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Analysis of emulsions concentration changes during imbibition in porous sorbents

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Abstract The stabilized emulsions removal from the aqueous systems is supposed to be an issue as important as the free oil products recovery. This work was conducted to investigate the mechanisms of oil-in-water emulsions sorption in a non-woven oleophilic/hydrophobic material forced by the capillary suction pressure, and the saturation level of such material during this process. It ensures the effective application of the sorbents and facilitates the development of alternative high-performance sorptive materials that can contribute to diminishing of the negative consequences of the aquatic environment contamination. The main aspect investigated in this research work was kinetics of the imbibition process in the porous media to define the optimal time of sorption and the height of the emulsions penetration. The measurement of the dispersed phase concentration changes with the increase in an emulsion front in the porous medium using the nephelometrical method is the advanced approach in the field of assessment of sorbents efficiency. The tendency of the imbibed emulsion concentration decrease versus the height was observed, which depended strongly on the viscosity and the initial composition of a penetrating liquid. The observed process was described by the mathematical model based on Hill equation.

Keywords Dispersed phase concentration · Emulsion · Hill equation · Imbibition · Porous sorbent · Saturation

Abbreviations

API	American Petroleum Institute
DPC	Dispersed phase concentrations
KO	Kerosene oil
VO	Vegetable oil

Introduction

Over the last decades, the contamination of the aqueous environment with oil and its derivative compounds has been recognized as a serious ecological problem. Such contaminants can be present in aqueous objects in the form of free spilled oil products or their emulsions. In the majority of cases, the penetration of different types of emulsions is a direct result of the surface run-off from the land-based objects and the discharge of industrial untreated effluents, i.e. from oil refinery facilities, objects of food industry, metal processing, refuelling and service stations, territories with storage tanks, and also during transportation operations (Wake 2005; Srinivasan and Viraraghavan 2010; Coca-Prados and Gutiérrez-Cervelló 2011). The reason of such contamination can also be oil spills caused mainly as a result of drilling processes, transportation, e.g. leakages from tankers, underwater and underground pipelines, and accidents on offshore platforms (Fingas 2011; Al-Majed et al. 2012). Following the oil and/or its refined products penetration into the aquatic environment, the sequence of physical, chemical, and biological weathering processes and contaminants translocation (i.e. spearing, drifting) occurs. The climatic and environmental conditions as well as the properties of oil-spill-derived hydrocarbons are recognized to be the dominating factors

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that define the kinetics and mechanisms of the oil transformation, including the emulsification and dispersion processes (Daling and StrØm 1999; Kingston 2002; Fingas 2011).

One of the initially required conditions for the above-mentioned alterations of thin layer of oil on water surface is a wind speed in a range 3–5 m/s. However, emulsification and dispersion of the spilled oil can also be intensified by a mixing intensity of waves and streams (Wei et al. 2003; Al-Majed et al. 2012). The oil-in-water dispersions and water-in-oil emulsions are reported to be formed on the surface and at near surface zone of a water column (Walker et al. 1993; Lewis et al. 1994; Xie et al. 2007).

The main consequences of such a contamination are economic losses and a wide range of negative impacts on the environment. Subject to the oily component properties of an emulsion, the threats can be represented by toxic, carcinogenic, and mutagenic effects on aquatic and coastal-terrestrial biota, an inhibition of the physiological activity of living organisms, a disruption of the food chains, and an irreversible degradation of the ecosystem due to the deterioration of its abiotic components quality (Kingston 2002; Wake 2005; Fingas 2011).

Presently, a great deal of different remediation approaches was elaborated for oil and its products removal from the aqueous media, which application depends on the scale, the character of the contaminated territory, and the spilled pollutants properties. Emulsions recovery process can be based on the technologies such as coagulation and flocculation, gravity separation, chemical treatment, dissolved air flotation, membrane processes, and integrated or hybrid methods (Fakhru'l-Razi et al. 2009). However, all of them feature some major disadvantages such as a low efficiency in small oil droplets removing, a high operation costs, and some difficulties in applying in situ (Fakhru'l-Razi et al. 2009; Coca-Prados and Gutiérrez-Cervelló 2011). In contrast, the mechanical extraction by use of suitable sorbents can be considered as one of the most effective method for emulsions removal due to its ease in handling and implementing in the contaminated areas. Furthermore, the mechanical recovery using sorptive materials is also regarded as a highly appropriate countermeasure due to the absence of risk concerning an additional environmental contamination.

Among different types of sorbents, i.e. natural, inorganic mineral, and synthetic, preferably used are the last ones because of a high-efficiency and a low-cost technology as well as numerous exploitation advantages. The results of researches related to the effectiveness of polypropylene, polyethylene, polystyrene and their modified variants as sorbents of oils, and its refined products from water surface were discussed in the scientific literature (Teas et al. 2001; Wei et al. 2003; Wei et al. 2005; Zhu et al. 2011; Lin et al. 2012; Wu et al. 2012).

Most of commercial polypropylene sorbents are in the form of non-woven materials that consist of webs created by consolidation of individual fibres. Such a structure provides a formation of voids that facilitates the penetration of a contaminant and its retention into the sorbents (Schmenk et al. 2000). Teas et al. compared the oil-sorption capacity of polypropylene with commercial types of perlite and cellulosic material. The synthetic material exhibited a high-performance absorption of light cycle and light gas oils in all sets of experiments in both cases of pure compounds and oils presence in water baths (Teas et al. 2001). Different samples of polypropylene non-woven materials were tested according to their initial oil-sorption capacities and oil-retention properties in another publication (Wei et al. 2003). Using the wasted plastic in the form of powders and sheets as a sorbent of oil products was also investigated. The polyethylene powder and sheets as well as polypropylene powder were recommended for heavy crude oils removing, while polypropylene sheets adsorbed light oils (Aboul-Gheit et al. 2006).

