



# Capillary pressure method for measuring lipophilic hydrophilic ratio of filter media

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## ABSTRACT

Lipophilic Hydrophilic Ratio (LHR) was defined based on Washburn equation. The LHR values of five filter media were calculated from the wetting rates of cyclohexane (apolar) and water (polar) through compact filter media beds measured by capillary pressure method. The surface structures of filter media were characterized by X-ray Photoelectron Spectroscopy (XPS) and Fourier Transform Infrared Spectroscopy (FTIR). It was confirmed by great regression coefficients and reproducibility of wetting rates that the values have a good reliability and the technique is applicable. The LHR values of nutshell, manganese sand, ceramic granule, quartz sand and ceramic sand are 66.87, 1.24, 1.22, 1.16 and 0.80, respectively, which shows that nutshell is much more lipophilic while manganese sand, ceramic granule and quartz sand are somehow more lipophilic than ceramic sand. This fact is consistent with the results of XPS and FTIR.

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## 1. Introduction

Filtration is a typical tertiary treatment method for oily wastewater, suitable for oil particles, which are smaller than 10  $\mu\text{m}$  and the lower oil concentration. As far as filtration treatment of oily wastewater is concerned, the oil removal efficiency in filter bed depends not only on filtration velocity and oil concentration, but also on the physical and chemical characteristics of filter media [1]. Wettability is one of the most important surface properties of filter media for water treatment, which affects the removal rate of oil in filtration. Therefore study on their wettabilities helps a lot in the evaluation, selection and development of more efficient filter media for oily water treatment.

Currently, the wettability of solid material surface is generally evaluated in terms of the contact angle formed by liquid on solid surface. For the solid with large and uniform surface, the traditional methods such as sessile techniques, tilting plate technique can be applied to the measurement of contact angle. But the particles of water treatment filter media are small and their shapes are very irregular and diversified, therefore, these methods cannot be applied. Because the method of liquid penetrating into porous bed has been successfully applied to measure the advancing contact angles of solid particles or powders such as mineral particles [2], drug particles [3] and fine coal [4], and in addition, filter particle packed bed is similar to powder bed to some extent given that

the porous columns are modeled as a bundle of uniform capillaries [5], the wettabilities of water treatment filter media were studied in our work by using dynamic permeating pressure method which is based on Washburn's equation.

## 2. Principle

Washburn's equation relates the capillary rise height of a liquid through a compact vertical bed of particles with small pore radius and the contact angle [6,7]:

$$h^2 = \frac{r_{\text{eff}} \gamma_{\text{LV}} \cos \theta}{2\eta} t \quad (1)$$

Here  $\eta$  is the viscosity of the penetrating liquid,  $\gamma_{\text{LV}}$  the surface tension of the penetrating liquid,  $r_{\text{eff}}$  the effective capillary radius,  $h$  the height of liquid penetrating the bed in time  $t$ , and  $\theta$  the advancing particle contact angle. Generally, water treatment filter medium particles are diversified in grade, shape and surface roughness, therefore, the effective capillary radii are different in different places of a filter bed, leading the velocities of capillary rise are different in the different capillaries of a filter bed and the frontline of wettability is not clear. Therefore it is difficult to measure the height of liquid penetrating the bed.

Because the air in filtration bed will be compressed when capillary rise takes place, so that the air pressure will increase, therefore Eq. (1) can be modified according to the relationship between the height and the pressure. After modification, Eq. (1) can be transformed into the following form and its pressure increase of air in

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the filter medium bed as a function of time:

$$(\Delta P)^2 = \left( \frac{\beta \gamma \cos \theta}{\eta} \right) t \quad (2)$$

