FENTON TREATMENT TO REMEDIATE SOIL CONTAMINATED WITH POLYCYCLIC AROMATIC HYDROCARBONS

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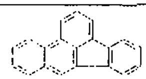
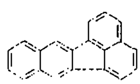
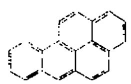
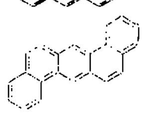
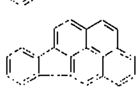
Introduction

Polycyclic aromatic hydrocarbons (PAHs) are persistent organic pollutants (POPs) according to a 1998 UN/ECE protocol. POPs must be strictly monitored because of their resistance to photolytic and biological degradation, low water solubility, and high lipid solubility that collectively result in bioaccumulation in fatty tissues of living organisms. Under this protocol, benzo(a)pyrene (BAP), benzo(b)fluoranthene (BBFT), benzo(k)fluoranthene (BKFT), and indeno(1,2,3-cd)pyrene (INDE) are considered as PAH indicators. The chemical properties of PAHs are given in Table 1.

Table 1 Chemical properties of PAHs[1,2,3]

Structure	PAH	Molecular weight	Boiling Point (℃)	Log K_{ow}	Vapor pressure at 25℃ (mmHg)	Carcinogenicity[a]
	BBFT	252.3	480	6.35	ND	88 ng/kg (skn-mus)
	BKFT	252.3	ND	ND	ND	2820 mg/kg (skn-mus)
	BAP	252.3	495	5.99	5.49×10^{-9}	25 ng/kg (skn-mus)
	DIB	278.4	ND	ND	ND	ND
	INDE	276.3	ND	6.58	1.00×10^{-10}	72 mg/kg (scu-mus)

[a] Toxic dose low, *i.e.*, the lowest dose of a substance introduced by any route other than inhalation, over any given period of time, to which humans or animals have been exposed and reported to produce any non-significant toxic effects in humans or to produce non-significant tumorigenic or reproductive effects in animals or humans.

[b] ND; no data available.

Because no effective technology currently exists for remediating common soil highly contaminated by PAHs, and because uncontrolled land disposal of PAHs is such a serious threat to the environment, here we describe a Fenton treatment method that can remove PAHs from soil such that Canadian soil standards for residential areas are satisfied (< 1 mg/kg). In addition, to elucidate the removal mechanism, we selectively compare PAH removal characteristics and Fenton treatment products using field soil and in pure ethanol, respectively.

Methods

PAH-contaminated soil was obtained from a petroleum refinery plant. The concentration of BAP, BBFT, BKFT, dibenz(a,h)anthracene (DIB) in soil was 62.1, 105.3, 29.0, and 44.2 mg/kg, respectively. No INDE was detected (< 0.2 mg/kg).

To evaluate the effect of ethanol addition on PAH removal, various amounts of ethanol (1.0–5.0 mL/g soil) were added to contaminated soil and the mixture was agitated for 24 h to dissolve absorbed PAHs. Fenton oxidation treatment was performed next, i.e., 30% H_2O_2 (1.0–3.7 mL/g soil) and 0.5 M Fe^{2+} (0.5–2.0 mL/g soil) were added and allowed to react in a sealed teflon reactor for 24 h at room temperature. Similar control experiments were performed to confirm recovery of PAHs, i.e., corresponding amounts of distilled water were substituted for 30% H_2O_2 and 0.5 M Fe^{2+}. We also combined ethanol (10 mL) with prepared solutions of BAP, BBFT, BKFT, DIB, or INDE (150 mg/L). In each experiment, pH was adjusted to 3.5 by adding 1 M H_2SO_4 or NaOH prior to adding 0.5 M Fe^{2+} (2.7 mL) and 30% H_2O_2 (4 mL). After various times, the reaction was terminated by lowering pH < 1 by adding 4–8 drops of conc. H_2SO_4. The concentrations of PAHs after Fenton oxidation were measured by a linear gradient of methanol/water—75–100% methanol for 25 min, then 100% methanol for 10 min—using HPLC-UV (LC-10AD VP, Shimadzu) with reverse phase separation (Tosoh TSK-Gel ODS-80 Ts, 25 cm–4.6 mm i.d.) at 254 nm, 1.0 $mLmin^{-1}$, and 25°C. All Fenton oxidation experiments were conducted in the dark at 30 °C.

Results and discussion

Ethanol addition before Fenton treatment substantially enhanced removal of PAHs, being most likely the result of ethanol increasing desorption of PAHs from the soil matrix. Table 2 shows PAHs concentrations under various Fenton treatment conditions. Under the best Fenton treatment conditions—5 mL of ethanol, 2 mL of 0.5 M of Fe^{2+}, and 3.7 mL of 30% H_2O_2 per 1 g of soil—the following removal efficiencies were obtained: BAP, 98.6%; BBFT, 72.0%; BKFT, 97.7%; and DIB, 99.5%. The resultant concentrations of BAP and BKFT satisfied Canadian soil standard for residential areas (< 1 mg/kg). The effect on PAH removal due to adding reagents was ethanol > H_2O_2 > Fe^{2+}. Although no products peaks after Fenton treatment of PAHs-contaminated soil were detected on HPLC-UV chromatograph (Fig. 1), BAP-1,6, -3,6-, and -6,12-dione were identified as products of Fenton treatment of BAP in pure ethanol (data were not shown). With the exception of BBFT, Fenton treatment of PAHs in soil and in pure ethanol followed a pseudo first-order reaction. Fenton treatment of soil effectively removed PAHs, even though the reaction order coefficient was smaller compared to that in pure ethanol. In addition, similar to ultraviolet degradation of a PAH mixture or individual PAHs, the removal efficiency of BBFT in soil was much higher than that in pure ethanol (72.0 vs. 14.6%).

