

Joint chemical flushing of soils contaminated with petroleum hydrocarbons

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Abstract

How to increase the efficiency of chemical flushing and decrease the remediation expenses of contaminated soils are two key scientific and technological issues to be solved. Joint chemical flushing was tested and compared with the water-flushing. The joint acid-flushing could effectively remove petroleum hydrocarbons in contaminated aquorizem and the dosage of washing powder as a flushing agent was greatly reduced, thereby, saving approximately 1200 US dollars of expenses relative to the water-flushing. The joint salt-flushing could be an optimal method for the cleanup of meadow burozem contaminated with petroleum hydrocarbons under the experimental conditions. Moreover, the amount of surfactant remained in the two washed soils after the joint acid-flushing and the joint-salt-flushing was minimal.

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1. Introduction

Petroleum hydrocarbons including straight and branched chain saturated alkanes from methane (CH₄), ethane (C₂H₆), and propane (C₃H₈) to C₇₆H₁₅₄, aromatic hydrocarbons, and other organic components containing nitrogen and sulfur are a prevalent type of soil contaminants that are harmful to the growth and development of plants and animals, and human health (Newton, 1990; Zhou, 1995; Sun et al., 2001; Guo and Zhou, 2003). Hydrocarbons that originated from oils have become one of the most important types of organic pollutants with the development of the petroleum industry. There are increasingly wide pollution of sources including leakage of fuel by transportation and traffic accidents, land disposal of residual lubricants, inappropriate storage of oils,

and discharge or leakage of organic solvents at industrial sites, particularly oil exploitation and abstraction. According to the data from the Liaoning Central Station of Environmental Monitoring in People's Republic of China, concentrations of petroleum hydrocarbons in some soils from the Liaohe Oil-Field Area, Liaoning Province in China were higher than 10,000 mg/kg, 20 times as much as the soil-critical value limiting the growth and development of plants (He et al., 1999; Sun et al., 2001). In the oil-extraction area, more than 1000 ha of agricultural land have been seriously contaminated by petroleum hydrocarbons (Song et al., 1999; Sun and Song, 1999). With wide application of petroleum and oil products to agricultural production and rural areas, contamination of soils by petroleum not only occurred in oil-field areas, but also took place in other types of land (Song et al., 1999; Zappi et al., 1996; Guo and Zhou, 2003).

As an important scientific and technological area, more and more attention has been paid to the remediation of contaminated soils (Zhou and Song, 2004). Although new methods of contaminated soil remediation have been extensively explored (Wei et al., 2003), the soil-flushing

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technique is still an important approach to the remediation of contaminated soils (Anderson, 1993; Zhou, 1998, 2002, 2003). In situ soil flushing floods contaminated soil beneath the surface level with flushing agents designed to flush out the contaminants into a zone from which they will be extracted. The efficiency of this technique is directly related to types and amount of flushing agents added to soils (Zhou and Song, 2004). Surfactant is an effective flushing agent to remove petroleum hydrocarbons from soils and ground-water (Brown and Burris, 1996; Bruell, 1997). However, large amounts of surfactant have to be applied to the contaminated soils and thus resulting in high costs. Moreover, second pollution of surfactant from washing powder often occurs to the soils (Zhou and Song, 2004). More studies are needed to increase the efficiency of soil flushing technology and decrease the dosage of surfactant and expenses of contaminated soil treatment.

2. Materials and methods

2.1. Tested soils

Soil contaminated with high concentrations of petroleum hydrocarbons, which is usually regarded as oil soil, was collected from the Liaohe Oil-Field Area, Liaoning Province in China. The soil is named as aquorizem in the US Soil Taxonomy. In the meantime, another oil soil based on meadow burozem was also collected. Some basic properties of the soils are listed in Table 1.

