \tag{1}$$

In this equation, n_{C} is the molar flow rate of the contaminants from the reactor in the effluent, N_{C} the number of moles in the water phase in the reactor, r_{ds} the rate of extraction, either by dissolution or by desorption, and r_{rxn} is the oxidative destruction rate. If r_{ds} in Eq. (1) is dissolution rate, then it can be written as

$$r_{\mathrm{ds}} = -\frac{\mathrm{d}q}{\mathrm{d}t} = \frac{C^{\mathrm{sat}}Q}{w_{\mathrm{s}}} \tag{2}$$

where q is the solid loading in mass contaminant per unit mass soil, C^{sat} the solubility in hot water (mass contaminant per unit volume), Q the water volumetric flow rate, and w_{s} is the mass of soil in the vessel. But if r_{ds} is the desorption rate, then:

$$r_{\mathrm{ds}} = -\frac{\mathrm{d}q}{\mathrm{d}t}, \quad q = f(C_{\mathrm{C}}) \tag{3}$$

To calculate the oxidation rate, concentration data from extraction-only experiments and combined extraction and oxidation experiments were fitted to smooth curves and then for each PAH component, the reaction curve was subtracted from

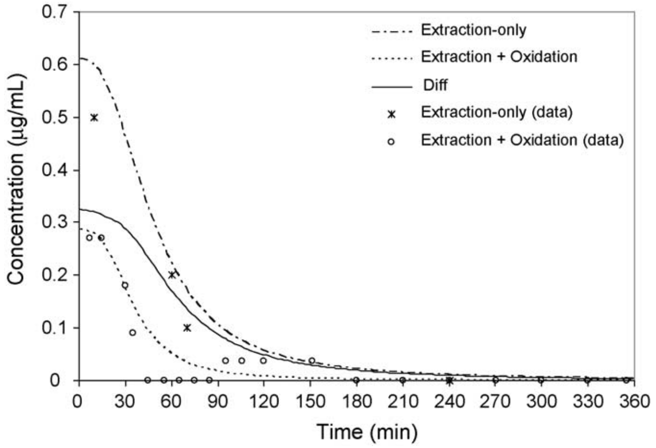

Fig. 13. Variation of acenaphthene concentration by time in effluent water in Experiments C1 and C8 with residence time = 1 h.

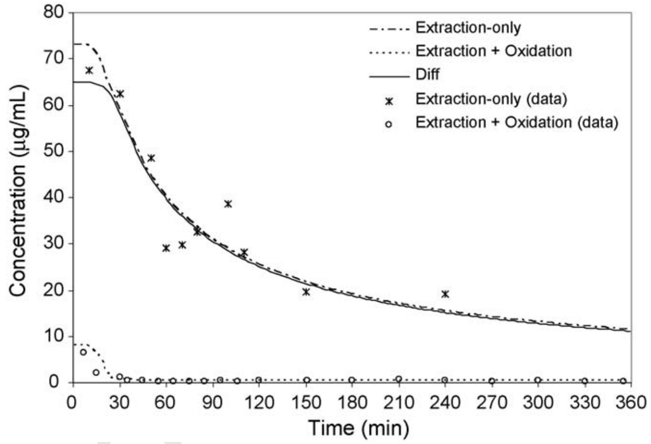

Fig. 15. Variation of total PAH concentration by time in effluent water in Experiments C1 and C8 with residence time = 1 h.

the extraction curve to find the amount of reacting material for each PAH as was described earlier (see Fig. 12). It is assumed that in extraction-only experiments, rate of oxidation is negligible, and in the combined extraction and oxidation experiments, the oxidant does not extract PAHs. Then for each PAH, this new set of data along with other two fitted concentration curves and the experimental data points were plotted on the same graph. This is done for results of experiments of 1 and 2 h residence times. Fig. 13 shows the resulting graph for acenaphthene for 1 h residence time. Then this concentration difference curve was differentiated versus time by calculation of slope at 2 min time intervals to find the instantaneous rates of oxidation. For acenaphthene and 1 h residence time, the resulting oxidation rate graph is shown in Fig. 14. Same procedure for calculating the oxidation rate was applied to other PAHs under study and the total PAH content in both 1 and 2 h residence time experiments. Figs. 15 and 16 show the resulting graphs for total PAHs in 1 h residence time experiments (Experiments C1 and C8). In all of the graphs illustrating the rate data, the rate increases, passes through a maximum, and then sharply decreases until the second and third hour of operation, and finally gradually decreases until the end of the experiment. This can be explained as follows: what is recorded as the reaction or extraction time is not the real starting time. As mentioned earlier, time was recorded immediately after the mixer and inlet pump were switched on, when the reactor has been heated to a temperature of nearly 250 °C. However, during the heating period the reactor was full of aqueous solution of hydrogen peroxide and soil, which led to a localized high concentration of dissolved PAHs and free oxygen just before starting the mixer and timer. This may be the reason for the initial higher rate and the decline after that. As a general trend concentrations and oxidation rates for various PAHs are lower in experiments with 1 h residence time. This is expected due to the more dilution in the 1 h residence time than experiments with 2 h residence time. As was already noted, in the 1 h residence time (Experiment C8), the total flow rate was double of the experiments with 2 h residence time; however, the quantity of hydrogen peroxide feed per unit time was the same in both set of experiments. For all oxidation rates, they were integrated

