Chemosphere 174 (2017) 28–38

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Removal of crude oil polycyclic aromatic hydrocarbons via organoclay-microbe-oil interactions

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HIGHLIGHTS

- Organo-montmorillonite and organo-saponite inhibit the biodegradation of dimethylnaphthalenes.
- Organo-saponite unlike organo-montmorillonite enhances the biodegradation of crude oil phenanthrenes.
- Organoclays sorb dimethylnaphthalenes extensively.
- Clays with relatively high CEC produces more hydrophobic organoclays and inhibit the biodegradation of PAHs.
- Unmodified montmorillonites enhances the biodegradation of PAHs except the LMWPAHs.

ARTICLE INFO

Article history:
Received 15 October 2016
Received in revised form
31 December 2016
Accepted 14 January 2017
Available online 23 January 2017

Handling Editor: Caroline Gaus

Keywords:
Polycyclic aromatic hydrocarbons
Biodegradation
Adsorption
Organo-clays,
Montmorillonite
Saponite

ABSTRACT

Clay minerals are quite vital in biogeochemical processes but the effect of organo-clays in the microbial degradation of crude oil polycyclic aromatic hydrocarbons is not well understood. The role of organo-saponite and organo-montmorillonite in comparison with the unmodified clays in crude oil polycyclic aromatic hydrocarbons (PAHs) removal via adsorption and biodegradation was studied by carrying out microcosm experiments in aqueous clay/oil systems with a hydrocarbon degrading microbial community that is predominantly *alcanivorax spp*. Montmorillonite and saponite samples were treated with didecyldimethylammonium bromide to produce organo-montmorillonite and organo-saponite used in this study. Obtained results indicate that clays with high cation exchange capacity (CEC) such as montmorillonite produced organo-clay (organomontmorillonite) that was not stimulatory to biodegradation of crude oil polycyclic aromatic compounds, especially the low molecular weight (LMW) ones, such as dimethylnaphthalenes. It is suggested that interaction between the organic phase of the organo-clay and the crude oil PAHs which is hydrophobic in nature must have reduced the availability of the polycyclic aromatic hydrocarbons for biodegradation. Organo-saponite did not enhance the microbial degradation of dimethylnaphthalenes but enhanced the biodegradation of some other PAHs such as phenanthrene. The unmodified montmorillonite enhanced the microbial degradation of the PAHs and is most likely to have done so as a result of its high surface area that allows the accumulation of microbes and nutrients enhancing their contact.

1. Introduction

So long as petroleum remains the main fossil fuel used as source of energy, spill incidents will likely remain inevitable. The spillage of crude oil and its fractions in the environment is responsible for many hydrocarbon polluted sites (Environmental agency, 2006). Soil contamination by hydrocarbons can cause extensive damage to the local ecosystems affecting vegetation and wildlife adversely. Such contamination can also present a serious public health threat and in extreme case, can render the contaminated area uninhabitable for humans (Sunggyu, 1995). Broadly speaking, there are three key sources of hydrocarbons through which releases of PAHs to the environment can occur, namely, petrogenic, pyrogenic and biogenic sources. PAHs in the environment as a result of oil spill and natural oil seeps are petrogenic whereas those arising from burning wood, volcanoes, petroleum products and forest fires could be regarded as pyrogenic. Biogenic sources include PAHs from biologic or diagenetic processes. Simpson et al. (1998) demonstrated that

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http://dx.doi.org/10.1016/j.chemosphere.2017.01.080
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the source of PAH input to the environment in the event of hydrocarbon contamination could be identified. Higher concentrations of retene and perylene in the environment are indicative of terrestrial organic inputs of biogenic origin while the predominant existence of lower molecular weight PAHs such as fluorene and acenaphthene indicates petrogenic origin. Higher concentrations of higher molecular weight PAHs (4–6 membered ring PAHs) such as fluoranthene, pyrene and benzo (a) pyrene in the environment are indicative of pyrogenic origin (Helfrich and Armstrong, 1986; Bence et al., 2007). Groundwater could also be at risk of contamination with PAHs from incidents of agricultural activities, improper waste disposal, underground oil storage tanks etc. Both natural and anthropogenic activities are responsible for the release of PAHs to the environment. Forest fires, volcanoes, biologic/diagenic processes and natural oil seepages etc represent the main natural sources of PAH in the environment while crude oil spills, municipal waste, and combustion of fossil fuels represent anthropogenic sources. PAHs are more recalcitrant to biodegradation than saturated hydrocarbons especially n-alkanes of equal molecular weight. The ability of PAHs to resist biodegradation in addition to their lipophilic nature account for why they persist in the environment and can penetrate tissues to bioaccumulate in organisms in the environment (Tuvikene, 1995; Boehm et al., 1981). Biomagnification of the PAHs takes place as they (the PAHs) are transferred to higher trophic levels in the food chain (Boehm et al., 1981). Very many PAHs have been reported to be mutagenic and carcinogenic making their control in the environment extremely important (ASTDR, 1995). The solubility of monoaromatic hydrocarbons such as benzene, toluene, ethylbenzene and xylene (BTEX) is higher than that of PAHs. Generally speaking, the solubility of aromatic hydrocarbons in water (though poor) decreases with increase in molecular weight and is the reason why the concentration of PAHs in water column is relatively low.

