Remediation of Hydrocarbon-Contaminated Sediments by Strong Mixing and Hydrophobic Aerogel Sorption

Mohammad Farshidy & Catherine N. Mulligan
Department of Building, Civil and Environmental Engineering,
Concordia University, Montreal, Quebec, Canada

ABSTRACT
This study was on the evaluation of a desorption-sorption process for remediation of hydrocarbon-contaminated sediments. Furthermore, the effect of two influential factors including retention time and solid load was studied. A laboratory scale system was designed and built for remediation of sediments in a short period of time. A strong turbulence vessel (about 16000 rpm) was used to increase desorption of hydrocarbon contaminants from sediments. A sorption packed column containing hydrophobic silica aerogel granules was used to remove the contaminants in order to improve the quality of the effluent slurry. After 45 minutes, 29.5% of total petroleum hydrocarbon (TPH) removal from sediments was achieved. Different applied ranges of retention time in the agitator (0.19 and 0.43 min) and sediment solid loads (5, 10 and 15 g/l) did not show a significant effect on the efficiency of the process. The processed sediment and water in effluent followed the allowed Canadian governmental and provincial environmental criteria for fresh water.

RÉSUMÉ
Cette étude portait sur l'évaluation d'un procédé de désorption-sorption pour l'assainissement de sédiments contaminés par des hydrocarbures. En outre, l'effet de deux facteurs influents, y compris le temps de rétention et la charge solide, a été étudié. Un système à l'échelle du laboratoire a été conçu et construit pour l'assainissement des sédiments en peu de temps. Un fort récipient de turbulence (environ 16 000 tr / min) a été utilisé pour augmenter la désorption des contaminants hydrocarbonés des sédiments. Une colonne remplie de sorption contenant des granules d'aérogel de silice hydrophobe a été utilisée pour éliminer les contaminants afin d'améliorer la qualité de la suspension d'effluent. Après 45 minutes, 29,5% de l'élimination des TPH des sédiments ont été réalisés. Différentes plages de temps de rétention appliquées dans l'agitateur (0,19 et 0,43 min) et charges solides de sédiments (5, 10 et 15 g/l) n'ont pas montré d'effet significatif sur l'efficacité du procédé. Les sédiments traités et l'eau contenue dans les effluents respectaient les critères environnementaux gouvernementaux et provinciaux canadiens pour les eaux douces.

1 INTRODUCTION

Clean up of contaminated sediments is a challenging practice in environmental remediation. Organic and inorganic contaminants are absorbed into the porous media of the sediment and form strong bonds. Due to the existence of strong forces between the contaminants and sediment matrix, the destruction, immobilization, separation, or extraction of the contamination is complicated (Fingas, 2011; Mulligan et al., 2010).

Petroleum products and their derivatives are among the most hazardous sediment contaminants due to slow rate of degradation, high toxicity and wide spreading in the environment (Reible & Lanczos, 2006). Spills of petroleum products caused by human error, equipment failure, accidents and climate disasters regularly occur around the world. Spills happen during the well drilling, extraction, transport, storage, refining, downstream transforming and usage. On average, for an oil-based product there are about 10 to 15 transfers between the oil well and the final consumer. In each transfer there is a risk for accidents, leakage or sabotage (Fingas, 2001).

Remediation of contaminated sediments is difficult and costly due to diversity of mechanisms of contaminant-sediment interaction. Conventional mechanical remediation methods increase the desorption rate of contaminants. These methods eliminate or reduce the necessity of washing aids. However, in the field, they are of low-efficiency or less cost-effective than heat- or chemical-based methods (Mulligan et al., 2010).

Many remediation methods for contaminated sediments have previously been applied for soil remediation. Selection of the remediation method is carried out based on numerous factors, particularly sediment and contaminant type (Mulligan et al., 2010; Reible & Lanczos, 2006).

Washing process is among the most common methods for decontamination of environmental solid media including soil, sediment, mine and oil sands tailings, coastal sands, solid sludge, buried and subaqueous wastes and oil well drilling mud (oil sludge). Washing has been applied for remediation of a wide range of environmental contaminants (Dermont et al., 2008; ICS-UNIDO, 2007; Mulligan et al., 2010).

