การบำบัดไพรีนในดินด้วยฟองก๊าซแอฟรอนที่เตรียมจาก สารลดแรงตึงผิวที่ย่อยสลายทางชีวภาพ

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บทคัดย่อ

งานวิจัยนี้ได้ศึกษาประสิทธิภาพการบำบัดไพรีนที่ปนเปื้อนในดินด้วยสารลดแรงตึงผิวที่ไม่เป็นพิษและย่อยสลายทางชีวภาพได้จำนวน 2 ชนิด ได้แก่ ไบโอโนเน็กซ์ (BioNonex) และ ไบโอโซล์ว (BioSolve) ในการทดลองใช้หินภูเขาไฟเป็นตัวแทนของดินที่ปราศจากสารอินทรีย์และทดลองเปรียบเทียบกับดินธรรมชาติโดยนำไปแช่ในสารละลายไพรีนที่ความเข้มข้นต่างๆ ในการศึกษาเบื้องต้นพบว่า สารละลายไบโอโนเน็กซ์สามารถบำบัดไพรีนได้ดีกว่าสารละลายไบโอโซล์วประมาณร้อยละ 20-30 ต่อมาได้ศึกษาการบำบัดไพรีนด้วยฟองก๊าซแอฟรอน (Colloidal Gas Aphrons, CGA) ที่เตรียมจากสารละลายไบโอโนเน็กซ์ในแพ็คคอลัมน์ซึ่งดำเนินการแบบไหลขึ้น (Up flow) จากการศึกษาพบว่าด้วยปริมาตรของสารที่เท่ากัน ฟองก๊าซแอฟรอนที่เตรียมจากไบโอโนเน็กซ์มีประสิทธิภาพในการบำบัดมากกว่าสารละลายไบโอโนเน็กซ์และน้ำกลั่น โดยที่การกำจัดเกิดขึ้นในอัตราที่สูงในช่วงแรกจากนั้นจึงลดลงหลังจาก 2 ชม. ฟองก๊าซแอฟรอนที่เตรียมจากไบโอโนเน็กซ์ร้อยละ 7 มีอัตราการกำจัดสูงสุดซึ่งอัตราการกำจัดลดลงจาก 120 มก./ชม. เป็น 40 มก./ชม. ภายใน 2 ชม.

คำสำคัญ : สารลดแรงตึงผิวที่ย่อยสลายทางชีวภาพ / ฟองก๊าซแอฟรอน / ไพรีน / หินภูเขาไฟ

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Removal of Pyrene in Soil by Colloidal Gas Aphrons of Prepared from Biodegradable Surfactant

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Abstract

Two commercial biodegradable and non-toxic surfactants (BioSolve and BioNonex) were studied for efficiency of pyrene removal from soil. Pumice was used as a model of natural soil with free of organic material. Natural soil taken from KMUTT campus was also used in the experiment. Pumice and natural soil were pretreated by soaking in pyrene solution to obtain the pyrene loading at various concentrations. In preliminary study, BioNonex solution could remove pyrene from pumice better than BioSolve solution at the same concentration. The removal of pyrene by colloidal gas aphron (CGA) of BioNonex was conducted in a packed column of pumice operated in continuous up-flow mode. It was demonstrated that BioNonex CGA could remove pyrene more efficiently than BioNonex solution and water particularly based on the aqueous volume. The initial rate of removal was high and retarded after 2 h. 7% BioNonex CGA provided the maximum rate of pyrene removal which decreased from 120 mg/h to 40 mg/h within 2 h.

Keywords : Biodegradable surfactant / Colloidal gas aphron / Pyrene / Remediation / Pumice

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a class of diverse organic compounds containing two or more fused aromatic ring of carbon and hydrogen atoms such as pyrene. These compounds are pollutants produced via natural and anthropogenic sources. They are harmful to environment and health of human being due to their high degree of mutagenicity and carcinogenicity. In Thailand, sediment from urban canals in Bangkok, street dust in urban area, and the Chao Phraya river estuary are contaminated with both petrogenic and pyrogenic PAHs. Boonyatumanond et al. [1] reported the distribution of PAH in riverine, esturine, and marine sediments as followings: the average total PAH concentration were 2,290 ± 2,556 ng/g in cannel, 263 ± 174 ng/g in the river, 179 ± 222 ng/g in the estuary, and 50 ± 56 ng/g in the coastal areas. Comparison of the concentration range with a worldwide survey of sedimentary PAH concentration ranked PAH contamination in Thai sediments as low to moderate.

