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IMPACT OF ROUGHNESS ON HYDROPHOBICITY OF PARTICLES MEASURED BY THE WASHBURN METHOD

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Wettability and penetration kinetics of liquid into porous material were studied by the capillary rise method. The mass gain of the penetrating liquid in a tube filled with glass beads was measured vs. time. Two types of glass beads surfaces: unmodified (smooth), modified (rough), were used to investigate the influence of porous material surface on wettability and penetration kinetics. It was found that the surface roughness has a significant effect on the penetration kinetics but not on the contact angle. The penetration rate of liquids into porous material with the rough surface was found to be over two-fold greater than that for porous materials with unmodified (smooth) surface. It is well known that the surface roughness has a significant effect on the macroscopic contact angle for flat surfaces. Our experiments showed that the contact angle of a collection of particles does not depend on their surface roughness. It may suggest that the surface roughness does not influence the microscopic contact angle.

Key words: roughness, capillary rise, penetration kinetics, porous media, flotation

INTRODUCTION

The wettability of surfaces is an important property in many applications including flotation and washing. The wettability is generally characterized by the contact angle between liquid, solid surface, and gaseous environment. The contact angle has been mostly studied for flat surfaces as a function of liquid drop size, heterogeneity and roughness of the surface (Kwok and Newmann, 1991; Miller *et al.*, 1996; Drelich and Miller, 1994; Adamson, 1967). For particulate materials, particles forming a bed and for porous material, however, the contact angle has not received the same attention.

The roughness has a significant effect on the macroscopic contact angle of flat surfaces (Adamson, 1967). However, no study on surface roughness of particles

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forming porous materials was found in the literature. The present study is an extension of the effort (Dang-Vu and Hupka, 2005; Dang-Vu et al., 2005) to investigate the contact angle of porous materials and penetration kinetics using the capillary rise method.

EXPERIMENTAL

The characteristics of the glass beads used to form a bed of particles resembling porous material is presented in Table 1. The glass beads were provided by the Interglass Ltd. Walbrzych, Poland.

Table 1. Characteristics of bed of particles

Symbol	Pore size [μm]	Porosity [m^3/m^3]	Bulk density [kg/m^3]	Surface property	Source
A	60 – 110	0.34	1589	smooth (unmodified)	*
B	150 – 250	0.33	1619	smooth (unmodified)	*
C	150 - 250	0.30	1678		*
D	150 – 250	0.36	1556	rough (modified)	this work

* - Dang-Vu and Hupka, 2005; Dang-Vu et al., 2005

Bed D was obtained after performing a surface modification, which can be summarized as follows (Dang-Vu, 2005):

1. Glass beads were dipped in 10 % hydrofluoric acid for 5 min
2. Then, they were dipped in etching solution for 10 min. The etching solution consisted of distilled water (35%), 40%-hydrofluoric acid (30%), potassium hydrofluoride (KHF_2) (35%)
3. Glass beads were again dipped in hydrofluoric acid for 3 minutes
4. Modified glass beads were then washed with distilled water and dried over night at 120°C

The characteristics of the wetting liquid used in this study is shown in Table 2.

Table 2. Characteristics of liquids used for capillary rise experiments (20°C)

Wetting liquid	Density [kg/m^3]	Viscosity [$\text{mPa}\cdot\text{s}$]	Surface tension [mJ/m^2]
Water	997	1.01	72.3
Toluene	862	0.55	27.8
Ethanol	785	1.20	22.0
Heptane	684	0.41	20.3
Octane	703	0.55	21.8
Decane	730	0.92	23.9

The capillary rise experiment, also called the Washburn method, was used to study the impact of surface properties of porous materials on wettability and penetration rate. The penetration height of the liquid in a 0.7 cm diameter glass tube filled with glass beads was measured vs. time. The increase of the penetrating liquid in glass beads bed was recorded every two seconds using an electronic balance. Details of the experimental apparatus and procedures are given elsewhere (Dang-Vu and Hupka, 2005).

RESULTS AND DISCUSSION

Electron scanning microscope images of the glass bead before and after surface modification are presented in Fig. 1. A dull surface of the glass bead after modification was clearly observed. The depth of the groove of the modified surface roughness is in the range of 5 to 15 μm . It is worth to note that after the surface modification the mass of particle decreased, however, its radius remained unchanged.

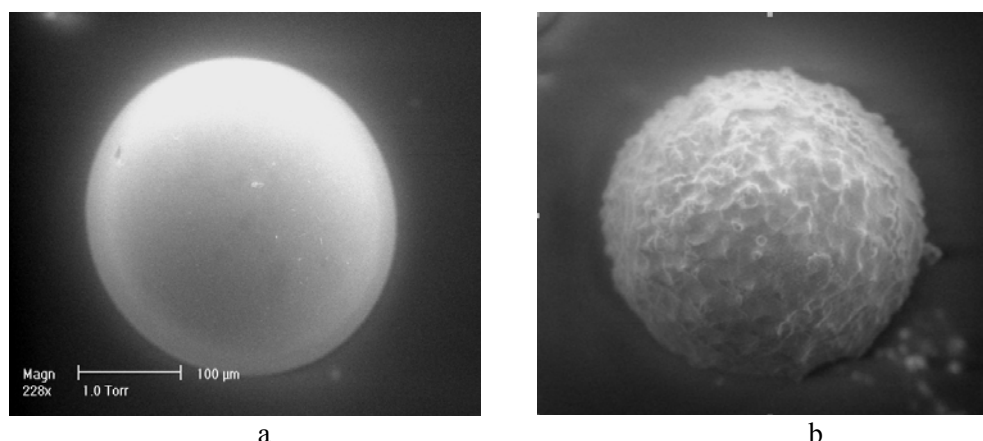


Fig. 1. The surface of glass beads before (a) and after (b) modification

The relationships between the square of liquid mass and penetration time for particles with the modified surface are shown in Fig. 2. As can be seen for all the wetting liquids, the relationships are linear and in good agreement with the Washburn equation. Water was the fastest penetrating liquid while ethanol was the slowest. The same relationships for beds A, B, and C have been presented previously elsewhere (Dang-Vu and Hupka, 2005).

