Sorption of phenanthrene by kaolin and efficacy of hydraulic versus electroosmotic flow to stimulate desorption

Ikrema Hassan[a,b,*], Eltayeb Mohamedelhassan[c], Ernest K. Yanful[a], Ze-Chun Yuan[b,d]

[a] Department of Civil and Environmental Engineering, Western University, London, ON N6A 5B9, Canada
[b] Southern Crop Protection and Food Research Centre, Agriculture and Agri-Food Canada, Government of Canada, London, ON N5V 4T3, Canada
[c] Department of Civil Engineering, Lakehead University, Thunder Bay, ON P7B 5E1, Canada
[d] Department of Microbiology and Immunology, Western University, London, ON N6A 5C1, Canada

ABSTRACT

Petroleum hydrocarbons are hydrophobic and tend to adhere to soil when released into the environment. Desorption of the contaminant from soil is necessary for most remediation technologies. In subsurface and for in-situ remediation, the dominant desorption mechanism is back diffusion.

In this study, three tests were conducted to establish sorption and desorption kinetics for phenanthrene as a contaminant and kaolinite as a soil matrix. Sorption isotherm tests were conducted at temperatures of 14, 22, and 30 °C using six phenanthrene solution containing concentrations from 300 to 800 μg/L. Freundlich equation constant, K_f, values of 0.147, 0.133, and 0.109 $\mu g L^n/g^{(1+n)}$ were determined for the three temperatures. Desorption tests were conducted using phenanthrene-free solution to determine desorption parameters at room temperature (~22 °C). In addition, two test series were performed to compare phenanthrene desorption by hydraulic and electroosmotic flows at room temperature. A fixed wall hydraulic permeability apparatus was used to generate a hydraulic flow rate of 1.4×10^{-3} mL/s at a pressure of 260 kPa, while a low level direct current density (0.3–0.43 mA/cm²) was applied to generate electroosmotic flow rate equivalent to the hydraulic flow. The phenanthrene concentration in effluent samples after desorption by electroosmotic flow was found to be three to four times the concentration after desorption by hydraulic flow. Moreover, the power required in the hydraulic flow test was three orders of magnitude higher than the consumed power in the electrokinetic flow test. These results show that phenanthrene desorption by electroosmotic flow is more efficient than by hydraulic flow.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

In the industrial era, the environment has been heavily affected by improper disposal of waste from petroleum extraction and anthropogenic activities. Polycyclic aromatic hydrocarbons (PAHs) are an important group of pollutants because some of them have been identified as mutagenic, carcinogenic, and/or teratogenic [1,2]. PAHs are characterized by their polarity and low solubility in water, both of which hinder their removal from soils [3,4]. The risk assessment and the evaluation of the fate of the contamination source are solely dependent on understanding the sorption and desorption characteristics of the pollutant. Sorption of a certain contaminant in the environment is commonly described by the distribution coefficient between sorbent (e.g. soil) and sorbate (e.g. aqueous phase), assuming the process is linear. The partition

coefficient depends on the environment and can be estimated by the product of contaminant and organic carbon partition coefficient (K_{oc}) and organic carbon fraction in the sorbent (f_{oc}). In the literature, reported values of K_{oc} vary over a wide range. For instance, log K_{oc} for phenanthrene ranges from 3.97 to 6.12, i.e. a variation of more than two orders of magnitude in K_{oc} [5]. Recent studies have shown that not only does the fraction of organic carbon in the sorbent control the sorption, but also the type of organic carbon (humin, humic acid, and fluvic acid) and the environmental conditions play a dominant role in the sorption partitioning phenomenon [6,7]. For example, Terashima et al. [8] demonstrated that the presence of high molecular weight humic acids results in high sorption of polycyclic aromatic hydrocarbons (PAHs). A study by Pan et al. [7] has shown that humin (HM) is responsible for slow sorption of PAH, whereas fulvic and humic acids are predominant in the initial sorption stage. The findings of the aforementioned researchers are in agreement with the concept of biphasic sorption, which has been discussed extensively in the literature [9–11]. There are several well established methods for

determining f_{oc}, such as wet oxidation and dry oxidation [12]. Although the values of K_{oc} and f_{oc} can be determined by any of the aforementioned techniques, the test can result in under or over estimation of the sorption process. This is because soils' organic matter fractions and organic matter types play a crucial role in the sorption and desorption capacity of the soil to petroleum hydrocarbons. Therefore, determining the sorption coefficient is essential to understand the behavior of contaminant and interaction between the contaminant 'sorbate' and the matrix 'sorbent' when the contaminant released in the environment.

In the last two decades, desorption of organic contaminants from soil has gained considerable attention in the literature as it is the key factor governing the bioavailability and consequently the biodegradation [13–18]. Many research studies have shown that batch desorption tests can result in less than 100% of the sorbate recovery; a phenomenon called hysteresis. For example, Kan et al. [18] research study has shown that because of the hysteresis between sorption and desorption for hydrocarbon organic contaminants, only 30–50% of sorbed PAHs was recoverable after a batch desorption test. At contaminated sites, desorption mechanism is slow and depends on many factors including: (i) sorbate concentration gradient inside the sorbent, which develops during the sorption phase with higher sorbate farther inside the sorbent, (ii) thickness of the double layer, (iii) sorbate chemical properties, and (iv) sorbent physico-chemical properties. It has been shown that PAHs partitioned into clay soil is highly susceptible to mobilization by groundwater and degradation by soil-micro-organisms [19].

