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A new kinetic model for absorption of oil spill by porous materials

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ABSTRACT

A new kinetic model has been presented, based on combination of linear driving force and fractal like approaches, for correct modeling of oil spill absorption by porous material. The derived kinetic equation is able to describe maximum capacity of porous material and diffusion coefficient of oil into pores. In this new model, the presence of various pores with different sizes is considered, accounting for real systems. The basis of this new model is the presence of different pores with different diffusion coefficients and also changes of pores filling with time based on their sizes. The presented equation has been used for kinetic modeling of oil spill absorption by different porous materials, very well.

1. Introduction

Unintentional discharge of oil in aquatic ecosystem, frequent oil spill accidents in the oil exploration, transportation and processing have been a major challenge on a global scale [1]. The oil spill contaminants must be cleaned quickly and efficiently because of their catastrophic effects on the ecosystem [2]. There are different methods including in-situ burning [3], skimmers [4] and utilization of oil absorbing material [5] for oil and organic solvents cleanup from water. Absorption by using porous materials is generally considered as one of the most effective techniques for removal of spilled oil.

Different hydrophobic materials are reported recently, which can be used effectively for oil spill cleanup, including porous carbon [6], porous aerogel [7,8], leophilic foams [9] and highly oleophilic and highly hydrophobic sponge [10]. The mechanism of oil collection by these materials is absorption, because oil is penetrate to pores of these materials and fill all of them.

One of the most important factors in oil spill cleanup by these materials is the rate of absorption, and it is clear that the higher rate is desirable. Most of researchers have investigated the time dependency kinetics of oil spill cleanup by prepared hydrophobic porous materials [6,8,10,11]. Some of researchers have tried for time dependency modeling of oil spill cleanup by porous materials using different kinetic models. One of these models is diffusion model [6].

$$m'_t = A\sqrt{t} + B \tag{1}$$

which considers a linear relationship between mass of absorbed oil per unit area of porous material (m'_t) and $\sqrt{t}$. This model is very simple but it is not valid for all systems and also does not give any information about maximum capacity of absorbent.

Two other models, having been used for kinetic of oil spill cleanup by porous materials are pseudo first order and pseudo second order models [7,8,11–15].

$$q_t = q_e\left(1 - e^{-k_1 t}\right) \quad \text{or} \quad \ln\left(1 - \frac{q_t}{q_e}\right) = -k_1 t \tag{2}$$

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \quad \text{or} \quad \frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 q_e^2} \tag{3}$$

Although, Eqs. (2) and (3) have been fitted successfully to experimental data from the mathematical viewpoint, but, in our opinion these fittings are questionable from physical viewpoint. Because these equations are basically for adsorption but not for absorption. As it was presented theoretically by our research group, both of these equations can be derived from Langmuir kinetic model [16] accounting for monolayer adsorption. Also other theoretical models for derivation of these equations are based on

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monolayer adsorption [17]. On the other hand, k_1 and k_2 are the rate coefficients of adsorption having been reported theoretically [16] and experimentally [18–21] that are dependent to the initial concentration of adspecies. But in the case of oil spill absorption, initial concentration is not meaningful, and therefore the physical meaning of k_i for this process should be modified. Also, for adsorption experiments, it has been found that q_e, as the equilibrium amount of adspecies, is a function of initial concentration of solute, which also is not meaningful for oil absorption. So, for oil absorption studies, instead of equilibrium adsorbed value, maximum absorbed value has to be defined.

The purpose of this work is to present a new simple kinetic model for time dependency modeling of oil spill cleanup by porous materials considering physical aspects of the process including: (a) "absorption" not "adsorption", (b) maximum capacity of absorbent, (c) physical meaning of the rate coefficient and (d) presence of different pores for absorption.

2. Theory

In the simplest form, it can be assumed that the driving force for migration of oil into pores of hydrophobic porous material is $m_{max}-m_t$, where m_t is the mass of oil absorbed per unite mass of absorbent at any time and $m_{\max}$ is the maximum oil capacity per unit mass of absorbent. Therefore $m_{max}-m_t$ refers to the available empty pores able to absorb oil at any time. If the rate of oil removal (dm_t/dt) has a linear relationship with the driving force ($m_{max}-m_t$), one has:

$$\frac{dm_t}{dt} = \beta(m_{\max} - m_t) \tag{4}$$

where β can be considered as an apparent mass transfer coefficient and is related to the apparent diffusion coefficient (D_{app}) of oil into the pores (i.e. $\beta \propto D_{app}$). Since the relation between the rate and the driving force is linear in Eq. (4), this equation can be called linear-driving force (LDF) model as similar to the adsorption models [22,23]. By integration of Eq. (4) at boundary conditions, $t = 0$, $m_t = 0$ and $t = t$, $m_t = m_t$, one arrives to:

$$m_t = m_{\max}[1 - \exp(-\beta t)] \tag{5}$$

or

$$\ln\left(1 - \frac{m_t}{m_{\max}}\right) = -\beta t \tag{6}$$

Although the Eq. (6) is mathematically similar to Eq. (2), but its constants have different physical meanings.