2.2. Flushing agents and flushing experiments

The main flushing agent used in the experiment was an ordinary washing powder used for washing clothes in daily life, which contains 14.8% of alkyl benzene sulfonate (ABS). Correspondingly, water, 0.001 N HCl and 1 M NH₄Ac solutions were chosen to be auxiliary washing agents on the basis of their extraction function. The flushing experiments were designed as follows:

- (1) Test I (single flushing: water-flushing): 1 kg of fresh oil soil+15, 20, 25, 30, 35 and 40 g of washing powder+1.0 liter of H₂O→fully mixed→equilibrated for 12 h→fully mixed again→equilibrated for another 12 h→separation of soil particles from the solution;
- (2) Test II (joint flushing 1: joint acid-flushing): 1 kg of fresh oil soil+15, 20, 25, 30, 35 and 40 g of washing powder+1.0 liter of 0.001 N HCl solution→fully mixed→equilibrated for 12 h→fully mixed again→equilibrated for another 12 h→separation of soil particles from the solution;

- (3) Test III (joint flushing 2: joint salt-flushing): 1 kg of fresh oil soil+15, 20, 25, 30, 35 and 40 g of washing powder+1.0 liter of 1 M NH₄Ac solution→fully mixed→equilibrated 12 h→fully mixed again→equilibrated for another 12 h→separation of soil particles from the solution.

2.3. Chemical determination

Oils remained in the washed soil were distilled and extracted according to Sun and Song (1999) and determined by HPLC (Ouyang et al., 1986). Surfactant remained in the washed soil was determined according to Shen (1997) and Song et al. (1999).

2.4. Calculation of removal rate

The removing ability of oils in soils is expressed by the removal rate that is calculated according to the following formula:

$$Y = \frac{C_{\text{remained}} - C_0}{C_0} \quad (1)$$

where Y is the removal rate (%), C_{remained} is the concentration (mg/kg) of petroleum remained in a soil after flushing, C_0 is the initial concentration (mg/kg) of petroleum in a contaminated soil. The removal rate (%) was statistically expressed using mean±standard deviation (S.D.).

3. Results and discussion

3.1. Single flushing

Soil flushing is a remediation technology used for extracting pollutants from soils by using a solution. It usually works by applying water to the soil. An additive is normally added to water to enhance the contaminant solubility. Pollutants dissolved in the flushing solution are leached into the groundwater and then extracted. In some cases, the flushing solution is injected directly into the groundwater. This raises the water table into the capillary fringe just above the surface of the water table, where high concentrations of pollutants are found. In many instances, surfactants (i.e., detergent-like substances) or solvents are used as flushing agents (Zhou and Song, 2004). In this sense, the effectiveness of this process is firstly dependant on types of flushing agents.

As a daily commodity, washing powder is a cheap surfactant to be examined for the remediation of soils contaminated with petroleum and oil products. The results of this study indicated that the removal rate of petroleum in the two oil soils was directly related to the amount of washing powder added to the soils. There were significant logarithmic relationships between the removal rate and

Table 1
Physical and chemical properties of the tested soils

Soil type	pH	Organic matter (%)	CEC (meq/100 g soil)	Clay (<0.001 mm, %)	Water content (%)	Oils (%)
Aquorizem	8.1	2.5	10.3	12.4	15.4	5.73
Meadow burozem	6.3	3.7	19.2	17.2	7.9	6.01

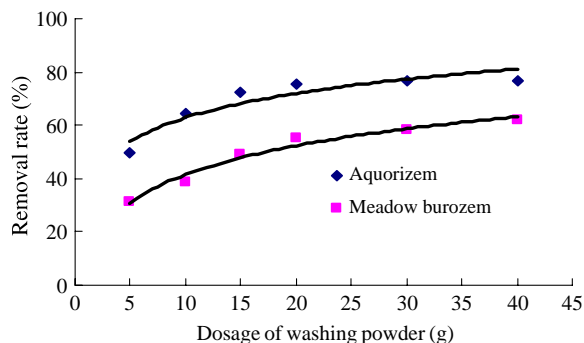


Fig. 1. Changes in the removal rate of petroleum hydrocarbons in aquorizem and meadow burozem by the water-flushing method.

the dosage of washing powder (Fig. 1). The regression equations for aquorizem and meadow burozem are listed as follows:

$$Y_1 = 13.1 \ln(X) + 32.6 \quad (r^2 = 0.879, n = 6) \quad (2)$$

and

$$Y_2 = 15.6 \ln(X) + 5.7 \quad (r^2 = 0.971, n = 6) \quad (3)$$

where Y_1 is the removal rate (%) of petroleum in aquorizem, Y_2 is the removal rate (%) of petroleum in meadow burozem, and X is the dosage (g) of washing powder added to soils. When the dosage of washing powder was lower than 15.0 g/kg wet soil whose moisture content was 31.8%, the removal rate of the oil soil based on aquorizem was greatly increased with the increase in the dosage of washing powder. When the dosage of washing powder was higher than 20.0 g/kg wet soil, the increment in the removal rate of the oil soil from aquorizem gradually decreased with the increase in the dosage of washing powder. Thus, the acceptable dosage of washing powder added to aquorizem in this single flushing could be 20.0 g/kg wet soil. According to the calculations using Eqs. (2) and (3), the dosage of washing powder added to aquorizem and meadow burozem should be higher than 171.6 and 421.9 g/kg wet soil respectively if the removal rate reaches 100% (although it is impossible).