A part of the literature is also dedicated to the methods of synthetic sorbents modification and estimation of their abilities to be applied for the oil-spill-derivative hydrocarbons removal (Ceylan et al. 2009; Qi et al. 2011; Zhu et al. 2011; Lin et al. 2012; Atta et al. 2013; Saleem et al. 2014). The efficiency of the macroporous polymeric material consisting of butyl rubber as a sorbent was investigated in laboratory conditions. Its sorption capacity for crude oil and petroleum products was defined in a range of 15–23 g/g (Ceylan et al. 2009). The commercial felt was modified by adding expanded graphite with an oil-sorption capacity of 80 g/g. The experimental results indicated that the absorption capacity of the obtained sample was remarkably improved, i.e. almost by 300 % in comparison with the application of the pure felt (Qi et al. 2011). The sorption capacity of a sorbent consisting of polyvinyl chloride (PVC) and polystyrene (PS) fibre prepared by an electrospinning process was investigated in the publication of Zhu et al. (2011). The results showed that the sorption ability of the PVC/PS sorbent for different oily liquids can be displayed in such order: motor oil > peanut oil > ethylene glycol > diesel (Zhu et al. 2011). Polystyrene produced by means of the electrospinning method and characterized with high specific surface of fibres was reported to be an excellent sorbent for vegetable and motor oils due to the combination of absorption and adsorption

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processes (Lin et al. 2012). On the other hand, reutilization of such sorbent and extraction of the imbibed liquid from fibres pores can become a quite challenging and complicated process. The efficiency of non-woven polyethylene terephthalate fibres modified by the adherence of cross-linked polymer coatings to the fibre surface was evaluated by means of oil absorption experiments with toluene and crude oil as the sorbed media (Atta et al. 2013). More recently, the diesel oil uptake process by a synthetic sorbent consisting of ultra-high molecular weight polyethylene has also received some attention (Saleem et al. 2014). Despite the high sorption capacity, the modified polymer sorbents have the following drawbacks: high production costs of these materials, fabrication mainly in laboratory scale, and finally, a low reusability level of multicomponent sorbents and these composed of nano-porous fibres.

The sorption process is based on the physical phenomenon known as the spontaneous imbibition forced by capillary rise. The capillary pressure is the main acting force of the imbibition, and it appears due to the wetting of the porous medium by a penetrating liquid, and consequent interactions of their surface energies (Zhmud et al. 2000; Hamraoui and Nylander 2002; Masoodi et al. 2007). There has been an ongoing interest in the imbibition process carried out by science and industry (Zhmud et al. 2000; Masoodi and Pillai 2010; Cai et al. 2012). The processes and mechanisms of porous media imbibition with single-phase liquids, for example, water (Hamraoui and Nylander 2002; Masoodi and Pillai 2010); deionized water and dimethyl silicone oil (Xue et al. 2006); dodecane and diethyl ether (Zhmud et al. 2000); and dodecane, hexadecane, and decane (Masoodi et al. 2007) were investigated experimentally and described in the literature. Moreover, the various models mainly based on fundamental equations such as Lucas–Washburn, Hagen–Poiseuille, and Laplace–Young were proposed to approximate the experimental data concerning single-phase liquids imbibition in the capillaries and different porous media. Many of such models consider the influence of dynamic contact angle on the capillary rise (Zhmud et al. 2000; Hamraoui and Nylander 2002; Digilov 2008; Hilpert 2010). Another type related to the spontaneous imbibition of a wetting permeant into gas-saturated porous media consisting of a complex structure of pores and based on fractal geometry (Benavente et al. 2002; Zhao and Li 2009; Cai et al. 2010, 2011, 2012). The effect of tortuosity and shape on the capillary imbibition in the wetting porous media is discussed in the publications of Cai et al. (2010, 2011, 2012), and this approach allowed to characterize the mentioned process in a wide range of porous structures, i.e. rocks, silica glasses, and fibrous material.

The emulsions are recognized as the heterogeneous multiphase systems, consisting of immiscible components, which can differ at least by viscosity and wettability. This allowed to assume that the process of porous media imbibition with emulsions differed from the one with single-phase liquids. Moreover, the previously mentioned models were applicable to describe transport phenomenon driven by the capillary pressure in case of single-phase permeants and disregarded the effect of composition heterogeneity and the structural changes of multiphase penetrating liquids in porous media.

The experiments reported in the present paper were undertaken in order to study the changes of two-phase liquids behaviour during the porous oleophilic/hydrophobic medium imbibition. The porous structure saturation versus the height of an imbibed permeant penetration and the influence of the initial dispersed phase concentrations were the objective of the discussion. Moreover, the phenomenon of an imbibed emulsion concentration changes with the increase in its front height was an issue investigated in this publication. The observed process was described by the mathematical models based on the fundamental sorption equations. The experiments were performed during 2015–2016 at the Department of Chemical Engineering in Lodz University of Technology (Poland). In practice, this investigation aims at estimating the imbibition mechanism of synthetic sorbents to predict the process of different multiphase liquids removal from the aquatic environment.

Materials and methods

Six types of oil-in-water emulsions were prepared by means of a homogenizer MSM–67170 (Bosch, Germany) during 600 s, which was sufficient to obtain the required degree of homogenization. According to the results of the microscopic images analysis (Microscope Leica DMI3000B with camera Lumenera Infinity1), the diameters of dispersed phase droplets in the obtained emulsions were in the range 1–20 μm, while 75–80 % of them had the size of 2–5 μm. One of the experimental liquids was emulsions composed of kerosene Shellsol D–60 (Chemia–Łódź S.A., Poland) and denoted as KO type. They represented low-viscosity oil products such as diesel oil, light crude oil, and gasoline. Using kerosene was promoted by its relatively non-volatility that minimized physicochemical properties changes of medium during the experiments.

Table 1 Properties of emulsions used in experiments ($T = 23 \pm 1$ °C)

DPC (%)	Viscosity (mPa s) KO emulsion	Density (kg/m^3)	Viscosity (mPa s) VO emulsion	Density (kg/m^3)
10	1.133 ± 0.021	973.1 ± 2.15	5.920 ± 0.140	992.2 ± 2.31
30	2.220 ± 0.050	932.2 ± 1.13	14.850 ± 0.23	978.9 ± 3.43
50	5.120 ± 0.003	890.8 ± 1.38	28.930 ± 0.24	961.9 ± 2.18

The kerosene API density was 52.74° ($\rho = 767.80 \pm 2.10$ kg/m^3), and viscosity was 1.23 ± 0.20 mPa s measured at 23 °C. The value of surface tension was 27 ± 1.8 mN/m. The emulsions of VO type consisted of the refined vegetable oil Uniwersalny (FHPU Marlibo Z.P.Chr., Poland), which served as a model liquid of high-viscous oil products. Its API density was equal to 21.97°, and density was equal to 922.00 ± 0.60 kg/m^3. The viscosity value for oil was 53.12 ± 0.44 mPa s, and surface tension was 32 ± 1.7 mN/m.

The dispersed phase concentrations (DPC) of the prepared emulsions were 10, 30, and 50 vol%. The emulsions were stabilized with a non-ionic surfactant—ethoxylated oleic acid (commercial name Rokacet O7, produced by PCC Exol SA, Poland). It was added in an amount of 2 per 100 ml of an emulsion.

The viscosity of the emulsions and the basic components was measured using a shear rheometer Bohlin CVO120 (Malvern Instruments, UK). The density was determined by means of the picnometric method. Three replications were carried out for each measured parameter of an emulsion, and results were presented as their mean values. The physicochemical properties of the prepared liquid media are shown in Table 1.

