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TRANSPORT OF EMULSIONS IN GRANULAR POROUS MEDIA DRIVEN BY CAPILLARY FORCE

Abstract
The transport of liquids driven by capillary suction-pressure and balanced by both viscous drag force and gravity acceleration is known as spontaneous imbibition. The prediction of spontaneous imbibition in porous media is of importance due to its relevance as a fundamental phenomenon in numerous industrial technologies as well as in nature. A vast majority of the experimental results and mathematical models concerning the imbibition process of single-phase liquids are considered and analyzed in the literature. The present research focuses on two-phase liquids transport in porous medium driven by capillary force. The penetrating liquids were surfactant-stabilized emulsions with the different dispersed phase concentrations. The discussed issues are the influence of porous bed composition and inner phase concentration on the height of an emulsion penetration, which allows to predict the velocity of imbibition process. From a practical point of view, the experimental results give the possibility to evaluate: productivity of granular sorbents applied to recover the environment, efficiency of building materials wetting with multiphase liquids, process of oil-derived pollutants migration in porous media, e.g. soil and other rock structures, etc.

Key words
emulsion, imbibition, kinetics, granular media, pore radius

Introduction

The liquids transport driven by capillary force and counterbalanced by viscous drag force and gravity acceleration is referred in literature as spontaneous imbibition or wicking [1-4]. The imbibition as a physical phenomenon occurs in porous structures on the condition that adhesion predominates a mutual force of attraction between molecules in a permeating liquid [3-5]. The prediction of the spontaneous imbibition in porous media remains of importance due to its relevance as a fundamental phenomenon in a variety of industrial technologies and in nature: oil recovery and removal of different oil-derivative products from the environment, paper coating, ink penetration process, drug delivery systems, hydrological regime of soil layers, and measuring of contact angle in surface chemistry [1, 2, 6].

The process of porous media imbibition with such single-phase liquids as water [1, 4, 7], and different inorganic substances, i.e. dimethyl silicone oil, dodecane, hexadecane, diethyl ether, was experimentally investigated and described in the literature [3, 5, 8]. There are numerous approaches used to describe the single-phase liquids wicking in various porous structures. A great deal of the discussed mathematical models considers the effect of a dynamic contact angle on capillary rise [4, 8, 9]. Another group predicts the spontaneous imbibition in the porous media regarding structural parameters, i.e. porosity, tortuosity and shape of pores [2, 10-12]. A lot of approaches confiders both factors: structure of voids and medium saturation [11, 13, 14]. This allows for the characterization of the imbibition process in a wide range of granular media such as sorbents, soil, silica glasses, and other rocks. The mentioned concepts are appropriate to predict imbibition process in case of various single-phase liquids, while there is lack of experimental results and mathematical models, which predict wicking of multiphase liquids in granular beds.

This research work focuses on the study of the imbibition process in case of oil-in-water emulsions as two-phase dispersions differed by wettability and viscosity. The experiments reported in the paper were undertaken to investigate the kinetics of imbibition in different granular beds in terms of the changes of penetration height as a function of time, i.e. $h_{im} = f(t_{im})$. The influence of the dispersed phase concentration and the composition of granular media on the kinetics of imbibition, velocity of this process, its instantaneous velocity as well as the maximal height of an emulsion front rise were also considered and discussed.

Materials and Methods

In these experiments, the spontaneous imbibition process was investigated experimentally using the wicking test, as described in details in the publication [6, 15]. The used experimental set-up is schematically represented in Figure 1. A sample of a granular medium (*2*) was directly immersed with one end into a reservoir with an emulsion (*1*) with a contact area of 0.00096 m^2. The changes of the emulsion mass m_{im} in a reservoir (*1*) were registered versus time t_{im} using an analytical balance (*3*) as well as the height of its penetration h_{im} by means of a ruler (*4*). The time when the mass of the emulsion in a reservoir (*1*) became steady was assumed as the final time of imbibition process t_{max}. The achieved height of the liquid front at t_{max} was denoted as the equilibrium height, denoted as h_{max}.