Here  $\Delta P$  is the pressure increase of air in filter medium particle bed,  $\beta$  is geometrical factor which is only based on the parameters of filtration bed and initial air pressure in filtration bed and is generally regarded to be constant as long as the packing and the particle size remain similar. Therefore the slope of measurement curve is as follows:

$$k = \frac{\beta \gamma \cos \theta}{\eta} \quad (3)$$

This slope can be experimentally determined for each type of particle packing. But the precise and accurate determination of  $\beta$  is essential for correctly calculating  $\theta$ . To obtain the parameter  $\beta$ , one totally wetting liquid has to be used (the contact angle in this situation is then assumed to be zero). A strict particle packing control with a reproducible procedure is also essential in order to ensure the geometric factor  $\beta$  for this totally wetting liquid is the same as for another liquid. Once the geometric factor  $\beta$  is determined, then the contact angle of another liquid for the filter particle could also be calculated by Eq. (3) from the later investigated curve slope.

However,  $\beta$  values are different for different filter media because their kinds, shapes and diameters are various, in addition, it is not easy in practice to find a totally wetting liquid for every kind of filter particle, namely, the factor  $\beta$  value is rather difficult to be determined in any case. Therefore, in order to obviate this problem, we define a concept of Lipophilic Hydrophilic Ratio (thereinafter called LHR) in this work:

$$\text{LHR} = \frac{\cos \theta_o}{\cos \theta_w} \quad (4)$$

There  $\theta_o$  and  $\theta_w$  are the contact angles of oil phase and water phase, respectively for one kind of filter medium. Combination of Eqs. (3) and (4) will result in:

$$\text{LHR} = \frac{k_o \eta_o}{k_w \eta_w} \cdot \frac{\beta_w \gamma_w}{\beta_o \gamma_o} \quad (5)$$

For a similar column packed by the same filter medium,  $\beta_o$  and  $\beta_w$  could be regarded as identical, thus Eq. (5) can be simplified as

$$\text{LHR} = \frac{k_o \eta_o}{k_w \eta_w} \cdot \frac{\gamma_w}{\gamma_o} \quad (6)$$

$k_o$  and  $k_w$  are the measurement curve slopes of oil and water wetting a filter medium, respectively. Obviously the LHR value, which reflects the difference of wettability selectivity of a filter medium to oil and water, depends not only on the penetrating rates of oil and water, but also on the values of viscosity, density and surface tension of wetting liquids. This paper applies Eq. (6) to investigate lipophilic and hydrophilic properties of several commonly used filter media in order to obtain some significant results about the wettabilities.

### 3. Experiment

#### 3.1. Materials and reagents

Five water treatment filter media, nutshell, manganese sand, ceramic granule, quartz sand and ceramic sand, having different shapes and different grade, were purchased from Songxin Filter Media Company, Henan Province of China. Size fractions of 0.6–0.9 mm were obtained by dry-sieving through stainless steel sieves. The sieved samples were well cleaned prior to use [8]. The cleaning procedure consisted of boiling the samples in deionized water for 30 min, washing several times with deionized water until the washed water no longer seemed turbid. Before use, the cleaned

**Table 1**

Characteristics of cyclohexane and deionized water at 20 °C.

Wetting liquid	Viscosity (mN m <sup>-2</sup> s)	Surface tension (mN m <sup>-1</sup> )
Cyclohexane	0.937	25.5
Deionized water	1.002	72.8

samples were dried at 60 °C and then baked in oven at 110 °C for 12 h.

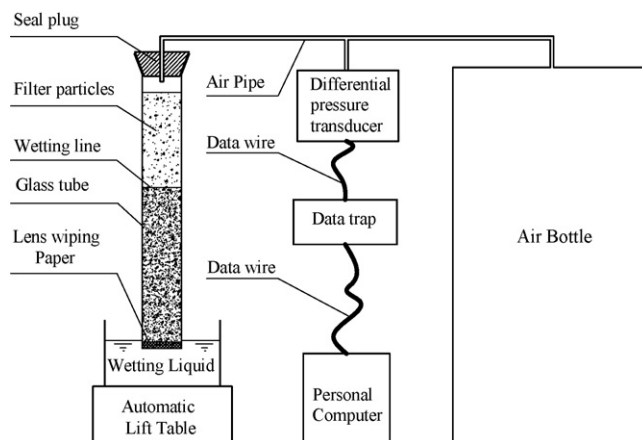
The reagents used in this work are apolar cyclohexane and polar deionized water, representing the oil phase and water phase, respectively [3,9]. Cyclohexane was purchased from Institute of Medicine Technology, Tianjing, China. It is an analytic grade reagent, and the content is more than 99.5%. The deionized water was produced by reverse osmosis, passage through two stages of mixed ion exchange resin bed followed by a filtration stage of activated carbon. Their characteristics are listed in Table 1.