The conventional remedies such as pump-and-treat have proven to be of limited practical value because of the hydrophobic nature of the polycyclic aromatic hydrocarbon (PAHs) compounds [2-7]. Therefore, significant efforts are devoted to develop efficient approaches for improve these techniques. One of the methods used to increase the solubility or decrease the surface tension of the PAHs in water is the application of surfactants [8-13]. Surfactants are especially useful for dissolving NAPL and enhancing NAPL mobility by lowering the interfacial tension between the NAPL and water [14-17]. The performance of a surfactant in the subsurface depends on temperature, sorption, degradation, the interaction of the compounds with the surfactants and soil, the partitioning of the compound with the surfactant micelle, the aqueous geochemistry of the injection water, and the surface chemistry of aquifer solids [18].

Surfactant can be introduced into the subsurface either in a conventional solution form or in the form of colloidal gas aphrons (CGAs) [19]. CGA are micro-bubbles (10-100 μm) encapsulated in a soapy film and created by intense stirring at 5,000-10,000 rpm. The attractive features of CGA are their small sizes, resulting in a large surface area to volume ratio, and the existence of a soluble film of surfactant encapsulating the gas, retarding the bubbles from coalescing. Moreover, there is no significant coalescence during transportation by pumping [20]. Some of the applications of CGA suspensions are flotation of organic contaminants, soil flushing, and in-situ bioremediation [3, 21-24]. CGA suspensions were found to be more efficient than surfactant solutions on the basis of weight of contaminant removed per gram of surfactant.

In this study, we used CGA and solutions of biodegradable surfactants (BioSolve and BioNonex) to remove pyrene as a model of PAH. The objectives of this study were to investigate the pyrene removal efficiency of the two biodegradable surfactant by varying surfactant type, concentration, and usage form.

2. Experimental

2.1 Materials

Pumice was purchased locally and used without further modification. Owing to the porous structure with free of organic material, we used pumice as a model in the experiment to eliminate effects of organic compounds in natural soil. The properties of pumice as received are shown in Table 1. Natural soil obtained from the KMUTT campus was used in a comparative study of pyrene removal with pumice. Pyrene (99% purity), a 4 benzene-ring polycyclic aromatic hydrocarbon, obtained from Aldrich Chemical Company, was selected as a target contaminant and used without further purification. Two commercial types of non-toxic and readily biodegradable surfactants, BioSolve (The Westford Chemical Corporation, Massachusetts, USA) and BioNonex (Apels Cheminvest AB, Mossv, Sweden) were used in this study to prepare surfactant solutions and CGA. The basic properties of both surfactants are listed in Table 2. They have been proven in the laboratory and in the field as cost effective, environmentally sound substances for remediation of soil and groundwater involving a wide range of contaminants.

2.2 Pretreatment of pumice

The purchased pumice was dried in an oven at 110°C for 6 h. It was then ground and sieved through US standard sieves (Mesh no. 5, 4, and 3). Three sizes of pumice particles in diameter, i.e., 4.0-4.8 mm, 4.8-6.3 mm and 6.3-8.0 mm were obtained. Five gram of each pumice particle size range were soaked in 10 ml of pyrene solutions in toluene with various concentrations. Then, the samples were shaken in the orbital shaker at 100 rpm for 3 h. The pyrene-loaded pumice particles were separated by a centrifuge and dried in an oven at 110°C for 6 h. The pyrene concentration in liquid phase was analyzed according to the Standard Methods 6440 B liquid-liquid extraction chromatographic for polycyclic aromatic hydrocarbons [25]. The GC analyses were accomplished with a HP-5890 Series II instrument equipped with a Chemipak PH SUS packed column (2 m length x 4 mm ID) working with carrier gas nitrogen at flow rate of 40 ml/min; injector and detector temperatures 280°C and 300°C, respectively. The pyrene adsorbed on pumice was calculated by mass balance. All data from these experiments were based on duplicate samples. The coefficient of variation for the pyrene concentration was ±2%.