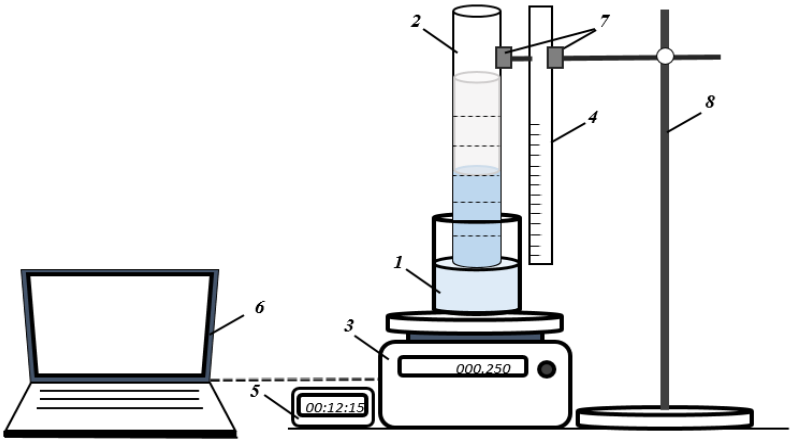

Fig. 1. Schematic illustration of the used experimental set-up for a granular medium: 1 – reservoir with an emulsion; 2 – granular bed; 3 – analytical balance; 4 – ruler; 5 – timer CDN TM15; 6 – computer to register data; 7 – fixators; and 8 – stand. The camera Nikon Coolpix L120 was used to record the changes of the height.
Source: Author's

Three types of oil-in-water emulsions were used in the current experiments. The emulsions were prepared according to the standard procedure. The dispersions differed by the inner phase concentration, which was equal to 10 vol.%, 30 vol.%, and 50 vol.%. They were stabilized with 2 vol.% of a non-ionic surfactant composed of ethoxylated oleic acid (commercial name Rokacet O7), obtained from PCC Exol SA (Poland). The defined volume of the distilled water, as a continuous phase, was mixed with the emulsifier and dispersed phase in a 500 ml beaker with a diameter d_{bk} of 0.08 m. The immiscible phases and surfactant were mixed by means of a high shear laboratory homogenizer with revolution of 12000 min^{-1} during 600 s.

Microscopic images analysis of the prepared emulsions was carried out by means of Microscope Leica DMI3000B with a Lumenera Infinity1 camera. The distribution of the dispersed droplet size in emulsions is shown in Fig. 2. According to the results, the diameters of dispersed oil droplets in the prepared emulsions were in the range 1–20 µm, while a majority of them (75–80%) had a size of 2–10 µm.

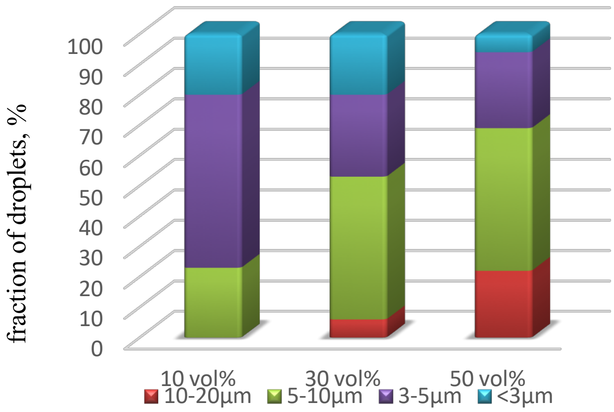

Fig. 2. Distribution of the dispersed droplet size in emulsions stabilized by the surfactant in concentration φ_s of 2 vol.%.
Source: Author's

The viscosity was measured using a shear rheometer Bohlin CVO120 (Malvern Instruments, UK). The density was determined using the picnometric method. The surface tension was measured using a tensiometer KRÜSS K12 (KRÜSS GmbH, Germany). The physicochemical properties of the emulsions components are shown in Table 1.

Table 1. Properties of emulsions components (T=23±1^{0}C)

Type of liquid	**Density (kg/m^3)**	**Viscosity (mPa·s)**	**Surface tension (mN/m)**	**HLB (-)**
Dispersed phase	922.1±0.6	53.12±1.44	32.2±1.7	-
Rokacet O7	908.0±2.7	50.21±0.62	36.2±1.8	10.6

Source: Author's

The porous medium was represented by a granular bed consisting of spherical granules, and characterized by the oleophilic/hydrophilic property. The beads were produced and obtained from "Alumetal-Technik" (Poland). The used porous media differed by a size of the particles, and their diameters ranged from 100–800 µm. The parameters of the granular media used are provided in Table 2.

