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A Preliminary Study for Removing Phenanthrene and Benzo(a) Pyrene from Soil by Nanoparticles

[1]Benjalak Karnchanasest and [2]Onarpar Santisukkasaem
[1]Environmental Research Institute,
[2]National Center of Excellence for Environmental and Hazardous Waste Management,
Chulalongkorn University, Phayathai Rd, Patumwan, Bangkok 10330, Thailand

Abstract: Nanoparticles (NPs) synthesized were amphiphilic polymer with hydrophilic outer surface and hydrophobic interior with 50-110 nm diameter which enabled them to sorb some lipophilic organic compounds successfully. Stirring condition was crucial and influenced the NPs size. The soil texture and its high Organic Carbons (OCs) exhibited strong affinity to the compounds and subsequently difficult to desorb by NPs particularly high lipophilic benzo(a)pyrene (BaP). It was evident by the soil-NPs partition coefficients (K_{SN}) for PHE (0.55±0.03) and BaP (0.36±0.02) that NPs have stronger affinity than the soil allowing them to attract the compounds from soil. Flushing out of NPs from soil column with electrolyte solution gave 94% recovery which demonstrated some of particles might be trapped in the micropore, adsorb on the soil and inaccuracy weighing method. Phenanthrene (PHE) and BaP removal from spiked soil column were more effective in discontinuous elution for high and low spikes and the latter spike gave approximately 90% PHE, 50% BaP, the best elimination for all cases. It was the limited NPs for removing concentrate PAHs since increase of NPs the removal rate was higher. Factors governing removal process comprised mainly contact time, NPs size, NPs and contaminant concentrations.

Key words: Partition coefficient, soil-nanoparticles, removal, PAHs

INTRODUCTION

PAHs are ubiquitous airborne organic contaminants resulting from natural and anthropogenic sources. They occur in natural media, i.e., soil, sediment, water and air. Their presence in the environmental matrices is of great concern due to their adverse effects to human health and the environment (Zhou and Zhu, 2005; WHO, 1998). Since soil acts as a sink of atmospheric pollutants and disposed further to the environment through plants or directly to the air, surface water and groundwater. Thus, several soil remediation methods have been undertaken such as bioremediation of soil contaminated with organic substances often utilized requires exploration of appropriate microbes, environmental conditions and nutrient supplements in order to accomplish successful reaction (Nazaroff and Alvarez-Cohen, 2001). Similarly, phyto-remediation method needs long time for plants to grow and subsequent required disposal of chemical-accumulated plants. Also, simple water washing method gives low organic pollutant removal efficacy (Viglianti *et al.*, 2005). Lately, surfactant enhanced extraction of organic pollutants seems the most practice for soil extraction, however, is mainly limited by the concentration and stability of surfactant. That is because the surfactant concentration used must exceed the Critical Micelle Concentration (CMC) and surfactant loss through adsorption on the soil matrix in order to perform effectively (Edwards *et al.*, 1991). Additionally, this approach requires compatible surfactants that can work proficiently (Zheng and Obbard, 2002). Later Kim *et al.* (2003) and Tungittiplakorn *et al.* (2004) synthesized amphiphilic polyurethane NPs which exhibited superior removal than surfactants due to no breakage through interaction with soil matrix and shown to desorb PHE, low MW PAH, with an exceptional high percentage. Objective of this study is therefore, to investigate further the desorption efficiency for higher MW PAHs which sorbs powerfully to soil particles than lower MW PAHs using BaP conducted parallel to PHE as test compounds. Firstly, the sorption strength of NPs is to verify for both PHE and BaP by conducting NPs-soil partition coefficient. Next is the column test on high and low MW PAHs for the removal efficiency. Influencing factors is also discussed.

