REMOVAL OF PETROLEUM FROM AQUEOUS SYSTEMS BY POLY(DIVINYLBENZENE) AND POLY(METHYL METHACRYLATE-DIVINYLBENZENE) RESINS: ISOTHERMAL AND KINETIC STUDIES

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Abstract. In this study, the performance of two polymer resins was evaluated, one composed of methyl methacrylate-divinylbenzene (MMA-DVB) and the other of only divinylbenzene (DVB), for adsorption of oil in synthetic oily wastewater. The tests were carried out using two processes: (i) continuous flow, to assess the quantity of oily water that can be eluted until reaching the saturation point of resins; and (ii) batch, to obtain information about the best-fitting kinetic and isotherm models for the two resins. The results for both resins showed better fits to the Freundlich isotherm model and the pseudo-second-order kinetic model. The low activation energy values found suggest physical adsorption between the resins and oil. Although DVB resin has presented slightly better oil removal efficiency than the MMA-DVB one, the results showed that DVB resin can be industrially replaced by MMA-DVB resin, due to the latter advantages: lower cost, lower toxicity and easy regeneration, as indicated by the kinetic and isotherm studies.

Keywords: oily water treatment, adsorption, porous polymer resins, isotherm model, kinetic model.

1. Introduction

The process of petroleum production is accompanied by continuous production of water. This produced water is a byproduct, the complex composition of which depends on the type of oil, age of the field and extraction procedure. In general, this water contains high concentrations of different salts, a large quantity of dispersed and emulsified oil, solids from the rock formation and chemical products added to improve the extraction process, such as biocides, antifoam agents and corrosion inhibitors [1-6]. Therefore, the produced water needs to be treated before being discharged in the environment because toxic properties or used for other purposes [7]. The treatment method depends on this final destination: discharge or reuse in other activities, such as irrigation, steam generation for tertiary oil recovery or power generation [8-10], and reinjection in producing wells [11-12]. For discharge, in Brazil the concentration of oil must be reduced to 0.029 kg/m^3, according to the rules issued by the National Environmental Council [13]. For reuse and reinjection, the levels of contaminants must be smaller than for discharge, making it necessary to use more complex treatment methods, such as nanofiltration and reverse osmosis membranes.

Produced water treatment by physico-chemical processes, involving gravitational separation, hydro-cycloning and/or ultrafiltration, is very common, but in some cases these methods are unable to reduce the concentrations of contaminants to acceptable levels, even for discharge. Various alternatives have been studied to "polish" this water, with processes involving adsorption being the most suitable and widely studied [14-15]. Among filtering methods, the use of crushed walnut shells and other plant materials can be mentioned. In adsorption processes, materials like charcoal, organic clays and polymer resins are being used [16-19]. Polymer resins have several advantages, such as thermal, mechanical and chemical stability and reusability. They can also be tailored to the type of contaminant to be removed [20-22]. In adsorption processes in general, polymer resins have presented satisfactory results, and although they can be obtained with varied compositions [23-26], those based on divinylbenzene (DVB) and styrene (STY) having the greatest application. Several studies of the use of STY-DVB resins to treat produced water have been published [27-29]. Since crude oil is a complex mixture of compounds with different characteristics, some studies have been published investigating the efficiency of resins made from methyl methacrylate (MMA) and DVB [30-32]. These resins show as advantages the lower

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toxicity of MMA in relation to STY and slightly more polar character of MMA [33], inducing more effective adsorption of other types of molecules that compose crude oil. In previous studies, preliminary tests of continuous flow treatment of oily water allowed establishing parameters to obtain the best efficiency of this type of resin to remove oil from synthetic wastewater samples [34-35]. However, to the best of our knowledge, no studies have been published involving the physico-chemical adsorption of oil by MMA-DVB resin, to shed more light on the interaction aspects. Therefore, this paper presents the results of tests to evaluate the removal of oil from synthetic oily water (oil-in-water emulsion) with an MMA-DVB polymer resin in comparison with a DVB resin, through continuous flow and batch processes, indicating the isothermal and kinetic parameters that best fit the systems. The study of these aspects is of great importance for more effective treatment of produced water so that it can be discharged or reused.