Organo-clays are mainly produced by the modification of 2:1 clay minerals such as smectites especially montmorillonites. The modification of clay minerals to produce organo-clays involves the replacement of the clay's interlayer exchangeable inorganic cation with a desired organic cation via ion-exchange reactions. This modification to produce organo-clay leads to a transformation from surface hydrophilcity to hydrophobicity (Hermosin et al., 1992; Groisman et al., 2004). Long chain alkyl ammonium cation such as didecyldimethylammonium (DDDMA) is used in the preparation of organoclay (Cornejo et al., 2008). Organoclays have been reported to be useful in the remediation of organic pollutants such as pesticides (Cornejo et al., 2008). However, it is not yet clear what role organoclays would play during the biodegradation of crude oil PAHs.

Previous organo-clay mediated biodegradation studies reported by different authors (Malakul et al., 1998; Biswas et al., 2015) involved only single PAHs as substrate such as naphthalene and phenanthrene respectively. It was demonstrated in these studies that organoclay enhanced the biodegradation of the above substrates. There are scarcely any known studies on the effects of organo-montmorillonites or organo-saponites on the biodegradation of mixed PAHs as found in crude oil. When studying the effect of organo-clays, or any other material, on the microbial degradation and adsorption of PAHs present in petroleum, it is essential to do so in the presence of numerous PAHs rather than individual PAH fractions so as to understand how the biodegradation and adsorption of the individual PAHs proceed in the presence of other PAHs. Hence, this study would seek to understand how the presence of other PAHs affects the removal of the individual PAHs via organo-clay mediated adsorption and biodegradation.

The effect of organoclays on the biodegradation of crude oil saturated fraction has been reported (Ugochukwu et al., 2013) however, our knowledge of the effect of organo-clays during biodegradation of crude oil PAHs is grossly limited. The result of the microcosm experiments carried out to investigate the ability of organo-clays in comparison with the unmodified clays to adsorb and stimulate or hinder the microbial degradation of crude oil PAHs is reported in this paper. The following objectives were pursued:

(i) To produce organo-clay with hydrophobic surface by having the DDDMA successfully intercalated
(ii) To investigate how the individual PAHs in crude oil respond to microbial degradation and adsorption on the organo-clays in the presence of other PAHs compared to unmodified clays?

2. Materials and methods

Bentonite (Berkbent 163) was supplied by Steetley Bentonite & Absorbent Ltd (now Tolsa UK Ltd; www.tolsa.com) while natural saponite was collected from the Orrock Basalt Quarry Burntisland, Scotland (National Grid Reference NT 218887; Cowking et al., 1983). Clay mineral samples used in this study were a saponite and a montmorillonite separated by fractionation from the altered basalt rock samples and from the reference bentonite Berkbent 163, respectively, following the method of Cowking et al. (1983) modified as follows: Approximately 1000 g of basalt rock was crushed to particle size less than 10 μm and soaked in a 5 L beaker filled with water to 4.5 L mark. This mixture was allowed to stand overnight and the supernatant liquid decanted and sonicated for 3 min. Gravity sedimentation was employed for the settling of the crushed Orrock Basalt rock so as to separate particle size less than 2 μm by progressive size fractionation applying Stoke's Law. The same procedure was repeated for Berkbent 163 Bentonite except that there was no crushing and overnight standing as this reference material is provided as a powdery material. The microbial communities that were involved in the microbial degradation of crude oil PAHs were isolated from beach sediment samples that were collected in sterilised glass bottle from a site at St Mary's Lighthouse near Whitley Bay, Newcastle Upon Tyne, United Kingdom (National Grid Reference: NZ 352 754) and stored at 4 °C in cold room until the commencement of the experiment. The microbial community has been reported to contain mainly Alcanivorax spp. as the dominant genera in another study carried out by Singh et al. (2009) conducted with exactly the same beach sediments as source of microbial cells.

The Bushnel-Haas (BH) broth as the nutrient source, nutrient agar and all other chemicals were supplied by Sigma Aldrich. The undegraded North Sea crude oil sample for the experiments was supplied by British Petroleum (BP).

2.1. Organo-clay preparation

The organo-clay minerals were prepared following the procedure reported in Ugochukwu et al., 2014a. Very succinctly, this procedure consisted in adding sufficient amounts of didecyldiammonium (DDDMA) bromide to the montmorillonite and saponite suspensions to reach 35% of their respective CEC followed by centrifugation, repeated washing of the clay with de-ionized water, drying and storing in a desiccator.

2.2. Characterization of the clay samples

2.2.1. XRD, FTIR, CEC, EGME-Surface area and TOC

The untreated saponite and montmorillonite and the prepared organo-clays were characterized in detail using various techniques. The method employed for the X-Ray Diffraction (XRD), Fourier