Corresponding Author: Benjalak Karnchanasest, Environmental Research Institute, Chulalongkorn University, Phayathai Rd, Patumwan, Bangkok 10330, Thailand

MATERIALS AND METHODS

Chemicals: (1) poly(tetramethylene glycol) (PTMG, Aldrich), (2) 2,4-toulene diisocyanate (TDI, Aldrich), (3) 2-hydroxyethyl methacrylate (HEMA, Fluka), (4) poly(ethylene glycol) (PEG, Fluka), (5) N,N dimethylacetamide (DMAc, Acros), (6) potassium persulfate (KPS, Acros), (7) hexane (J.B. Beaker), (8) acetone (J.B. Beaker), (9) dichloromethane (DCM, Mallinkrodt), (10) anhydrous sodium sulfate (Na_2SO_4, Merck), (11) silica gel (Merck), (12) calcium sulfate ($CaSO_4$, Carlo), (13) sodium azide (NaN_3, Aldrich).

Test compounds: Phenanthrene (PHE 98%, Fluka) and Benzo(a)Pyrene (BaP, Ehrenstorfer) were used as test compounds. Due to unavailable radioactive treatment in the laboratory, Pyrene (PYR 98%, Fluka) was used as an internal standard.

Nanoparticles: The synthesis was modified from Tungittiplakorn *et al.* (2004) and carried out in the laboratory of Environmental Research Institute. The mixture comprised 2:1:1:1: TDI: PTMG: HEMA: PEG and steps for the reaction was as following.

- **Synthesis of precursor:** 6.954 g TDI was mixed with 20.002 g PTMG in a reactor, stirred at 35°C for 30 min and stirred again 5 h at 45°C. The containment was cooled down to 20°C, 2.603 g HEMA was then added while stirring for 30 min and another stir of 3 h at 45°C. Finally, 40 g PEG in 0.25% DMAc was introduced and the mixture was increased to 65°C with stirring 12 h. During the synthesis, 99.99% nitrogen gas was continuously purged to avoid any oxygen in the system. The complete product of precursor obtained, poly(ethylene)glycol modified urethane acrylate (PMUA), was confirmed by the disappearance of NCO group at the wavelength of 2270 cm^{-1} measured by fourier transform infrared spectrometer.
- **Formation of NPs:** Deionized water was dropped on the precursor at 35°C with vigorous stirring until emulsion of nanoparticles was formed.
- **Cross-linked reaction:** At 65°C, 5% KPS was added on the emulsion in a round bottom flask equipped with magnetic stirrer and purged with nitrogen gas and stirred 8 h. The nanoparticles attained were measured by particle size distribution analyzer after filtering out 450 nm size through GFC and then adjusted pH from 2 to 7 using NaOH.

The particles synthesized have hydrophobic interior region enable to sorb lipophilic chemicals and hydrophilic at the surface which promote particle mobility in the soil.

Soil: Soil surface (10-15 cm) was collected from uncontaminated area, outskirt of Bangkok, in dry season of April, 2006. The soil samples were mixed, sieved through 0.5 mm and stored in air-tight clean glass containers at room temperature. The soil was analyzed in our laboratory for pH (soil: water = 1:1), texture (sieve analysis), moisture content (gravimetric method), Cation Exchange Capacity (CEC) (ammonium saturation and distillation), OC content (Walkley-Black method) and any PHE, PYR and BaP contamination (USEPA method 3546).

Experimental procedures

Extraction and isolation: The soil was extracted with 30 mL 1:1 hexane:acetone in a microwave extractor and continued for isolation as detailed in Karnchanasest and Jailuk (2004).

Quantification: The concentrates were quantified by GC-FID, Hewlett Packard HP 6890 equipped with 7683 autosample injector and HP-5 capillary column (30×320 μm id $\times$ 0.25 μm). The optimal condition gave the running time of 30 min: an initial column temperature at 80°C ramped at 25°C min^{-1} to 160°C and stayed for 5 min and again at 5°C min^{-1} to 300°C stayed for 5 min.

