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EXPERIMENT SIMULATING THE WASHED-OUT BEHAVIOR OF ALKYLPHENOLS DURING WATERFLOODING

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Summary

The contact of injection water and crude oil during the water injection process leads to the leaching of water-soluble phenolic compounds available in oil composition. The rate of decline in alkylphenol concentration in the injection water due to leaching depends on many factors related to the oil - water partition coefficient, oil saturation, interstitial velocity of phases, and dispersion coefficient.

This paper presents an experimental study combined with an analytical model to evaluate the relationship between washed-out rate and partition coefficients of some short-chain alkylphenols during oil - water interaction. The water - oil displacement experiment was carried out on a column packing glass beads, in which the packed column was initially saturated with Su Tu Nau crude oil at a temperature of 40°C. Our research results show that in a given flow regime the washed-out rate of alkylphenols differentiates from each other mainly due to the partition coefficient, thereby suggesting the possibility of using alkylphenols as a tracer to determine residual oil saturation in the sweeping area of the injection water.

Key words: Alkylphenol, partition coefficient, washed-out rate, oil saturation.

1. Introduction

Short-chain alkylphenols (C_0 - C_3) are commonly found in organic sedimentary compounds, including crude oil. In the 1990s, the initial presence of alkylphenols in crude oil was believed to originate from alkylation reactions and isomerization of precursor compounds in source rocks during the petroleum formation process. However, this approach did not explain the origin of all the observed alkylphenols in crude oil [1 - 3]. Recently, a wealth of experimental evidence suggests that the formation of alkylphenols may be linked to the hydroxylation of alkylbenzenes catalyzed by Lewis acids in sedimentary environments [4 - 6]. Accordingly, depending on the source of organic matter, the concentration of alkylphenols in crude oil varies significantly [7, 8]. After formation, the concentration and relative proportions of alkylphenol isomers are primarily controlled by partitioning between phases [9, 10]. The presence of the hydroxyl group in the molecule makes alkylphenols readily distribute from the oil phase to the water phase and mineral matrix both at the surface and subsurface conditions. The concentration of phenol (C_0) and cresols (C_1) in water tends to dominate over C_2 - C_3 alkylphenols, while higher isomers are typically more abundant in oil. Laboratory studies on the oil - water partition properties of alkylphenols had been conducted by Taylor, Bennett, and Larter [11, 12].

The impact of partitioning on the concentration of alkylphenols during the interaction of oil with injected water in the exploitation process, more specifically, results in alkylphenols being washed away from the oil phase into the water phase at the oil - water interface, leading to a gradual decrease over time in their concentration in both phases [13]. The rate of decrease in concentration (or wash-out rate) of alkylphenols in the produced water provides information about fluid velocity, oil - water interaction process, and oil saturation. The efforts to harness the potential use of alkylphenols as natural tracers in assessing oil saturation and determining the contribution of injection wells to production wells have been carried out by the Tracer Laboratory at the Center

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for Applications of Nuclear Technique in Industry (CANTI) for several years [14, 15]. Recently, an analytical model describing the transport of alkylphenols as they leach from oil phase into water phase during waterflooding has been proposed by Huong et al [16]. Currently, this study investigates the correlation between the wash-out rate and the partition coefficient of alkylphenols regarding their concentration history using both analytical and experimental models. Validating the above correlation will form the basis for proposing a methodology to determine residual oil saturation by matching the production profiles of alkylphenols with a mathematical model.

2. Materials and methods

2.1. Laboratory column experiment

A laboratory experiment to simulate the leaching process of alkylphenols was conducted through a water - oil displacement regime on a column packing glass beads. The experimental setup is presented in Figure 1, under experimental conditions at a temperature of 40°C and atmospheric pressure.

The physical model used in this study is a stainless steel column (SS316L) with a length of 30.5 cm and an inner diameter of 1.57 cm. The column is packed with laboratory-grade glass beads with an average diameter of 100 - 150 µm and a bulk density of 2.7 g/cm^3. The porosity of the packed column is 41.2%, corresponding to a pore volume (PV) of 24.3 cm^3.