2. Experimental

2.1. Chemicals

The crude oil sample was donated by the Petrobras Research Center (CENPES), Rio de Janeiro, Brazil, and is identified as "Petroleum B" (density 927 kg/m^3 and °API = = 20.35, at 293 K). Hexane, sodium chloride and calcium chloride (P.A. purity grade) were supplied by Vetec Química Fina Ltda, Duque de Caxias, Brazil, and used as received. Two kinds of mesoporous polymer resins, previously synthesized and characterized, were used as adsorbents: (i) polydivinylbenzene (DVB) (surface area 567·10^3 m^2/kg; pore volume 1.28·10^{-4} m^3/kg; pore diameter 79.5 Å); and (ii) poly(methyl methacrylate-divinyl benzene) (MMA-DVB) (molar ratio 77–23; surface area 72·10^3 m^2/kg; pore volume 3.9·10^{-4} m^3/kg; pore diameter 218.9 Å). Distilled and deionized water was produced with a Gehaka OS10LX reverse osmosis system.

2.2. Preparation of the Water Contaminated with Crude Oil

Firstly, synthetic saline water was prepared containing NaCl and CaCl$_2$ in the ratio of 10:1, respectively, with the total salt concentration of 55 kg/m^3. The salts were dissolved in half the total volume of water, by magnetic stirring, and after their total dissolution the rest of the water was added to the system [31, 35]. This concentration of salts was chosen because it is near the salinity of the water typically found in oil fields [36]. The crude oil was then slowly added to half the volume of the saltwater, under stirring at 13,000 rpm with an Ultra-Turrax T-25. Finally, the remaining saltwater was poured into the system and stirred for 900 s at 15,000 rpm [31, 35].

2.3. Determination of Total Oil and Grease (TOG) by Fluorescence Spectroscopy

Fluorescence spectroscopy was used to analyze the total oil and grease (TOG) concentration, using a Turner Designs TD-3100 bench top fluorometer [31, 34, 36]. Aliquots of 4.5·10^{-5} m^3 of oily water were collected in 5·10^{-5} m^3 graduated cylinder tubes, followed by addition of 5·10^{-6} m^3 of hexane. The tubes were shaken vigorously for about 300 s to extract the maximum of the oil phase by the hexane.

After complete separation of the phases, the organic phase (containing oil and grease) was isolated for subsequent analysis. The excitation wavelength was set at 350 nm and the emission spectra were obtained in the range of 360–600 nm, in line with the data obtained in a previous study [34]. The fluorescence emission of the mono and polyaromatic hydrocarbons contained in crude oil typically occurs in the region of (430 ± 30) nm. The device was calibrated using the reading for pure hexane and a solution of oil in hexane at the concentration of 0.025 kg/m^3, as specified in the instruction manual.

2.4. Batch Adsorption Experiments

In these experiments, we evaluated the following factors that influence the adsorption process: contact time, adsorbent mass, and temperature. The equilibrium data were fitted in two isotherm models: Langmuir and Freundlich [39], in their linearized versions. The kinetic data were fitted in the pseudo-first-order and pseudo-second-order models [40, 41].

The analysis was carried out by immersing the adsorbent in the oily water and mechanically shaking the solution in a Haake SWB25 shaker, at 100 rpm. The temperature was thermostatically controlled using a bath coupled to the shaker (Thermo Haake C25P). All analyzes were done in duplicates for the two systems studied.

2.4.1. Equilibrium adsorption studies

For this study, five test tubes were prepared, each containing 50 lL of oily water at 0.030 kg/m^3 and a different mass of resin (5·10^{-5}, 1·10^{-4}, 3·10^{-4}, 7·10^{-4}, 1·10^{-3} kg). The tubes were agitated at 298, 308, 318 and 323 K. The oily concentration in solution, C_e (kg/m^3) was quantified by fluorescence.

2.4.2. Adsorption kinetics studies

To analyze the adsorption kinetics, six test tubes were prepared, each containing 5·10^{-5} m^3 of the oily water at 0.15 kg/m^3 and 3·10^{-4} kg of resin. The tubes were agitated at 298, 308, 318 and 323 K, with different contact times: 900, 1800, 3600, 5400, 7200 and 14400 s. The oil concentration in solution, C_e (kg/m^3), was quantified by fluorescence.