#### 3.2. Equipment and approach

The experimental equipment used in this work is illustrated in Fig. 1. It mainly consists of CYB11W differential pressure transducer (Xingmin Electron Technology Company, Xian, China), USB-4.0 data trap and software for date processing (Xingmin Electron Technology Company, Xian, China), Fangzheng PC computer (Fangzheng Company, Beijing, China), Washburn glass tube which is cylindrical and equipped with a sintered glass sieve plate of controlled porosity at its lower extremity (made in our laboratory, 10 mm × 150 mm) and so on.

Before measurement, the fixed quantity of filter particles is weighed and put into a cleaned Washburn glass tube. A filter paper is placed between the sintered glass sieve plate and the filter particle in order to avoid the fall of particles into the pores. It was noted that the packing procedure is the most important operation of this method, and great care must be taken when preparing the columns in order to ensure reproducible results [10]. In this work, the packed Washburn glass tube is manually impacted hundreds times until it meets all parameters in Table 2.

The Washburn glass tube packed with filter particles is fixed on an iron stand. A glass beaker loading testing liquids, with temperature kept strictly around 20 ± 0.5 °C, is placed on the automatic elevator-platform. Start this elevator-platform to make the glass beaker rise slowly, once the surface of liquid get in touch with the bottom of the Washburn glass tube, the rising of elevator-platform is stopped immediately, then the capillary rise takes place that the front of the liquid rises through the porous bed causing the pressure of air in packed bed start to increase. This information is send, via



**Fig. 1.** Schematic diagram of the measuring system for pressure approach.

**Table 2**  
Characteristics of filter media in packed bed.

Filter name	Density (g cm <sup>-3</sup> )	Weight (g)	Packed height (cm)	Packed fraction ( $\Phi^*$ )
Nutshell	1.20	4.5	8.1	0.590
Manganese sand	3.20	10.0	7.1	0.560
Ceramic granule	2.40	8.0	6.5	0.653
Quartz sand	2.55	8.0	6.3	0.634
Ceramic sand	2.30	8.0	6.9	0.642

$\Phi^*$  calculated from the height and weight of packed bed (Prestidge et al. [3]).

differential pressure transducer and data trap, to a personal computer where the pressure changes are recorded 30 times per second with 5 Pa of sensitivity automatically. The elevator-platform must be raised slowly with a very low speed of 10 mm min<sup>-1</sup> controlled by the motor until the sintered glass filter extremity just touches the testing liquids. The experimental data, pressure increases and times, are collected until the liquid front does not advance any more.

### 3.3. Particle characterization

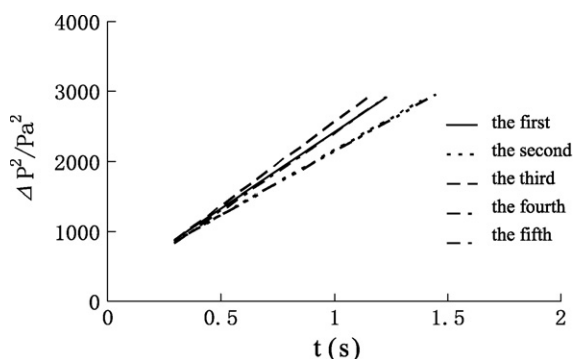
XPS spectra of the five filter particles were recorded using a PerkinElmer PHI Model 5702 X-ray photoelectron spectrometer with an Al K $\alpha$  X-ray source operated at 14 kV and the pass energy of 29.35 eV, which was made in American Physical Electron Company. Surface atomic concentrations were determined from peak intensities and the corresponding sensitivity factors.