Table 2. Parameters of the granular media

Type of medium	**Range of beads diameter (µm)**	**Average diameter of beads, d_a (µm)**	**Porosity, ε**
GS 100	100–200	180±10.9	0.35±0.010
GS 200	200–300	245±12.3	0.36±0.011
GS 600	600–800	650±9.2	0.37±0.013

Source: Author's

All experiments were conducted at 23±1^{0}C and atmospheric pressure. Three independent replications were carried out for each experiment, and results were presented as their mean values.

Result and Discussion

The results concerning the change of the emulsion penetration height h_{im} as a function of time t_{im} for the different granular beds are represented in Figure 3. The used granular beds were composed of spherical grains with sizes in the ranges of 100–200 µm, 200–300 µm, and 600–800 µm. The data were obtained for emulsions with the different dispersed phase concentrations of 10 vol%, 30 vol%, and 50 vol%.

As shown in Figure 3, the emulsions differ significantly by the height of penetration, thus a fraction of beads size and consequently, radii of pores in a granular bed causes the strong influence on the height of the emulsion front rise. The hydraulic radius of pores r_h was calculated according to Kozeny-Carman theory as a relation between medium porosity and average diameter of beads [16]. Thus, it was 16.2±0.16 µm for a medium with particles diameter d_b in a range of 100–200 µm, 23.0±0.38 and 63.6±0.18 µm for GS 200 and GS 600, respectively. To compare used granular beds, all emulsions tended to wick higher in case of medium with lower value of r_h. In contrast, the dispersed phase concentration is recognized initially as a less important factor.