2.5. Data Analysis

For both the equilibrium and kinetics studies, the concentration of adsorbed solute per mass unit (q_e) was calculated by Eq. (1):

$$q_e = \frac{(C_i - C_e) \cdot V}{m} \tag{1}$$

where C_i is the initial solute concentration in the solution, kg/m^3; C_e is the solute concentration in the solution under equilibrium, kg/m^3; V is the solution volume, m^3; and m is the adsorbent mass, kg.

2.5.1. Isotherm models

The Langmuir and Freundlich isotherm models were adopted to analyze the equilibrium data. The Langmuir isotherm is valid for monolayer adsorption and serves as the starting point for many adsorption studies in catalytic applications [39]. The Langmuir model is described by Eq. (2):

$$\frac{1}{q_e} = \frac{1}{Q_0} + \frac{1}{bQ_0C_e} \tag{2}$$

where q_e is the mass of adsorbate per unit mass of adsorbent, kg/kg; Q_0 indicates the maximum adsorbate mass that can be retained in the adsorbent; b is the Langmuir constant, which is related to the bonding energy; and C_e is the solute concentration in equilibrium, kg/m^3.

Eq. (3) describes the equilibrium of heterogeneous adsorption systems proposed by the Freundlich isotherm model [39]:

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \tag{3}$$

where q_e is the mass of adsorbate per unit mass of adsorbent, kg/kg; K_F is a constant that indicates the relative adsorption capacity of the adsorbent, kg/kg; n is a dimensionless constant that indicates the adsorption intensity; and C_e is the solute concentration in equilibrium, kg/m^3).

2.5.2. Kinetic models

The pseudo-first-order model follows Eq. (4):

$$\ln (q_e - q_t) = \ln q_e - K_1 t \tag{4}$$

where q_e is the mass solute adsorbed per unit of adsorbent mass in equilibrium, kg/kg; q_t is the concentration of solute adsorbed per unit of adsorbent mass (kg/kg) at time t (s); and K_1 is the adsorption velocity constant, s^{-1}.

The angular coefficient of $\ln(q_e - q_t)$ *versus* time plot provides the first-order velocity constant (K_1). The values of $\ln(q_e - q_t)$ were calculated from the linear portion of the graph of q_t *vs. t*. The activation energy of the process was obtained by plotting the graph of $\ln K_1$ as a function of $1/T$ from the Arrhenius equation (Eq. (5)) [42, 43].

$$\ln K_1 = -\frac{E_a}{RT} + \ln A \tag{5}$$

where K_1 is the adsorption velocity constant, s^{-1}; E_a is the activation energy, kJ/mol; R is the universal gas constant (8.314 J/mol·K); and A is the pre-exponential factor.

The pseudo-second-order model follows Eq. (6):

$$\frac{t}{q} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e}t \tag{6}$$

where q_e is the concentration of solute adsorbed per unit of adsorbent mass in equilibrium, kg/kg; q is the concentration of solute adsorbed per unit of adsorbent mass at time t, kg/kg; and K_2 is the pseudo-second-order velocity constant, kg·kg·s^{-1}.

2.6. Retention Experiments Under Continuous Flow

The resins were first placed in water to swell for 24 h at room temperature. Then with the aid of a packing tool, stainless steel columns (11 mm inner diameter × 30 mm height – bed volume equal to 2.85·10^{-6} m^3) were packed with resins at the water flow rate of 1.67·10^{-8} m^3/s for 3600 s, using a Jasco PU-1580 chromatographic pump. At each hour, the flow rate was increased by 8.3·10^{-9} until reaching 1.67·10^{-7} m^3/s. The system was kept at this condition for 1 h and then 1 h more at 1 ml/min.

Oily water at concentrations of about 0.2 kg/m^3 (previously quantified) was eluted through the column at the flow rate of 1.17·10^{-7} m^3/s. After each 2.0·10^{-4} m^3 of solution, aliquots were collected to determine TOG by fluorimetry.

3. Results and Discussion

3.1. Studies of Oil Retention by Batch Adsorption

The batch experiments had the objective of obtaining the parameters for fitting an isotherm model, for efficient interpretation of the equilibrium and kinetics of the resins. The relative errors were of the order of 5 %.

3.1.1. Adsorption equilibrium

To assess the influence of resin mass on the adsorption efficiency, experiments were performed in which the mass and temperature were varied, maintaining the initial adsorbate concentration and adsorbate-adsorbent contact time constant. This experiment allowed obtaining information on the minimum quantity of adsorbent needed to achieve maximum adsorption.