FTIR spectra of the five filter particles in the wave number range of 400–4000 cm<sup>-1</sup> were obtained by IFS66V/S infrared spectrometer which was made in German Bruker Company.

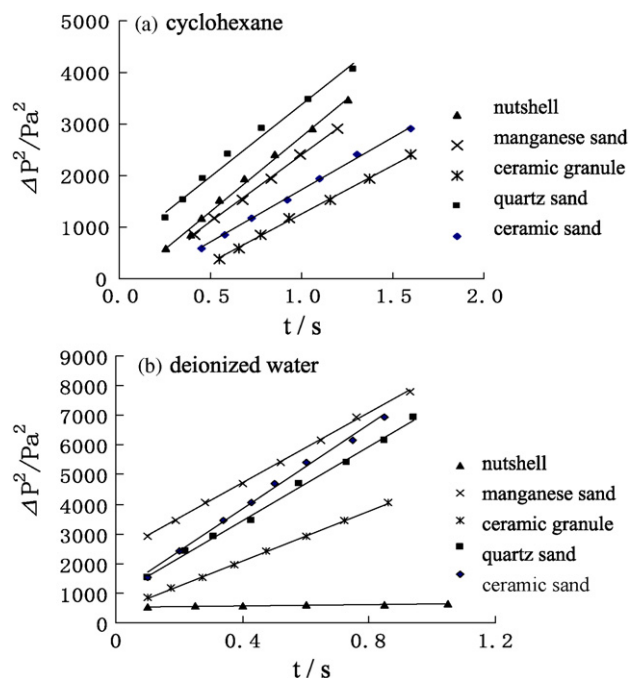
## 4. Results and discussion

### 4.1. Feasibility of the method

Generally speaking, the diameters of filter medium particles for water treatment are much greater than that of solid powders, and they are very irregular and diversified in grade, shape and surface roughness, therefore whether or not dynamic permeating pressure method can be applied to measure wettabilities of filter medium must be verified by experiment. The Feasibility of this method should mainly depend on the result reproducibility and the linearity. As an example, Fig. 2 shows the five time experiment curves of water wetting ceramic sand. The average slope and mean error are 2002.88  $\pm$  152.02. Therefore it can be concluded that both the reproducibility and the linearity are good, and the method is feasible.



**Fig. 2.** The reduplicity tests of ceramic sand for cyclohexane as wetting liquid.



**Fig. 3.** The linear stages of the wetting curves of different filter media.

### 4.2. Wetting rates and LHR values

Linear stages obtained from the wetting curves about between 0 and 2 s are segmented and given in Fig. 3. Linear least-square fits for all wetting rates gave regression coefficients of more than 0.99. The slopes of these lines  $k$  are collected in Table 3. Fig. 3 and Table 3 indicate that the wetting rate of water to different filter particles is in the order as follows: ceramic sand > quartz sand > manganese sand > ceramic granule > nutshell, but the wetting rate of cyclohexane to different filter particles is in the order as follows: nutshell > quartz sand > manganese sand > ceramic sand > ceramic granule.

As previously mentioned,  $\beta$  values are different for different filter media, in addition, it is not easy in practice to find a total wetting liquid for every filter medium, thus in order to compare the differences of wettabilities of apolar liquid (oil phase) and polar liquid (water phase) for these five filters, the LHR concept is brought forward here and the values of filter media are calculated by Eq. (6) and also listed in Table 3. The LHR Value conceptually reflects the wettability difference between oil phase and water phase for the same filter medium, namely, the greater the LHR value, the more lipophilic is the filter medium, and vice versa. Then we can find from Table 3 that nutshell is the most lipophilic, its LHR value reaches to 66.87; the LHR values of manganese sand, ceramic granule and quartz sand are 1.24, 1.22 and 1.16, respectively; ceramic sand is the most hydrophilic, its LHR value is only 0.80.

