



Research article

Desorption and mobility mechanisms of co-existing polycyclic aromatic hydrocarbons and heavy metals in clays and clay minerals

Mohsen Saedi^{a,*}, Loretta Y. Li^a, John R. Grace^b^a Department of Civil Engineering, The University of British Columbia, 6250 Applied Science Lane, Vancouver, British Columbia, Canada, V6T 1Z4^b Department of Chemical and Biological Engineering, The University of British Columbia, 2360 East Mall, Vancouver British Columbia, Canada, V6T 1Z3

ARTICLE INFO

Article history:

Received 16 December 2016

Received in revised form

16 February 2018

Accepted 16 February 2018

Keywords:

Heavy metals

PAHs

Desorption and mobility

Clayey minerals

Kaolinite

Bentonite

ABSTRACT

The effects of soil components such as clay minerals and as humic acids, as well as co-existing metals and polycyclic aromatic hydrocarbons, on desorption and mobility are examined. Three types of artificially blended clay and clay mineral mixtures (pure kaolinite, kaolinite + sand and kaolinite + sand + bentonite), each with different humic acid content, were tested for desorption and mobility of acenaphthene, fluorene and fluoranthene by three extracting solutions CaCl₂ (0.01 M) and EDTA (0.01M) with non-ionic surfactants (Tween 80 and Triton X100). Heavy metals (Ni, Pb and Zn) were also studied for desorption and mobility. The influence of co-present metals on simultaneous desorption and mobility of PAHs was investigated as well. The results showed that <10% of metals in the clay mineral mixtures were mobile. Combined EDTA and non-ionic solutions can enhance the desorption and mobility of PAHs to >80% in clay mineral mixtures containing no sand, while in the same soils containing ~40% sand, the desorption exceeded 90%. Heavy metals, as well as increasing humic acids content in the clay mineral mixtures, decreased the desorption and mobility of PAHs, especially for soils containing no sand, and for fluoranthene compared with fluorene and acenaphthene.

© 2018 Elsevier Ltd. All rights reserved.

1. Introduction

Soil contamination by polycyclic aromatic hydrocarbons (PAHs) is widespread in most developed countries such as Canada and USA (USEPA, 2004; CCME, 2010). The number of contaminated sites was estimated to be 294,000 and 30,000 in the US (USEPA, 2004) and Canada (NRTEE, 2003), respectively. In the UK, the total number of contaminated sites needing remediation is 511, while 30,000 to 40,000 sites are affected by contamination (EUGRIS, 2016). The main contaminant sources are bitumen and oil from production plants, combustion processes, fuel and storage facilities and spills of petroleum and petroleum products during transportation (Abdel-Shafy and Mansour, 2016; CCME, 2010; Choi et al., 2009). Many of these anthropogenic sources of PAHs, particularly those from the oil and related industries, also release toxic heavy metals (HMs) into the environment. As a result, PAHs often co-exist with HMs in contaminated soils (Wang et al., 2004; Morillo et al., 2008; Thavamani et al., 2011, 2012). There is evidence that there are synergistic effects when PAH and HM contaminants co-exist, with

greater toxicity and decreased natural attenuation (Thavamani et al., 2011). As soil contamination with mixed contaminants has increased (Maliszewska-Kordybach and Smreczak, 2003; Saedi et al., 2012), rapid and effective removal of mixed contaminants to minimize adverse effects is emerging as a critical issue.

Current remediation technologies are mostly intended and designed for either organic or inorganic compounds. Rarely can they be applied efficiently for both organics and inorganics (Wick et al., 2011). Technologies to treat mixed PAHs (organic) and HMs (inorganic) contaminants are limited and more challenging for low-permeability soils due to high clay content (Reddy and Cameselle, 2009). Hydraulic fracturing is commonly used to enhance the formation permeability by creating fractures filled with high-permeability materials to deliver reactive agents to the subsurface. However, most traditional technologies fail to remediate mixed contaminants efficiently (Reddy and Cameselle, 2009). To devise an appropriate technological approach to remediate mixed contaminants in soil based on the extraction and mobilization of contaminants, synergistic effects among HM and PAH mobility, biodegradation and desorption in soil must be better understood.

The mobility of contaminants and their subsequent removal depend on their sorption affinities and kinetics in the soil. Soil

* Corresponding author.

E-mail address: msaedi@iust.ac.ir (M. Saedi).

properties, mineralogy and organic content also influence desorption and mobility of mixed contaminated soil. The quantity and form of organic matter in soil, humic substances and humic and fulvic acids all affect HM mobility, complexing and precipitation (Kaschl et al., 2002).

The mobility of PAHs may be influenced by both soil properties and the presence of other co-contaminants such as heavy metals, particularly at high concentrations (Weber et al., 2002). Non-ionic organic contaminants such as PAHs interact with soil organic matter (SOM) (Bancha-Szott et al., 2014; Saparpakorn et al., 2007). Heavy metal cations are also complexed by the organic molecules in soil solids or released into soil water systems (Gao et al., 2003, 2006; Zhang and Ke, 2004). Thus heavy metals in soil may play an important role in desorption, mobility and fate of PAHs in soils.

Fonseca et al. (2011) showed that the presence of phenanthrene as a co-contaminant can prolong the residence time of Pb in soil. Experiments to study Pb as a single contaminant and in the presence of phenanthrene were conducted using synthetic solutions such as (ethylenedinitrilo)-tetraacetic acid disodium salt (Na-EDTA) and/or polyethylene glycol dodecyl ether (Brij[®] 35 P) or polyethylene glycol sorbitanmonooleate (Tween[®] 80). Extraction levels close to 100% were obtained for soil contaminated only by Pb by applying EDTA or EDTA/B35, while only 48% and 55% of Pb and phenanthrene were extracted, respectively, with EDTA/B35 solution for co-contaminated soil. Fonseca et al. (2011) suggested that custom-composed solutions could enhance the solubilization of mixed organic and inorganic contaminants in soil.