2.3 Preliminary study

Removal of pyrene from natural soil

Five grams of soil samples with particle size of 4.0-4.8 mm in diameter obtained from the KMUTT campus were loaded with pyrene solution by soaking in 10 ml of 1,000 mg/l pyrene solution for 3 h as explained in 2.2. The concentration, and volume of pyrene solution remained in the Erlenmeyer flask were quantitatively determined by GC. The pyrene adsorbed on the soil was calculated by the mass balance. The soil samples loaded with pyrene were put in 10 ml of 5%vol BioNonex solution. All samples were shaken in an orbital shaker at 100 rpm for 3 h. After extraction, the soil particles were separated by a centrifuge at 3,000 rpm for 5 min. The concentration of removed pyrene in the solutions was determined by GC. All experiments were conducted at 30 °C.

Solubilization of pyrene in surfactant solution

Approximately 0.5 g of pyrene was put into 20 ml of surfactant solution of BioNonex and BioSolve at concentration of 1, 3, 5, 7 and 10 % vol. They were shaken by an orbital shaker at 100 rpm for 24 h. The solutions were then centrifuged at 3,000 rpm for 5 min in order to separate undissolved pyrene. The concentration of pyrene in the solutions was determined by GC.

2.4 Removal of pyrene from pumice

Batch operation

Effect of surfactant type and concentration

The pyrene-loaded pumice particles at various concentrations were prepared by the same procedure as above-mentioned. Pumice with particle size of 4.0-4.8 mm were soaked in 10 ml of pyrene solution (concentration of 1,000 mg/l) for 3 h. Pyrene adsorbed onto pumice was calculated by the same method as above-mentioned. Then, they were put in 10 ml of BioSolve and BioNonex solution at concentrations of 1, 3, 5, 7 and 10 %vol, respectively, and shaken in an orbital shaker at 100 rpm for 3 h. After extraction, the pumice particles were separated by a centrifuged at 3,000 rpm for 5 min. The pyrene in the surfactant solution was determined by GC.

Continuous operation

The schematic diagram of the system for continuous removal of pyrene is shown in Fig. 1 Acrylic columns (55 cm long and 5 cm diameter) [26] were used for all pumice flushing experiments. The outlet and inlet ends of the column were fitted with wire meshes (1 x 1 mm) to prevent pumice from being washed out of the column and to distribute the flow uniformly across the pumice bed. Then, 260 g of pyrene-loaded pumice particle (size of 4.8-6.3 mm and concentration of 1,300 mg-pyrene/kg-pumice) was packed in the column. Before experiment, the column was flushed with water in order to remove any residue toluene. The continuous operation was conducted as upflow mode with 3 and 7 %vol BioNonex solution or CGA (prepared from 3 and 7 %vol BioNonex solution) at a fixed flow rate of 100 ml/min with all experiment, respectively. The preparation of CGA was described elsewhere [27]. The duplicate samples of effluent were then collected every 30 min until 20 h. They were centrifuged at 3,000 rpm for 5 min to separate pumice particles that might be washed along with the effluent. Finally, the extracted pyrene concentration was analyzed by GC.