At the initial conditions, the packed column is saturated with Su Tu Nau crude oil (°API = 39.8). The density of the crude oil under experimental conditions is 0.82 g/cm^3. The crude oil contains six alkylphenol compounds, including phenol (P), 4-methylphenol (4MP), 2-methylphenol (2MP), 3,4-dimethylphenol (34DMP), 2,4-dimethylphenol (24DMP), and 4-ethylphenol (4EP), with initial concentrations ranging from 100 to 500 mg/L. Laboratory-grade deionized water is used as the injection fluid in this experiment. The density of the water under experimental conditions is 0.992 g/cm^3. The partition coefficients (K_d) of the alkylphenol compounds (APs) are measured under static contact between the oil - water phases at the experimental conditions.

The deionized water is pumped into the saturated oil column at a flow rate of 0.3 mL/min, and the water sample is collected separately over time until it almost reaches the state of residual oil saturation (66.8%) at a cumulative injection volume of 11 PV (pore volume). The concentration of alkylphenols in water samples is analyzed using a Dionex UltiMate 3000 high-performance liquid chromatography (HPLC) system with a DAD detector and a C_{18} column at the Laboratory of Physical Chemistry (VILAS-609) of the Center for Applications of Nuclear Technique in Industry (CANTI). The detection limit is approximately 10^{-7}, with a 95% confidence level and a measurement error of 3 - 5%. The analysis procedure for these alkylphenols was researched and completed by CANTI as part of the project funded by Vietnam's Ministry of Science and Technology [17]. Under the analytical conditions, the chromatogram on HPLC/DAD shows good separation for the six alkylphenol compounds, including phenol (P), 4-methylphenol (4MP),

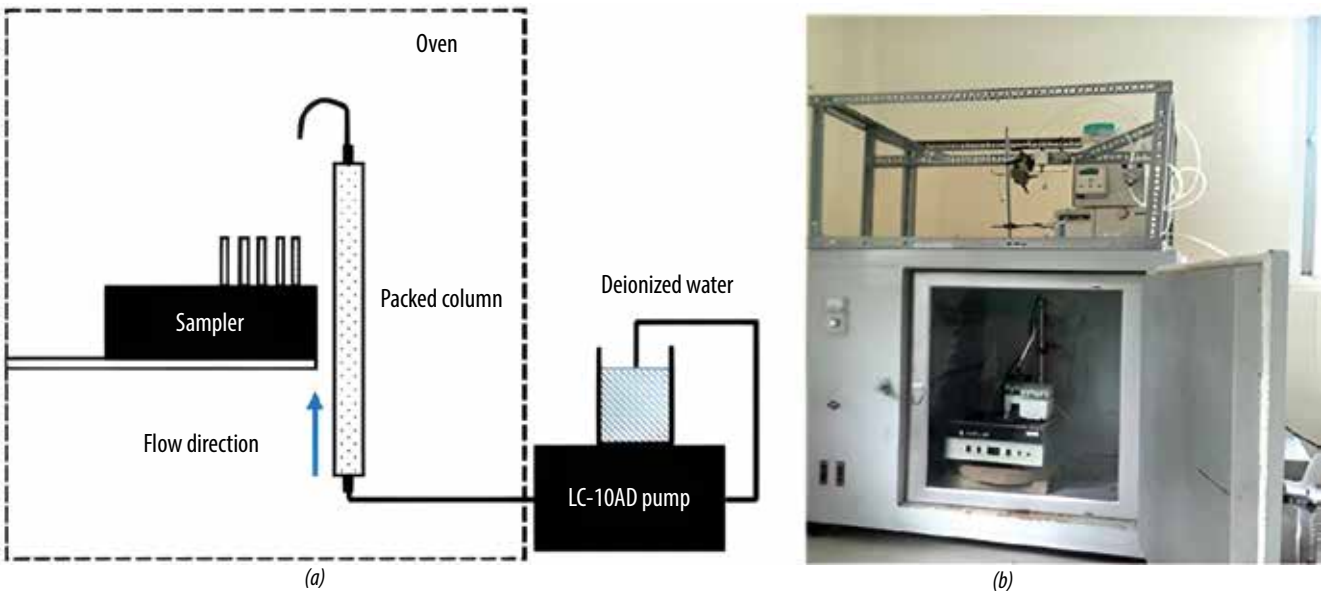


Figure 1. *Experimental setup diagram (a) and the experimental system at the Tracer Laboratory (CANTI) (b).*