3.2. Joint acid-flushing

In situ soil flushing is an innovative treatment technology that floods contaminated soils with a solution to move the contaminants to an area where they are removed. “In situ” meaning “in place” refers to treating the contaminated soil without digging up or removing it. The specific pollutants in the soil at any particular site determine the type of flushing solution needed in the treatment process. The flushing solutions are typically two types: (1) water only; or (2) water plus additives such as acids, bases or surfactants (such as detergents). It was reported that acids and sour solutions are effective flushing agents for contaminated soils with cadmium, copper, amines, ethers and anilines. In view of the cognition, an acid combined with a surfactant was examined to remedy contaminated soils with petroleum hydrocarbons.

Joint acid-flushing greatly improved the removing ability of petroleum hydrocarbons in the tested soils. Joint flushing of washing powder and 0.001 N HCl solution (joint acid-flushing) was particularly an effective method to remove petroleum hydrocarbons in aquorizem. The highest removal rate of petroleum

Table 2

Removal rate of petroleum hydrocarbons in aquorizem by three flushing methods

Dosage of washing powder (g)	Removal rate (%)		
	Water-flushing	Acid-flushing	Salt-flushing
5	49.7±1.90	57.1±2.69	53.8±0.78
10	64.5±1.91	76.9±1.25	68.4±1.48
15	72.3±2.57	82.6±1.71	77.1±1.84
20	75.6±2.18	85.5±1.60	78.8±2.01
30	76.4±1.55	85.7±2.26	79.3±3.41
40	76.8±2.41	85.7±1.32	80.6±1.59

hydrocarbons in aquorizem under the experimental conditions reached 85.7% (Table 2).

When the removal rate of the oil soil based on aquorizem reached 76.8%, the dosage of washing powder in the single flushing was four times as much as that in the joint acid-flushing. Addition of 0.001 N HCl solution in joint acid-flushing reduced the dosage of washing powder needed (Table 2). The reduced amount was up to 10.0 g/kg wet soil. The oil-removal efficiency can be greatly enhanced by the joint acid-flushing method. Significant logarithmic relationships (Fig. 2) between the removal rate of joint acid-flushing and the dosage of washing powder added to the oil soils were expressed by the following regression equations:

$$Y_1 = 13.3 \ln(X) + 41.9 \quad (r^2 = 0.804, n = 6) \quad (4)$$

and

$$Y_2 = 16.7 \ln(X) + 16.7 \quad (r^2 = 0.993, n = 6) \quad (5)$$

Thus, the dosage of washing powder added to aquorizem and meadow burozem could be calculated and it dropped to 78.9 and 146.6 g/kg wet soil respectively if the removal rate reaches 100%.

3.3. Joint salt-flushing

Successful application of flushing technique to soil remediation depends on the effectiveness of flushing agents. Contaminants in soils are partitioned into flushing agents by mechanisms such as solubilization, emulsification and chemical reaction. For biodegradable contaminants, it may be possible to add nutrients and

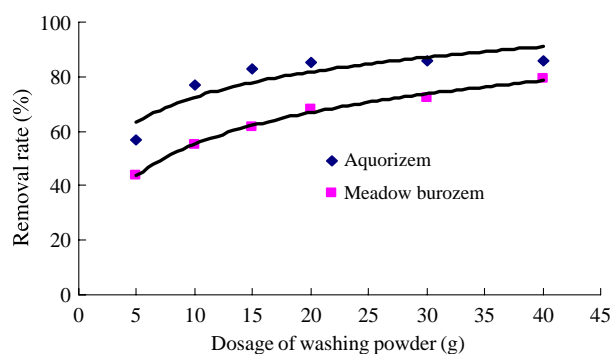


Fig. 2. Changes in the removal rate of petroleum hydrocarbons in aquorizem and meadow burozem by the joint acid-flushing method.

distribute flushing agents into the soil to promote contaminant bioremediation. Some salt solutions as nutrients for living microorganisms may be effective when combined with a surfactant to promote partition of soil contaminants into flushing agents.

