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Running Title: PETROLEUM REMOVAL FROM SOIL

Combining Solvent Extraction and Bioremediation for Removal of Weathered Petroleum in Soil [*1]

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ABSTRACT

This study aimed to remediate a highly contaminated soil with weathered petroleum using an integrated technology combining solvent extraction and biodegradation. Soils were washed using a composite organic solvent consisted of hexane and pentane (4:1 v/v) and then bioremediated in microcosms which were bioaugmentated with *Bacillus subtilis* FQ06 strains and/or rhamnolipid. The optimal solvent extraction conditions were determined as extraction for 20 min at 25 °C with solvent-soil ratio of 6:1 (v/w). On this basis, total petroleum hydrocarbon was decreased from 140,000 to 14,000 mg kg^{-1}, which was further reduced to < 4000 mg kg^{-1} by subsequent bioremediation for 132 days. Sustainability assessment of this integrated technology showed its good performance for both short- and long-term effectiveness. Overall results encouraged its application for remediating contaminated sites especially with high concentration weathered hydrocarbons.

Key Words: solvent extraction, TU-A solvent , bioremediation, *Bacillus subtilis*, rhamnolip

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INTRODUCTION

Most of the existing oil fields in China have been exploited for more than ten years and residual petroleum hydrocarbons concentrations in some soils can exceed 10 000 mg kg^{-1} (Zhou *et al.*, 2005). Remediating these contaminated sites could provide more land available for housing development, which is a continued concern in China due to the sustained growth of population and the lack of residential land. Therefore, there is an increasing demand for development of soil

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remediation technologies that offer both pragmatic cost effective solution and sustainable regeneration of contaminated land.

Among the various remediation technologies currently available, solvent extraction is one of the most attractive ones due to its high efficiency. A great deal of investigations on solvent extraction showed that oil removal efficiencies ranged between 75 and 99% (Heemken *et al.*, 1997; Khodadoust *et al.*, 2000; Saifuddin and Chua, 2003; Silva *et al.*, 2005; Risdon *et al.*, 2008). Typically, either an individual solvent or a mixture of solvents is used to extract or wash petroleum from contaminated soils (Risdon *et al.*, 2008; Gan *et al.*, 2009). Advancements within this field include using non-toxic and biodegradable extraction agents such as cyclodextrins and vegetable oil as well as using supercritical and subcritical fluids (Wu *et al.*, 2011). The two steps involved in the extraction of the chemicals of concern (CoC) from a solid matrix are desorption from the binding site in (or on) the solid matrix followed by elution from the solid into the extraction fluid, which implies that the CoC are only transferred from the solid phase to the liquid phase. Therefore, the extracting fluid and the residual soil need further treatment to remove or destroy the remaining CoC.

In order to address this drawback, solvent extraction complemented with bioremediation is an attractive approach because bioremediation has the ability to inexpensively treat wide range of organics in all environmental media, generating little or no residues with a low carbon footprint, and causing minimal, if any, ecological effects (Atlas and Cerniglia, 1995; Allard and Neilson, 1997; Lohner *et al.*, 2009). But it is generally perceived that soil contaminated with high TPH concentrations will not be amenable to most biotreatment approaches if pretreatment(s) are not employed to lower concentration and toxicity (Khodadoust *et al.*, 2000). Therefore, this study investigated a combined approach where solvent extraction was coupled to surfactant addition and bioaugmentation in order to improve the performance of conventional soil remediation process for heavily oil contaminated sites.

Benefits of such combined approach have been previously demonstrated with coal tar-contaminated soils that were pre-extracted with acetone and ethanol in a batch mode bioreactor (Lee *et al.*, 2001). However, it remains unclear whether this approach would be efficient with high level contamination, as the hydrocarbons concentrations were relatively low (< 5 000 mg kg^{-1} soil) compared to those reported in our previous study which were ≥ 140 000 mg kg^{-1} (Wu *et al.*, 2011). To the best of our knowledge, there are not yet any combined approaches that have been successfully used to remediate highly contaminated sites with weathered oil. This is partly due to two challenges: (i) ageing processes result in the incorporation of organic compounds to soil organic matter, slow dissolution into nano- and micro-pores, and formation of semi-rigid films around the non-aqueous phase liquid (NAPL) that causes a high resistance to mass transfer (Trindade *et al.*, 2005); and (ii) the explicit NAPL would become one of the most significant compartments for distribution of hydrocarbons, which results in the infinite degradation half-lives because of the toxicity to microorganisms, lack of water, nutrients and oxygen to support degradation (Coulon *et al.*, 2010) .

Therefore, the objectives of this study were: (i) to evaluate the efficacy of a combined remedial approach based on solvent extraction and biological transformation of soils contaminated with high levels of weathered hydrocarbons, and (ii) to assess the practicality and sustainability of such approach.