In the next step, we are going to improve Eq. (5) or (6) for more realistic systems. It is clear that porous materials have different pores with dissimilar sizes or shapes. Therefore, the rate of diffusion of a liquid into these pores is different.

It has been reported that liquids at first penetrate to smaller pores [24,25]. So, in the process of oil spill absorption by foams, aerogel or other porous materials at first oil fills the smaller pores and subsequently to the bigger ones. In order to account this fact in Eq. (5) or (6), it is considered a schematic of pores in Fig. 1a showing typically three pores (*A, B, C*) with different diameters in a solid sample. Since, their sizes are different, the corresponding diffusion coefficients (D_A, D_B, D_C) are different too, i.e.

$$D_A > D_B > D_C \tag{7}$$

The time progress of oil absorption into pores is presented in Fig. 1b–e. As shown in these Figures, the fluid, at first fills the smaller pores, then, the medium and finally the bigger one. So, by switching of filling from one pore to other pores, the diffusion coefficient changes too. For the case of Fig. 1c, the apparent diffusion coefficient, D_{app}, is:

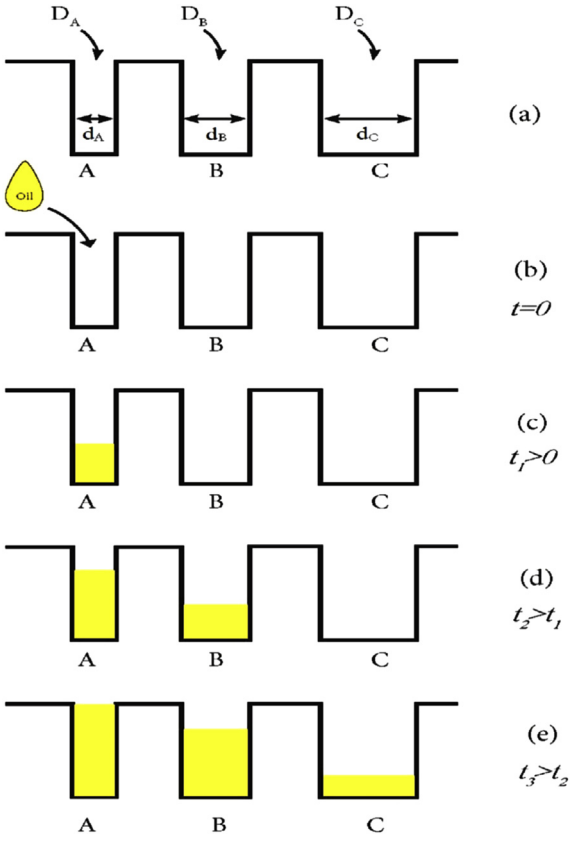

Fig. 1. Schematic representation of oil absorption process as a function of time in various pores. A, B, C are three pores with different diameters for absorption of oil.

$$D_{app} = D_A \quad (\text{for } t_1 > 0) \tag{8}$$

For Fig. 1d is

$$D_{app} = \omega_{A(t)}D_A + \omega_{B(t)}D_B \quad (\text{for } t_2 > t_1) \tag{9}$$

where $\omega_{A(t)}$ and $\omega_{B(t)}$ are the weight factors for diffusion coefficients of absorption into pores *A* and *B*, respectively. It should be noted that $\omega_{A(t)} + \omega_{B(t)} = 1$. The subscript (t) for $\omega_{(t)}$ indicates that the weight factors are changing with time.

For Fig. 1d, the apparent diffusion coefficient is:

$$D_{app} = \omega_{A(t)}D_A + \omega_{B(t)}D_B + \omega_{C(t)}D_C \quad (\text{for } t_3 > t_2) \tag{10}$$

In this case $\omega_{A(t)} + \omega_{B(t)} + \omega_{C(t)} = 1$ but $\omega_{A(t)} < \omega_{B(t)} < \omega_{C(t)}$. Eq. (10) is valid for a solid with three different pores, while a real solid includes a lot of pores having different sizes. So, for a real solid one can write:

$$D_{app} = \sum_{i=A}^{n} \omega_{i(t)}D_i \tag{11}$$

with the following constrain:

$$\sum_{i=A}^{n} \omega_{i(t)} = 1 \quad (i = A, B, C, \ldots, n) \tag{12}$$