On the other hand, various technologies based on sorption phenomenon are commonly used in the cleaning processes in environmental remediation and protection (Chiou, 2002; Inglezakis & Poulopoulos, 2006; Mota & Lyubchik, 2008; Mulligan et al., 2010; Zhang et al., 2009). Sorption is one of the key remediation technologies in the present and future (Yang, 2003).

Nanostructured sorbents will be extensively applied in remedial technologies in the future. Silica aerogels are considered as new adsorbents for spill containment. Bearing characteristics such as low toxicity, light weight and excessive hydrophobicity makes this type of aerogels a proper material for absorption of organic contaminants.

Aerogels are manufactured as films, granulates, powders, blocks or from organic or inorganic substances (Buschow et al., 2001). So far, aerogels are among the lightest man-made materials. The most prominent type of aerogels are silica aerogels. They have been studied more than the other types aerogels due to their non-toxic nature and high sorption capacity (Griffin, 2014; Tomczyk, 2014). The silicon-oxygen bridges form the network skeleton in silica aerogels ($\equiv$Si-O-Si$\equiv$). Following the discovery of silica aerogel, other types of aerogels have been invented. Examples of other types of aerogels are carbon aerogels, carbon nanotube aerogels, inorganic hollow nanotube aerogels, organic polymer aerogels, alumina aerogels, gold aerogels and clay aerogels.

The aim of the present study is evaluation of a desorption-sorption process for remediation of hydrocarbon-contaminated sediments.

2 EXPERIMENTAL STUDY

2.1 Desorption-Sorption Setup

A closed-loop system was designed and built to cleanup hydrocarbon-contaminated sediments in a short period of time while minimizing the concentration of contaminates in the effluent to avoid releasing into the environment. To enhance desorption of contaminants from sediments a vigorous turbulence (near 16000 rpm) was applied. A sorption column containing modified silica aerogel was utilized in the process to remove the desorbed contaminants in order to enhance the quality of the effluent slurry (Figure 1).
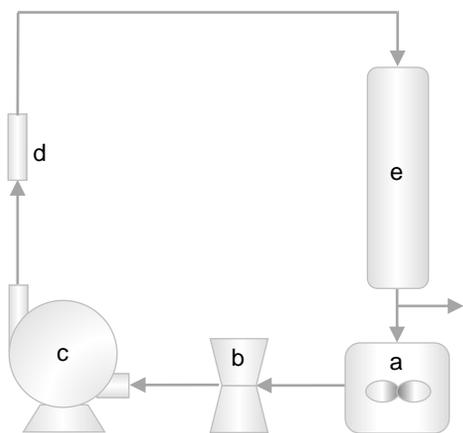
Figure 1. Sorption-desorption setup including the (a) agitation vessel, (b) liquid-gas separation chamber, (c) pump, (d) flow meters and (e) adsorption column

The adsorption column was made of a glass tube with 4.9 cm internal diameter and up to 25 cm length. The arrangement of piping allowed the slurry stream to flow into the column upward or downward. A sampling port and a purge port were implemented for sampling and working in semi-batch configuration. Two relief valves allowed release of the small bubbles of air from the column. Hydrophobic surface-modified silica aerogel was used as a typical adsorbent to adsorb and sink the contamination. The arrangement of several bypasses and 22 valve streams could enable experiments in different flow directions, flow rates and contact times.

During the preliminary experiments it was revealed that submerged aerogel granules strongly repel the water and tend to have a layer of air around them. Therefore, a special mechanism and several air bubble traps were placed in the system to ensure that the inlet slurry to the adsorption column does not have visible and large air bubbles.