MATERIALS AND METHODS

Soil

The soils used in this study were obtained from a typical oilfield in China that had a long history of contamination with high concentration of petroleum hydrocarbons. Soil samples were collected at depth of 20 cm approximately using spade, transported and stored in tarpaulin bags at 4 °C. Soil samples were air-dried, protected from sunlight to minimize any potential reaction, and homogenized by screening through 40 mesh sieves to remove extra vegetable roots before physicochemical characterization.

Soil pH was measured by 1 M NaCl on pH meter. Water content was determined gravimetrically after drying soil samples at 105 °C for 8 h. Soil organic matter (SOM) content was measured by placing samples (2 g) in the crucible, weighed and heated in a furnace at 500 °C for 2 h to allow the organic matter to burn away. After removal from the oven, the crucibles were allowed to cool before being weighed again. The weight after baking was subtracted from the initial weight to give the weight of organic matter in each sample. Total organic carbons (TOC) was tested by weighing 5 g of sample into a small silver-foil capsule and adding 4 M hydrochloric acid drop by drop until any visible reaction stopped. After dried at 90 °C for 4 h, the capsule was packed into a larger aluminium-foil capsule and was heated at 900°C on a flow of oxygen gas. TOC was determined by carbon dioxide released that was measured by thermal conductivity detector. Bulk density, tap density and soil grain size were tested using Laser Particle Sizer (LG-Malvern).

Solvent extraction process

Composite TU-A solvent used in this study consisted of hexane and pentane (4:1) as described by Lian *et al.* (2008). The influence of operating parameter settings including temperature, extraction time and solvent volume on solvent extraction efficiency were evaluated as described by previous studies (Urum *et al.*, 2004; Han *et al.*, 2009).

The solvent extraction process is shown in Fig. 1. Briefly, soil samples (10 g) were weighed into a cylinder (50 mm × 50 mm internal diameter) filled with a certain amount of organic solvent as shown in Table I. After extraction at a constant temperature for 5, 10, 15, 20, 25 and 30 min on a side-to-side shaker, the concentration of TPH remaining in the soil was measured. Based on these experimental results, the optimal temperature, solvent volume and extraction time were determined. Samples for subsequent bioremediation were prepared by an extra set of extractions under the optimized conditions.

Fig. 1

Fig. 1 Schematic of the solvent extraction and biodegradation experiments

TABLE I

Operation parameters in solvent extraction

Parameters	Values

	1	2	3	4	5	6
Temperature (°C)	20	30	40	50	-	-
Solvent volume (mL)	20	40	60	80	-	-
Extraction time (min)	5	10	15	20	25	30

Analysis of TPH

TPH concentration in the soil was determined using infrared spectrophotometric method which was a rapid and cheap technique for measuring TPH in soil and water (US EPA Method 418.1). Briefly, soil samples (0.25 g) were chemically dried using 0.25 g of anhydrous Na_2SO_4 and ultrasonically extracted with 10 mL of CCl_4 at 20 °C for 20 min followed by vacuum filtration in sand core funnel fitted with glass receiver tube. This step was repeated twice. After rinsing the conical flask with 10 mL of CCl_4 in triplicate, the extract was adjusted to 50 mL with CCl_4. The silica gel cleanup was then performed by passing the extract through a silica gel column (200 mm × 10 mm internal diameter) before analysis on F2000-I Infrared Spectrophotometer (China Jiling Oer, Ltd.). Calibrations were carried out using oil standards dissolved in CCl_4 solution ranging from 80 to 400 M.

Fractionation of TPH into aromatic, aliphatic, asphaltene and NSO (nitrogen, sulfur and oxygen-containing compounds) was done by silica gel column chromatography followed by gravimetric analysis (Das and Mukherjee, 2007). TPH extracts were dissolved in *n*-pentane and separated into soluble and insoluble fractions (asphaltene). The soluble fraction was loaded on the top of a silica gel column. The alkane fraction was eluted with 100 mL of hexane followed by the aromatic fraction with 100 mL of toluene. The NSO fraction was eluted with 100 mL of methanol and chloroform.

Batch biodegradation experiments

Bacillus subtilis (B. subtillis) FQ06 strains obtained from Liao Oilfield, China, was used in this study due to its ability of degrading crude oil (> 2 g mL^{-1}) under laboratory conditions (Yang, 2010). The processes of bacteria screening and acclimating, and the preparation and maintenance of bacteria suspension were carried out as described by Yang (2010).

As shown in Fig. 2, triplicate microcosms were established in sterile Bunsen beakers (100 mL) containing 60 g of solvent washed soil and 15 mL of sterile water (natural attenuation: Scenario 1); 60 g of solvent washed soil and 15 mL of *B. subtilis* FQ06 strains suspension with a cell density of 10^8 cell mL^{-1} (bioaugmentation: Scenario 2); and 60 g of solvent washed soil, 13 mL of *B. subtilis* FQ06 strains suspension and 2 mL of rhamnolipid solution (bioaugmentation/biostimulation: Scenario 3). The rhamnolipid (3 g L^{-1}) was bought from Wotaisi Chemicals Co., Ltd., China.

