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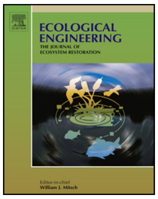

Assessment of sepiolite as a low-cost adsorbent for phenanthrene and pyrene removal: Kinetic and equilibrium studies

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ABSTRACT

The objective of this work is to identify and evaluate reactive materials that can serve as permeable reactive barriers to PAHs. The ability to of sepiolite to remove model PAHs, such as phenanthrene and pyrene, was tested in batch assays. The reactive material was assayed for individual PAHs and a mixture of PAHs at concentrations ranging from 50 to 400 μM. Initially, kinetics studies aimed at determining the behaviour of the system and the equilibrium concentration were conducted. The adsorption processes followed pseudo-second-order kinetics, with rate constants of 0.5027 and 0.2478 g μmol^{-1} h^{-1} for phenanthrene and pyrene, respectively. Moreover, it was determined that the mechanism that controls the sorption rate was the pore diffusion rate in this study system. Subsequently, equilibrium data were analysed by evaluating their Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherms. In all cases, the Freundlich isotherm exhibited the best fit to the experimental sorption data, suggesting that stronger binding sites on a heterogeneous surface are occupied first and that the strength of binding decreases with an increasing degree of site occupation. Finally, several successive batches were assayed using the same sepiolite to evaluate the behaviour of the clay matrix as a permeable reactive barrier. The conclusion of this study is that sepiolite can adsorb phenanthrene and pyrene. This finding has interesting implications for environmental treatment applications, such as providing a source of low-cost reactive material for groundwater treatment using permeable reactive barriers.

1. Introduction

Groundwater is a limited natural resource that may be considered as one of the most important components of our socio-economic framework. Groundwater provides enormous quantities of high-quality water for human activities such as agriculture, domestic uses and industry. Nevertheless, there are several sources of groundwater pollution as a result of anthropogenic activities, including septic tanks, agricultural areas where fertiliser or pesticides are used, underground storage tanks, and unauthorised dump sites. Thus, one of the consequences of groundwater pollution is the degradation of environmental quality, which poses a risk to public health (EPA, 1980).

In recent years, the amounts of emerging organic pollutants, such as polycyclic aromatic hydrocarbons (PAHs), found in the environment have increased (Pergent et al., 2011). PAHs primarily enter the environment as a result of anthropogenic activities, such as the combustion of fossil fuels, and their low solubility does not prevent their persistence in water bodies (Manoli and Samara, 1999). According to Mackay and Gschwend (2001), the hydrophobic organic compounds (HOCs) that are mobile in groundwater include both dissolved and colloid-associated species. Dissolved forms may include HOC molecules that are solvated by water or mixtures of water and non-aqueous solvents. The colloid-associated species include HOC molecules that are associated with macromolecular humic substances, biogenic exudates, micelles, microorganisms, and nanometre-to-micrometre-sized suspended mixed-phase solids. As result of the impacts of PAHs on the environment, these compounds are included in a list of pollutants provided by the United States Environmental Protection Agency and the EU Water Framework Directives (2000/60/EC) (EU, 2000; Haritash and Kaushik, 2009). In addition, current Spanish regulations allow only a small concentration of PAHs in waters, approximately 0.1–0.01 μM (Miñana et al., 2008).

The use of permeable reactive barriers (PRBs) for the treatment of a range of contaminants found in polluted groundwater is widespread throughout the world (Warner, 2011). The most common procedure for installing a PRB is to dig a trench in the

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Nomenclature

q_t	uptake (μmol g^{-1})
q_e	equilibrium uptake (μmol g^{-1})
q_m	maximum uptake (μmol g^{-1})
t	time (h)
C_e	equilibrium concentration (μM)
k_1	pseudo-first-order equilibrium rate constant (h^{-1})
k_2	pseudo-second-order equilibrium rate constant (g μmol^{-1} h^{-1})
α and β	Elovich coefficients
K_i	intra-particle diffusion rate constant (μmol (g h$^{0.5}$)$^{-1}$)
I	parameter of intra-particle diffusion model
k_L	Langmuir constant (μmol g^{-1})
b	Langmuir coefficient
k_F	Freundlich constant (μmol g^{-1}) μM)$^{-1/n}$
n	Freundlich coefficient
α	Dubinin–Radushkevich parameter (μmol^2 J^{-2})
ε	Polanyi potential
A	Temkin isotherm equilibrium binding constant (L g^{-1})
B	Temkin constant related to the heat of sorption (J μmol^{-1})

polluted area and fill it with an appropriate reactive material (Cobas et al., 2013). As contaminated groundwater flows through the structure, the reactive material removes the pollutants by adsorption, ion exchange, precipitation or oxidation–reduction reactions (Thiruvenkatachari et al., 2008). This technology has been widely studied for the removal of inorganic compounds such as metals or nitrates (Fiore and Zanetti, 2009; Moraci et al., 2011). However, the use of this treatment to remove emerging organic pollutants such as PAHs is in the initial stages, and the number of reactive mediums available for this type of pollutant remediation is limited.