With respect to the efficiency in removing each mass of adsorbent at a given temperature (Fig. 1), the DVB resin was more efficient than the MMA-DVB resin. At 298 K, with 5·10^{-5} kg of DVB (Fig. 1a), the adsorption efficiency reached 50 %, while with 7·10^{-5} kg the efficiency was 80 %. For masses above this value, no substantial increase in efficiency was observed. In the case of MMA-DVB (Fig. 1b), there was a greater dependence

between the mass and adsorption efficiency. The initial efficiency was 23 % with $5 \cdot 10^{-5}$ kg of resin, which increased to the maximum of 58 % with resin mass of $1 \cdot 10^{-3}$ kg. The performance profile was the same for all the other temperatures tested, where larger resin masses produced higher adsorption efficiencies. This behavior can be attributed to the larger surface areas due to the increase in mass.

The better efficiency of DVB resin *versus* MMA-DVB resin can be explained by the higher specific surface area of DVB in relation to MMA-DVB. This is an important factor for a material to be a good adsorbent. The DVB resin has a specific surface area about eightfold that of MMA-DVB. However, the adsorption results for MMA-DVB were not proportionally lower in relation to its smaller surface area, showing that the adsorption depends not only on specific surface area, but also on other factors, such as pore size and volume, particle size and type of

adsorbent-adsorbate interaction in terms of polarity, hydrophobicity and crosslinking degree, among other factors [44, 45].

With respect to the effect of temperature on the oil adsorption capacity of the resins, this capacity for both resins declined with rising temperature (Fig. 1). This can be attributed to the fact that adsorption is exothermal [46].

These data were used to plot the adsorption isotherms, providing information on how effectively the resins adsorb the oil present in the water, by estimating the quantity adsorbed in function of concentration in equilibrium (C_e). For both adsorbents, the concentration of solute adsorbed per unit of mass (q_e) was initially calculated according to Eq. (1), and these values were used to plot graphs of q_e *versus* C_e (Fig. 2), which depict the adsorption isotherms of oil in the DVB and MMA-DVB resins at all studied temperatures.
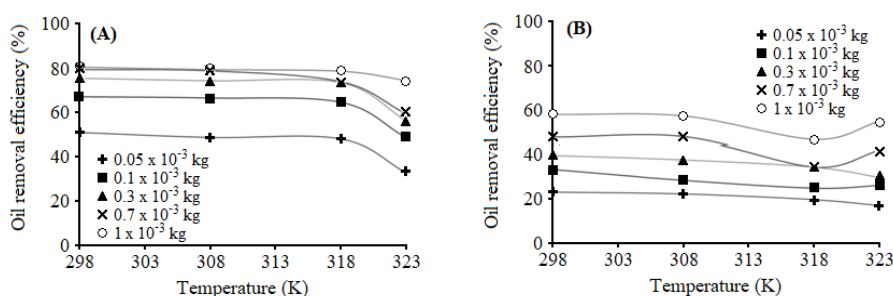

Fig. 1. Effect of temperature on the oil adsorption efficiency of DVB (a) and MMA-DVB (b), using resin masses of $0.05 \cdot 10^{-3}$, $0.1 \cdot 10^{-3}$, $0.3 \cdot 10^{-3}$, $0.7 \cdot 10^{-3}$ and $1.0 \cdot 10^{-3}$ kg and oil concentration of 0.03 kg/m^3
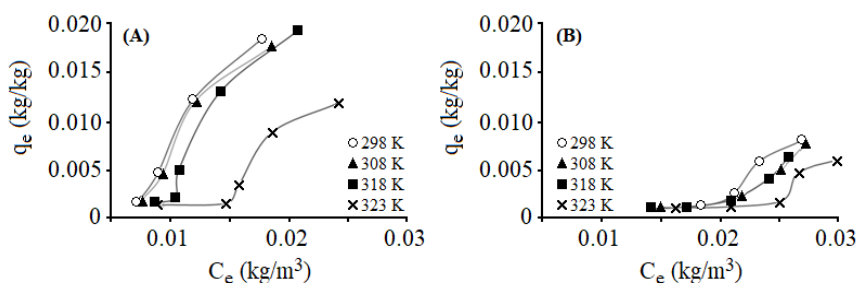