A commercial non-woven polypropylene material (Sintac©–Polska Sp.z o.o., Poland) with an average porosity equal to 0.93 ± 0.01 was used as the porous sorptive medium. This material is recognized as an appropriate sorbent for oil products removal from the environment. It revealed to have a sufficient sorption capacity of oily components of the investigated emulsions (i.e. 20 g/g for the vegetable, 15 g/g for kerosene oil), but it was not imbibed with water. The density of the investigated material was equal to 63.84 kg/m^3. Such polypropylene sorbents are characterized by high level of physical and chemical resistance, reusability, and possibility to recover the absorbed oil. For the experimental purposes, the stripes were cut from a polypropylene sheet which had a width of 0.035 m and a length of 0.20 m. The mean thickness of each stripe was equal to 0.0019 m.

Determination of the maximal mass and height of an imbibed liquid

For the imbibition process investigation, the prepared emulsions were poured into a beaker and its initial mass m_o was measured using an analytical balance (Radwag WTB 200, Poland) with an uncertainty of ± 0.001 g. A stripe of polypropylene was directly immersed with one end into emulsion to a depth of 0.02 m (Sęk et al. 2015). The contact area of porous material with an emulsion was equal to 0.0014 m^2. The changes of the emulsion mass in a beaker were registered as a function of time starting when the sorbent stripe was submerged and the process of imbibition initiated. The time when the mass of the emulsion in a beaker became steady was assumed as the final time of imbibition process t_{max}. The achieved height of the liquid front at t_{max} was accordingly denoted as the equilibrium height, h_{max} (Sęk et al. 2015). Afterwards, the sample of sorbent imbibed with an emulsion was removed and the mass m_f of the emulsion left in the beaker was measured. The difference between the initial m_o and final mass was defined as the maximal imbibed mass: $m_{max} = m_o - m_f$. For each type of emulsion, at least three independent experiments were conducted and the mean values were calculated. All experiments were conducted at 23 ± 1 °C.

Determination of an emulsion concentration changes during sorption process

These experiments allowed to define the variation of an emulsion concentration with its front raise in the porous media during the imbibition and to evaluate the influence of the following factors: initial dispersed phase concentration and properties of the oil used as an internal phase in the emulsions. The experiments were conducted for the maximal time of process t_{max}, which in this case was equal to 1800 s, and also for shorter intervals t_{im} such as 300, 900, and 1200 s. There was no considerable difference between the results for 1200 and 1800 s; therefore, only the
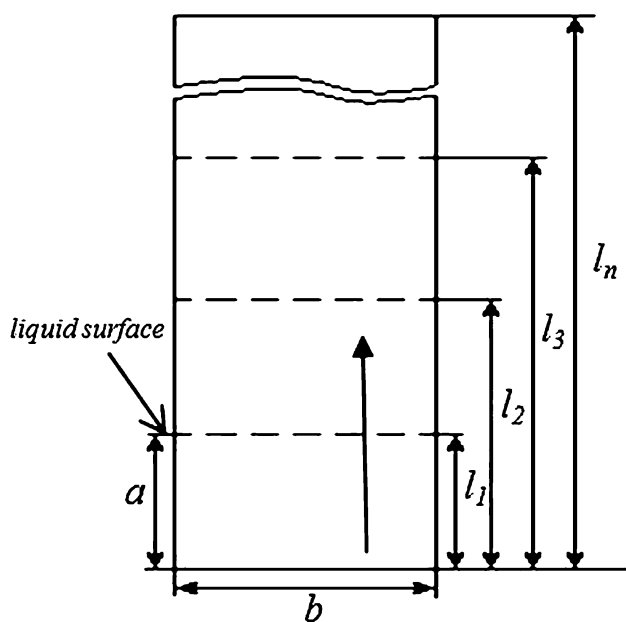
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Fig. 1 Scheme of the sorbent sample division: a the height and b the width of a sorbent fragment

last data point was used for plotting the results. After such a defined time, a sorbent stripe was removed from the beaker, and its soaked part was cut into fragments. The principle of a sorbent division is shown in Fig. 1.

Each fragment had identical dimensions, i.e. the height a of 0.020 m and the width b of 0.035 m. The first fragment L_1 visualized a submerged part of material, and its height range was from 0 to 0.02 m. The height boundaries of next fragments were calculated according to the formula: $L_n = l_n - l_{n-1}$; thus, L_2 represented the height in the range 0.02-0.04 m, for L_3, it was equal to 0.04-0.06 m etc. (Fig. 1).

The samples of material were washed out after imbibition with 10 ml of distilled water. After that, the mass of the washed out liquid and a part of retained liquid in the material fragment were measured. The nephelometrical method was applied to determine concentrations of the dispersed phase in the obtained samples of liquids. The back-scattering rate (BSR) of light in an emulsion was measured by means of the optical analyzer TurbiscanTM LAB (Formulaction, France). The concentration of the dispersed phase in the obtained samples was determined using the calibration curves that describe the functional dependence between BSR of the light in an emulsion and

its concentration, as described elsewhere (Lemarchand et al. 2003).

Results and discussion

Changes of the height of an emulsion front versus time

The height of an imbibed emulsion front is an important parameter that characterizes the level of penetration inside the porous sorbent defining the effectiveness of the used material. The results of height changes with time are shown in Table 2.

These results clearly show that for time 300 s, the highest levels of penetration were observed for 50 % emulsions, i.e. KO-50 — 0.045 m; VO-50 — 0.042 m, in comparison with others, while the lowest heights of the emulsions front were in the case of VO-10 and KO-10 (Table 2).

For $t_{im} = 900$ s, the height of the front in porous medium was maximum for emulsions with lower dispersed phase concentrations, viz. KO-10 — 0.098 m and VO-10 — 0.066 m (Table 2). The same tendency was noticed for the maximal time t_{max}. Thus, for 10 % emulsions, the height values were in the range 0.120-0.122 m, whereas for others, it was lower, i.e. 0.102-0.105 m for 30 % and 0.08 m for 50 % emulsions (Table 2).

In summary, the height of imbibed emulsion front in the porous sorbent decreased with increasing the initial concentration of the dispersed phase at time $t_{im} \geq 900$ s. The observed tendency can be explained by oleophilic/hydrophobic characteristics of the investigated porous sorbent. Consequently, emulsions with higher content of oleic substances as the dispersed phase would be absorbed higher level during first 300 s. After that, the imbibition process began to slow down possibly due to the penetration

Table 2 Maximal height of the investigated emulsions penetration in the porous sorbent, [m]

Time (s)	Type of imbibed emulsion					
	VO-10	VO-30	VO-50	KO-10	KO-30	KO-50
300	0.030	0.041	0.042	0.042	0.043	0.045
900	0.066	0.064	0.062	0.098	0.096	0.075
1800	0.120	0.102	0.080	0.122	0.105	0.080

paths blocking with oil droplets or/and the increase in the balancing force. In case of 10 % emulsions, oil is present in a low concentration and wet pores walls creating path for continuous phase that can explain lower height of penetration. Thereafter, these emulsions can penetrate at higher levels due to their low viscosity in comparison with 50 % emulsions and possibly, the absence of significant paths obstruction with oil droplets.