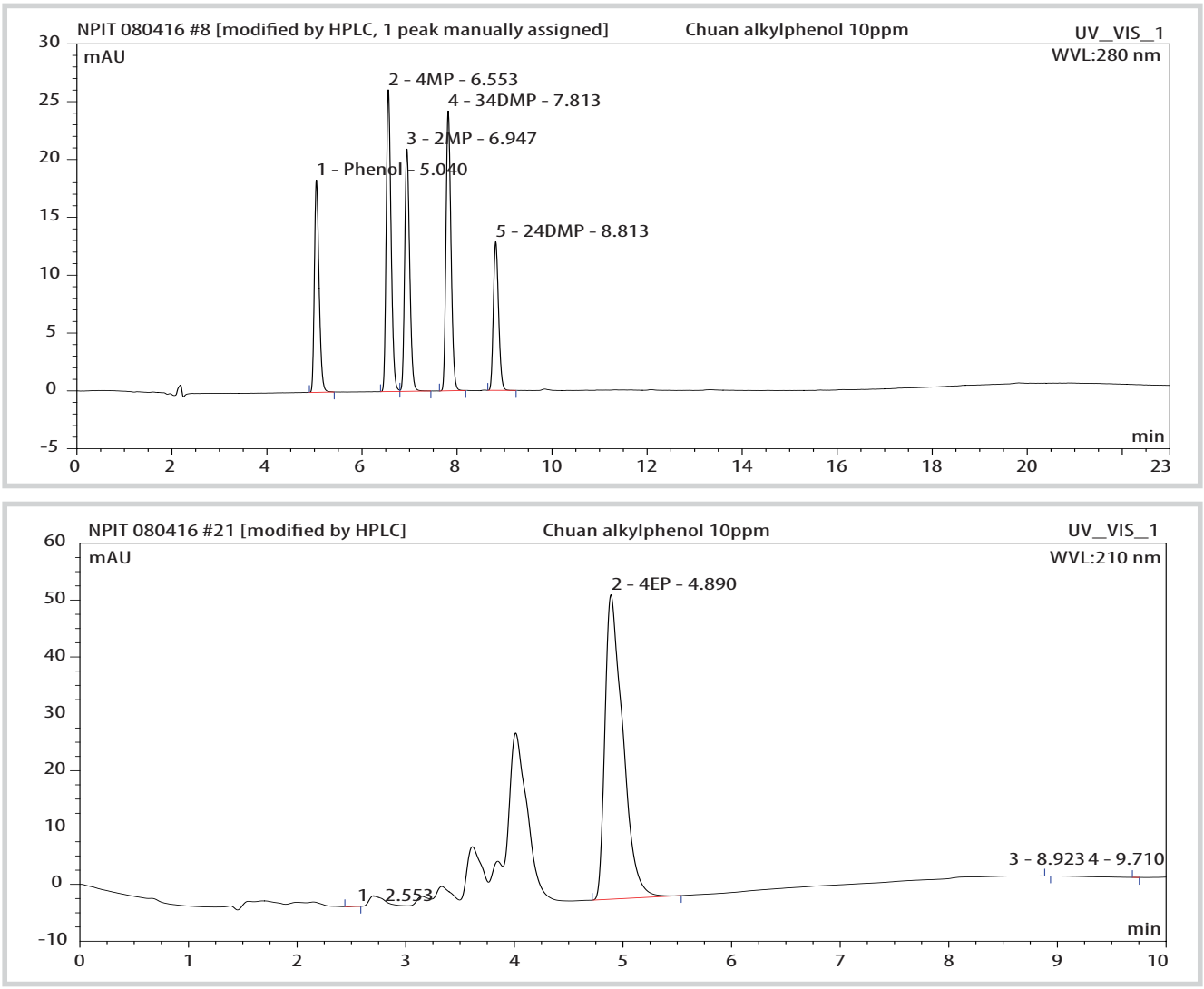


Figure 2. *Chromatographic analysis of standard samples of six alkylphenol compounds, including phenol (P), 4-methylphenol (4MP), 2-methylphenol (2MP), 3,4-dimethylphenol (34DMP), 2,4-dimethylphenol (24DMP), and 4-ethylphenol (4EP), on HPLC/DAD.*

2-methylphenol (2MP), 3,4-dimethylphenol (34DMP), 2,4-dimethylphenol (24DMP), and 4-ethylphenol (4EP), as illustrated in Figure 2.

2.2. Analytical model

Analytical model is used to analyze the leaching process of alkylphenols obtained from the experiment.

The transport of alkylphenols in porous media can be modeled using the advection-dispersion equation with a term of partitioning instantaneously between oil and water phases [18]. Suppose that the porous media is infinite homogeneous, the saturation of the two phases is constant, and the interstitial velocity of phases is constant in the pore, a one-dimensional (1D) analytical solution describing the concentration of alkylphenols in water phase $C_w(x, t)$ is expressed as equation (1) [16]:

$$\frac{C_w(x,t)}{C_0} = \frac{1}{2} \times \left[1 + Erf\left(\frac{x - \frac{C^*}{A} \times t}{2 \times \sqrt{\frac{B \times t}{A}}} \right) \right] \quad (1)$$

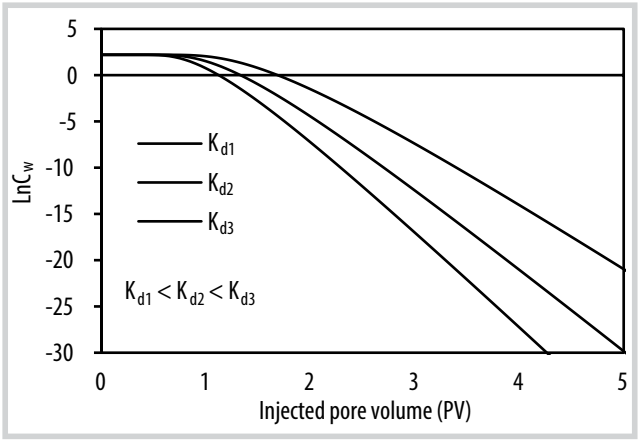
In which, C_0 is the initial concentration of alkylphenol in water phase [M/L^3]; A, B and C* are parameters depending on alkylphenol partition coefficient, oil saturation, dispersion coefficient in phases, and pore velocity of water and oil:

$$A = 1 + (K_d - 1) \times S_o$$

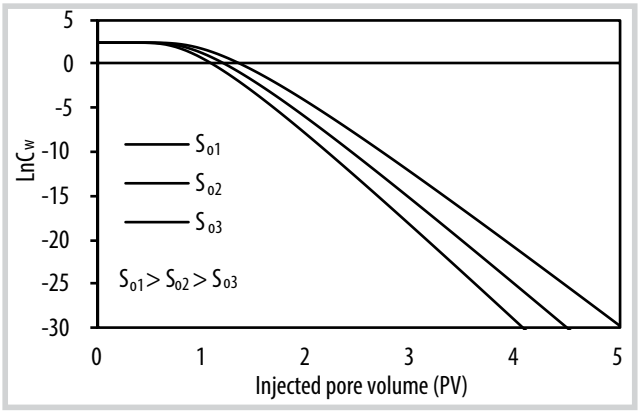
$$B = (1 - S_o) \times D_{Lw}^* + K_d \times S_o \times D_{Lo}^*$$

$$C^* = (1 - S_o) \times v_{wx}^* + K_d \times S_o \times v_{ox}^*$$

C_w is the alkylphenol concentration in water phase [M/L^3]; So is the saturation of oil phase (S_w = 1 - S_o is the saturation of water phase); K_d is the alkylphenol