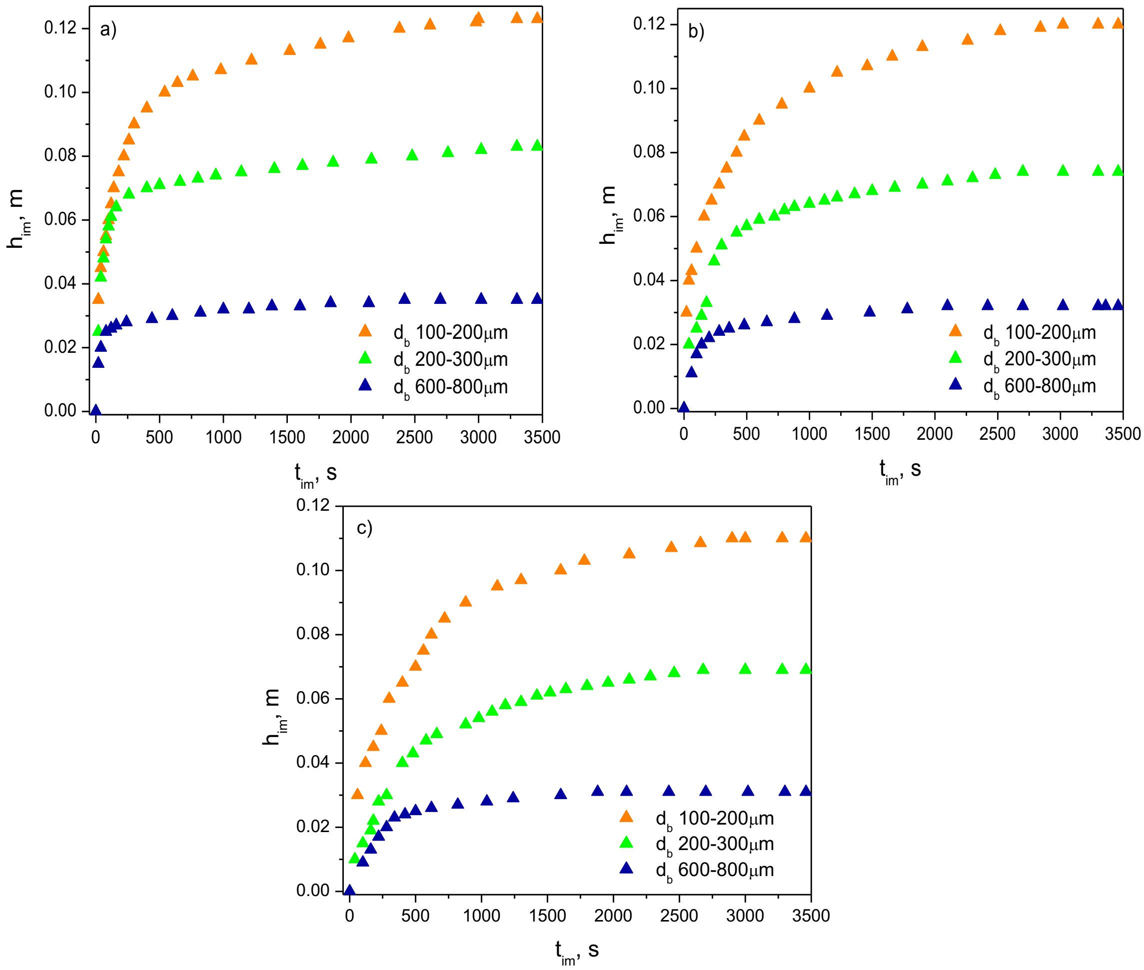

Fig. 3. Changes of emulsion front height h_{im} versus time t_{im} during the imbibition process in the different granular media in case of: a – 10% emulsions; b – 30% emulsions; c – 50% emulsions.
Source: Author's

The experimental data allowed to define the maximal height of emulsions penetration in the different granular media, and the results are shown in Table 3.

Table 3. The maximal height h_{max} of the imbibed emulsions

Type of medium	**Dispersed phase fraction, φ_d**		
	10 vol%	**30 vol%**	**50 vol%**
GS 100	0.123	0.120	0.110
GS 200	0.083	0.074	0.069
GS 600	0.035	0.032	0.031

Source: Author's

The maximal height tends to decrease slightly, i.e. maximum up to 17 %, with the enlarging of the dispersed phase concentration. Such tendency was observed for porous beds with different compositions. The experimental results shown that the highest values of h_{max} were obtained in case of the granular medium composed of beads with d_b in a range of 100–200 μm, i.e. 0.123, 0.12, and 0.11 m for 10%, 30%, and 50% emulsions, respectively. Consequently, the lowest values were derived for the spontaneous imbibition process in a granular medium with d_b of 600–800 μm.

The changes of the imbibition velocity as $v_{imh} = f(t_{im})$ on the base of height values in the used granular beds are shown in Figure 4.