Saturation of the porous sorbent with imbibed emulsions

The saturation characterizes the sorbent efficiency and defines a level of free volume filling. The porous sorbent saturation was calculated according to the following equation:

$$S_f = \frac{(V_w + V_r) - V_s}{V_f \varepsilon} \tag{1}$$

where S_f is the degree of saturation in a fragment of a polypropylene stripe, [–]; V_w is the volume of an emulsion washed out from a fragment [ml]; V_r is the volume of a liquid retained in a fragment after washing out [ml]; V_s is the volume of the added water (in this case equal to 10 ml); V_f is the volume of the investigated fragment [ml]; and ε is the porosity of a sorbent material.

The results of saturation changes versus the height for the equilibrium time t_{max} are represented in Fig. 2.

At 1800 s, in the first fragment (L_1), the volume of the imbibed and further extracted emulsions exceeded the potentially available free volume of porous medium in all investigated cases and sorbent was supposed to be oversaturated with the emulsions, i.e. $1 \leq S_{f1} \leq 1.4$ (Fig. 2).

This phenomenon can be explained by the fact that a part of emulsions was absorbed on the external surface creating a thin covering layer. In the second fragment ($0.02 < h_{im} \leq 0.04$ m), the saturation level was equal to 1.0 for VO-50 and 0.93 for KO-50 emulsion. However, for 30 % emulsions, its values were in a range 0.86-0.87, and finally, for 10 %, it was 0.76-0.77 (Fig. 2). For a height of 0.08 m, all kerosene-based emulsions nearly had the same saturation values, which were 0.33-0.36. While for vegetable oil-based emulsions, the corresponding values are 21 - 27 % higher and spanned in the range 0.40-0.46.

At height of 0.10 m, the average value of saturation was equal to 0.20-0.25 for all investigated liquids, besides 50 % emulsions which permeated only to the height ≤ 0.08 m (Fig. 2; Table 2). Three emulsions, viz. KO-10, 30 and
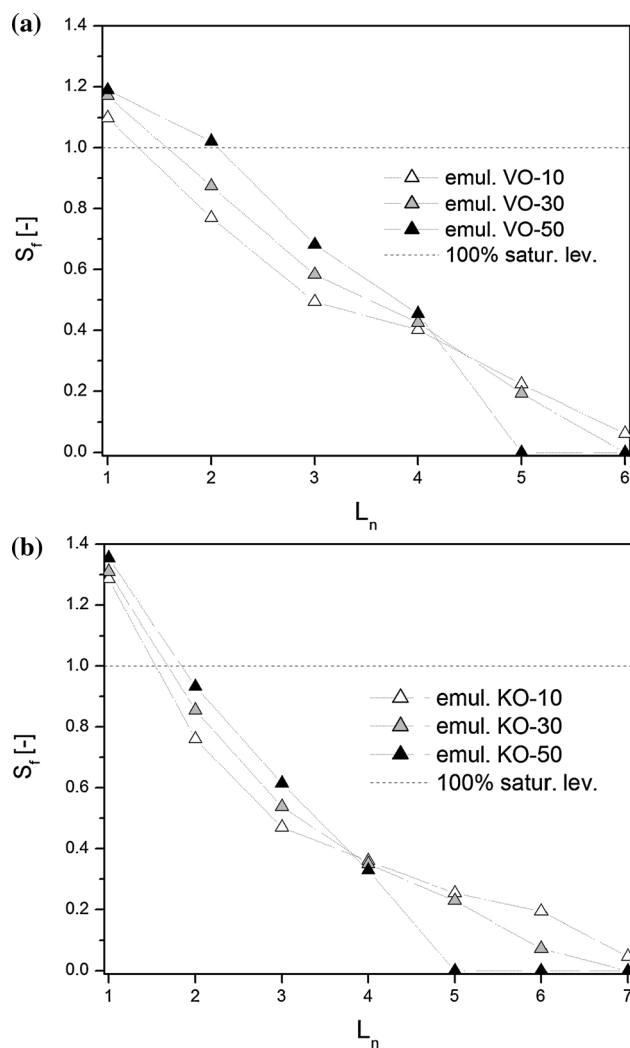

Fig. 2 Changes of saturation with the height of an imbibed emulsion front for $t_{im} = 1800$ s: **a** for VO emulsion type; **b** for KO emulsion type

VO-10, reached the height 0.1-0.12 m, and levels of porous material saturation were equal to 0.19, 0.073, and 0.062, respectively.

As mentioned previously, only KO-10 achieved the highest value of maximal height in porous medium, i.e. 0.122 m, but the observed sorbent saturation level was minimum in this case and was less than 0.05 (Fig. 2; Table 2).