(a)



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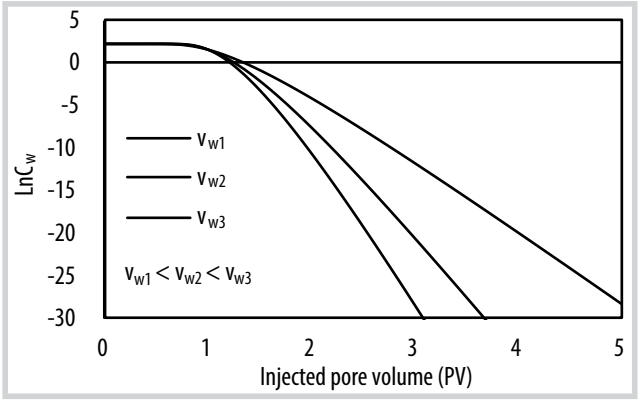


(c)

Figure 3. *Influence of the partition coefficient (a), oil saturation (b) and water interstitial velocity (c) on the decrease of LnCw according to the injected pore volume.*

partition coefficient defined as the ratio of alkylphenol concentration in oil phase and water phase at equilibrium conditions; v_w and v_o are the interstitial velocity of water phase and oil phase, respectively [L/T]; D_{Lw} and D_{LO} are the dispersion coefficient of alkylphenol in water phase and oil phase, respectively [L^2/T]; t is time [T]. When the injected volume is sufficiently large, LnC_w becomes nearly linear over time, with the slope of $\frac{C^{*2}}{4 \times A \times B}$ $[T^{-1}]$ representing the wash-out rate (a) of alkylphenols during water sweeping.

The analytical solution above shows a good agreement with the results of the numerical simulation of ¼ 5-spot model using the UTCHEM simulator [16]. The wash-out rate is inversely proportional to the partition coefficient of alkylphenols and the oil amount within the sweep zone of the injection water (as shown in Figure 3a, 3b). The increase in interstitial velocity of the water phase enhances the bulk movement of alkylphenols and mechanical dispersion related to local velocity variations in pore space. As a result, alkylphenols can be washed away more rapidly, as illustrated in Figure 3c. The typical interstitial velocity of the water phase during waterflooding in an oil field is approximately 10^{-5} m/s; under these circumstances, molecular diffusion does not significantly influence the transport of solutes within the reservoir [19, 20].

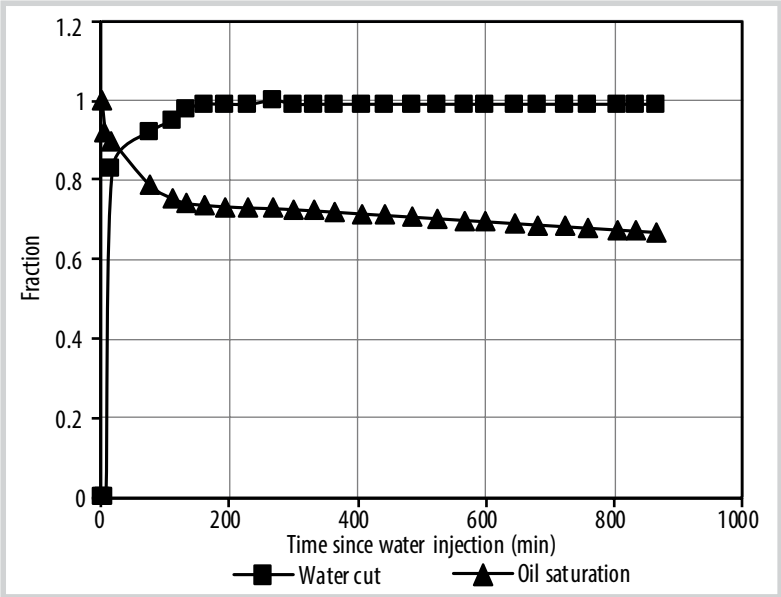
3. Results and discussion

Initial concentrations of six alkylphenol compounds in the oil phase and their partition coefficients (K_d) at the experimental conditions are detailed in Table 1.