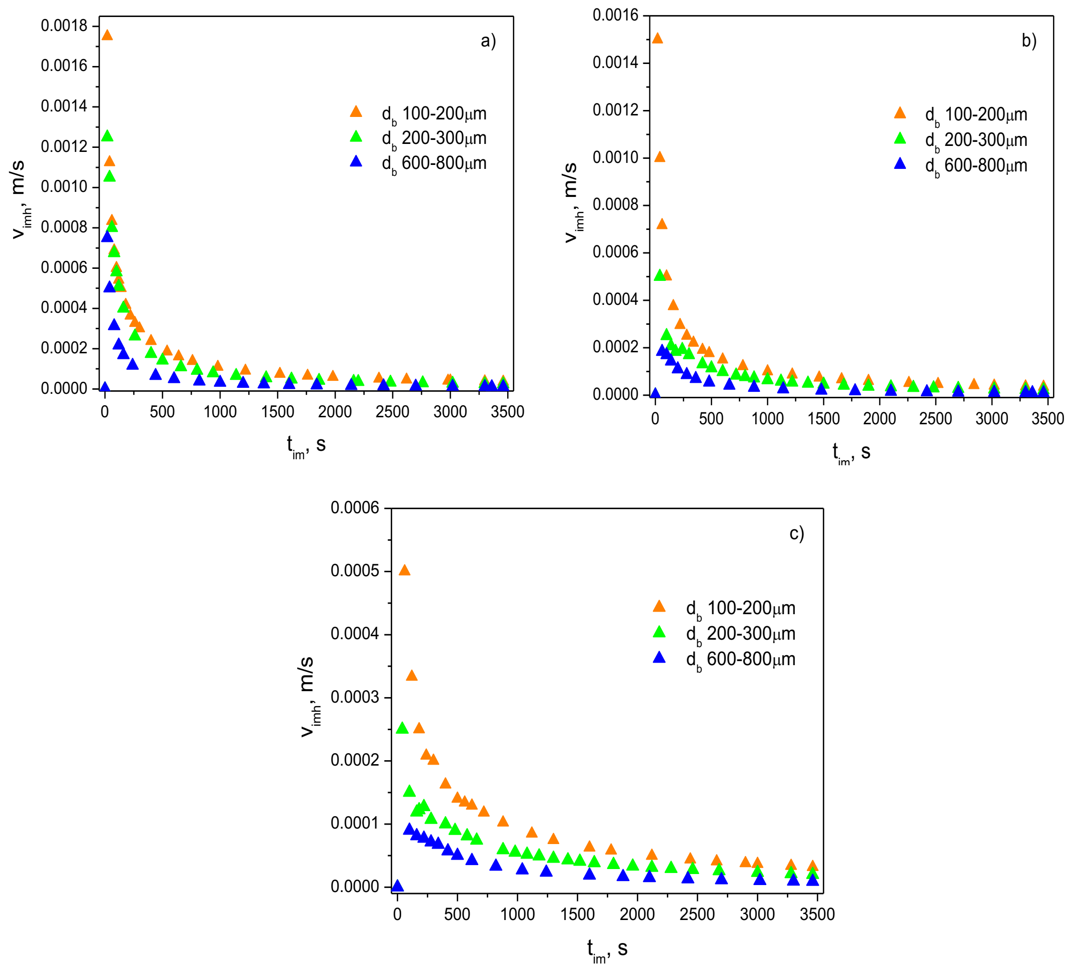

Fig. 4. Changes of the imbibition velocity v_{imh} versus time t_{im} for: a – 10% emulsions; b – 30% emulsions; c – 50% emulsions
Source: Author's

The imbibition velocity v_{imh} tends to rise rapid and after that decreases as shown on the graphs. It can be explained by growth of the counterbalancing force, i.e. gravity acceleration, due to increase of an imbibied emulsion mass. The values of the maximal velocity v_{max} of the wicking process and time $t(v_{max})$, when it was reached, are represented in Table 4.

Table 4. The maximal velocity v_{max} of the imbibition process

Dispersed phase concentration, φ_d	**GS 100**		**GS 200**		**GS 600**	
	v_{max}, m/s	**$t(v_{max})$, s**	**v_{max}, m/s**	**$t(v_{max})$, s**	**v_{max}, m/s**	**$t(v_{max})$, s**
10 vol%	0.00175	20	0.00125	20	0.00075	20
30 vol%	0.00150	20	0.00050	40	0.00018	60
50 vol%	0.00050	40	0.00025	40	0.00009	100

Source: Author's

In all investigated cases, the highest maximal velocity values were obtained in case of the dispersions with the lowest inner phase concentration. It can be explained by the difference in viscosity, and lower value is less influence of the viscous drag force. Thus, the prepared emulsions have the following viscosities: for 10% it was equal to 6.1 mPa·s, in case of 30% this parameter was near 14.8 mPa·s, and the largest value was obtained for 50% dispersion, i.e. 48.4 mPa·s.

As shown in Table 4, it is equal to 0.00175 m/s for the porous bed with d_b of 100–200 µm, 0.00125 m/s for 200–300 µm, and consequently, 0.00075 m/s for 600–800 µm. To compare, the lowest values of v_{imh} were observed for 50% emulsions in all used granular beds. The maximal velocity was registered at t_{im} = 20 s for 10% emulsions, however it tends to growth with increase of the inner phase concentration. The enlargement of grains size and consequently, hydraulic radius of pores causes the increase of time needed to obtain the maximal velocity, i.e. up to 20 s ≤ t_{im} ≤ 100 s (Table 4).

The changes of instantaneous velocity v_{inh} with time t_{im} was additionally calculated relating to average velocity of the imbibition process. It represented as velocity of a liquid in motion at the specific point of time process. The results of the instantaneous velocity variations are performed in Figure 5.