Fig. 2. Adsorption isotherms of DVB (a) and MMA-DVB (b). Initial oil concentration of 0.03 kg/m^3, temperature range of 298–323 K, contact time of 18000 s; q_e is the mass of oil adsorbed per mass of adsorbent in equilibrium, and C_e is the concentration of oil in water in equilibrium

Table 1

Parameters of the Langmuir and Freundlich models of adsorption of oil by the DVB and MMA-DVB resins, at initial oil concentration of 0.03 kg/m^3, masses of $5 \cdot 10^{-5}$ and $1 \cdot 10^{-3}$ kg and contact time of 18000 s

Adsorbent	Temperature, K	Model					
		Langmuir			Freundlich		
		b	Q_0, kg/kg	R^2	K_F	n	R^2
DVB	298	-62.35	-0.0022	0.8390	104.71	0.45	0.9211
	308	-59.81	-0.0022	0.8110	1348.96	0.36	0.8982
	318	-51.66	-0.0022	0.7920	2511.89	0.34	0.8684
	323	-31.02	-0.0030	0.7530	112.20	0.40	0.7902
MMA-DVB	298	-33.62	-0.00094	0.9020	6309.60	0.26	0.8870
	308	-31.81	-0.0010	0.9542	1995.30	0.28	0.9204
	318	-31.91	-0.0010	0.9526	501.20	0.31	0.9042
	323	-25.98	-0.0012	0.8289	199.50	0.33	0.7825

As previously mentioned, the profile of the isotherms shows that the quantity of oil adsorbed was inversely proportional to the increase in temperature, explained by the exothermal nature of the adsorption processes, and the difference in the isotherm profiles of the two resins is probably due to factors like porosity and chemical structure of the adsorbents [47]. The data from the isotherms were fitted to the Langmuir and Freundlich models to identify the one that best represented the adsorption process of the systems studied. We employed the equations of Langmuir (2) and Freundlich (3) in their linearized forms to obtain the parameters of each isotherm model (Table 1).

For the Langmuir model, the MMA-DVB resin presented the highest correlation values, but they were not very close to 1. Besides this, for both resins the calculated values for the parameters b and Q_0 were negative, suggesting that the systems studied cannot be represented well by this model. In turn, for the Freundlich model, the resins presented correlation coefficient values that were not very high (< 0.95), indicating that the isotherms were unfavorable and revealing a weak interaction between the resins and oil. Of the parameters obtained, n is related with the interaction of the adsorbate and adsorbent and K_F is related with the adsorption capacity. We also observed that the temperature has a stronger influence on the adsorption of MMA-DVB, because with increasing temperature, the values of K_F decreased.

3.1.2. Adsorption kinetics

Figs. 3a and 3b show the results of the mass of oil adsorbed per mass of adsorbent (q_e) in function of contact time, for DVB and MMA-DVB resins, respectively. From these data on adsorption efficiency in function of contact time it is possible to predict the behavior of the adsorbents through kinetic models.

Initial analysis of the graphs allows noting that the largest removal occurred in the initial contact periods. The adsorption took place quickly at first and then gradually slowed until reaching the equilibrium, at about 60 min for DVB and 30 min for MMA-DVB. The latter resin, although less efficient in adsorbing oil, reached equilibrium in less time. This can be explained by the porosity characteristics, where although MMA-DVB has smaller surface area than DVB, the average pore diameter is larger, allowing easier access of the oil particles to the pores.