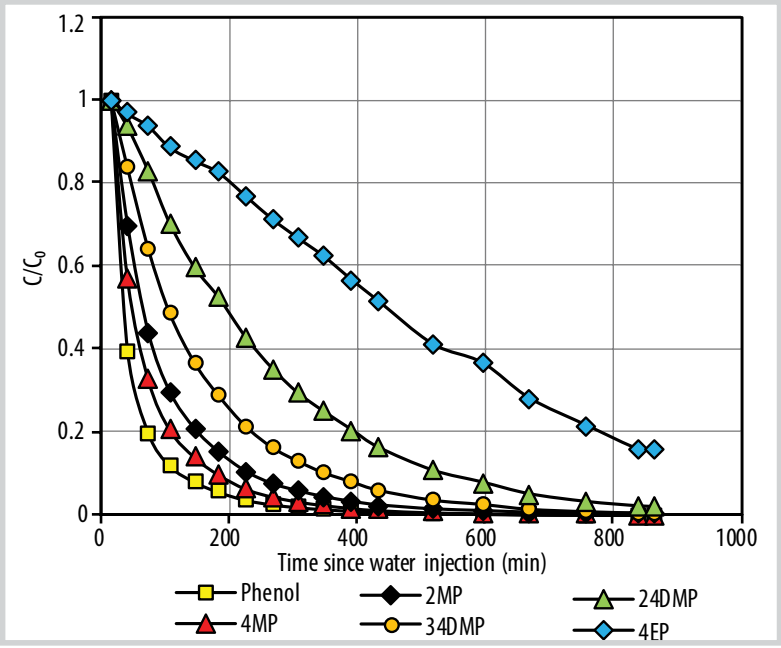
The process of displacing oil by water occurs over more than 14 hours, corresponding to an injection volume of 11 PV (pore volume). The water cut and oil saturation are plotted as functions of time in Figure 4a. The state of residual oil saturation is considered the condition where the remaining oil is trapped in the pore space and cannot be further recovered under the same injection conditions. In this experiment, the residual oil saturation is considered to reach 66.8% when there is a 1% difference between two consecutive oil saturation values.

The relative concentration (C/C_0) of six alkylphenols in water phase at the column outlet over injection time are shown in Figure 4b; C is the alkylphenol concentration and C_0 is the alkylphenol concentration at the beginning of water injection. The data show that the concentration of alkylphenols in the water phase gradually decreases during the injection, as depicted in Figure 4b. In a such clear representation, the decrease in the concentration of alkylphenols differentiates from each other. This washed-out rate characterizes the interaction between oil and water and can be analyzed using analytical model.

The relative concentrations C/C_0 obtained from both the experiment and the analytical model in equation (1) are compared and contrasted, as expressed in Figure 5a. In equation (1), interstitial velocity and dispersion coefficient are defined as follow:



(a)



(b)

Figure 4. *Experimental results: Water-cut and oil saturation in fraction (a), and alkylphenol relative concentration in water phase at the column outlet over injection time (b).*

- Interstitial velocity of water phase (i = w) and oil phase (i = o) are determined as a function of flow rate (Q), phase fraction (f_i), cross-sectional area (A_s), porosity (ϕ) and phase saturation (S_i):

$$v_{xi}^{*} = \frac{Q \times f_i}{A_s \times \varphi \times S_i} \quad (2)$$

- Hydrodynamic dispersion of alkylphenols in water phase (i = w) and water phase (i = o) are expressed as equation (3):

$$D_{Li}^{*} = \frac{D_{m,i}}{F \times \varphi} + \alpha \times v_{xi}^{*1.2} \quad (3)$$

In which, $F = \phi^{-m}$ is the formation factor (m = 1.3 for glass-bead [21]); α is the dispersivity; v_i^* is the interstitial velocity of phase. This study utilizes the molecular diffusion coefficients of alkylphenol in water phase of $D_{m,w} = 7.8 \times 10^{-10}$ (m^2/s) and in oil phase of $D_{m,o} = 3.8 \times 10^{-10}$ (m^2/s) which are referenced from O. Huseby [18].