**Table 3**  
Wetting kinetics and LHR values of filter media.

Filter name	Cyclohexane		Deionized water		LHR
	Slope of the line (Pa <sup>2</sup> s <sup>-1</sup> )	R <sup>2</sup>	Slope of the line (Pa <sup>2</sup> s <sup>-1</sup> )	R <sup>2</sup>	
Nutshell	2882.24	0.991	119.49	0.994	66.87
Manganese sand	2445.82	0.993	5459.60	0.996	1.24
Ceramic granule	1825.66	0.993	4152.97	0.996	1.22
Quartz sand	2790.84	0.991	6643.16	0.997	1.16
Ceramic sand	2002.88	0.993	6937.78	0.993	0.80

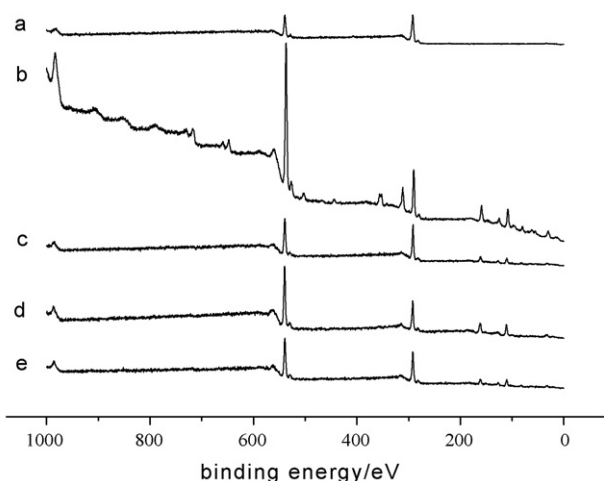


Fig. 4. XPS of five filter media. (a) Nutshell, (b) manganese sand, (c) ceramic granule, (d) quartz sand, and (e) ceramic sand.

#### 4.3. Surface analysis by XPS and FTIR spectroscopy

In this work, XPS analysis of the five filter samples was employed to elucidate the differences in surface chemistry responsible for the observed wetting rates and calculated LHR values. The XPS spectra of the filter samples are presented in Fig. 4. The analyzed results of atomic concentration data for nutshell are with carbon (291.6 eV) of 83.38%, oxygen (539.2 eV) of 16.62%; for manganese sand are Si (111.3 eV) of 17.22%, O (539.6 eV) of 74.22%, Fe (714.3 eV) of 5.12% and Mn (69.7 eV) of 3.45%; for ceramic granule are Si (111.0 eV) of 22.31%, O (539.3 eV) of 71.96%, Al (72.3 eV) of 5.73%; for quartz sand are Si (111.0 eV) of 25.83%, O (539.3 eV) of 72.20%, Al (72.3 eV) of 1.97%; for ceramic sand are Si (111.0 eV) of 22.47%, O (539.3 eV) of 70.26%, Al (72.3 eV) of 6.32%, Fe (714.1 eV) of 0.94%.

The FTIR spectra of five filter particle are shown in Fig. 5. For nutshell, the absorption at 2927.4 and 2884.9  $\text{cm}^{-1}$  belong to  $-\text{CH}_2-$  stretching vibration, 1452.1–1465.6  $\text{cm}^{-1}$  represents its deformation vibration, 1616.1–1658.5  $\text{cm}^{-1}$  represents  $\text{C}=\text{C}$ , 1511.9  $\text{cm}^{-1}$  belongs to nitrogen group, 1384.4–1446.3  $\text{cm}^{-1}$  belongs to carboxylic group, 1274.7  $\text{cm}^{-1}$  belongs to aliphatic group, 1051.0  $\text{cm}^{-1}$  belongs to aether and alcohol groups [11]; for manganese sand, the strong and broad absorption at 1078.0  $\text{cm}^{-1}$  is due to stretching vibration of Si–O, and 470.5  $\text{cm}^{-1}$  is due to its deformation