By applying the kinetic pseudo-first-order model [48] (Eq. (4)), in its linearized form (Eq. (5)), it was possible to obtain graphics (Fig. 4) with good correlation coefficients. For DVB, the values were nearer to 1, while for MMA-DVB they varied from 0.92 to 0.98. These results indicate that the oil adsorption process of the adsorbents evaluated can be represented by the Lagergren model. Based on the data from the graphs in Fig. 4, we calculated the constant K_1 (adsorption velocity constant) and $q_{e(calc)}$ (concentration of solute adsorbed per unit of adsorbent mass in equilibrium), presented in Table 2.
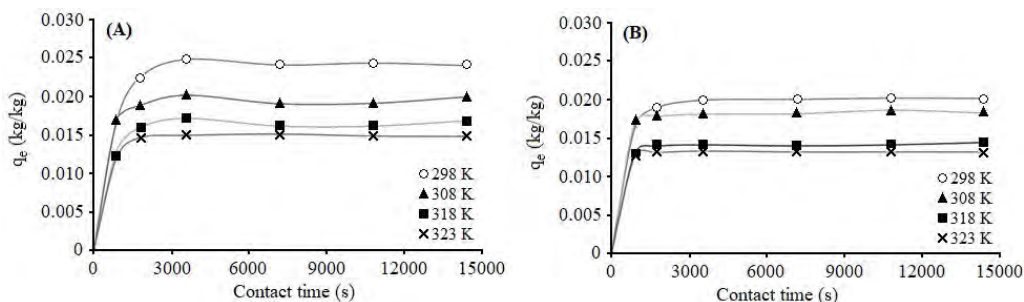

Fig. 3. Adsorption kinetics of DVB (a) and MMA-DVB (b). Initial oil concentration of 0.15 kg/m^3, resin mass of $3 \cdot 10^{-4}$ kg and temperature range of 298–323 K; q_e is the mass of oil adsorbed per adsorbent mass
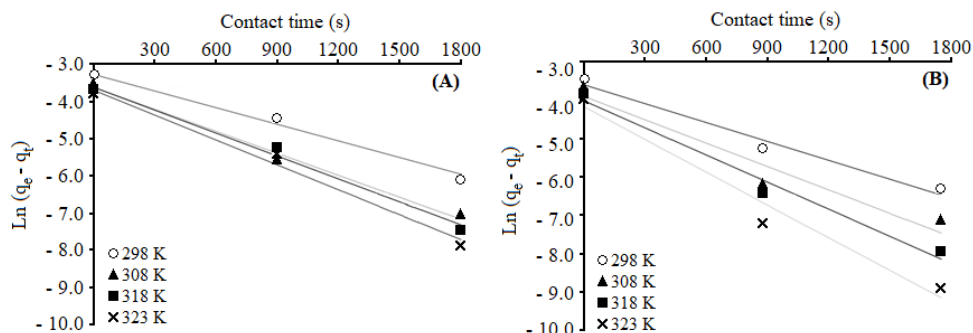

Fig. 4. Linearization of the pseudo-first-order adsorption kinetics of DVB (a) and MMA-DVB (b). Initial oil concentration of 0.15 kg/m^3, resin mass of $3 \cdot 10^{-4}$ kg and temperature range of 298–323 K

Comparison of the values of R^2 and $q_{e(calc)}$ of the two kinetic models studied indicates that the pseudo-second-order better describes the kinetic behavior of the systems evaluated than the pseudo-first-order model. According to the literature, the pseudo-second-order model is able to describe the adsorption kinetics in a wide time range, but only for low solute concentrations, unlike the other model [40, 49, 50].

The initial adsorption velocity values (h) indicate that in general the velocity increased with rising temperature and that MMA-DVB adsorbed the oil molecules in water faster than DVB at all temperatures studied.
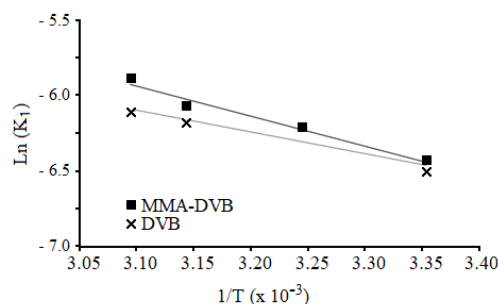
Fig. 5. Determination of the activation energy for adsorption of oil in the DVB and MMA-DVB resins

Table 2

Pseudo-first-order kinetic constants for adsorption of oil by the adsorbents DVB and MMA-DVB

Adsorbent	Temperature, K	K_1	$q_{e(exp)}$, kg/kg	$q_{e(calc)}$, kg/kg	R^2
DVB	298	0.0015	0.02415	0.02545	0.9964
	308	0.0020	0.01937	0.01791	0.9942
	318	0.0021	0.01637	0.01801	0.9921
	323	0.0022	0.01492	0.01668	0.9909
MMA-DVB	298	0.0016	0.01992	0.01825	0.9899
	308	0.0020	0.01818	0.01348	0.9221
	318	0.0023	0.01410	0.01199	0.9820
	323	0.0028	0.01314	0.01026	0.9712