The beakers were well sealed by multi-layer gauze to prevent cross contamination with other microorganism and incubated at 25 °C. The pH value ranged from 7.2 to 7.6 during all the experiments. Sterile water was supplemented periodically to saturate the soils which drained to the field capacity without leaching. The soil slurry system was thoroughly agitated manually every 10 days. Residual TPH concentration was determined before the onset of the incubation and after 7, 12, 20, 25, 35, 45, 54, 64, 74, 84, 94, 105, 118 and 132 days.

Modelling biodegradation kinetics

The first-order degradation reaction equation was used to predict the biodegradation kinetics with absence of surfactant (Scenarios 1 and 2) as follows:

$$dC/dt = -k \cdot C \quad (1)$$

where *K* represents the first-order proportionality constant. *C* is TPH concentration. Integrating this equation over time yields:

$$\ln C = -k \cdot t + A \quad (2)$$

where *A* is Napierian logarithm of TPH concentration at t_0.

In the case of Scenario 3, it was assumed that a residual amount of contaminants (C_m) partitions into the surfactant micellar phase and thereby it is not bioavailable to the bacteria (Guha and Jaffé, 1996). In other words, degradation occurs only in water phase. On this basis, the term C of the Eq. (2) was substituted by an effective concentration defined as the concentration (C) subtracting the concentration of contaminants bound to micellar phase (C_m). The mass balance equation can then be written as follows:

$$\ln(C - C_m) = -k \cdot t + A \quad (3)$$

The goodness of fit of the models was assessed by calculating t-statistic, correlation coefficient squared R^2 and F-ratio via analysis of variance (ANOVA; Field, 2009).

Statistical analysis

ANOVA was carried out using Tukey test to evaluate the effects of factors on the efficiency of solvent extraction and the changes of TPH during biodegradation. The difference between outcomes was recognised as significant where $P < 0.05$. All tests were performed using SPSS 13.0 for Windows.

RESULTS

Soil characterization

The physicochemical properties of the sandy soil are presented in Table II. The high TOC implies that the bioavailability of the TPH could possibly be enhanced by the addition of an organic solvent and a biosurfactant, as there is a strong positive correlation between the solubilisation effectiveness of solvent on petroleum hydrocarbons and the logarithm of the organic carbon partition coefficients (log *K*oc) (Lee *et al.*, 2001). The relatively low moisture content and SOM suggests that such type of soil would not be considered as promising candidates for bioremediation without pre-treatments due to the unfavourable conditions for microbial degradation. Therefore, potential strategies would be the addition of nutrients that limit the growth or activity of the microorganisms and the amendment of microorganisms with desired bioremediation capabilities.

The level of TPH contamination was estimated to be 140,000 ± 20,000 mg kg^{-1} of soil. The

alkanes (50%) represented the largest fraction of the solvent extracted TPH, followed by the aromatic (21%), the NSO (18%) and the asphaltene fractions (11%).

TABLE II

Physicochemical characteristics of the soil

pH	SOM [a)] (%)	CEC [b)] (mmol·kg^{-1})	Moisture content (%)	TOC [c)] (%)	Soil class (%)			BD [d)] (g·cm^{-3})	TD [e)] (g·cm^{-3})
					Clay	Sand	Silt		
8.0	0.7	164.0	1.7	7.0	25.3	40.4	34.3	1.4	2.8

[a)] Soil organic matter, [b)] Cation exchange capacity, [c)] Total organic matters, [d)] Bulk density, and [e)] Tap density

Effects of solvent extraction parameters

Removal efficiencies at different extraction time indicated oil removal was a very fast process and over 80% of TPH was removed within 5 min (Fig. 2a). Maximum removal rate (up to 96%) was reached after 15 min and barely increased ($P > 0.05$) after 20 min, suggesting that the equilibrium time was reached.

The oil removal rate was enhanced from 88% to 96% as the temperature increased from 20 °C to 50 °C (Fig. 2b). The increase of temperature resulted in a decrease of oil viscosity, which could improve oil mobility (Urum *et al.*, 2004). In the meantime, the addition of heat was observed to alter the component molecules of natural SOM resulting in phase transitions of SOM from the condensed glassy to the expanded rubber state (Pignatello, 1998). Consequently, the hydrocarbons previously bound to SOM are more easily desorbed and released to the solvent phase. However, temperature higher than 40 °C is unfavourable in this study as hexane and pentane would be lost by evaporation. Therefore, operating design at room temperature was recommended in practical terms.