The employed treatment process for remediating soil contaminated with PAHs is considered to be effective for meeting Canadian soil standards for residential areas (< 1 mg/kg), and it can be successfully applied to PAH-contaminated soil that does not contain high concentrations of BBFT; a case requiring further study.

Table 2 PAHs concentration after Fenton treatment*

Treatment conditions	Addition amounts (mL)**			BAP		BBFT		BKFT		DIB	
	Ethanol	30% H_2O_2	0.5 M Fe^{2+}	mg/kg	Removal (%)	mg/kg	Removal (%)	mg/kg	Removal (%)	mg/kg	Removal (%)
1	1.0	1.0	0.5	17.2	72.3	96.5	8.4	19.1	35.9	40.1	9.3
2	1.0	2.0	0.5	9.4	84.9	91.4	13.2	21.3	28.5	33.5	24.2
3	2.0	1.0	0.5	1.2	98.1	79.4	24.6	11.0	63.1	18.4	58.4
4	2.0	2.0	0.5	1.6	97.4	72.7	31.0	9.2	69.1	5.5	87.6
5	3.0	1.0	1.0	1.5	97.6	74.4	29.3	7.3	75.5	3.2	92.8
6	3.0	2.0	1.0	1.1	98.2	57.1	45.8	3.9	86.9	1.4	96.8
7	5.0	3.7	2.0	0.9	98.6	29.5	72.9	0.7	97.7	< 0.2	> 99.5
Control	2.0***	3.0	1.0	0.8	18.2	94.6	10.2	20.2	32.2	41.3	6.6

*: Initial concentration of BAP, BBFT, BKFT, and DIB were 62.1, 105.3, 29.8, and 44.2 mg/kg, respectively
**: Based on 1 g of soil
***: Distilled water

References

1. Martha, W., B. Susan, Y.S. Lorraine and N.F. Margaret (1983) The Merck Index. 10th ed., pp. 1107, Merch&Co.Inc, New York, U.S.A.
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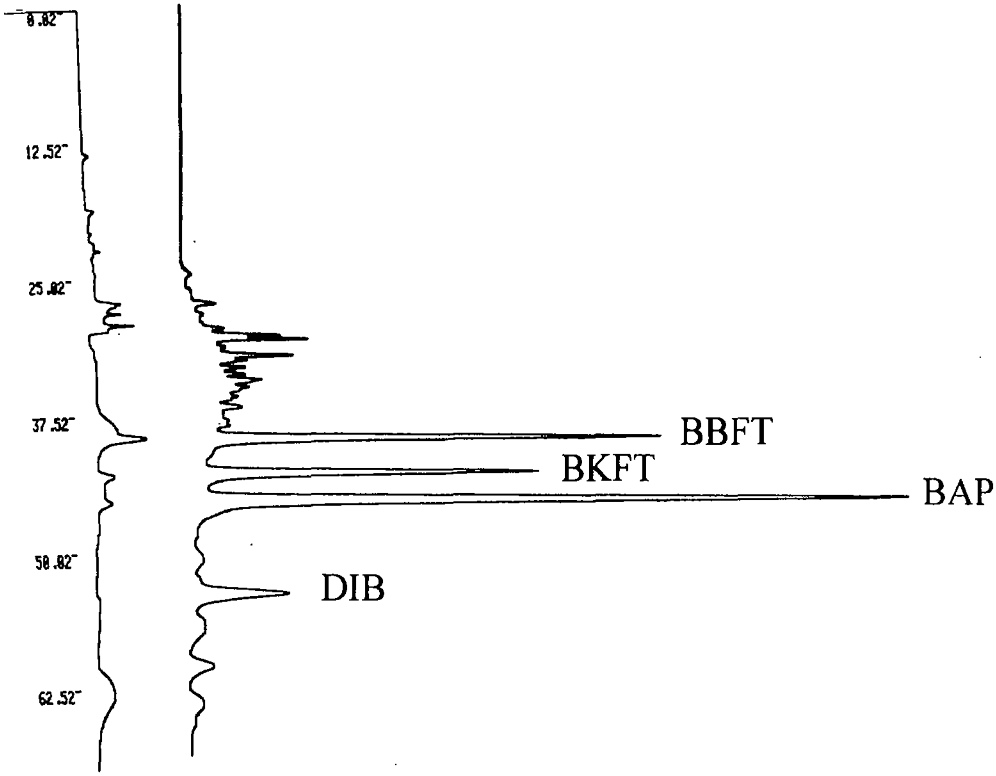

Fig. 1 Chromatograph of HPLC-UV before (right) and after (left) Fenton treatment of PAHs-contaminated soil.