The root mean square error (RMSE) between the relative concentrations (C/C_0) obtained from the experiment and the analytical model falls within the range of 0.02 to 0.2 when the water cut, f_w, is close to unit (2 - 11 PV, corresponding to 162 - 864 minutes). Detailed results are presented in Table 2. The matching result also indicates the dispersivity of the porous media as α = 10 cm.

In the late stage of waterflooding (f_w is close to 1), the wash-out rate of alkylphenols (a) is quantified through the slope coefficient representing the linear relationship of $Ln(C_w)$ over time, with a maximum value of 0.009

Table 1. *The concentration of alkylphenols in the oil phase and their corresponding partition coefficients under experimental conditions*

APs	Partition coefficient $K_d = C_o / C_w$	Initial concentration in oil phase (mg/L)	Detection limit of APs in water phase (mg/L)
Phenol	1.0	134	0.03
4-methylphenol (4MP)	1.3	128	0.06
2-methylphenol (2MP)	1.5	137	0.03
3,4-dimethylphenol (34DMP)	2.1	194	0.10
2,4-dimethylphenol (24DMP)	3.1	291	0.04
4-ethylphenol (4EP)	7.5	491	0.05

(1/s) for phenol (K_d = 1.0) and a minimum value of 0.002 (1/s) for 4EP (K_d = 7.5). Thus, when examining the transport process of alkylphenols under identical conditions, a higher partition coefficient corresponds to a lower wash-out rate. The experimental results demonstrate a relationship of $a = 0.009 \times K_d^{-0.807}$ with a correlation coefficient $R^2 > 0.999$ (Figure 5b).

According to the above results, the analytical solution proposed by Huong et al. (2021) [16] provides a good description of the leaching process of alkylphenols from the oil phase to the water phase. The transport of alkylphenol compounds was experimentally studied by O. Huseby et al. (2003) [18], focusing on the diffusion process of these compounds from immobile bypassed oil during waterflooding. However, they demonstrated a collapse of the relative concentration data (C/C0) for the various compounds onto a single curve. Although the authors proposed semi-empirical equations describing the concentration decline of alkylphenol compounds over time during water injection using exponential functions, they did not clarify the contribution of dynamic parameters affecting this decline. Different from the above approach, the present experiment focuses on the leaching process of alkylphenols from residual oil in the sweeping area of the injection water. Based on the excellent agreement between the experimental data and the mentioned analytical solution [16], this study provides a clearer understanding of the factors influencing the decline in alkylphenol compared to the previous semi-empirical formula. This suggests that the residual oil saturation can be completely determined by matching the trendline of the wash-out rate of alkylphenols and their partition coefficients measured in the laboratory under reservoir conditions.