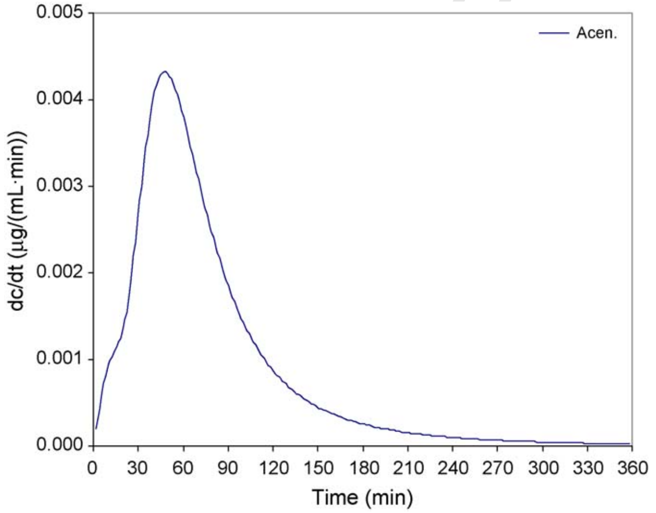

Fig. 14. Oxidation rate of desorbed acenaphthene in the hot subcritical water, residence time = 1 h, average rate = 8.98×10^{-4} μg/(mL min).

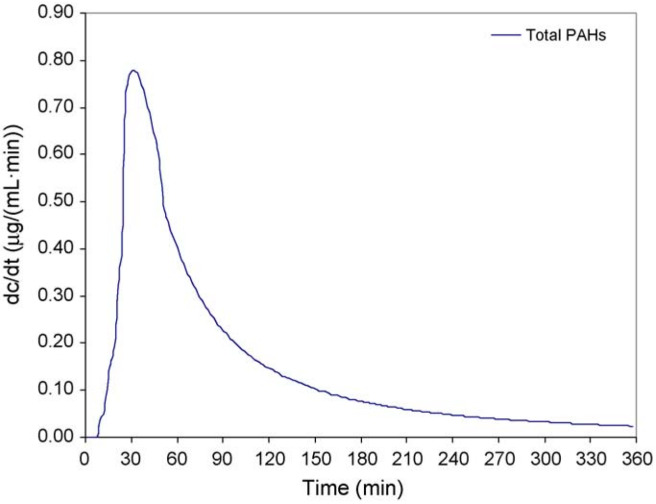

Fig. 16. Oxidation rate of total PAHs in the hot subcritical water, residence time = 1 h, average rate = 0.151 μg/(mL min).

Table 4
Average oxidation rates for individual and total PAHs over the 6 h period for 1 and 2 h residence times

PAH	Average oxidation rate (μg/(mL min))	
	1 h Residence time	2 h Residence time
Acenaphthene	8.98×10^{-4}	4.16×10^{-3}
Phenanthrene	1.46×10^{-2}	2.20×10^{-2}
Fluoranthene	5.77×10^{-2}	1.05×10^{-1}
Pyrene	4.65×10^{-2}	9.93×10^{-2}
Chrysene	8.87×10^{-3}	2.88×10^{-2}
Benzo(a)pyrene	1.47×10^{-2}	9.74×10^{-3}
Total PAHs	1.51×10^{-1}	2.57×10^{-1}

Table 5
Rate parameters for total PAH oxidation

K	3.28×10^{-4} (1/min)(μg/mL)$^{-1}$
N	2
R^2	0.9758

over the entire period of time (which are actually areas under the rate curves) and divided over the integration time period to get the average oxidation rate. Table 4 lists these average rates.

For total PAH oxidation, the rate of reaction was fitted to a power law expression as is shown in Eq. (4):

$$r_{rxn} = kC^n \tag{4}$$

Then by plotting the ln(rate) versus ln(total PAH concentration), k and n parameters are found (Table 5).

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