In the process of joint salt-flushing, logarithmic relationships (Fig. 3) between the removal rate and the dosage of washing powder added to soils were also significant. The regression equations are as follows:

$$Y_1 = 12.7 \ln(X) + 37.5 \quad (r^2 = 0.863, n = 6) \quad (6)$$

and

$$Y_2 = 11.8 \ln(X) + 45.4 \quad (r^2 = 0.969, n = 6) \quad (7)$$

When the removal rate of the oil soil based on aquorizem reached 76.8%, the dosage of washing powder in the single flushing was three times as much as that in joint salt-flushing. The dosage of washing powder added to aquorizem and meadow burozem could be 137.2 and 102.2 g/kg wet soil respectively if the removal rate reaches 100%. Compared with the water-flushing method, the joint salt-flushing was more adequate to remedy soils contaminated with petroleum hydrocarbons.

3.4. Influences of soil types

The effectiveness of the soil flushing process not only depends on types of flushing agents, but is also restricted by hydrogeologic variables such as soil type, soil moisture and other factors. In this study, the removal efficiency of petroleum hydrocarbons in meadow burozem with high clay content (<0.001 mm, %) and organic matter seemed to be low with the water-flushing method, only 31.2–61.8% were obtained under the experimental conditions (Table 3). The difference in the removal rate of petroleum hydrocarbons may mainly depend on the contents of clay and organic matter in soils. Clay can adsorb petroleum hydrocarbons more tightly than other soil components and high organic matter is disadvantageous to the desorption of petroleum hydrocarbons from the soil particles.

The removal rate of petroleum hydrocarbons in meadow burozem with low pH was lower than that in aquorizem with high pH when the joint acid-flushing method was used. Thus, the method was not an effective method when applied to remediation of meadow burozem contaminated with petroleum hydrocarbons. In other words, the joint acid-flushing method is inapplicable to cleanup of petroleum hydrocarbons in acidic soils, because H^+ in

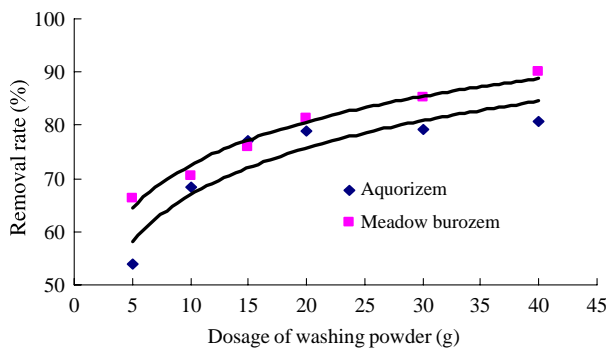


Fig. 3. Changes in the removal rate of petroleum hydrocarbons in aquorizem and meadow burozem by the joint salt-flushing method.

Table 3

Removal rate of petroleum hydrocarbons in meadow burozem by three flushing methods

Dosage of washing powder (g)	Removal rate (%)		
	Water-flushing	Acid-flushing	Salt-flushing
5	31.2±1.71	43.7±1.00	66.3±1.82
10	38.7±0.95	55.2±3.70	70.4±1.30
15	49.1±1.44	61.6±2.69	75.8±2.38
20	55.3±2.93	68.3±2.38	81.3±3.61
30	58.4±4.93	71.9±3.67	85.1±1.91
40	61.8±3.39	79.3±2.55	90.2±2.21

acidic soils can perhaps counteract the effect of 0.001 N HCl solution in the method.

The joint salt-flushing of meadow burozem contaminated with petroleum hydrocarbons was perhaps the best method under the experimental conditions. The highest removal rate was up to 90.2%. The good removal efficiency may be attributed to the action of CEC (meq/100 g soil) of soils. At least, high CEC is advantageous to exchange of petroleum hydrocarbons with ions ionized from salts.