The oil removal was significantly enhanced ($P < 0.05$) as solvent volume increased from 20 to 80 mL (Fig. 2c). The raise of liquid-solid ratio facilitated the diffusion of the desorbed contaminants into the aqueous phase, thus improved the oil removal. On the other hand, using excessive solvents would increase the cost of subsequent solvent recycling. Accordingly, a liquid-solid ratio of 6:1 (v: w) is suggested in terms of practicality.

Based on these findings, the optimal solvent extraction conditions were determined at ambient temperature (25 ± 2 °C) for 20 min with an initial solvent concentration of 6 mL g^{-1} soil. Thereby an extra set of triplicate solvent extraction was carried out in which TPH concentration was reduced to 14 000 ± 3 000 mg kg^{-1}.

Fig. 2

Fig. 2 Influence of extraction time, temperature and solvent volume on the removal efficiencies of TPH.

Bioaugmentation effectiveness on the degradation of the residual TPH

As expected, the natural attenuation (Scenario 1) was very slow and the greatest degradation rate was only 18% by day 118 (Fig. 3). In contrast bioaugmentation of the microcosms with *B. subtilis* (Scenario 2) significantly enhanced the TPH removal ($P < 0.01$) suggesting that the

proportion of the hydrocarbon-degrading bacteria within the indigenous community was insufficient to effectively sustain the degradation of a complex mixture of hydrocarbons. It also suggests that *B. subtilis* can significantly accelerate the degradation of heavy hydrocarbons in contaminated soils. This finding is in good agreement with Das and Mukherjee (2007).

Addition of rhamnolipids (Scenario 3) further enhanced the removal of TPH by one order of magnitude compared to the natural attenuation (Scenario 1). This suggested that the bioavailability of the substrate has been enhanced by reducing the surface tension of phase boundaries. The biosurfactant contributed to wreck the stable structure of asphaltenes coagulation formed by presence of TU-A solvent as discussed previously, which facilitated the transport of residual oil from soil and non-aqueous phases to aqueous phase where microorganisms are present.

Fig. 3

Fig. 3 Percentage degradation of TPH over 132 days

Biodegradation kinetics

The kinetic equations and associated parameters are shown in Table III. Confidences in the hypothesis that the predictor variable contributes significantly to the ability of the model to estimate concentration of contaminants during biodegradation process were obtained by t-statistic test ($P < 0.001$). The first order biodegradation proportionality constant k increased from 0.008 to 0.051 d^{-1} in presence of biosurfactant. In addition the calculated half-life of the bioaugmented microcosms was decreased from 347 to 87 days and further decreased to 20 days by addition of biosurfactant (Table III).

TABLE III

Calculated parameters of the regression equations

Scenario	Equation	Parameter	Estimated	Std. Error	t-statistic	Sig.	Half-life (d)	R^2	Adjusted R^2
1	lnC = -kt + A	K (d^{-1})	0.002	0.000	16.070	0.000	346.6	0.952	0.948
		A (mg g^{-1})	2.638	0.007	372.639	0.000			
2	lnC = -kt + A	K (d^{-1})	0.008	0.001	34.156	0.000	86.6	0.848	0.836
		A (mg g^{-1})	2.281	0.067	0.850	0.000			
3	ln(C-Cm) = -kt + A	K (d^{-1})	0.051	0.005	-	-	20.2	0.995	0.979
		A (mg g^{-1})	2.336	0.044	-	-			
		C_m (mg g^{-1})	2.965	0.211	-	-			

Concentrations predicted were similar to those measured as presented in Fig. 4. A smaller correlation coefficient squared (0.848) was observed in Scenario 2. The F-ratios of the three models (Table IV) were much greater than 1 indicating that the improvement due to fitting the regression models is much greater than the inaccuracy within the model and there was less than 0.1% chance that such large F-ratios would happen if the null hypothesis were true ($P < 0.001$). Therefore, it is concluded that the regression models overall predict the biodegradation kinetics significantly well.

Fig. 4

Fig. 4 Comparison of the calculated TPH concentration with the observed data

TABLE IV

Analysis of variance of the kinetic models

	Model	Sum of squares	Degree of freedom	Mean squares	F-ratio	*P*-value
1	Regression	0.064	1	0.064	258.230	0.000
	Residual	0.003	13	0.000		
	Total	0.067	14			
2	Regression	1.599	1	1.599	72.248	0.000
	Residual	0.288	13	0.022		
	Total	1.887	14			
3	Regression	553.284	3	184.428	723.247	0.000
	Residual	3.056	12	0.255		
	Total	556.340	15			