Partitioning between the soil and NPs: The equilibrium time was pre-determined using 3 g soil, 50 mL of 0.5 g L^{-1} NPs and 25S PAH concentrations. This condition was presumed to cover the reaction between stronger NPs solution and lower PAH concentrations carried out in the partitioning process. A set of three flasks was taken at the end of each shaking time of 6, 12, 24, 48 and 96 h for further extraction and quantification. The plots of PAHs in soil and NPs against shaking time demonstrated equilibrium attainment was reached at 48 h. The batch experiments of soil- NPs were conducted similarly in triplicate, at 27°C, using 50 mL of 0.5, 2.5 and 5 g L^{-1} NPs, 3 g soil and 4 concentrations of PAHs (0.05, 0.12, 0.18 and 0.25S). They were shaken for 48 h. The soil was filtered out and the filtrate was extracted and quantified for PAHs. Since only 50 mL DI water involved in the partitioning system and ¼ S concentration selected for the experiment contains very low amount of PAHs, therefore, the water phase can be neglected. Only two phases of soil and NPs were considered.

Elution of soil column: Pore Volume (PV) and porosity: 2.5×10 cm glass column was filled with soil (70 g) and the

soil volume was measured. The soil in the column was saturated with DI, weighed then drained out and weighed again. PV equal to the drained DI was 30 mL. The soil pore volume to soil column volume multiplied by 100 gave soil porosity of 65%.

Nps recovery: The soil column feeded with 30 mL 12 g L^{-1} Nps was rinsed with electrolyte solution of 5 mM $CaSO_4$ and 0.02% NaN_3 at 20 mL h^{-1}, 27°C. The effluent was collected every PV and dried at 50°C for 48 h to determine NPs residue.

Elution condition: PAHs in the range of 0.3-1.8 mg kg^{-1} was often found in roadside soil. Working concentrations of PAHs therefore were used accordingly. Seventy gram soil samples were pre-spiked with 0.125 (1.79 mg kg^{-1} soil) and 0.025 mg PAHs (0.36 mg kg^{-1} soil), packed separately in the columns. Each soil sample was pre-eluted with electrolyte solution to reduce colloidal solution and inhibit microbial activity. Twelve gram per liter NPs solution was feeded upwardly into soil columns at 20 mL h^{-1} 27°C. Every 30 mL effluent was collected using fraction collector, extracted and quantified. The experiments were operated separately in two elutions; (1) continuously and (2) discontinuously with 48 h stoppage for each PV eluting.

RESULTS

Property of nanoparticles: The precursor PMUA formed has hydrophilic poly (ethylene oxide) chains anchored to the particles surface as pendent chains which cause the PMUA particles uncharged and stable. These hydrophilic polymer chains of hydroxyl end groups prevent Van der Waals attraction among the particles. Emulsifying PMUA in DI water force the precursor chains to form nano size. The final step of cross-linking of the particles prevents their breakage to occur during interaction with soil matrix (Tungittiplakorn *et al.*, 2004). They have not any affect from high ionic strength. The NPs obtained are of colloidal form, micelle-like colloidal particles and mostly in the size of 50-110 nm (50.52% v v^{-1}) (Table 1).

Property of soil: The soil samples were sandy loam soil (67.8% sand, 20.2% silt and 12% clay) and found no contamination of the test compounds or internal standard. The moisture content is 8.5% and pH 7.9. CEC was 7.9 cmolec kg^{-1} and OCs 2.34% considered strong affinity to hydrophobic compounds (Chiou, 1999).

Soil-NPs partition coefficients (K_{SN}): The partition coefficient of an organic compound between two phases developed from very low concentrations of the compound can be obtained from the slopes of the relationship

Table 1: Size of nanoparticles and their volume synthesized in this study

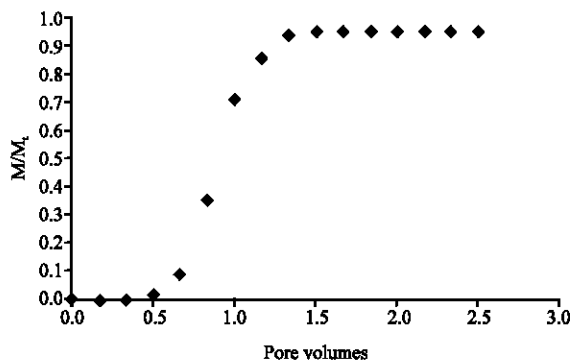| Size (nm)	Volume (%)
50	2.66
60	5.45
70	8.28
80	10.77
90	12.07
110	11.29
130	8.45
150	4.88