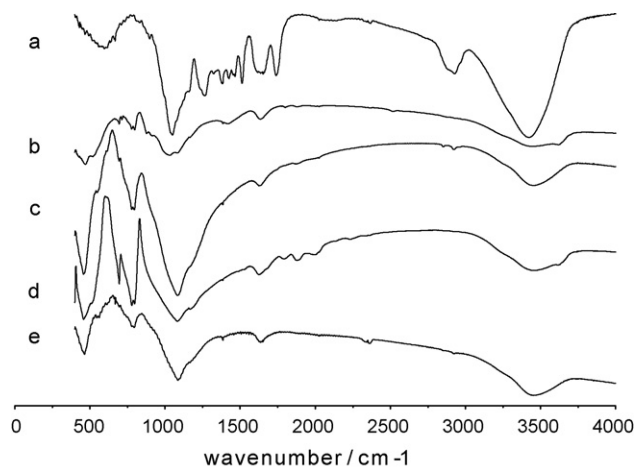


Fig. 5. FTIR of five filter media. (a) Nutshell, (b) manganese sand, (c) ceramic granule, (d) quartz sand, and (e) ceramic sand.

vibration, 875.5  $\text{cm}^{-1}$  is due to  $\text{MnO}_4^{2-}$ , 694.2  $\text{cm}^{-1}$  is due to  $\text{Fe}_3\text{O}_4$ ; for ceramic granule, the strong and broad absorption at 1085.7  $\text{cm}^{-1}$  represents Si–O stretching vibration, and 464.8  $\text{cm}^{-1}$  represents its deformation vibration, 777.2  $\text{cm}^{-1}$  represents Al–O stretching vibration; for quartz sand, the strong and broad absorption at 1076.1  $\text{cm}^{-1}$  is for symmetry stretching vibration of Si–O–Si, 690.4  $\text{cm}^{-1}$  is for asymmetry stretching vibration of Si–O, and 459.0  $\text{cm}^{-1}$  is for its deformation vibration, 779.1  $\text{cm}^{-1}$  is for stretching vibration of Al–O; for ceramic sand, 1083.8  $\text{cm}^{-1}$  represents symmetry stretching vibration of Si–O–Si, 464.8  $\text{cm}^{-1}$  belongs to deformation vibration of Si–O, 779.1  $\text{cm}^{-1}$  belongs to Al–O stretching vibration. The broad adsorption at 513.0–694.2  $\text{cm}^{-1}$  belongs to  $\text{Fe}_3\text{O}_4$  [12].

Obviously the XPS data and FTIR spectra identify significant qualitative and quantitative differences in the surface chemistry of the different filter media samples. Nutshell surface is mainly made up of carbon and oxygen elements, which combine into some weakly polar organic functional groups and make nutshell more wettable for apolar cyclohexane than water. While manganese sand, ceramic granule, quartz sand and ceramic sand surfaces contain polar Si–O, and minor Al–O, Fe–O, Mn–O species which make them hydrophilic and accordingly water would excel cyclohexane for wetting them. Therefore it can be concluded that the results of surface characterization are consistent with LHR values determined above.

## 5. Conclusions

The capillary rises of filter medium were measured by using dynamic permeating pressure method. Linear least-square fits gave regression coefficients of more than 0.99, confirming the suitability of the experimental method for filter medium particles and further validating Washburn's theory. The wettabilities for different filter medium particles with the same size fraction of 0.6–0.9 mm were evaluated by comparing their LHR values calculated from penetrating kinetics. The LHR values for nutshell, manganese sand, ceramic granule, quartz sand and ceramic sand are 66.87, 1.24, 1.22, 1.16 and 0.80, respectively, which means nutshell particles are lipophilic, while manganese sand, ceramic granule, quartz sand are hydrophilic comparatively, and ceramic sand is the most hydrophilic one. These differences would probably be attributed to the differences of surface chemistries, namely, nutshell surface seems weakly polar and other particles contain more polar hydrophilic species.

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