Thus, these results suggest the following trends. Firstly, the sorbent saturation with an imbibed emulsion changes with the height of its front, and the minimal one was observed at the maximal achieved height. The analogous tendency was observed for all investigated emulsions.
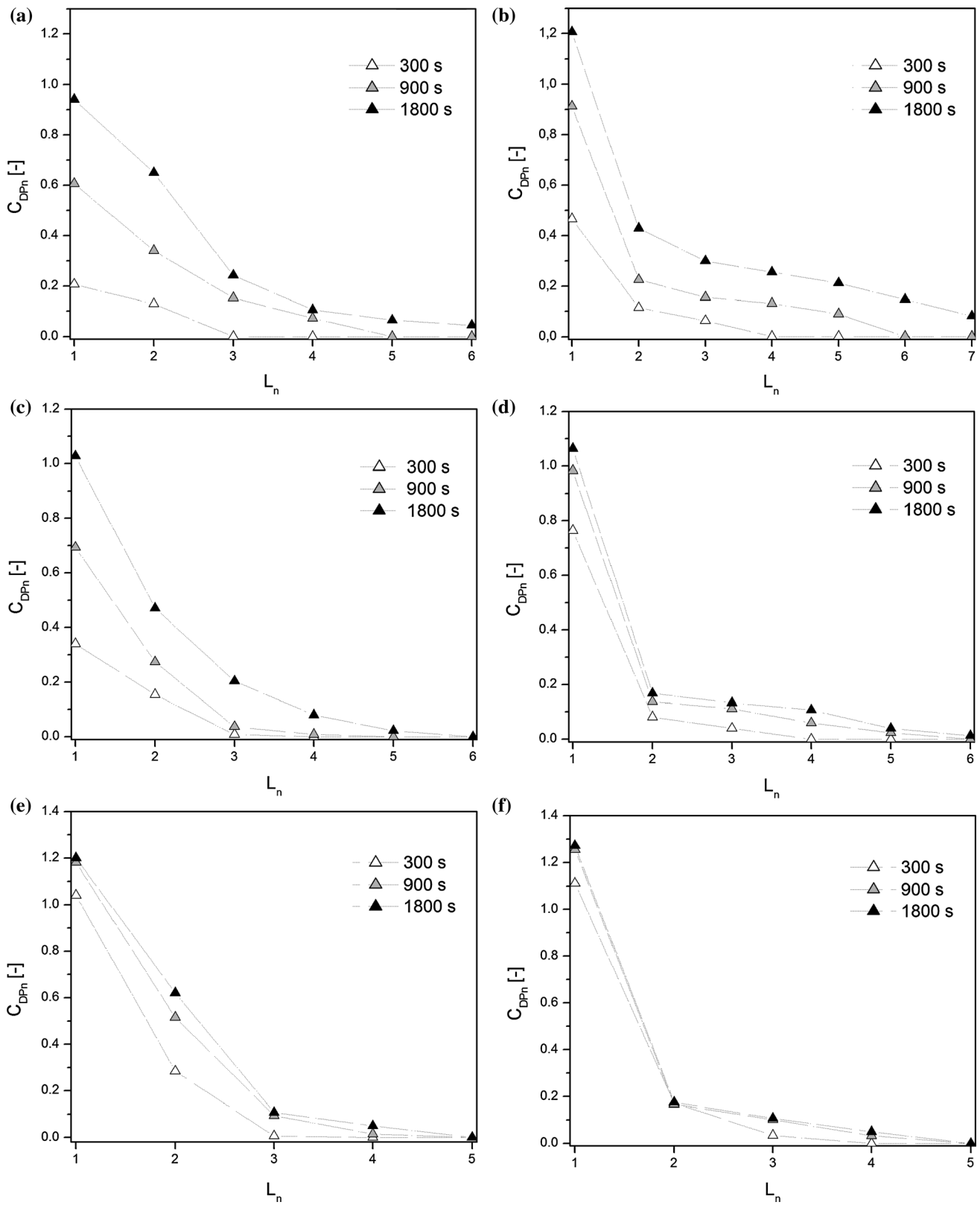
Fig. 3 Changes of the dispersed phase concentration versus the height at t_{im} = 300, 900 and 1800 s for emulsions: **a** VO-10; **b** KO-10; **c** VO-30; **d** KO-30; **e** VO-50; and **f** KO-50

Secondly, the specific points were determined, for which saturation of polypropylene sorbent with the investigated emulsions was almost identical. Such point was defined at the height of 0.08 m, and for VO emulsions, the average saturation level was equal to ~ 0.43, whereas for KO emulsions, it was approximately 0.35 (Fig. 2).

Changes of the dispersed phase concentrations versus the height of emulsions penetration in a sorbent

The emulsion concentration changes with the height for different times of the imbibition are shown in Fig. 3. The vertical axis on the graph represents the values of the normalized dispersed phase concentration which was denoted as C_{DPn} and calculated according to the expression:

$$C_{DP_n} = \frac{C_{DP}}{C_{DP_0}}, \quad (2)$$

where C_{DP_0} is the initial concentration of the emulsion in a beaker before imbibition experiment and C_{DP} is the concentration of an imbibed emulsion at the defined height measured by the nephelometrical method.

The obtained concentrations of the dispersed phase were lower in the case of kerosene-based emulsions in comparison with another type (Fig. 3).

As shown in Fig. 3a, b, for $t_{im} = 1800$ s, the dispersed phase concentration in case of KO-10 was 2.4 times lower at the $h_{im} = 0.04$ m, than at the height of 0.02 m, while for VO-10, this difference equalled 1.4 times. For emulsions with an initial concentration of 30 %, this difference was equal to 6.3 and 2.1 times for kerosene-based and vegetable oil-based emulsions, relatively (Fig. 3c, d). In the case of 50 % emulsions, this value equalled 7.3 for KO type and 2.2 for VO type (Fig. 3e, f). Thus, the observations revealed that the process of an emulsion concentration decreasing is more gradual for vegetable oil-based emulsions rather than for kerosene-based ones.

Figures 4, 5 and 6 represent the results describing the difference between the changes of the dispersed phase concentration vs the height at the given value of time of the imbibition process. For the shortest investigated time, i.e. 300 s, the highest emulsion concentrations were observed for both 50 % VO and KO emulsions (Fig. 4), whereas for $h_{im} \leq 0.02$ m, the dimensionless dispersed phase concentrations differed significantly from each other. Thus, its values for vegetable oil-based emulsion were equal to 0.21 for 10 %, 0.34 for 30 %, and finally, 1.04 for 50 % (Fig. 4a). In case of kerosene-based emulsion, the obtained
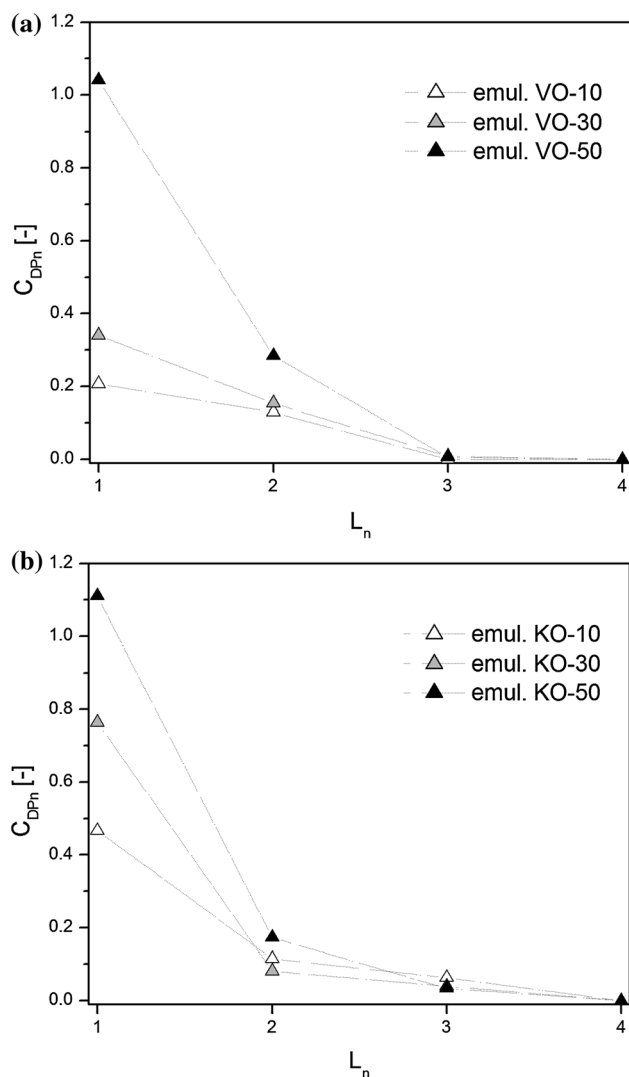

Fig. 4 Changes of the dispersed phase concentration with the height of an emulsion front for $t_{im} = 300$ s: **a** for VO emulsions; **b** for KO emulsions

values of C_{DPn} at the same height were a little bit higher, i.e. 0.47 for 10 %, 0.76 for 20 %, and 1.11 for 50 % (Fig. 4b). For $h_{im} > 0.04$ m, the rapid decreasing emulsion concentration was registered in this samples set. Moreover, the imbibed KO emulsions had almost identical concentrations of the dispersed phase for the height of 0.06 m (Fig. 4b).