To minimize the loss originated from the adsorption or leaching of hydrocarbons by the exposed wall surfaces, a Teflon pump and Teflon-lined tubing was used. The agitation vessel was made from stainless steel 316 which is one the best-suggested materials for hydrocarbon laboratory tests. The adsorption column and separation chamber were made from glass. The tubing joints were made from Teflon or stainless steel 316. A control system was designed and built to control the agitation vessel and pump and ensure the safety of the personnel and system simultaneously. As the agitator rotated in speeds of higher than 10,000 rpm, to avoid the overheating the motor, a cyclic timer was installed on the control panel to turn ON/OFF the agitator intermittently. The time intervals were adjusted for 20 second ON and 60 seconds OFF. The flow rate of the slurry entering to the column could be adjusted by either series of valves which enabled recycle of the stream, two liquid flow meters (high range 0.95-9.5 l/min and low range 0.1-1.5 l/min) or an electrical pump controller on the control panel. A main stream of water from tap water was installed to wash inside the whole setup after every experiment. The electrical current passing through the agitator and pump was indicated by two ampere meter on the board. During the experiments, the temperature of agitator, pump electromotor and other parts could be measured by a laser thermometer (model Mastercraft). A cooling water coil was installed around the pump to prevent overheating. A series of circuit-breakers were embedded in the control panel for the sake of safety. The system could be shut-down with a main emergency switch in the case of an incident.

In the pre-determined time intervals (0, 3, 30, 60, 120 and 180 min), 300 ml of slurry were taken from the setup by a graduated cylinder and weighed by a laboratory balance. The slurry was divided in six 50-ml metallic centrifuge tubes and centrifuged at 3700 rpm for 30 minutes. To avoid adsorption of tiny amounts of hydrocarbons on the wall, the conventional polyethylene centrifuge tubes were not used. The supernatant was separated carefully and collected for liquid-liquid extraction by hexane for further gas chromatographic (GC) analysis.

2.2 Materials

The sediment samples were collected from sector 103 of the Port of Montreal. Sector 103 is located on the northern coastline of the river and has been a ground for various industrial activities, particularly oil and metal refining, for over five decades. The concentration of total petroleum hydrocarbon (TPH) in sediment was 678.7 ± 21.0 mg/kg.

Granular aerogel type P300 was purchased from Cabot Co. The surface of this type of aerogel is covered with tri-methyl-silyl groups (-Si(CH3)$_3$) and is strongly hydrophobic.

Gas chromatography grade hexane Optima with a minimum purity of 99.9% was obtained from Fisher Scientific Canada. Anhydrous sodium sulfate ACS with 99% purity and 10/60 mesh for analysis, anhydrous magnesium sulfate with at least 99% purity for analysis and extra pure silica gel with 70-230 mesh were obtained from Fisher Scientific Canada.

The C10-C50 soil standard was purchased from the Quebec Expertise Environmental Analysis Center (Centre d'expertise en analyse environnementale du Québec).

2.2 Methods

A gas chromatograph coupled with a flame ionization detector (FID) (model Varian CP-3800) was used to measure the total petroleum hydrocarbon content in solid environmental samples and water. A capillary DB-5 column (Agilent Technologies) was used in the GC.

The concentrations of total petroleum hydrocarbon (TPH) in sediment, pore water and processed water were measured applying the C10-C50 analysis protocol established by the government of Quebec (MA. 400 – HYD. 1.1; Détermination des hydrocarbures pétroliers (C10 à C50): dosage par chromatographie en phase gazeuse couplée à un détecteur à ionisation de flame, 2013). This protocol was selected for its accuracy and safety. In brief, sediment samples were dried with 3.5 g magnesium sulfate and extracted by hexane in an ultrasonic bath for 15 minutes. Magnesium sulfide were divided and added to the wet sediment at the bottom of tubes to dry the solid and to remove it from the tubes. The coarse mixture of sediment and magnesium sulfate was weighed and ground to a fine powder with a handheld electrical grinder modified for small sediment samples. The powder extracted by hexane.