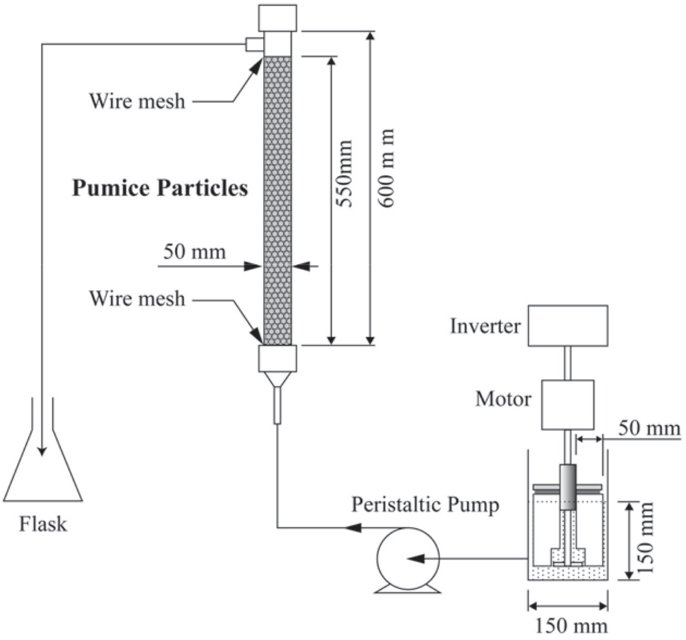

Fig. 1 Schematic diagram of continuous removal of pyrene system.

2.5 Pumice particle characterization

Intact pumice and pyrene-loaded pumice particles were characterized by N_2 adsorption at 77 K by Gas Sorption Analyzer model Nova-1200, Quantachrome Corporation in order to calculate the BET surface area. The total pore volume was determined from the amount of vapor adsorbed at a relative pressured of 0.95.

3. Results and discussion

3.1 Preliminary study

Pyrene removal from natural soil and pumice

The removal of pyrene from natural soil was investigated in order to study the effect of organic materials and to justify the usage of pumice as a model. The soil containing 3% by weight of organic material could adsorb 400 mg-pyrene/kg-soil while pumice adsorbed 750 mg-pyrene/kg-pumice. Pyrene removal from pumice and natural soil by 5 %vol BioNonex solution is shown in Fig. 2 We found that the rate of pyrene removal from pumice was slightly higher than that of natual soil at initial stage. After 20 h, the percentage of pyrene removal from pumice was 55% while that of from the natural soil was around 50%. In addition, the organic materials in the natural soil should also be removed by the solution. According to the results, organic matter does not seem to affect the pyrene removal as we presumed. Since pumice is easier to handle than natural soil and the natural soil can cause pressure drop in the continuous operation, we therefore used pumice instead of natural soil afterward.

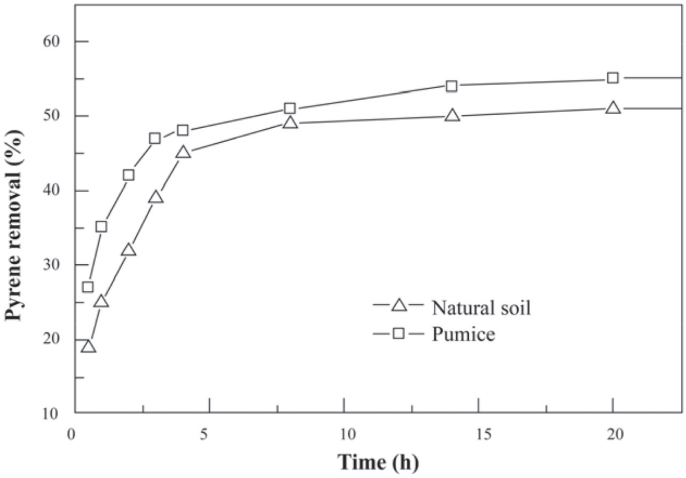

Fig. 2 Pyrene removal from pumice and natural soil using 5 %vol BioNonex solution in batch experiment at pyrene initial concentration of 1,000 mg/l..

Solubility of pyrene in surfactant solutions

The solubilization of pyrene in 1-10 %vol BioNonex and BioSolve solutions is shown in Fig. 3. All experiments were conducted at 30°C. Pyrene solubilization increased with increasing surfactant concentration of both BioNonex and BioSolve. This may be explained that as more solubilizate is incorporated in the core of the micelle, the core becomes more like the solubilizate, resulting in higher the solubilizing capacity of the core [22]. At the same concentration of both surfactants, pyrene solubilization in BioNonex is superior to that in BioSolve. This may be ascribed to the lower CMC value of BioNonex should enhance the solubility of pyrene.