Fig. 1: Nanoparticles mass recovery from 70 g soil column at the flow rate of 20 mL h^{-1} (M and M_t represents accumulated mass of particles in the effluent and total particles mass added to the soil column)

between the concentrations in those two phases (Connell, 1990). Thus, K_{SN} values for PHE and BaP in this study read out from the slopes of the linear relationships (R^2 = 0.93-0.96) are as low as 0.55±0.03 and 0.36±0.02 L kg^{-1}, respectively (Figure not shown). The results indicate sorption capacity in NPs (0.025 g), 2-3 times stronger than in soil (0.07 g OCs). The results confirm NPs can attract PAHs from those adsorbtion on soil.

Removal of PAHs by NPs: NPs recovery from soil is to determine by the plots of M Mt^{-1} versus PV (Fig. 1). The result indicates 12 g L^{-1} NPs can be flushed out only 94% from the soil column within about 1.6 PV or 48 mL.

Figure 2 and 3 shows that removal process of both cases of PAH concentrations require the flow to be interrupted in order to achieve high adsorption in NPs. Interruption of 48 h is adequate. It should be noted that diffusion of intraparticles and intraorganic matter could occur in extended time of eluting particularly with high OCs in soil and cause desorption slow down (Shor *et al.*, 2003). From calculation, about 576 g NPs can desorb successfully 90 and 50% of 1 mg of each PHE and BaP or 0.36 mg kg^{-1} soil with discontinous flow option (Table 2 and 3). With the same amount of NPs and flow option, elimination of 5 times higher concentration of PAHs (1.8 mg kg^{-1} soil) reduces to one third of former

Table 2: Percentage removals of phenanthrene and benzo (a) pyrene from soil column with 0.25 mg and 0.125 mg PAHs spiked by 12 g L^{-1} nanoparticles with two types of elutings

	12 g L^{-1} nanoparticles eluent			
	0.025 mg PAHs spiked		0.125 mg PAHs spiked	
PAHs	Continuous eluting	Discontinuous eluting	Continuous eluting	Discontinuous eluting
PHE	72	90	17.7	29
BaP	35	50	3.8	15

Table 3: Mass (mg) removals of phenanthrene and benzo (a) pyrene from soil column with 0.25 mg and 0.125 mg PAHs spiked by 12 g L^{-1} nanoparticles with two types of eluting

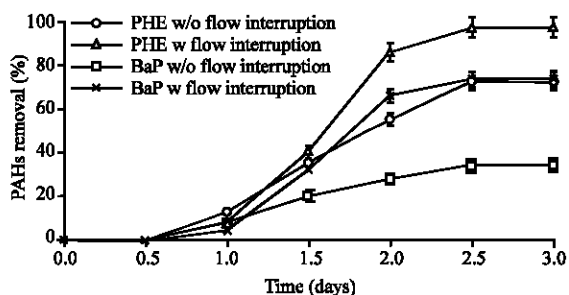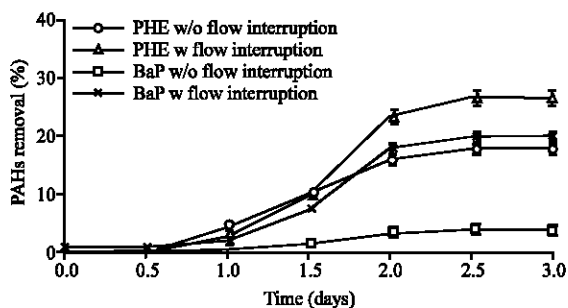|	12 g L^{-1} nanoparticles eluent			
	0.025 mg PAHs spiked		0.125 mg PAHs spiked	
PAHs	Continuous eluting	Discontinuous eluting	Continuous eluting	Discontinuous eluting
PHE	0.0181	0.0226	0.0221	0.0363
BaP	0.0088	0.0125	0.0048	0.0191