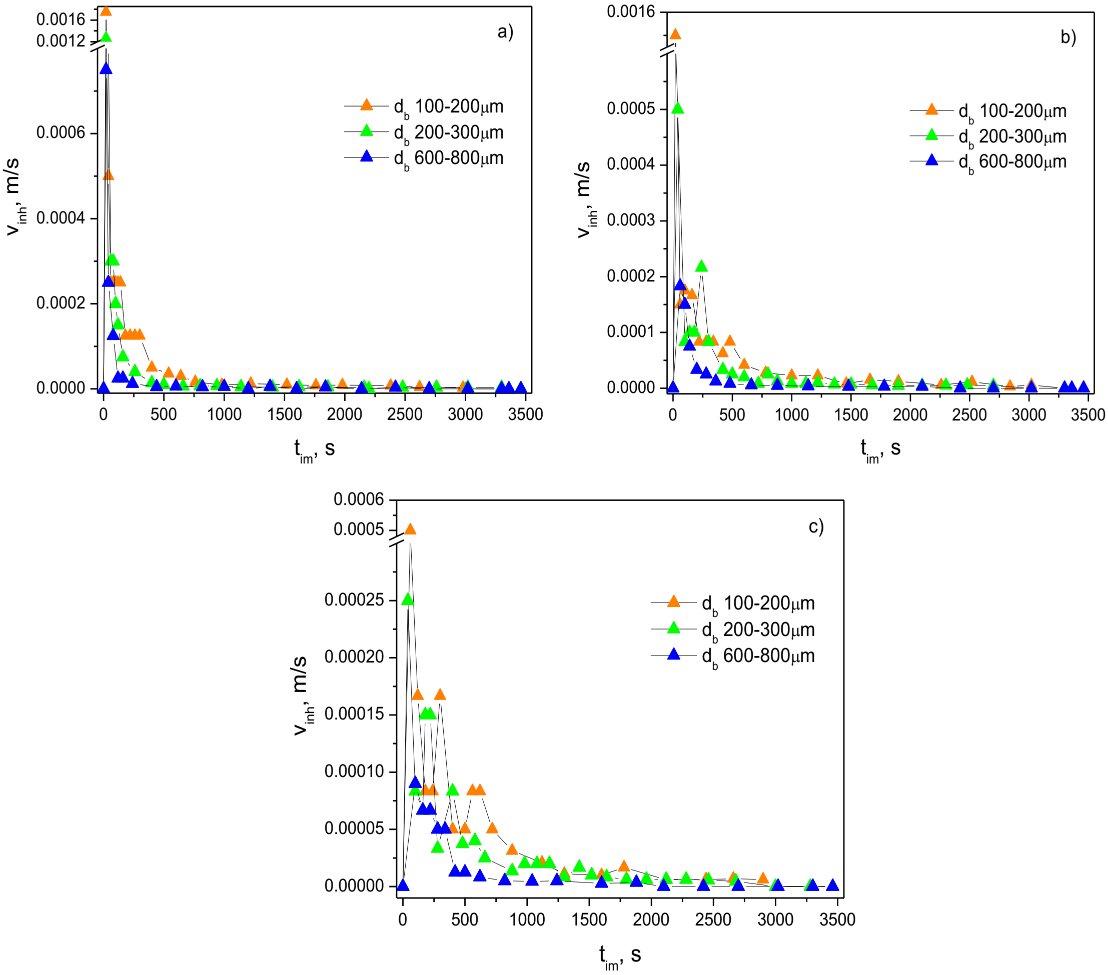

Fig. 5. Changes of the instantaneous imbibition velocity v_{inh} versus time t_{im} for: a – 10% emulsions; b – 30% emulsions; c – 50% emulsions.
Source: Author's

As show in Figure 5a, the higher instantaneous imbibition velocity was obtained for 10% emulsions in all granular beds investigated as in the case of the imbibition velocity v_{imh}. In contrast, the lowest values were derived for 50% dispersions. According to the results, the stronger influence of a bed composition is also observed for emulsions with the inner phase concentration of 50 vol%. In case of 10% emulsions, the instantaneous imbibition velocity becomes almost the same after t_{im} = 800 s (Fig. 5a).

To conclude, the emulsions imbibition in terms of the penetration height depends considerably on the composition of a granular bed. On the one hand, the dispersed phase concentration causes less significant influence on the height of an imbibed emulsion wicking in a granular media. On the other hand, the composition of the dispersed phase effects the imbibition velocity as well as instantaneous one.

Summary and conclusions

The discussed issues were the influence of porous bed composition and dispersed phase concentration on the height of emulsion penetration, which allows to predict velocity of the imbibition process and the maximal height of dispersion rise in a granular bed. According to results, the height of an emulsion front permeation in a granular medium forced by the capillary pressure depends more strongly on the composition of this bed than on the initial concentration of the dispersed phase. However, the effect of a porous medium structure was more considerable in case of 50% dispersions. From a practical point of view, the experimental results give the possibility to predict the productivity of granular sorbents applied to recovery the environment, the building materials wetting with dispersions, i.e. paints, antifungal liquid, and pollutants migration in various porous media, i.e. soil layers, sands and other rock structures.

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