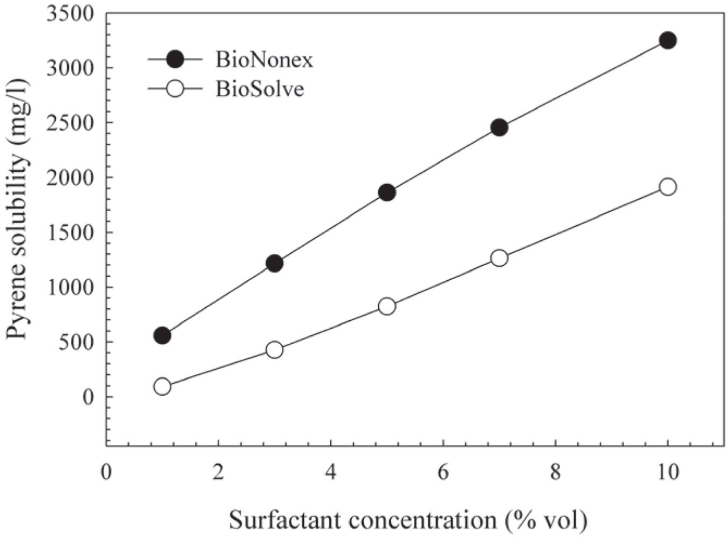

Fig. 3 Pyrene solubilization by 1-10 %vol BioNonex and BioSolve solutions at 30°C.

3.2 Batch removal of pyrene

Effect of surfactant type and concentration

The effects of surfactant type and concentration on pyrene removal by using 1-10 %vol BioNonex and BioSolve solutions are shown in Fig. 4. It can be seen that pyrene removal increased with increasing surfactant concentration of 1-7 %vol for both BioNonex and BioSolve. With increasing surfactant concentration, the number of micelles should be increased. This enhanced the pyrene solubilization [23]. However, at surfactant concentrations higher than 7 %vol, pyrene removal did not change significantly. This may be attributed to the change of surfactant concentration should affect the hydraulic conductivity and pore geometry of the pumice matrix [22]. The excessive surfactant concentration might cause pore blocking that prevented the wash media from reaching all pore spaces. The removal of contaminant decreased consequently [28]. Moreover, at the same concentration, pyrene removed by BioNonex was higher than that by BioSolve. These should be the same results as described in 3.1. Hence, we focused on BioNonex in the next experiments.

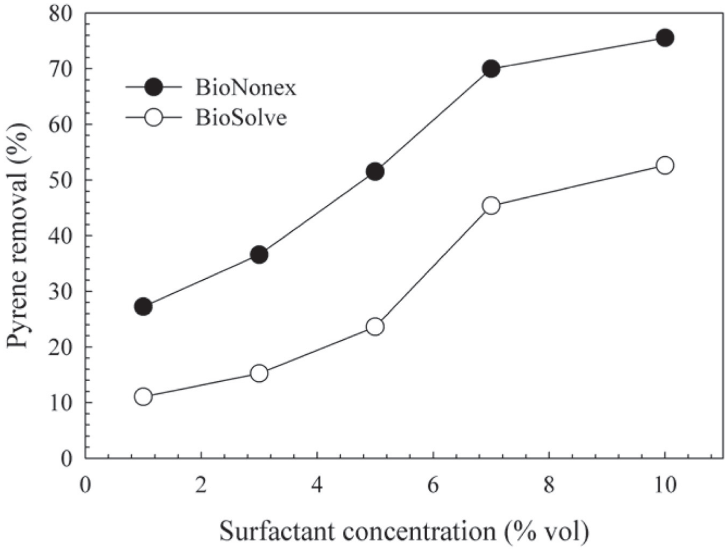

Fig. 4 Comparison of the pyrene removal in batch operation with 1-10 % vol BioNonex and BioSolve solutions.