DISCUSSION

This study clearly indicated that TU-A solvent is a promising mixture providing significant decrease of extraction time compared to other studies (Khodadoust *et al.*, 2005; Ahn *et al.*, 2008; Han *et al.*, 2009) in which the solvent washing of weathered oil required considerable time (1--48 h) to reach equilibrium. It can be inferred that all of the aliphatic and aromatic fractions have been removed after solvent extraction, although not being quantitatively confirmed, and the remaining insoluble fractions (14 000 mg kg^{-1}) were most likely asphaltenes as 15 000 mg kg^{-1} (11% of TPH) were quantified before extraction. This is evidenced by the chemical structure and properties of asphaltenes, which is believed to be polycyclic aromatic ring compounds bearing alkyl side chains composed of small amounts of heteroatoms (S, N, and O) and traces of vanadium and nickel (Ali and Alqam, 2000; Ancheyta *et al.*, 2002). They are soluble in liquids having a surface tension above 25 dynes cm^{-1} (such as benzene, pyridine, carbon disulfide and CCl_4), but insoluble in nonpolar solvents with a surface tension lower than 25 dynes cm^{-1} (such as petroleum ether, pentane, isopentane and hexane) (Speight and Moschopedis, 1994). Therefore, TU-A solvent was inefficient to remove asphaltenes by solubilisation. Moreover, coagulation of asphaltenes tend to be stimulated by low molecular weight hydrocarbons (i.e. hexane and pentane) that would take up the ‘stable space’ previously formed when colloid molecules in the crude oil were adsorbed on the surface of asphaltenes (Leontaritis and Mansoori, 1989; Chang and Fogler, 1994). This led to the formation of a thermodynamic stable structure, in which asphaltenes were sequestrated and became hardly transferable from the inner parts to the outer parts of the soil particles (Hu *et al.*, 2000). Future works are needed to better understand the solvent-asphaltenes interaction mechanisms and develop strategies for regenerating the solvent sequestrated in the formulated coagulation.

Results revealed that bioaugmentation with *B. subtilis* FQ06 and rhamnolipid was beneficial for TPH removal. However, use of biosurfactant for the purpose of improving biodegradation

should be further investigated as various studies reported contradicting results. For instance, the addition of rhamnolipids to hexadecane stimulated the biodegradative capabilities of *P. aeruginosa* strains UG2, ATCC15528 and PG201 as well as *R. erythropolis* ATCC 19558 while the degradative activity of *R. erythropolis* DSM 43066 was inhibited and no effect on the strain BCG112 was observed (Bruheim *et al.*, 1997; Noordman and Janssen, 2002). This demonstrated that stimulation, inhibition or no effects on biodegradation by exogenous addition of biosurfactants depend on the property of surfactant added and the type of biosurfactant producing organisms in the soil.

Biodegradation dynamics suggested that oil degradation was co-limited by the number of oil degraders and hydrocarbon bioavailability at the early stage. After 54 days, neither the addition of bacteria nor the emulsification of hydrocarbons via addition of biosurfactant would increase the degradation (Fig. 3), suggesting that hydrocarbon bioavailability was no longer a co-limiting factor at the final stage. It is likely that nutrients became a limiting factor since the carbon source available to microorganisms was gradually reduced and harmful substances resulted by metabolism were continuously accumulated. This was supported by McKew *et al.* (2007) that increasing bioavailability of the oil by emulsification will have a minimal effect if nutrients were limiting.

The first order biodegradation rate constants (Table III) were one order of magnitude lower than that of Lee *et al.* (2001). Therefore, the residual TU-A solvent was inferred to inhibit biodegradation, although biodegradation experiments without pre-extraction were not carried out in this study because such a high initial TPH concentration was toxic to microorganisms and would cause loss of degradation efficiency. This finding sounds opposite to several studies (Brusseau *et al.*, 1991; Pignatello and Xing, 1996; Lee *et al.*, 2001) in which organic solvents resulted in the enhancement of PAH bioavailability by solubilisation and consequently increased the first order biodegradation rate constants. This may be attributed to two concomitant effects resulted from TU-A solvent addition: (i) enhancement of bioavailability by solubilisation that causes faster biodegradation, and (ii) coagulation phenomena that makes hydrocarbons less or unavailable to microorganisms. The latter is likely the dominant kinetic factor limiting the transfer of highly recalcitrant hydrocarbons from solvent to water phase. Therefore, removal of the residual TU-A solvent in the extracted soil before bioremediation could be an important strategy since bioavailability is a co-limiting factor at the early stage of biodegradation. In order to gain more insights into the selectivity on different hydrocarbons during biodegradation, future works are needed to focus on biodegradation and bioavailability of various hydrocarbon fractions and indicator compounds instead of TPH when implementing this technology.