Table 3

Activation energy values (E_a) for the adsorbents DVB and MMA-DVB

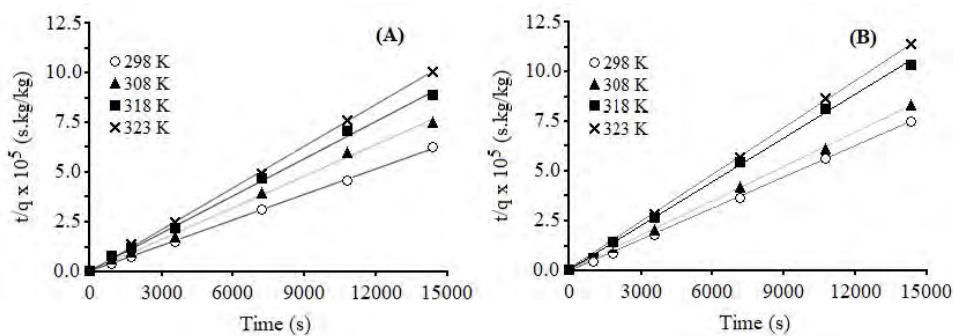| Adsorbent	Equation	$-E_a/R$	E_a, kJ/mol	R^2
DVB	$y = -1403.2x + 1.7475$	-1403.2	11.67	0.8791
MMA-DVB	$y = -2101.1x + 0.5858$	-2101	17.47	0.9131

Fig. 6. Linearization of the pseudo-second-order adsorption kinetics of DVB (a) and MMA-DVB (b). Initial oil concentration of 0.15 kg/m^3, resin mass of 3·10^{-4} kg, temperature range of 298–323 K, and contact time of 14400 s

Table 4

Pseudo-first-order kinetics constant for adsorption of oil by the adsorbents DVB and MMA-DVB

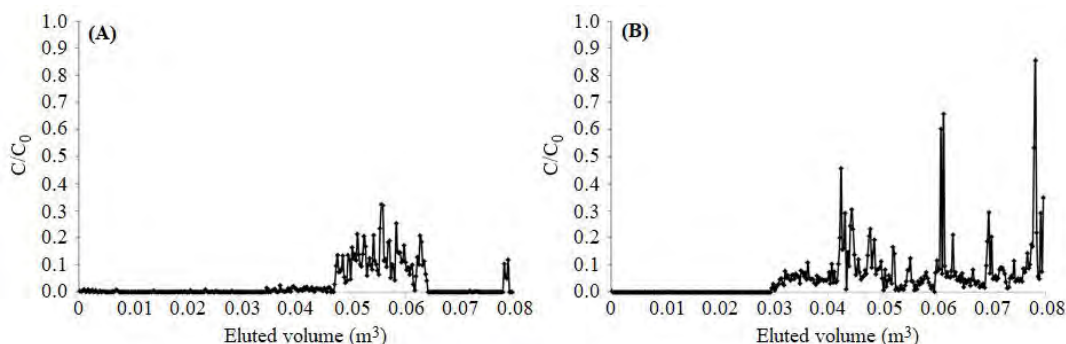| Adsorbent	Temperature, K	K_2, kg·s^{-1}	$q_{e(exp)}$, kg/kg	$q_{e(calc)}$, kg/kg	h, kg/kg^{-1}·s^{-1}	R^2
DVB	298	0.3464	0.024	0.024	0.00021	0.9992
	308	0.5650	0.019	0.020	0.00022	0.9989
	318	0.5575	0.016	0.017	0.00016	0.9988
	323	1.5767	0.015	0.015	0.00035	0.9997
MMA-DVB	298	0.5031	0.019	0.020	0.00020	0.9999
	308	1.2686	0.018	0.18	0.00042	0.9998
	318	0.9469	0.014	0.014	0.00019	0.9997
	323	11.0777	0.013	0.013	0.00187	1.0000

Fig. 7. Oil removal profile of DVB (a) and MMA-DVB (b) by the continuous flow process

3.2. Studies of Oil Retention Under Continuous Flow

The objective of this investigation of adsorption under continuous flow was to determine the saturation point of the adsorbents. Although this point is normally defined as the point where the quantity of oil in the water after treatment is the same as before treatment, here we considered the saturation point to be that where the concentration of oil in the eluted water was greater than or equal to 0.029 kg/m^3.