As shown in Fig. 5a, b, the dispersed phase concentrations were much higher for time equal to 900 s in comparison with the results obtained for 300 s. At the height of 0.06 m (i.e. L_3), the value of C_{DPn} for VO-10 equalled approximately 0.15 that was a higher concentration than in case of other emulsions, i.e. 0.037-0.094 (Fig. 5a). A
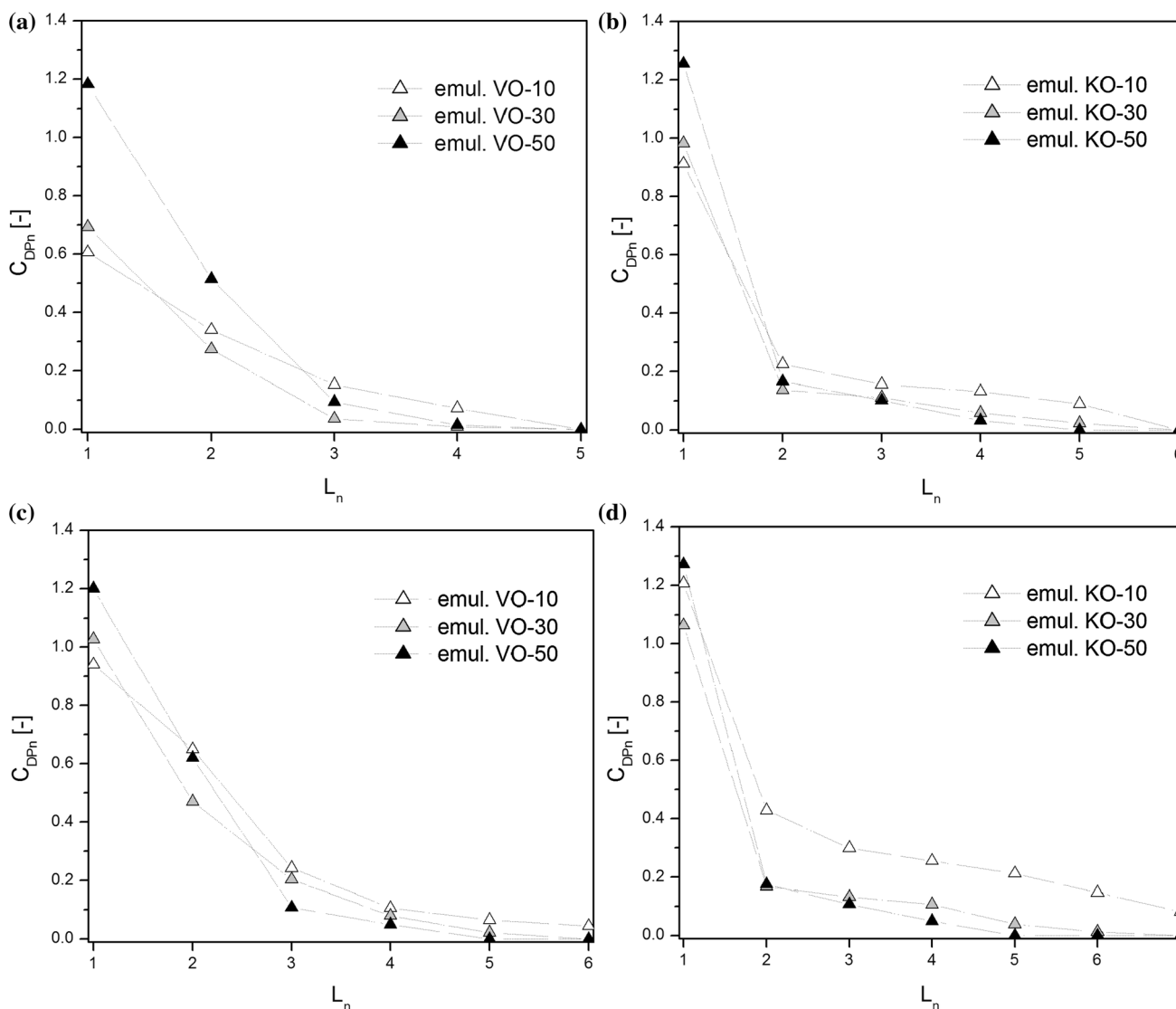
Fig. 5 Changes of the dispersed phase concentration with the height for: **a** VO emulsions, $t_{im} = 900$ s; **b** KO emulsions, $t_{im} = 900$ s; **c** VO emulsions, $t_{im} = 1800$ s; and **d** KO emulsions, $t_{im} = 1800$ s

similar tendency was noticed for kerosene-based emulsions, but at $h_{im} \leq 0.04$ m, viz. L_2 (Fig. 5b) and for all investigated emulsions in case of maximal imbibition time, i.e. 1800 s (Fig. 5c, d). The difference between concentrations for the same emulsions, but for process times of 900 and 1800 s, was relatively small (Fig. 5).

To sum up, the decrease in the dispersed phase concentration in relation to its initial value occurred slower for 10 % emulsion than for other investigated liquids after the first 300 s of the imbibition time.