The impacts of Zn, Cu, Al and Fe on partitioning and bioavailability of phenanthrene in soil were examined by Obuekwe and Semple (2013). Sequential extractability of 14C-phenanthrene was investigated using calcium chloride (CaCl₂), hydroxypropyl-β-cyclodextrin (HPCD) and dichloromethane (DCM). The presence of Cu and Al was found to result in larger amounts of 14C-phenanthrene being extracted by CaCl₂ and HPCD. The authors concluded that the presence of high concentrations of some metals can affect the mobility and accessibility of phenanthrene in soil, directly influencing the risks posed by PAH-contaminated soils.

The effects of other heavy metals (Cd, Cu, Pb and Zn) on the extractability of 14C-phenanthrene were studied by Saison et al. (2004) who reported higher adsorption in the presence of metals. They noted that this may be related to changes in the structural conformation of organic molecules in soils. Their results demonstrated that the fate of phenanthrene and PAHs in soil cannot be easily predicted, due to heavy dependence on co-pollution with metals. Such interactions had not been reported widely before, and the mechanisms of interaction of the different soil constituents with PAHs and metals are still not well known. These authors recommended that co-pollution should be taken into account when remediating contaminated soils, and proposed further studies to verify their assumptions.

Other studies (Zhou and Zhu, 2005; Cao et al., 2013) have also found that desorption of organics and some inorganics could be enhanced by chelating and surfactant solutions. High efficiencies of contaminants removal by surfactants have been reported. The remediation rate was shown to be accelerated, and a wide variety of contaminants could be removed. Limitations of this enhancement include low soil permeability, heterogeneity and insoluble contaminants such as PAHs (Bezza and Nkhalambayausi-Chirva, 2015). Another limitation is that surfactants are mostly effective on PAHs and chelating solutions on metals. None of the single solutions showed good efficiencies for both types of contaminants. Most recent work focuses on removal/desorption of specific PAHs (particularly phenanthrene), solely, or in the presence of a limited number of metals, using a variety of chelating agents, surfactants and other chemicals (Bezza and Nkhalambayausi-Chirva, 2015;

Song et al., 2008; Wang et al., 2008; Yan and Lo, 2013).

The aim of this paper is to investigate the impact of heavy metals (such as Ni, Zn and Pb, abundant in petroleum-contaminated sites) and humic acids (HA), solely and together, on desorption of both HMs and PAHs to improve the understanding of desorption and mobility of co-existing contaminants in various clay and blended clay minerals.

Our research tested artificially blended clay minerals. Heavy metals used in the experiments were those dominant in crude oil and petroleum products and most contaminated sites (Ni, Pb and Zn). PAHs studied were acenaphthene (ANA), fluorine (FL) and fluoranthene (FLAN) as they are abundant in contaminated sites and are among the 16 USEPA priority PAH pollutants. There is little information and published work on the mobility and desorption/remediation of these three PAHs, especially when they are mixed with heavy metals.

Our findings may be useful in remediation of fine contaminated soils containing co-existing metals and natural organic matter content, particularly when chemical desorption technologies are considered. We show that, even when the metal contents are less than those of soil criteria, the desorption efficiency of extracting solutions for PAHs removal may be considerably lower than expected. This paper also indicates decreased desorption efficiency resulting from the co-existence of selected heavy metals and humic acids.

2. Materials and methods

The clay-size components greatly influence the physical, chemical and biological activities of soil (CLBR, 1993). Clay minerals are dominant components of many Canadian soils (CLBR, 1993). Loamy, clayey and very fine clayey soils usually contain considerable amounts of clays, from about 27 to >60% (OMAFRA, 2016). Therefore, it can be expected that clay minerals are major components in many contaminated sites.

Because the remediation of PAHs co-existed by heavy metals in fine clayey soils is a challenge and needs to be better understood, this study focused on desorption and mobility characteristics of these mixed contaminants in clay mineral mixtures. Therefore, we selected the blending proportions of kaolinite, bentonite and sand so that all three resulting mixtures could still be classified as clayey soils. Two common clay minerals (kaolinite and bentonite) and sand were tested. By blending different proportions of these three base materials, three types of fine-grained clay mineral mixtures containing different proportions of clay were prepared. The first was pure kaolinite. Compared with other clay minerals, kaolinite has lower buffering and cation exchange capacity. It has been widely used as the model of clayey soil in laboratory experiments (Yuan et al., 2006, 2007; Ko et al., 1998). The second mineral mixture was kaolinite+sand, a coarser mixture with a lower content of kaolinite (60% w/w), but still clayey. The third type was a mixture of 43% w/w kaolinite, 42% w/w sand and 15% w/w bentonite, blended in such a way that the resulting mixture was clayey, but contained a small proportion of montmorillonite (the major constituent of bentonite).

2.1. Minerals, chemicals and enhancing agents

Kaolinite was obtained from International Laboratory, India (product number 1098578). Bentonite was purchased from Iran Barite Falat (P.L.C), Tehran, Iran. The sand, supplied by Amittis Azma Co., Tehran, Iran was a standard sand, with specification of ASTM C778 (ASTM, 2006). These three base materials had very low organic contents (<0.5%) and were uncontaminated. All three base materials were characterized for their mineralogy by X-ray

Download English Version:

<https://daneshyari.com/en/article/7477643>

Download Persian Version:

<https://daneshyari.com/article/7477643>

[Daneshyari.com](https://daneshyari.com)