Desorption of contaminants from the sorbent by the effect of ground water flow has a fundamental role in mitigation of contaminated sites [20]. For instance, natural attenuation remediation technique depends solely in desorption by ground water flow as a major mechanism for degradation of the contaminants [21]. In this method the concentration of the contaminant in soils and ground water is monitored in the source zone and in the contaminated plume. Due to the fact that the groundwater flow rate is very slow, the decrease in contaminant concentration by desorption (the effect of groundwater) may take centuries until it reaches the regulatory requirements or the standards [22–24]. Electroosmotic flow, associated with electrokinetics, creates flow within the Stern layer in the double layer. The Stern layer is next to the soil matrix (sorbent) where the sorption of organic contaminants takes place. The electroosmotic flow in this region can enhance back diffusion of the contaminant from the soil matrix to the pore fluid and accelerate desorption of the contaminant, which can result in reducing the amount of time required for mitigation of contaminated sites. According to the Helmholtz–Smoluchowski model, the most commonly used theory to describe electroosmosis, the width of the electroosmotic flow tube in a soil mass extends beyond the free water to the interface between the fixed and mobile parts of the electrical double layer [25]. In contrast, the hydraulic flow takes place in the zone of the free water alone. Since adsorbed PAH compounds are held very close to the surface of the soil, a flow generated within the electrical double layer may facilitate desorption of these compounds. Furthermore, electrokinetic remediation has a high potential for generating electroosmotic flow in fine-grained soils in which the groundwater flow rate is very slow so these soils are difficult to cleanup using conventional methods [26]. From the above discussion, the potential of electrokinetics in promoting desorption of contaminants by electroosmotic flow makes the technique a suitable candidate to be coupled with natural attenuation to enhance the outcome of natural attenuation. Electrokinetics requires a direct current (DC) power supply to produce the necessary power for the process, which arguably can increase the cost of the hybrid technique (electrokinetics natural attenuation). Studies by Yuan et al. [27] and Hassan et al. [28] have shown that solar panels can be used to generate enough power for electrokinetics remediation processes with the former study finding the cost of power by the solar panels to be less than that from the grid in China. This makes the hybrid technique, if successful, an excellent option to be used in contaminated sites at remote areas where electrical power lines are not abundant or absent.

Recent review articles by Yeung and Gu [29] and Gill et al. [30] have discussed various techniques to enhance electrokinetic remediation along with electrokinetics coupled with other remediation techniques. None of the aforementioned articles, however, has discussed the coupling of electrokinetics with natural attenuation. Desorption of PAH by electroosmotic flow to enhance natural attenuation has not been well studied. In fact, there are very few articles in the available literature that have studied the role of electroosmotic flow in desorption of PAHs from soil [17,31]. A study by Shi et al. [17] has shown that desorption of phenanthrene from glass beads by electroosmotic flow is more efficient than desorption by hydraulic flow.

In the present study, phenanthrene is selected as a model polycyclic aromatic hydrocarbon, and its sorption by kaolinite clay soil is investigated. Desorption of the sorbate (phenanthrene) resulting from hydraulic flow is compared to desorption driven by electroosmotic flow. One application of this study would be coupling electrokinetic remediation with natural attenuation. To the best of the authors' knowledge, this is one of the first studies that has compared the effectiveness of electroosmotic and hydraulic flows in desorption of PAH from a clay soil.

2. Materials and methods

Inorganic kaolinite clay soil, 96–99.9% kaolinite (EPK case number 1332-58-7), purchased from (EdgarMinerals, Florida, US) was used as the sorbent in the experiments. Table 1 shows the physical and chemical properties of the soil. Atterberg limits (liquid and plastic limits) were determined following ASTM D4318-10 [32]. The maximum and the minimum void ratios were determined using ASTM D4254-00 [33] and ASTM D4253-00 [34]. Maximum void ratio (e_{max}) is the void ratio (that is, volume of voids divided by the volume of solids) of the soil in its loosest state. It is determined by allowing a soil sample to settle by gravity in a graduated cylinder, cover the cylinder with latex sheet and turn the cylinder upside down slowly, and then the soil volume is measured [35]. The minimum void ratio (e_{min}) is the void ratio of the soil in its densest state, and is determined by measuring the volumes of soil voids and solids after compaction using the modified Proctor test [36]. Sieve analysis on the soil revealed that all the particle sizes were less than 0.075 mm (passed no. 200 sieve). Accordingly, hydrometer analysis was conducted to obtain particle size distribution, in accordance with ASTM D422-63 [37]. Total organic carbon analyzer (TOC-V$_{CPN}$, SHIMADZU, Kyoto, Japan) was used to determine the organic carbon fraction (f_{oc}) in the soil. Soil pH was determined using ASTM D4972-13 [38]. For cation exchange capacity, ammonium acetate and potassium chloride were used as extractants to obtain first the soluble salts and then the bound or

Table 1
Soil physicochemical properties.

Soil property	Measured value
Liquid limit	64
Plastic limit	35
e_{max}	3.1
e_{min}	0.87
Organic carbon content (f_{oc})	0.45%
pH	5.2
Cation exchange capacity	3.75 meq/100 g of soil
Specific surface area	28.75 m^2/g