3.3 Continuous removal of pyrene

Effect of surfactant usage form and concentration

The influence of surfactant usage form at various concentrations on pyrene removal efficiency is shown in Fig. 5. It can be seen that pyrene removal rate in all cases was high at initial stage (0-5 h). After that, the rate decreased and reached steady state. The high rate of pyrene removal at beginning may be ascribed to desorption of some pyrene that was attached loosely on the outer surfaces of pumice. The rate retarded after 5 h flushing may be due to the mass transfer resistance of pyrene in the inner pores of pumice. Pyrene removal efficiency was 55 and 47% when flushing with 3 %vol BioNonex CGA, and 3 %vol BioNonex solution for 20 h, respectively. Moreover, when increasing surfactant concentration to 7%vol, pyrene removal increased to 78 and 68% for BioNonex CGA and BioNonex solution, respectively. However, only 11% of pyrene was removed by flushing with pure water. These results could be caused by the hydraulic conductivity of pumice in water is low compared with surfactant solution as shown in Table 1. Therefore, 7 %vol BioNonex CGA drastically enhanced the efficiency of pyrene removal.

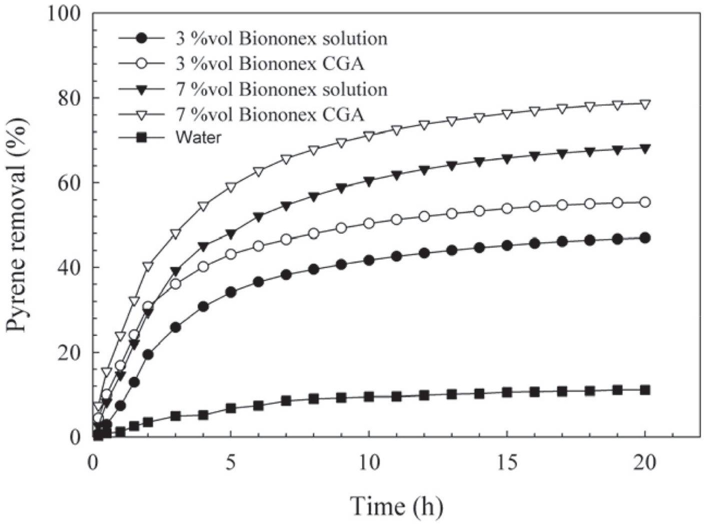

Fig. 5 Profiles of pyrene removal by different flushing media.

Table 1 Physical properties of pumice

Property	Value
Specific surface area, m^2/g (BET)	4.37
Pore volume, cm^3/g (BET)	1.92×10^{-3}
Moisture % (ASTM D 2216-98)	5
pH	7
Specific gravity (ASTM D854-06)	2.28
Hydraulic conductivity (ASTM D7100-06)	
(in water), cm/s	0.073 ± 0.002
(in 3 %vol Biosolve solution), cm/s	0.110 ± 0.002
(in 3% BioNonex solution), cm/s	0.114 ± 0.003

It can be seen that the percentage of pyrene removal by BioNonex CGA was higher than that of BioNonex solution. The density of CGA is different from solution, i.e. the specific gravity of CGA suspensions is in the range of 0.3-0.4 [29], hence we have to compare the removal efficiency on the same aqueous volume basis. The aqueous volume of CGA was obtained by collecting effluent CGA at the outlet in a measuring cylinder. Then, aphrons coalesced and turned to aqueous solution resulting in measurable aqueous volume. By plotting the percentage of pyrene removal against the volume of flushing media as shown in Fig. 6, we can find the explicit efficiency of CGA on pyrene removal. BioNonex CGA in both 3 and 7 %vol required less fluid volume than BioNonex solution to attain the same percentage of pyrene removal. Total liquid volume of CGA and conventional surfactant solution was around 60 and 120 l, respectively. Based on the results, CGA not only enhanced pyrene removal but also decreased volume of surfactant fluid.

Although CGA is homogeneous fluid and stable quite a long time (half-life of 8-11 min), the coalescence of CGA occurs during passing through porous media, resulting in a two-phase flow system. The phenomenon was observed as drainage at bottom of the column. The collapse of CGA bubbles in the column depends on several factors such as the flow rate, pore structure and the type of medium. The gas and liquid phases propagate through the porous medium at different rates with the liquid advancing faster than the gas phase [3].