Fig. 2: Percentage removal of PHE and BaP from soil column pre-spiked with 0.025 mg PHE/BaP on 70 g soil and eluted by 12 g L^{-1} nanoparticles at the flow rate of 20 mL h^{-1} with continuous and discontinuous elutions

Fig. 3: Percentage removal of PHE and BaP from soil column pre-spiked with 0.125 mg PHE/BaP on 70 g soil and eluted by 12 g L^{-1} nanoparticles at the flow rate of 20 mL h^{-1} with continuous and discontinuous elutions

elimination. Similar study but on an increase of 5 times of NPs (60 g L^{-1}) amount give the elimination to 91% PHE and 53% BaP (Figure not shown).

DISCUSSION

NPs obtained in this study have slight larger size as compared to other studies synthesized the same NPs with similar method which is due to the speed and duration of stirring in the NPs formation step (Table 4). Thus, reproducing the particles could have various sizes and should be conducted in one synthesis with adequate amount for use. Alternatively, composite of few syntheses before use is also possible. The resulting NPs are therefore suitable for soil remediation supported by their water soluble chains residing on the surface allowing particle mobility in soil and hydrophobic interior to permit attraction to PAHs.

The soil-NPs partition coefficients in comparison to other similar systems, i.e., K values of PHE for soil-nonionic surfactant (tritonX100) and soil-copolymer (ethylene oxide-propylene oxide, EO-PO) exhibit 10.5 and 8.6-47.6 L kg^{-1} respectively (Paterson *et al.*, 1999). This indicates tritonX100 and copolymer perform sorption of PHE in somewhat lesser extent as compared to NPs used in this study. It should be noted that larger amount/concentrations of NPs emulsion would raise its sorption capacity due to more adsorption sites and as a consequence, K_{SN} values lower than obtained.

NPs recovery rate indicating removing efficiency is less than the work of Tungittiplakorn *et al.* (2004) (100%) which may be influenced by about 4 times OCs content and higher silt and clay percentage in this study (20.2% silt and 12% clay compared to 4.32% silt and 1.77% clay (Tungittiplakorn *et al.*, 2004). Demars *et al.* (1999) supported that larger amount of fine texture of sand and silt tend to exhibit stronger affinity and subsequently hard to desorb. Loss of approximately 6% could be caused by adsorption on soil high organic carbon, trap of particles in the micropore and inaccuracy of quantifying method. However, they are only good at extracting organic chemicals which have mild lipophilic characteristics, or in other words low MW (PHE in this study). Stronger lipophilic compounds (BaP in this study) are removed in lesser extent by the NPs but rotation or shaking the content could accelerate the elimination at some level.

Conclusively, key factors for the removal process are the soil sorption strength (as shown by OCs in the soil), lipophilicity of organic compounds contaminated in the soil (expressed by log K_{OW}), type of NPs synthesized (also size and concentrations), adequate contact time between the soil and the NPs. In actual situation, PAHs can be reduced further by the activity of available microbes in the soil. Appropriate proportion of PAHs and NPs should be further investigated in order to achieve high efficiency extract by carrying out the compound

Table 4: Comparison of nanoparticles size obtained in this study to other studies

Type of nanoparticles	Particle size (nm)	References
APU 700 with UAN chain	Aggregated-32.10	Kim *et al.* (2003)
APU 1000 with UAN chain	23.40	Kim *et al.* (2003)
APU with UAA chain	15-60	Tungittiplakorn *et al.* (2004)
APU with PMUA chain	60-80	Tungittiplakorn *et al.* (2004)
APU with PMUA chain	50-150	This study

APU: Amphiphilic polyurethane nanoparticles; UAN: Urethane acrylate nonionomer; UAA: Urethane acrylate anionomer; PMUA: Poly (ethylene glycol)-modified urethane acrylate

solubilization in a series of particles concentrations. It should be aware that there would be other available organic contaminants in the soil and could compete with our target compounds leading to an unexpected low removal capacity. Since NPs are reusable, research on utilizing local microbes to degrade PAHs in the NPs is strongly recommended.

ACKNOWLEDGMENTS

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