3.5. Feasibility

The following factors may limit the applicability and effectiveness of the soil flushing process (Ouyan et al., 2002; Zhou and Song, 2004: (1) the flushing solution must be compatible with the in situ environment; (2) subsurface heterogeneity can interfere with uniform distribution of flushing solutions; (3) low-permeability soils are difficult to treat; (4) surfactants can adhere to soil and reduce effective soil porosity; (5) the flushing solution injection and collection systems must be designed and operated to limit the spread of contaminants to clean areas; (6) the flushing solution must be recovered and treated; (7) complex waste mixtures (e.g., multiple contaminant classes) increase the difficulty of formulating a flushing solution. In particular, flushing agents may leave small residuals in the soil or groundwater, and should be evaluated on a site-specific basis. In the gross, surfactant added to the tested soil in this study did not persist in the washed soil. A majority (89.1–99.8%) of applied surfactant was washed out with petroleum hydrocarbons, particularly under acceptable levels of washing powder and conditions of joint chemical flushing. The main mechanism is that petroleum hydrocarbons in soils are strongly adsorbed by surfactant and detached from soil particles. Both simultaneously entered into solutions. These results indicate that joint chemical flushing could not result in secondary contamination of surfactant.

Economic effectiveness of soil flushing should be of crucial importance in considering whether an improvement in flushing agents could be widely adopted in practice. According to the acceptable dosage (20.0 g/kg of wet soil) of aquorizem by the single flushing method, the price (about \$0.25 per bag in China, 400 g of washing powder per bag) of washing powder and soil weight of plower layer (1.89×10^6 kg/ha), approximately \$2500 are needed to remedy 1 ha of contaminated aquorizem (if 10% of plower-layer soil can be fully mixed with washing powder). Only about \$1250 are spent for remediation of 1 ha of contaminated aquorizem by using the joint acid-flushing method. In other words, \$1250 can be saved if the new method is applied to contaminated aquorizem.

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References

- Anderson WC. Innovative site remediation technology: soil washing/soil flushing. Annapolis: American Academy of Environmental Engineers; 1993.
- Brown MJ, Burris DR. Enhanced organic contaminant sorption on soil treated with cationic surfactants. *Ground Water* 1996;34(4):734–43.
- Bruell CJ. Laboratory evaluation of a biodegradable surfactant for in situ soil flushing. *J Soil Contam* 1997;6(5):509–23.
- Guo GL, Zhou QX. Advances of research on combined pollution in soil-plant systems. *Chin J Appl Ecol* 2003;14(5):823–8.
- He L, Wei D, Zhang W. Research of microbial treatment of petroleum contaminated soil. *Adv Environ Sci* 1999;7(3):110–5.
- Newton JPE. Remediation of petroleum contaminated soils. *Pollut Eng* 1990;12:46–52.
- Ouyan Y, Cho JS, Mansell RS. Simulated formation and flow of microemulsions during surfactant flushing of contaminated soil. *Water Res* 2002;36(1):33–40.
- Ouyang L, Zhang Z, Li L, Li B, 1986. Environmental monitoring and analysis. Changsha: Hunan Scientific and Technological Press; 1986. p. 426–7.
- Shen S. Surfactant. In: Wei F, et al, editor. A guild to monitoring and analytical methods for water and wastewater. Beijing: China Environmental Science Press; 1997. p. 317–25.
- Song YF, Sun TH, Xu HX. Influences of surfactant TW-80 biogradation of PAHs in soils. *Chin J Appl Ecol* 1999;10(2):230–2.
- Sun TH, Song YF. Phytoremediation of PAHs and oils. *Chin J Appl Ecol* 1999;10(2):225–9.
- Sun TH, Zhou QX, Li PJ. Pollution ecology. Beijing: Science Press; 2001.
- Wei SH, Zhou QX, Zhang KS, Liang JD. Roles of rhizosphere in remediation of contaminated soils and its mechanisms. *Chin J Appl Ecol* 2003;14(1):143–7.
- Zappi ME, Rogers A, Teeter CL, Gunnison D, Bajpai R. Bioslurry treatment of a soil contaminated with low concentrations of total petroleum hydrocarbons. *J Hazard Mater* 1996;46(1):1–12.
- Zhou QX. Ecology of combined pollution. Beijing: China Environmental Science Press; 1995.
- Zhou QX. Research progress on in-situ remediation of polluted land. *Pollut Control Technol* 1998;11(4):207–11.
- Zhou QX. Technological reforge and prospect of contaminated soil remediation. *Tech Equip Environ Pollut Control* 2002;3(8):36–40.
- Zhou QX. Progress in pollution eco-chemistry and its strategic expectation. *Bull Chin Acad Sci* 2003;18(5):338–42.
- Zhou QX, Song YF. Principles and methods of contaminated soil remediation. Beijing: Science Press; 2004.