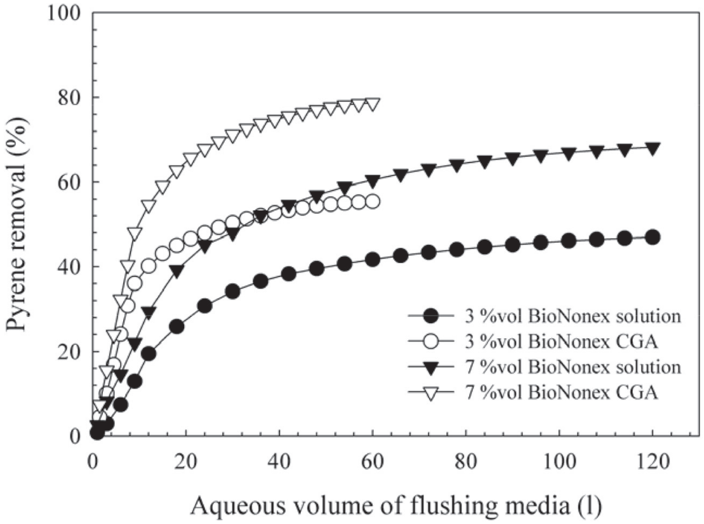

Fig. 6 Pyrene removal in column operation as a function of aqueous volume of flushing media.

Table 2 Properties of BioNonex and BioSolve

BioNonex		**BioSolve**	
Boiling point	100°C	Boiling point	130°C
Melting point	<0°C	Melting point	32°C
Solubility w/ water	100%	Solubility w/ water	100%
Density	Approx. $1.0\text{x}10^3$ kg/m^3	Specific Gravity	1.00±.01
pH	9.1±0.3	pH	Approx. 7
Biodegradable	yes	Biodegradable	yes
Interfacial tension (at CMC, mN/m)	31.12	Interfacial tension (at CMC, mN/m)	28.12
CMC (%vol)	0.03	CMC (%vol)	0.07
Appearance	Clear Liquid	Appearance	Clear Liquid
Ordor	Pleasant Fragrance	Ordor	Pleasant Fragrance

CGA bubbles should have the same charges on the surfaces as the surfactant from which it is generated. The surface area provided by the CGA bubbles may also play a significant role in the removal of pyrene from pumice pore spaces [21, 30]. The small CGA bubbles should move through the pores of pumice effectively and enhance pyrene removal due to the difference in density of CGA and conventional solution.

Pyrene removal rate

Figure 7 shows pyrene removal rate from column flushing of 1,300 mg-pyrene/kg-pumice. The removal rates in all the cases were high at initial period (0-2 h). They declined rapidly after 4 h until no pyrene presented at the end. The removal rates of BioNonex CGA at 3 and 7 %vol were around 2 times higher than that of BioNonex solution. However, flushing by CGA cannot enhance the pyrene removal rate after 2 h.

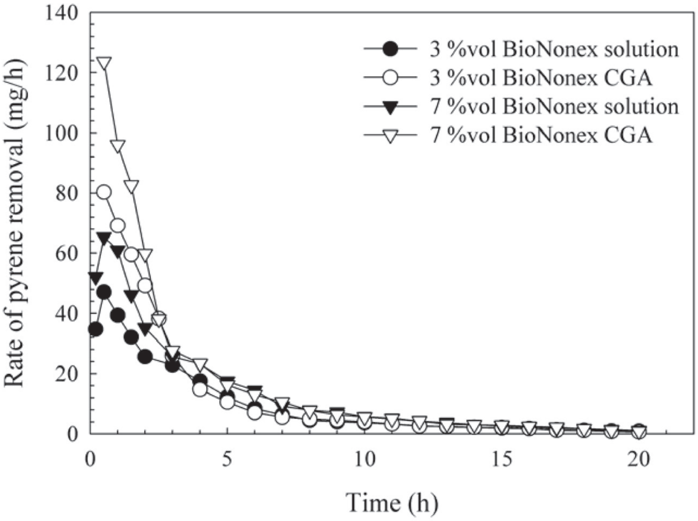

Fig. 7 Pyrene removal rate in column operation with different flushing media.