The flow rate of slurry could be adjusted by two flow meters (low range and high range). The working volume in the agitator was calculated by measuring the dimensions of parabolic profile (h$_0$, H and R) of the spinning water-air mixture according to Figure 2 and Equation 1 where H is maximum height of the liquid (m), h$_0$ is minimum height of the liquid (m), ω is rotational speed (1/s), R is radius of rotation (m), and g is gravity acceleration (9.8 m/s^2).

$$H-h_0 = (\omega^2 R^2)/2g \qquad [1]$$

HRT was measured by applying the Equation 2 where HRT is hydraulic retention time (sec), V is working liquid volume (m^3), and F is flow rate (m^3/s).

$$HRT = V/F \qquad [2]$$
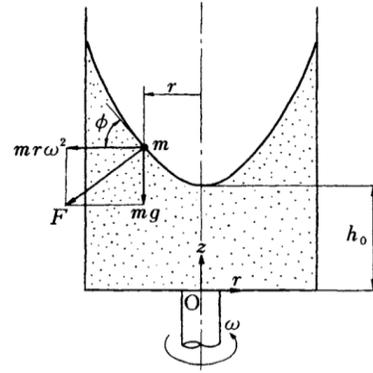
Figure 2. Parabolic profile of the liquid surface during the rotational movement in the mixer

The flow rate of sediment slurry in the desorption-sorption experiments was 4.5 l/m. This flow rate was the minimum flow rate that the pattern of adsorption column stayed a packed bed and not an inverse fluidized bed. To investigate the effect of retention time, the experiments were performed in flow rate of 2 l/m. This flow rate was the minimum flow rate that the pump could work without a large head loss to interrupt the flow because of the pressure drop. The hydraulic retention times in the agitator for these flow rates were 11.5 and 26 seconds (0.19 and 0.43 min), respectively.

The effect of solid load was studied by processing the sediment under different sediment to water weight ratios (5, 10 and 15 g/l) in the desorption-sorption test setup. The measurements were performed in duplicate.

The rotation speed of the impeller in the mixer was measured using a stroboscopic laser tachometer rotation speed meter (model DT 2234C+). A small piece of a shiny sticker (1x1 cm) was attached to a blade of agitator and the sensor of tachometer was pointed perpendicular to the sticker. The number displayed on the tachometer was recorded in rpm. The measurements were repeated 10 times and the average value was calculated as the rotation speed.

3 RESULTS AND DISCUSSION

3.1 Desorption-Sorption Remediation Experiments

The results of processing the sediment by the desorption-sorption process in 3 hours (including net 45 minutes of agitation) with the rpm of 15900 and flow rate of 4.5 l/min are presented in Figures 3 and 4. The final remediation of the hydrocarbon pollution in sediment was 29.5%. All TPH content of the pore water was extracted and adsorbed onto the aerogel. Also, the leaching of the hydrocarbon contaminant from the sediment was measured in two other conditions: with presence of only vigorous agitation; and with the absence of agitation and aerogel as control tests. Figure 3 indicates that in this case the increase in the TPH content of process water is almost completely due to the release of TPH from pore water into the process water.
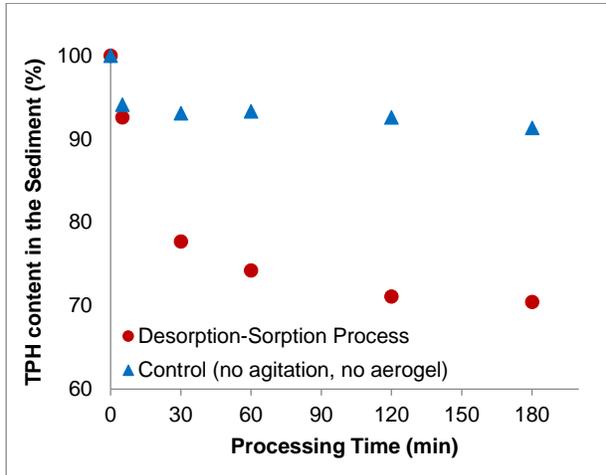
Figure 3. The effect of applying 3-hour agitation and adsorption on remediation of sediment; the average values of duplicate measurements are presented (error margin ≤ 4%).
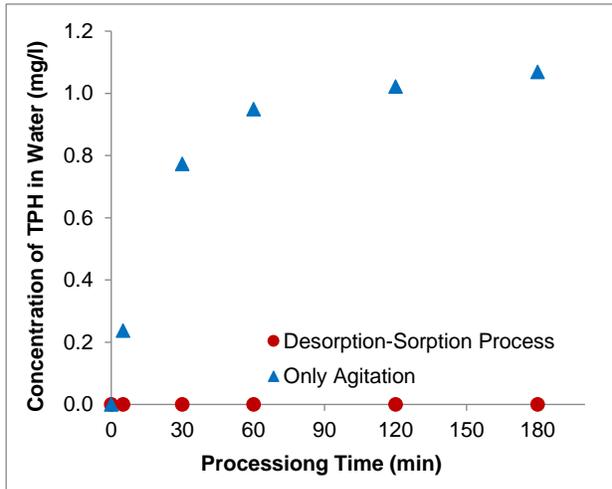
Figure 4. Effect of applying 3-hour agitation and adsorption on concentration of TPH in water; the average values of duplicate measurements are presented (error margin ≤ 4%).