The tests were conducted using synthetic oily water at 0.2 kg/m^3, where the total oil and grease (TOG) concentration was measured before and after elution, allowing plotting C/C_0 *versus* volume eluted graphs. C/C_0 corresponds to the ratio between the TOG in the eluted water (C) and the water before elution (C_0). Aliquots of eluted water were collected each $2.0 \cdot 10^{-4}$ m^3.

Both resins showed high efficiency in removing oil from the water. In the system composed of the MMA-DVB resin (Fig. 7b), the removal efficiency was 100 % after elution of the first 30 l of water (10,316 bed volumes). After this volume, oil started to be detected in the eluted water, but the TOG value higher than 0.029 kg/m^3 was only detected after elution of approximately $4.2 \cdot 10^{-2}$ m^3 of water, corresponding to 14,700 bed volumes.

In turn, for the system formed by DVB, 100 % adsorption efficiency was achieved after elution of 47 l of oily water, corresponding to approximately 16,500 bed volumes. As of that point, the TOG concentration of the eluted water increased, with subsequent return to concentrations near zero, as shown in Fig. 7a.

The differences in the elution profiles of the two resins can be associated with their structures. MMA-DVB, because it contains ester groups, has higher polarity than DVB, which is basically composed of aromatic rings. These are probably capable of establishing more favored interactions with the compounds present in the oil, allowing better adsorption. The tests with both resins were conducted until elution of $8.0 \cdot 10^{-2}$ m^3 of oily water, the volume at which a sharp saturation peak was observed for MMA-DVB.

4. Conclusions

Both systems, DVB and MMA-DVB (70:30), adsorb oil in multilayers through physisorption, since their behaviors better fit the isotherm model proposed by Freundlich than that proposed by Langmuir. The adsorption occurring by physical interactions was confirmed by the kinetic study, whose results better fitted to the pseudo-second-order model, and low activation energy values for the adsorbate-resin interactions were obtained. For both resins, the adsorption process was fast, allowing their industrial application through the continuous flow process. The DVB resin presented slightly better oil removal efficiency than the MMA-DVB resin, probably because the larger surface area presented by the former: the water eluted through the columns contained 5 % of the original quantity of oil in eluted volumes of $4.8 \cdot 10^{-2}$ m^3 for DVB and $3.2 \cdot 10^{-2}$ m^3 for MMA-DVB. Such difference can be counterbalance by using slightly larger amount of the MMA-DVB in the column. Therefore, DVB resin can be industrially replaced by MMA-DVB resin to remove oil from oily water, due to the follwoing advantages: lower cost, lower toxicity and easy regeneration, as indicated by the kinetic and isotherm studies.

Acknowledgments

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ВИДАЛЕННЯ НАФТИ З ВОДНИХ СИСТЕМ ПОЛІДИВІНІЛБЕНЗЕНОВИМИ ТА ПОЛІМЕТИЛМЕТАКРИЛАТ-ДИВІНІЛБЕНЗЕНОВИМИ СМОЛАМИ: ІЗОТЕРМАЛЬНІ ТА КІНЕТИЧНІ ДОСЛІДЖЕННЯ

Анотація. Досліджені метилметакрилат-дивінілбензенова (ММА-ДВБ) та дивінілбензенова (ДВБ) смоли для адсорбції нафти в штучному середовищі нафта-вода. Дослідження проводили для двох процесів: (і) безперервний процес для оцінювання кількості води з нафтою, яку можна елююювати до досягнення межі насичення смол; і (іі) періодичний процес для одержання кінетичної та ізотермічної моделі двох смол., Встановлено, що для обох смол результати найкраще відповідають ізотермі Фройндліха та кінетичній моделі псевдодругого порядку. Знайдені значення низької енергії активації свідчать про фізичну адсорбцію між смолами та нафтою. Показано, що незважаючи на непогану ефективність ДВБ смоли щодо видалення нафти, її можна замінити промисловою смолою ММА-ДВБ, завдяки таким перевагам як менша вартість, токсичність та легкість регенерації.

Ключові слова: оброблення нафтовмісної води, адсорбція, пористі полімерні смоли, ізотерма, кінетична модель.