3.4 Pumice particle characterization

The results of the specific area and pore volume of examined samples are shown in Table 3 concerning pyrene removal by BioNonex. In the cases of samples B and C (pumice loaded with pyrene 1,300 and 12,000 mg-pyrene/kg-pumice), the specific surface area decreased from 4.37 (intact pumice) to 3.84 and 2.36 m^2/g, and pore volume decreased from 1.92 x 10^{-3} (intact pumice) to 1.52 x 10^{-3} and 1.32 x 10^{-3} ml/g, respectively. This could be attributed to the adsorption of pyrene molecules into pumice pores. It caused by pore blocking, resulting in decreasing of pore volume. Water washing had a slight effect on specific area and total pore volume for samples D and E. However, when samples B and C were washed with 7 %vol BioNonex solution (denoted as sample G and H), the specific area and total pore volume significantly increased. This should be caused by the effective solubilization of pyrene and other materials in pumice by BioNonex.

Table 3 Specific surface area and average pore diameter of samples obtained from BET analysis

Sample Identification	Description	Specific surface area (m^2/g)	Total pore volume $x10^3$ (ml/g)	Average pore diameter (nm)
A	As received	4.37	1.92	2.20
B	Sample A+ 1300 mg-pyrene/kg-pumice	3.84	1.52	2.10
C	Sample A + 12000 mg-pyrene/kg-pumice	2.36	1.32	1.99
D	Sample B+ water wash	3.86	1.59	2.12
E	Sample C+ water wash	2.57	1.37	1.99
F	Sample A+7 %vol BioNonex wash	4.66	1.95	2.20
G	Sample B+7 %vol BioNonex wash	5.80	1.96	2.20
H	Sample C+7 %vol BioNonex wash	4.98	1.86	2.19

3.5 Mass balances of pyrene

Mass balance analysis of pyrene in this study was demonstrated by the Sample B (pyrene loading 1,300 mg-pyrene/kg-pumice) as shown in Fig. 8. Here we define pyrene in the system removed by flushing media and toluene extraction as 'removable pyrene', while pyrene as the result of the mass balance calculated by subtracting removable pyrene from initial pyrene loaded was defined as 'residual pyrene'. Figure 10 illustrates that the increment of surfactant concentration enhanced the pyrene solubilization, i.e., in the case of BioNonex, the removal efficiency increases from 50 to 70% with increasing surfactant concentration from 3 to 7 %vol. However, we found that there was about 20% of pyrene or 'residual pyrene' left in the pumice after extracted with toluene. This amount of 'residual pyrene' is derived from the mass balance calculation. Hence, some undetectable pyrene lost from the system could be included in this value. However, this work was conducted at room temperature and the volatilization of pyrene could not be detected.

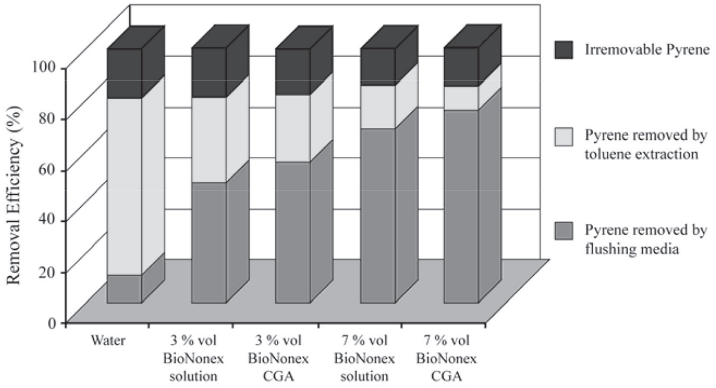

Fig. 8 Mass balance of pyrene in the experiments using 1,300 mg-pyrene/kg-pumice pyrene-loaded pumice.

4. Conclusions

The biodegradable surfactant, BioNonex was superior to BioSolve in pyrene solubilization at the same concentration over the range of 1-10 % vol. BioNonex in CGA form could remove pyrene more efficiently than BioNonex in solution form particularly based on the aqueous volume. The removal rate at beginning (0-2 h) was high due to the readily desorption of pyrene adsorbed on the outer surface of pumice. The retarded rate after 2 h is attributed to the mass transfer resistance of pyrene in the inner pores.

5. References

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