3.2 Effect of Retention Time in Agitation Chamber

The effect of retention time in the agitation chamber on the content of TPH in sediment and water is shown in Figures 5a and 5b. Retention time did not show any significant effect on the concentration of contaminant in the sediment. The desorption-sorption process was a closed-loop system and flow rate was high in comparison with the total volume of the system. Therefore, all the slurry circulated in the system several times every minute. By increasing the flow rate the average retention time for every particle of sediment or small control volume of water becomes shorter, but the number of passes through the agitation

a

b
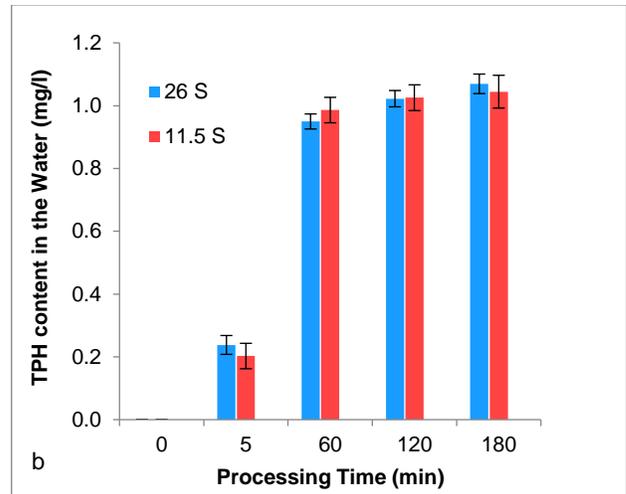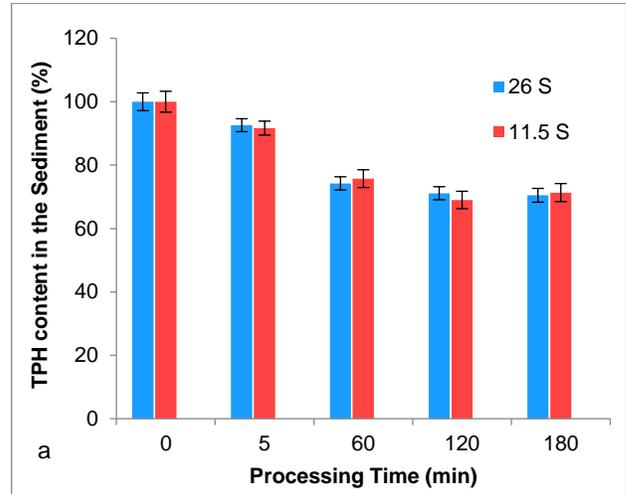
Figure 5. a. The effect of retention time in agitation chamber in the desorption-sorption process on the TPH content in sediment; and, b. The effect of retention time in agitation chamber in the presence of vigorous agitation rates and absence of aerogel on the concentration of TPH in water

chamber increases, which neutralizes the short residence time.

