Chemical Engineering Journal 233 (2013) 251–257

Contents lists available at ScienceDirect

Chemical Engineering Journal

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

Removal of polycyclic aromatic hydrocarbons from surfactant solutions by selective sorption with organo-bentonite

Wenjun Zhou [a,b,*], Xuehao Wang [a], Cuiping Chen [a], Lizhong Zhu [a,b]

[a] Department of Environmental Science, Zhejiang University, Hangzhou, Zhejiang 310058, China
[b] Zhejiang Provincial Key Laboratory of Organic Pollution Process and Control, Hangzhou, Zhejiang 310058, China

HIGHLIGHTS

- Organo-bentonite can selectively remove PAHs from nonionic surfactant solution.
- Surfactant recovery is feasible via selective sorption with organo-bentonite.
- Selectivity for surfactant recovery depends on the properties of surfactant and PAHs.
- The recycled CTMAB-bentonite can greatly increase surfactant recovery efficiency.

ARTICLE INFO

Article history:
Received 7 June 2013
Received in revised form 9 August 2013
Accepted 12 August 2013
Available online 21 August 2013

Keywords:
Selective sorption
Organo-bentonite
PAHs
Recovery
Surfactant solution
Soil washing

ABSTRACT

Surfactant-enhanced soil washing is known to be an effective remediation approach for contaminated soils and groundwater. However, the recovery of surfactant solutions after soil washing is required for reducing the operation costs of the soil washing process. In this study, selective sorption with organo-bentonite was employed for the removal of polycyclic aromatic hydrocarbons (PAHs) from aqueous surfactant solution as a potential means of recovering surfactant solution after soil washing. The sorption of phenanthrene onto organo-bentonite from surfactant solution was well described by the pseudo-second-order kinetic model and the linear sorption isotherm model, respectively. PAHs can be effectively removed by organo-bentonite from surfactant solutions in a high proportion relative to the sorption loss of surfactant under all experimental conditions. The selectivity for PAH removal to surfactant sorption increased with increasing PAH hydrophobicity and surfactant hydrophilicity, but decreased with increasing surfactant concentration. However, increasing the organo-bentonite dose did not have obvious effect on the selectivity for surfactant recovery since it synchronously enhanced phenanthrene removal and surfactant sorption. The sorbent of organo-bentonite could be repeatedly used for recovering surfactant solution, which greatly reduced the sorption loss of surfactant and subsequently increased the selectivity for surfactant recovery considerably. The results suggest that selective sorption with organo-bentonite provides an alternative means of recovering surfactant solution after soil washing.

1. Introduction

Contamination of soils and groundwater by toxic and/or hazardous organic pollutants is a widespread environmental problem. The remediation of contaminated soils with hydrophobic organic compounds (HOCs) has become a major serious concern as the toxic, mutagenic, or carcinogenic properties of some HOCs, and most of HOCs are strongly and long-lastingly sorbed to soils due to their water-insoluble characteristics, making them unavailable for the remediation process. Recently, surfactant-enhanced soil washing has been suggested as a promising remediation technology for contaminated soils and groundwater because surfactants can greatly increase HOCs solubilization in aqueous solution by partitioning them into the hydrophobic cores of surfactant micelles, thereby enhancing the desorption and removal of HOCs from contaminated soils [1–5]. During the soil washing process, however, large volumes of waste soil washing solution containing HOCs are generated; such a solution pose potential toxic hazards to the environment and must be treated after soil washing. In addition, surfactant-enhanced soil washing is often not economically acceptable due to the high cost of the washing agent. These factors are expected to potentially influence the practical implementation of soil washing technology.

Recovering and then recycling surfactant solutions is one of the most economical and effective strategies for treating waste soil washing solutions and reducing operation costs for soil washing

---

* Corresponding author at: Department of Environmental Science, Zhejiang University, Hangzhou, Zhejiang 310058, China. Tel./fax: +86 571 88982591.
E-mail address: wenjunzhou@zju.edu.cn (W. Zhou).

1385-8947/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.cej.2013.08.040

technology. In recent years, some technologies and methods were tested in order to recover surfactant solutions, including precipitation, ultrafiltration, solvent extraction, photochemical treatment, and electrochemical treatment [6–11]. However, most of these methods are limited by a high energy requirement, complex operating process, limited application range, or high treatment cost [12]. Therefore, it is necessary to develop alternative treatment approaches of recovering surfactant solutions after soil washing that are more simple, economical, and effective.

Sorption treatment has been regarded as a promising separation and purification method, as it has the advantages of high efficiency, lower cost, and easy operation. Selectively removing HOCs from waste soil washing solution by sorption treatment may be a simple and economical method for the recovery of surfactant solution. For this, it is crucial to overcome the problem of the retention of surfactant micelles for HOCs in aqueous solution and to selectively remove HOCs from aqueous solutions in a high proportion, relative to the sorption of surfactant onto adsorbent. Hence, the selection of an appropriate sorbent is the key factor for efficient surfactant recovery by the sorption process. In some previous studies [12–15], activated carbon was investigated to selectively remove HOCs from surfactant solutions and it exhibited high selectivity for HOC removal. However, the high price, low saturated adsorption capacity, competitive adsorption of coexisting HOCs, and difficulties in regeneration may limit the practical application of activated carbon. Hence, more alternative sorbents need to be investigated for their performance in surfactant recovery as they may offer more promising properties.