Overall results demonstrated both short-term and long-term effectiveness of the integrated technology. The short-term performances include: (i) more than 90% of TPH was removed within 15 min at room temperature, which was much more effective than previously reported solvent extraction methods with an extraction time raging from 1 to 48 h and temperature ranging from 70 to 100 ˚C (Khodadoust *et al.*, 2000; Khodadoust *et al.*, 2005; Ahn *et al.*, 2008; Han *et al.*, 2009); (ii) instruments used in traditional methods such as ultrasonic probes, freeze-dryer and Soxhlet equipments were not required, which kept capital outlay low and minimized the consumption of energy and other natural resources; (iii) significant amount of oil could be recovered by solvent extraction if the field-scale application of this method is successful to a site previously contaminated with extremely high concentration of oil; and (iv) negative impacts on environments associated with the utilization of solvent extraction are overcome as the subsequent biodegradation allows more complete removal of the unsolved waste, which is consistent with the recognition by the US and UK Sustainable Remediation Forums (SURF) encouraging the use of remedial technologies that permanently destroy

contaminants (Ellis and Hadley, 2009; Bardos *et al.*, 2011).

The long-term performances are as follows: (i) the ultimate residues remaining in the soil are water and the untreated asphaltenes (< 4000 mg kg^{-1}), because up to 99% of the solvent used in the solvent extraction could be recycled and reused by water wash technology (Wu *et al.*, 2011); (ii) water is recognized as 'green solvent' and its disposal is regarded as benign with little affect on the environment; (iii) although toxicity and carcinogenicity of asphaltenes have been recognized (Wess *et al.*, 2004), the potential toxicity of highly recalcitrant asphaltenes would diminish as they become less available to ecological receptors in soil (Alexander, 2000). Further bioaccumulation of asphaltenes would be highly unlikely because of their low water solubility and high relative molecular weight. The residual contaminants may potentially be left in place without creating additional environmental risk.

CONCLUSIONS

The performance of an integrated remedial approach coupling solvent extraction to bioremediation to treat soils contaminated with high concentrations of weathered petroleum hydrocarbons was investigated using TU-A solvent and *B. subtilis* FQ06 strains. The solvent extraction was proved to be fast and effective which removed over 80% of TPH in 5 min at room temperature. All of extraction time, temperature and solvent volume significantly influenced the extraction efficacy. The optimal extraction conditions were determined at 25 °C for 20 min with a solvent-soil ratio of 6:1 (v/w). On this basis, TPH were decreased from 140,000 to 14,000 mg·kg^{-1} d.w. soil. However, an inherent limitation of the solvent extraction lies in the fact that some extremely recalcitrant hydrocarbons such as asphaltenes are insoluble in the TU-A solvent. Therefore the residual oil was further removed by biodegradation. Bioaugmentation and surfactant addition enhanced significantly the degradation of the residual TPH (< 4000 mg·kg^{-1}) after 132-day of experiment. Biodegradation kinetics demonstrated that removal of residual solvent in the extracted soil at the early stage of degradation could be an important strategy. The overall results of the integrated remedial technology are in good agreement with the US and UK SURF-frameworks that incorporate sustainable concepts throughout the remedial action process. Importantly, it is easy and simple to reproduce. It should be encouraged at contaminated sites for reducing remediation time, enhancing efficacy, improving sustainability and restoring previous contaminated sites especially with high concentration weathered hydrocarbons.