3.3 Effect of Solid Load

The effect of sediment loading on the content of TPH in sediment and water in various process configurations is shown in Figures 6.a and 6.b. Solid load affected proportionally the release of TPH into the water but did not have any visible effect on the concentration of contaminant in the sediment.

Previous research indicated that the critical impeller speed for the complete suspension of floating solid particles does not significantly change with solid load (Kuzmanić, 2008). On the other hand, Feng et al. (2001) used a jet reactor, ultrasound and attrition washing to
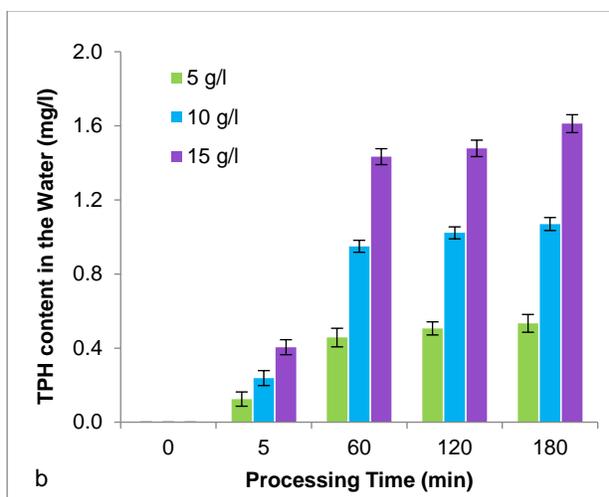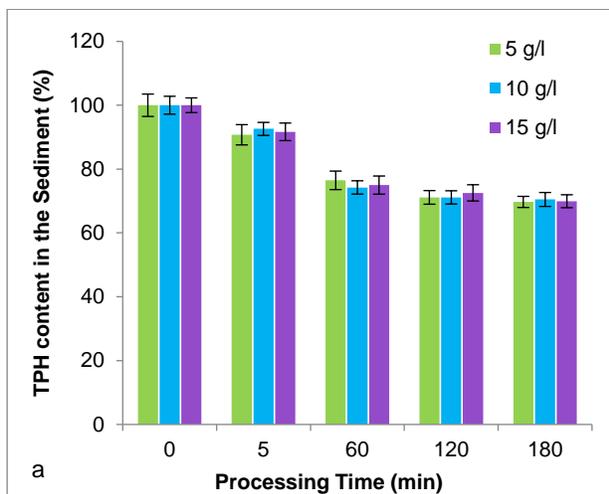
Figure 6. a. Effect of solid load in desorption-sorption process on the TPH content in sediment; and, b. Effect of solid load in the presence of vigorous agitation and absence of aerogel on the concentration of TPH in water

remediate a soil contaminated with diesel. They used high solid concentration ranges from 10% to 20% for jet reactor, 20% to 70% for ultrasonic washing, and from 70% to 90% for attrition washing. The three methods did not follow the same pattern. By increasing the soil content, the efficiency of diesel removal in the jet reactor washing reached a maximum and then decreased, whilst in ultrasound and attrition washing, the removal efficiency decreased to a minimum and then increased. They concluded that for diesel removal at lower solid concentrations, by increasing the solid/liquid ratio, the effect of interparticle scrubbing increases and becomes dominant over particle-water shear. In the current study, the concentration of solids is much lower when particle-to-particle scrubbing comes in to effect (5 to 15 g/l). Therefore, the particle-water shear governs the desorption process.

3.4   Quality of Effluent Sediment and Water

The maximum allowed concentration of TPH for freshwater and marine sediments in Canada is 500 mg/kg. In the province of Ontario, the highest allowed concentration of TPH in ground and potable water is 0.17 mg/l. In the province of Nova Scotia, this threshold is 0.1 mg/l for fresh and marine water. The concentration of TPH in effluent sediments and water exiting the desorption-sorption process respectively was 478.4 mg/kg and about 0.05 mg/l which met the Canadian environmental quality criteria.

4   CONCLUSIONS

The application of a closed-loop process including a strong mixing and a sorption process can be considered as a new methodology for remediation of contaminants in sediments.

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