Organo-bentonites have been widely employed for the removal of organic pollutants from aqueous solution over the last few decades, owing to their high efficiency and cost-effectiveness [16,17]. They have also shown high removal capabilities for organic pollutants, especially for HOCs [16–19], because the modification of natural bentonite with a surfactant creates a favorable organic partition medium for HOCs [20,21]. Some previous studies also indicate that the surfactant-derived organic medium on organo-bentonite is more effective for HOC partition than surfactant micelles in aqueous solution [22,23]. More advantageously, organo-bentonite can simultaneously remove many types of HOCs by the partition mechanism, and organo-bentonite samples can be repeatedly used for HOC removal due to their high sorption capacity for HOCs. Therefore, organo-bentonites would be excellent adsorbents for selectively removing HOCs from soil washing solution and recovering surfactant solutions after soil washing. However, there is limited information available on the performance of organo-bentonites for selectively removing HOCs from surfactant solutions.

In this study, selective sorption of polycyclic aromatic hydrocarbons (PAHs) from nonionic surfactant solutions by an organo-bentonite was investigated for various surfactant concentrations, sorbent doses, types of PAHs, and surfactants. Further, the feasibility and efficiency of selective sorption with organo-bentonite used for surfactant recovery were evaluated by using a parameter of selectivity for PAH removal to surfactant sorption. The recycling of organo-bentonite for PAH removal and surfactant recovery was also investigated. The objectives were to investigate the performance of selective sorption with organo-bentonite in selectively removing HOCs from surfactant solutions, and to then develop an alternative method of recovering surfactant solutions after soil washing.

2. Materials and methods

2.1. Materials

Phenanthrene, pyrene, fluorene, and acenaphthene were selected as representative PAHs to model HOCs, and obtained from Acros Organics (USA) at 98+% purity. Three Triton series surfactants, Triton X-114 (TX114), Triton X-100 (TX100), and Triton X-305 (TX305), were selected as model nonionic surfactants (Acros Organics, USA) and used without further treatment. Selected physicochemical properties of PAHs and surfactants are presented in Table 1.

A natural bentonite (Na^+-montmorillonite) was collected from Inner Mongolia, China. The organic carbon content, specific surface area (BET-N_2), and cation exchange capacity (CEC) of natural bentonite are 0.040%, 60.9 m^2/g, and 105 mEq/100 g, respectively. A cationic surfactant of cetyltrimethylammonium bromide (CTMAB, $CH_3(CH_2)_{15}(CH_3)_3NBr$) was obtained from Sigma–Aldrich Company (USA) at reagent grade. Organo-bentonite was prepared by modifying the natural bentonite with CTMAB at 1.0 times CEC using the methods described by Zhu et al. [18], and the final product was labeled as CTMAB-bentonite.

2.2. Batch sorption experiments

All batch sorption experiments were conducted in triplicate with 22-mL Corex centrifuge tubes (Teflon-lined screw caps), in which a certain amount of CTMAB-bentonite was mixed with 20 ml of aqueous solutions containing PAHs and surfactants. These tubes were equilibrated on a reciprocating shaker for 6 h at 20 ± 1 °C and then centrifuged at 3000 rpm for 20 min. An appropriate aliquot of the supernatant was removed and analyzed for PAHs and surfactants by HPLC. The sorption amounts of PAHs and surfactants on CTMAB-bentonite were calculated according to the difference between their initial and equilibrium concentrations in aqueous solutions.

Sorption kinetics experiments were conducted to determine equilibrium time for the sorption of phenanthrene onto CTMAB-bentonite from TX100 solutions, for which the tubes with aqueous solutions containing phenanthrene (20.0 mg/L), TX100 (2.0 or 4.0 g/L), and CTMAB-bentonite (1.0 or 2.0 g/L) were shaken for 12 h, and the sorption amounts of phenanthrene were measured at specified time intervals by the methods mentioned above.

All batch experiments for PAH sorption and removal were conducted at a fixed concentration of 20.0 mg/L for PAHs, which corresponds to the maximum concentration of PAH in the washed surfactant solution for the contaminated soils with 200 mg/kg of PAH after soil washing in a solid-aqueous ratio of 1:10, and the effects of surfactant concentration and sorbent dose were determined with a fixed CTMAB-bentonite dose of 1.0 g/L or TX100 concentration of 4.0 g/L. The effect of surfactant structure and PAH properties were also examined at fixed surfactant concentration of 4.0 g/L and CTMAB-bentonite dose of 1.0 g/L. All the batch sorption experiments in this study were conducted at the nature pH or ionic strength of surfactant solutions and did not use buffer or salt solution.

Table 1
Selected physicochemical properties of PAHs and surfactants.[a]

Compounds	Molecular formula	Molar mass	Log K_{ow}[b]	HLB[c]	CMC[d] (mg/L)
Acenaphthene	$C_{12}H_{10}$	154.21	3.92	–	–
Fluorene	$C_{13}H_{10}$	166.22	4.18	–	–
Phenanthrene	$C_{14}H_{10}$	178.23	4.57	–	–
Pyrene	$C_{16}H_{10}$	202.26	5.18	–	–
Triton X-114	$C_8H_{17}C_6H_4O(OCH_2CH_2)_8H$	558.75	–	12.3	117
Triton X-100	$C_8H_{17}C_6H_4O(OCH_2CH_2)_{9.5}H$	625	–	13.5	194
Triton X-305	$C_8H_{17}C_6H_4O(OCH_2CH_2)_{30}H$	1526	–	17.3	1770

[a] PAHs data from Yaws [24]; surfactants data from Zhou and Zhu [25].
[b] K_{ow}, octanol–water partition coefficient.
[c] HLB, hydrophile–lipophile balance.
[d] CMC, critical micelle concentration.