Determination of the maximal mass of the imbibed emulsions

The maximal mass of an imbibed emulsion m_{max} was measured experimentally and referred as a practically important parameter used to specify the effectiveness of the sorptive material. However, the obtained data concerning the saturation and the dispersed phase changes also allowed to calculate the maximal masses of imbibed liquids M_{max} in a sorbent and the following equation was used:
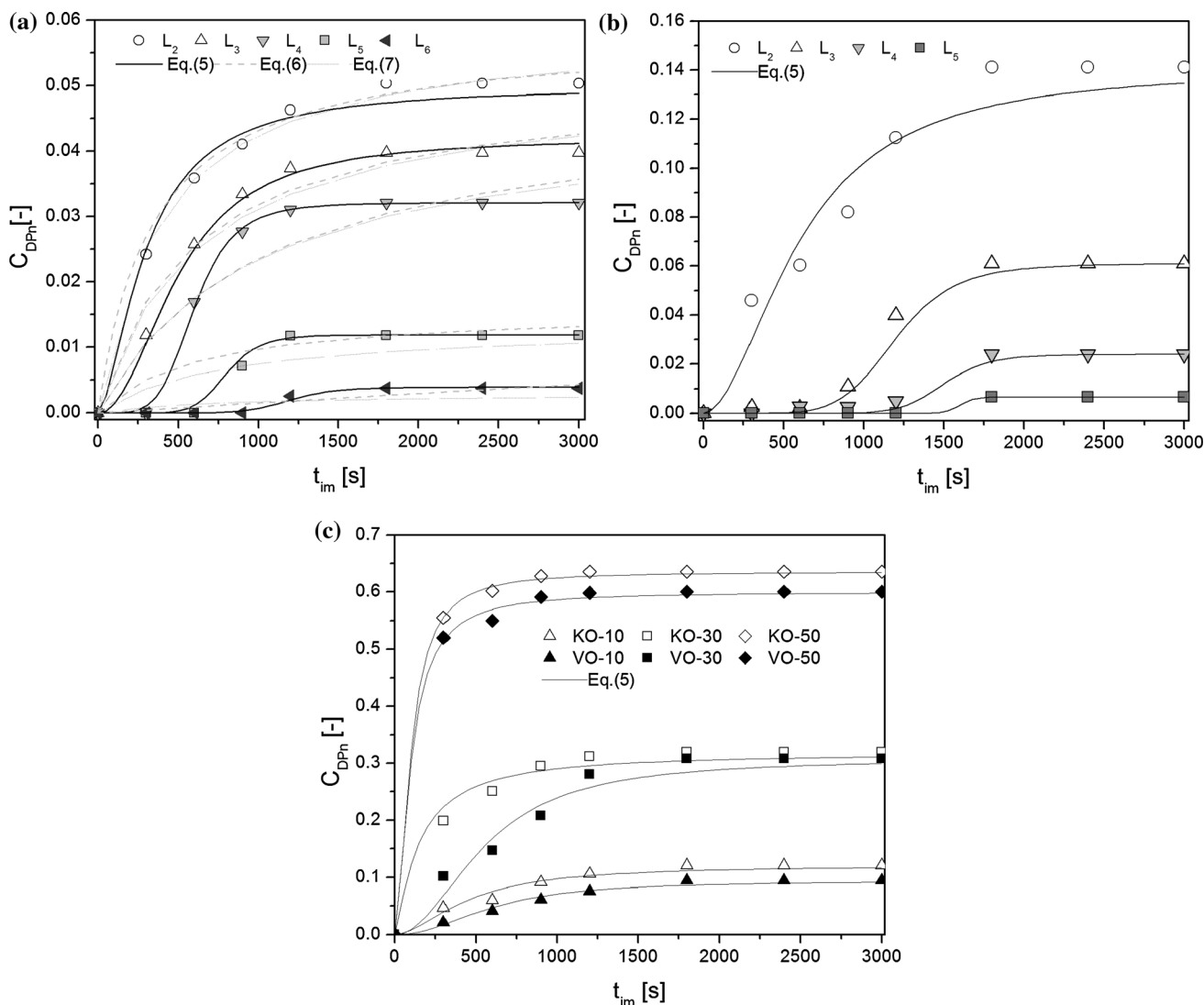
Fig. 6 Approximation of the experimental data for $t_{im} = 3000$ s: **a** 30 % kerosene oil-based emulsion; **b** 30 % vegetable oil-based emulsion; and **c** all emulsions ($h_{im} \leq 0.02$ m)

Table 3 Maximal masses of emulsions imbibed in the porous sorbent, (g)

Method	Type of imbibed emulsion					
	VO-10	VO-30	VO-50	KO-10	KO-30	KO-50
Experimental (m_{max})	4.15	4.38	4.47	4.53	4.44	4.15
Analytical (M_{max})	4.23	4.49	4.56	4.62	4.53	4.20

$$M_{max} = (V_1\varphi_{d1}\rho_d + V_1\varphi_{c1}\rho_c) + \cdots (V_n\varphi_{dn}\rho_d + V_n\varphi_{cn}\rho_c) \quad (3)$$

where V_n is the volume filled with an imbibed liquid in a fragment n and defined as $S_f V_f$; φ_{dn} is the fraction of the dispersed phase in a fragment n; ρ_d is the density of the dispersed phase; φ_{cn} is the fraction of the continuous phase in a fragment n; and ρ_c is the density of the continuous phase.

The comparison of the maximal analytical mass and one obtained experimentally is represented in Table 3.

As shown in Table 3, the value of experimental mass differed slightly from calculated one, and the divergence was in a range 0.05–0.11 g, i.e. $\sim$1.2–2.21 %.

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Modeling of the dispersed phase concentration changes versus time

The experimental data concerning the increase of an emulsion concentration versus time in the fragments of sorbent were approximated by equation based on fundamental descriptive-deterministic models such as Hill (Goutelle et al. 2008; Gesztelyi et al. 2012) and Michaelis–Menten (Johnson and Goody 2011) relating the reaction velocity as a function of the substrate concentration, and Langmuir adsorption model (Zhang and Wang 2010). The models were chosen due to their mathematical form and common use in the fields of sorption processes description during which changes of a concentration occur.

The Hill equation is originally used to define the reactions kinetics and includes such parameters as the maximal reaction rate, V_{max}; half-maximal concentration constant, K, and n defined as the Hill coefficient. The classical form of equation is represented as follows:

$$V = V_{max} \frac{[S]^n}{K^n + [S]^n},$$ (4)

where V is the rate of reaction per unit time, S is the substrate concentration (Goutelle et al. 2008; Gesztelyi et al. 2012). In the presently discussed case, the parameter of the reaction rate was substituted by a dimensionless parameter of concentration $C_{DPn}(t)$, and the substrate concentration, correspondingly by the time of an imbibition, t_{im} [s]. Finally, after rearranging, one obtains such form of modified equation:

$$C_{DP_n}(t) = C_{max} \frac{t_{im}^{\Psi}}{t_k^{\Psi} + t_{im}^{\Psi}},$$ (5)

where C_{max} is the dimensionless value of the maximal achieved concentration of oil phase in the fragment L_n at the equilibrium time, [–]; t_k is the time of an imbibition process, when the C_{DPn} is equal to a half of C_{max} [s]; and ψ is defined as a coefficient of the given equation. Other proposed mathematical equations on the base of Langmuir and Michaelis–Menten models had the following form, respectively:

$$C_{DP_n}(t) = \alpha \frac{k \cdot t_{im}}{1 + k \cdot t_{im}}$$ (6)

$$C_{DP_n}(t) = C_{max} \frac{t_{im}}{\beta + t_{im}}$$ (7)

where α, k are defined as coefficients of Eq. 6, and β is a coefficient of the last equation.