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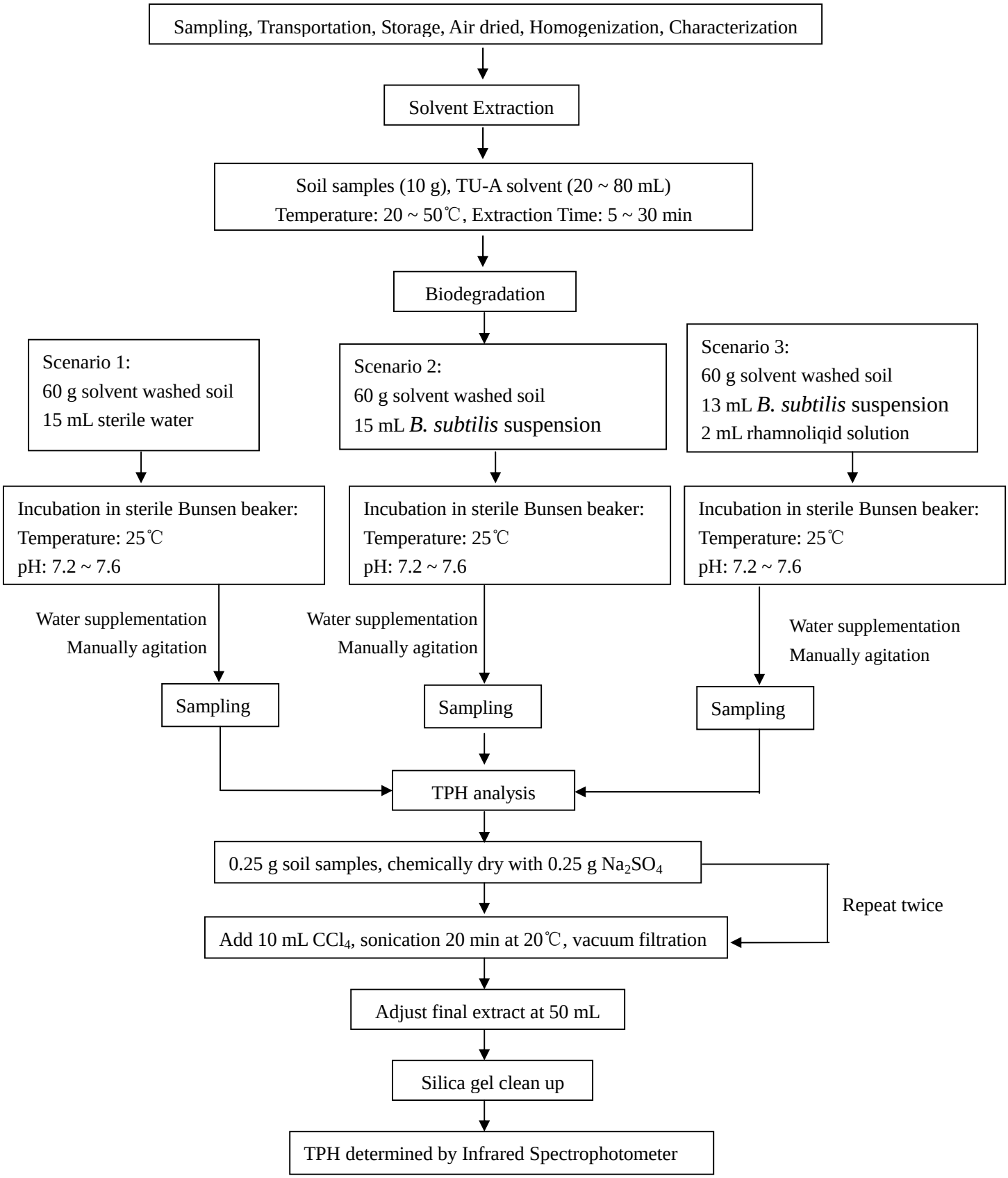


Fig. 1 Schematic of the solvent extraction and biodegradation experiments

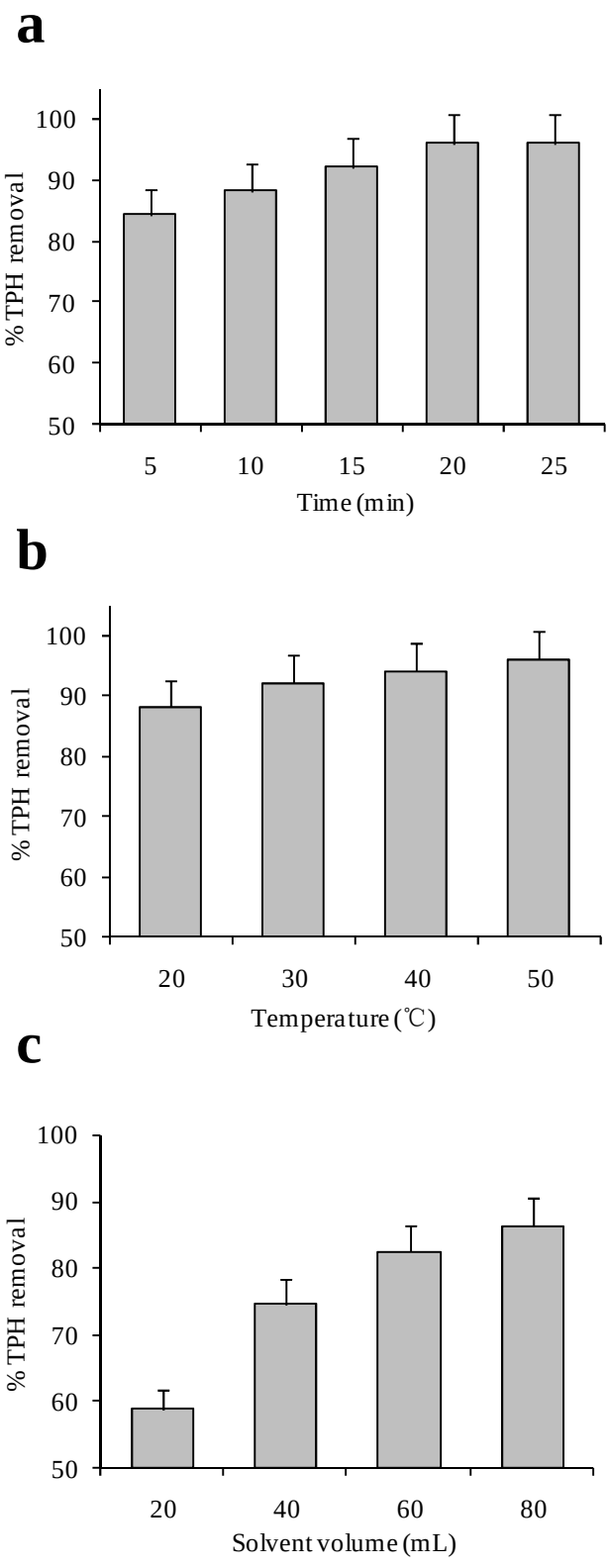


Fig. 2 Influence of extraction time, temperature and solvent volume on the removal efficiencies of TPH (Each value represents the mean removal percentage of TPH from duplicate samples ± standard deviation)