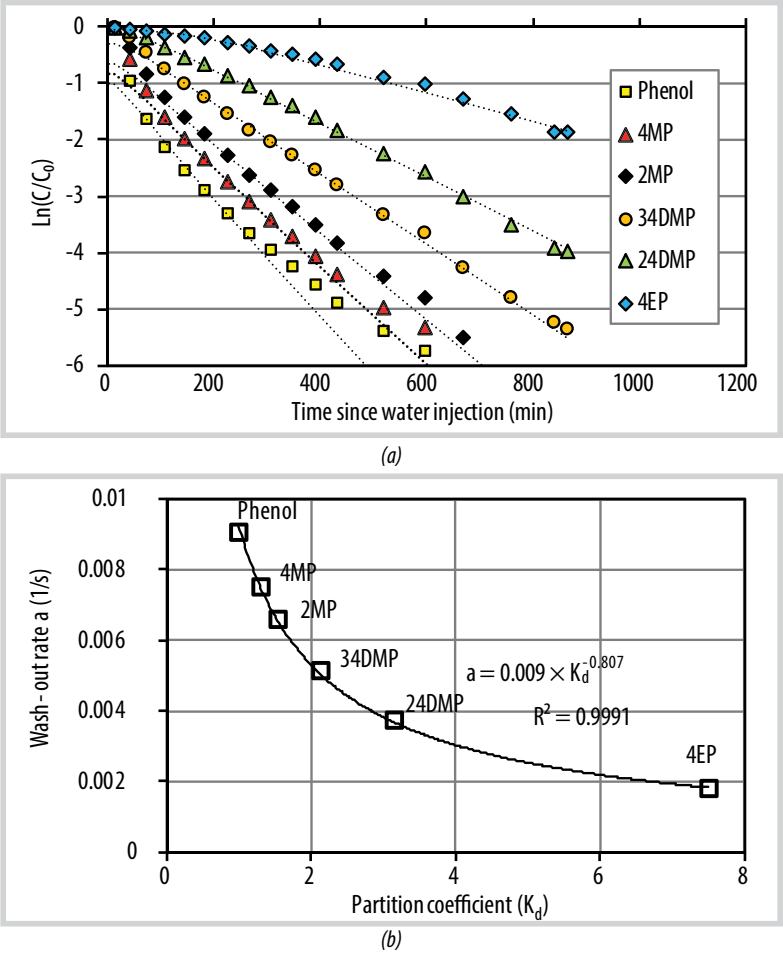


Figure 5. *The analytical solution (dashed line) describing the leaching process of alkylphenols in comparison to the experimental data points (a) and the wash-out rate of alkylphenols under experimental conditions (b).*

4. Conclusions

The leaching process of six alkylphenols naturally existing in crude oil into water has been studied experimentally in integration with analytical modeling. Initially, the packed glass-bead column was saturated with crude oil. During experimental water - oil displacement, the reduction rate of

Table 2. *The root mean square error (RMSE) between the relative concentrations (C/C_0) obtained from the experiment and the analytical solution during the injection stage (PV)*

PV	Phenol (K_d = 1.0)	4MP (K_d = 1.3)	2MP (K_d = 1.5)	34DMP (K_d = 2.1)	24DMP (K_d = 3.1)	4EP (K_d = 7.5)
0-2	0.46	0.48	0.47	0.43	0.33	0.22
2-4	0.06	0.06	0.06	0.20	0.10	0.20
4-6	0.06	0.07	0.05	0.09	0.06	0.13
6-8	0.05	0.05	0.04	0.06	0.05	0.05
8-11	0.03	0.02	0.02	0.02	0.02	0.06

alkylphenols concentration in water phase, acting as the wash-out rate, depends on the effect of partitioning the oil - water phases.

The experimental results are well-explained by a simple 1D analytical model when taking into account the partitioning process, especially at the late stage of waterflooding. The analytical model shows a clear relation between the wash-out rate of alkylphenols, partition coefficients, oil saturation, dispersion coefficients, and interstitial velocities. With the help of analytical model, the wash-out rate of alkylphenols under the experimental conditions shows an excellent agreement with partition coefficient in the form of a negative power function.

This shows that in cases where the wash-out rate of alkylphenols and their partition coefficients under reservoir conditions are known, the residual oil saturation in the sweeping area of the injection water can be estimated using the analytical model. The results here represent a first step toward a practical approach in using alkylphenols as natural tracers for estimating phase saturations in oil reservoirs. One of the key issues in the application is the analysis of the concentration of alkylphenols in the water phase under reservoir conditions at production wells. However, in reality, the water sample collected at the wellhead is under surface conditions, causing the concentration of alkylphenols in the collected sample to not reflect their actual value under reservoir conditions. Therefore, developing a method to convert the alkylphenol concentration in the wellhead sample to the concentration under reservoir conditions will be conducted and presented in future research, aiming to apply this method at a field-scale.

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