The suitability of a reactive material depends, in part, on its cost-effectiveness in comparison with other materials. Thus, the assessment of alternative low-cost materials as potential sorbents for the removal of pollutants has recently received a significant amount of attention within the scientific community (Ali et al., 2012; Doke and Khan, 2013).

Activated carbon is a highly preferred sorbent because it is one of the most effective sorbents, yields high-quality treated water, and can be used for a variety of contaminants, including metals, phenols, dyes, pesticides, PCBs, detergents and a variety of organic compounds, such as PAHs (Gupta et al., 2009; Yadav et al., 2013). However, activated carbon presents some disadvantages associated with the high cost and the difficulties related to its regeneration and/or reuse (Marchal et al., 2013). Thus, low-cost sorbents such as agricultural wastes, clay materials, biomass, and seafood-processing wastes have been studied (Irem et al., 2013; Kocaoba, 2009).

For the selection of an appropriate reactive material, the general requirements of a porous structure, environmental suitability, mechanical stability, hydraulic conductivity, and transport retardation should be satisfied. Therefore, the material considered in this work as a potentially suitable reactive material for use in PRB technology was the natural clay sepiolite, which has already been studied in terms of its adsorption of inorganic pollutants and dyes (Gupta et al., 2009; Yuan et al., 2011). This material has a high sorption capacity and selectivity because of its high porosity and molecular-sieving properties (Liu et al., 2013). Furthermore, this clay is available in large quantities and at a low-cost (Ongen et al., 2012). To date, there have been a number of studies that have used modified sepiolite as a sorbent (Dimos et al., 2012; Malamis and Katsou, 2013), but the present study employs a natural sepiolite because the modification process would increase the price of a sepiolite PRB.

The objective of this work is to identify and evaluate the natural clay sepiolite as a reactive material for use in PRBs installed for the treatment of PAHs. To evaluate the potential of this low-cost material, studies of the kinetics, adsorption mechanisms and isotherms were conducted.

2. Materials and methods

2.1. Materials

In this study, phenanthrene (PHE) and pyrene (PYR) were used as the model PAHs. Both were obtained from Sigma Aldrich; the PHE and PYR had purities of 98% and 99%, respectively. The natural sepiolite clay was supplied by TOLSA, S.A (Spain). This sepiolite had a specific surface area of 263 m^2 g^{-1}. The mean pore diameter was 20.4 nm, and the pore size distribution was 0.04 cm^3 g^{-1} (micropores), 0.32 cm^3 g^{-1} (macropores) and 0.98 cm^3 g^{-1} (mesopores) (Belzunce et al., 1998).

2.2. Material characterisation

The elemental analysis of sepiolite was obtained by X-ray fluorescence with a Siemens SRS-300. The sepiolite surface was observed by obtaining electron microscopy images with a JEOL JSM-6700F using an accelerating voltage of 20 kV. Fourier-transformer infrared (FTIR) spectra were recorded (KBr) on a Jasco FTIR-4100 Model Fourier-transform infrared spectrometer to determine the surface modifications after adsorption of PAHs. These analyses were performed in the Scientific-Technological Research Support Centre (CACTI) at Vigo University.

2.3. Adsorption kinetics and equilibrium isotherm studies

The ability of sepiolite to remove representative PAHs, i.e., PHE and PYR, was tested in batch assays. The assays were performed in 250-mL Erlenmeyer flasks by mixing sepiolite with aqueous PAH solutions in a ratio of 1:50 (g/mL). The PAH solutions were prepared at the desired concentration (ranging from 50 to 400 μM of each PAH) using 2% acetone and 1% Tween 80 to assure the complete solubilisation of PAHs. This approach removes any influence of PAH solubility, which can be a factor in nature, as described by Mackay and Gschwend (2001). The flasks were agitated in a shaking incubator at 150 rpm and the temperature was maintained at 298 K.

The adsorption kinetics studies were conducted with initial PAH concentrations of 50 μM, for each individual PAH and with a mixture of the two PAHs 50 μM of each. The PAH concentration was measured periodically until the equilibrium concentration was achieved. To avoid disturbing the equilibrium, each experimental treatment was stopped at varying contact times. The adsorption equilibrium isotherm assays were performed with initial PAH concentrations that ranged from 50 to 400 μM, with the same concentrations of both PAHs in the individual and mixture solutions. The samples were extracted after reaching the equilibrium concentration (32 h).

The adsorption kinetics and equilibrium isotherm assays were performed in duplicate, and the reported results are the mean values.