1

2

3

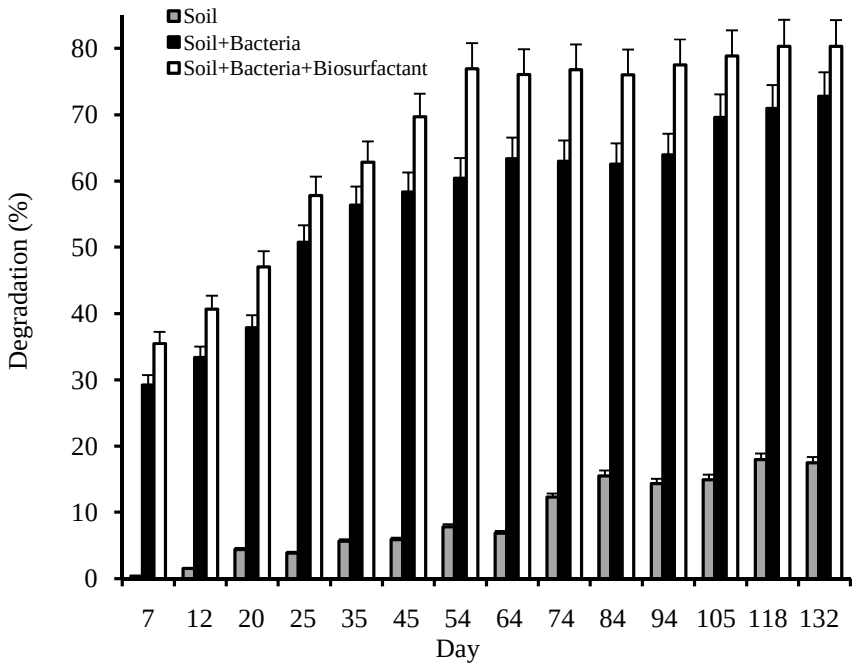


Fig. 3 Percentage degradation of TPH over 132 days (Each value represents the mean degradation percentage of TPH from duplicate samples ± standard deviation).

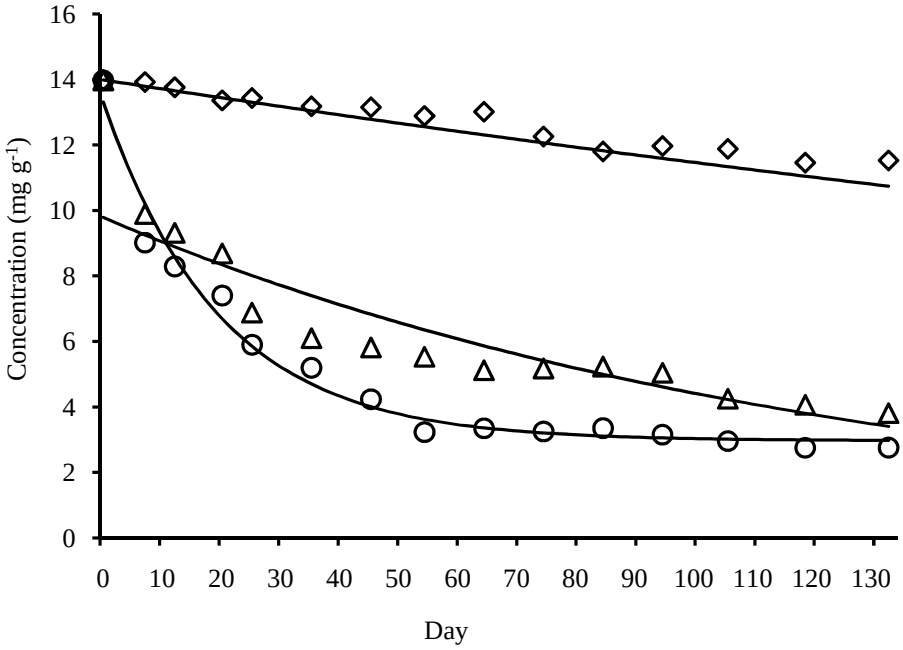


Fig. 4 Comparison of the calculated TPH concentration with the observed data. The symbols (◇: Soil, △: Soil + Bacteria; ○: Soil + Bacteria + Biosurfactant) represent the experimental data and the continuous lines are the model results of TPH concentration.



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Combining solvent extraction and bioremediation for removing weathered petroleum from contaminated soil

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