The obtained results of the dispersed phase concentration changes are plotted as a function of the process time. One example of such plots is given in Fig. 6a and presents data for 30 % kerosene oil-based emulsion and their approximation by the proposed Eqs. (5), (6), and (7). The dots depict the experimental results, while dashed lines show the values calculated by means of the proposed equations. The maximum observation time was assumed to be equal to 3000 s; however, after the maximum sorption time of 1800 s, only negligible changes of the emulsion front height were registered, i.e. $h_{im} < 0.001$ m per 300 s. As shown in Fig. 6a, the most accurate fitting and highest accuracy was obtained in case of Eq. (5) appropriate for sigmoidal tendencies, which can describe the trend of the process at all investigated height of the permeant penetration in a sorbent. Considering this fact, only this mathematical equation was used to approximate the other experimental results. Other investigated liquids were characterized with the same high accuracy of fitting.

The analysis of a part of the sorbent samples, which were in contact with the emulsion allowed to define the common trends of the observed process for emulsions with the same initial concentration (Fig. 6c). The values of the parameters used for fitting with Eq. (5) are displayed in Table 4.

The adequacy of equation application for the experimental data fitting was estimated by means of the correlation coefficient, R, and the normalized root-mean-square error (NRMSE) (Gmurman 2004). The calculated values of the normalized root-mean-square error were in a range 0.013 - 0.085 for all emulsions composed of vegetable oil and 0.031-0.086 for KO-10 and KO-30. However, the lowest one was obtained for 50 % kerosene-based emulsion, i.e. 0.007-0.024. The values of the correlation coefficient were found to be in the range 0.950-0.999 for emulsion VO-10; 0.905-0.999 for VO-30; 0.904-0.996 for VO-50; and 0.910-0.999 for emulsion KO-10; 0.977-0.998 for KO-30; 0.900-0.999 for KO-50. Therefore, the accuracy of the model can be accepted from the engineering point of view. Obviously, the values of parameters were different, whereas analogue tendencies in their changes were observed for both types of emulsions. Considering the results, one may assume that this equation gives a reasonable approximation of the experimental data because of the narrow boundaries within which solutions are found and adequate values of accuracy.

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Table 4 Parameters of the applied equation

Fragment	Parameters								
	C_{max}	t_k	ψ	C_{max}	t_k	ψ	C_{max}	t_k	ψ
	Emulsion VO-10			Emulsion VO-30			Emulsion VO-50		
L_1 (l_1)	0.094	600	2.16 ± 0.26	0.308	550	2.08 ± 0.36	0.600	100	1.64 ± 0.09
L_2 $(l_2–l_1)$	0.065	750	2.65 ± 0.49	0.141	600	1.89 ± 0.37	0.310	350	1.83 ± 0.26
L_3 $(l_3–l_2)$	0.024	800	5.73 ± 0.71	0.061	1200	6.52 ± 1.73	0.117	950	2.94 ± 0.70
L_4 $(l_4–l_3)$	0.011	850	6.02 ± 1.58	0.024	1500	10.87 ± 3.78	0.070	1250	8.92 ± 1.36
L_5 $(l_5–l_4)$	0.007	1100	9.42 ± 2.89	0.007	1600	27.55 ± 3.53	–	–	–
L_6 $(l_6–l_5)$	0.005	1500	11.1 ± 2.22	–	–	–	–	–	–
	Emulsion KO-10			Emulsion KO-30			Emulsion KO-50		
L_1 (l_1)	0.121	450	1.79 ± 0.29	0.319	150	1.32 ± 0.13	0.636	100	1.77 ± 0.05
L_2 $(l_2–l_1)$	0.043	650	2.17 ± 0.46	0.050	300	1.61 ± 0.15	0.100	100	1.78 ± 0.09
L_3 $(l_3–l_2)$	0.030	750	2.52 ± 0.46	0.040	500	2.61 ± 0.29	0.054	350	4.29 ± 0.32
L_4 $(l_4–l_3)$	0.026	900	3.42 ± 0.47	0.032	600	4.89 ± 0.35	0.025	850	8.88 ± 0.75
L_5 $(l_5–l_4)$	0.021	1200	4.38 ± 1.25	0.012	800	7.53 ± 1.54	–	–	–
L_6 $(l_6–l_5)$	0.015	1400	9.74 ± 0.82	0.004	1200	8.50 ± 3.34	–	–	–
L_7 $(l_7–l_6)$	0.008	1500	11.1 ± 2.22	–	–	–	–	–	–

Conclusion

The process of porous sorbent imbibition with two-phase emulsions differs from that one with single-phase liquids. The height of an emulsion permeation in a porous medium forced by capillary pressure depends on an initial concentration of the dispersed phase. For example, the height in case of 10 % emulsions was ~ 18 and ~ 50 % higher than for 30 and 50 % emulsions relatively, when the process time was equal to 1800 s. Thus, to remove emulsions with low concentrations, i.e. ≤ 10 %, applied sorbents should be a half higher in both cases of light and heavy oily components, than sorbent used for emulsions sorption with higher concentrations, i.e. ≥ 30 %.

The concentration of an emulsion during the imbibition process decreased with the increase in its front height in the porous sorbent in case of a non-immersed sorbent part, $h_{im} > 0.02$ m. Moreover, the kerosene-based emulsions were characterized by a quicker decreasing oil phase concentration with the height compared to another type of emulsions.

For a sorbent fragment with $h_{im} < 0.02$ m, an exceeding of its initial value of oil phase by 20-30 % was observed for time of 1800 s in case of 10 and 30 % emulsions, while for 50 % emulsion, this phenomenon was registered even at minimal observation time, i.e. $t_{im} = 300$ s. Thus, it is possible to assume that droplets were retained in lower layers of the sorbent causing obstruction of the penetration paths.

The saturation degree is recognized as one of the substantial parameters to evaluate the efficiency of pores volume filling and as a consequence, the polypropylene sorbent application. The oversaturated zone was defined at $h_{im} < 0.02$ m for all investigated emulsions. The observed exceeding of free pores volume of the material by 10-20 % was explained by an extra layer formation on the sorbent external surface. In case of the non-submerged part, the maximal saturation was observed for a height value in range $0.02 < h_{im} < 0.04$ m (i.e. L_2). It was equal to 100 for 50 % emulsions, while for 30 %, it was 86-87 %, and near 77 % for emulsions with the dispersed phase of 10 %. It proved once again that a larger part of the imbibed emulsions was retained in the lower part of a sorbent.

The experimental data concerning the dispersed phase concentration changes vs time for the different heights of an emulsion permeation in porous medium were approximated adequately by means of the modified Hill equation.

The present experimental results allow to define the appropriate time of sorption for non-modified polypropylene sorbent with an average porosity of 0.93 ± 0.01. Thus, its application time should not exceed 1800 s, because after the equilibrium state of the system was observed that was proved by the unchangeable values of imbibed mass and height.

Compliance with ethical standards

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