It is worth note that in our previous report (Dang-Vu and Hupka 2005) in the case of the unmodified glass beads with mean radius of 60 – 110 μm the relationship between the squared mass of liquid and penetration time was linear, but for that with mean radius of 150 – 250 μm the relationship between the squared mass vs. time was parabolic for the some wetting liquids. In the present study, although the particles

have large mean radius (150 – 250 μm), the relationship m^2 vs. t is linear for all tested liquids, indicating the effect of surface roughness on the penetration kinetics. This can be explained by the fact that an intergranular space between particles with rough surface is more even than that of unmodified surface. The penetration of liquid becomes more even resulting in a linear relationship between the squared liquid mass and penetration time.

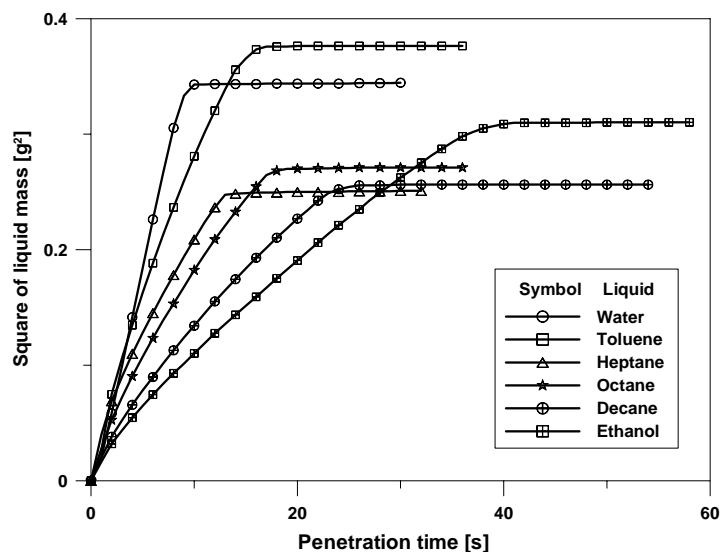


Fig. 2. Relationship between the square of liquid mass and penetration time for bed D

Pictures showing penetration of liquids into beds D and B are presented in Fig. 3. As can be seen in Fig. 3 the liquid penetrated more evenly into bed D than bed B. In the case of bed D (rough surface), liquid penetrated to the top of the bed surface and wetted the whole top surface at the same time. However, in the case of bed B (smooth surface), the liquid penetration is not even. In the top of the bed surface only some wetting regions were observed.

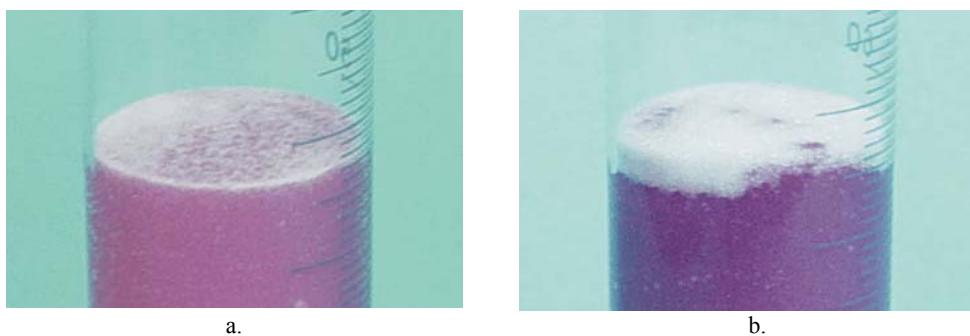


Fig. 3. Penetration of liquid into bed D (a) and B (b)

The effect of surface roughness of particles on penetration rate can be also observed in Fig. 4, which presents the slope of the m^2 vs. t curve for different beds. The results for unmodified particles (bed A, B, and C) were from our previous report (Dang-Vu and Hupka, 2005). As can be seen, the order of the slope for the wetting liquid in bed D is the same as that in bed A, B, and C. However, the value of the slope for bed D is over two-fold greater than that for the rest of the beds. Liquid penetrates into bed D over two-fold faster than beds A, B, C, indicating a significant effect of the surface roughness on the penetration rate.

As shown in Fig. 4 for alkane hydrocarbon, the penetration rate decreases with the chain length (number of carbon atom in the chain). A similar result has been reported in literature (Dang-Vu *et al.*, 2002; Gonzalez-Martin *et al.*, 2001; Prestidge and Tsatouhas, 2000, Hupka *et al.*, 2003)

It can be concluded from Fig. 2 that water penetrates the beds faster than toluene. The slope for toluene was calculated and used for determination of the contact angles of the studied liquid in relation to the toluene which was arbitrarily taken as the reference liquid due to its largest product of $\frac{m^2}{t} \cdot \frac{\eta}{\rho^2 \gamma}$ (Dang-Vu, 2005). The results of calculations are presented in Table 3.

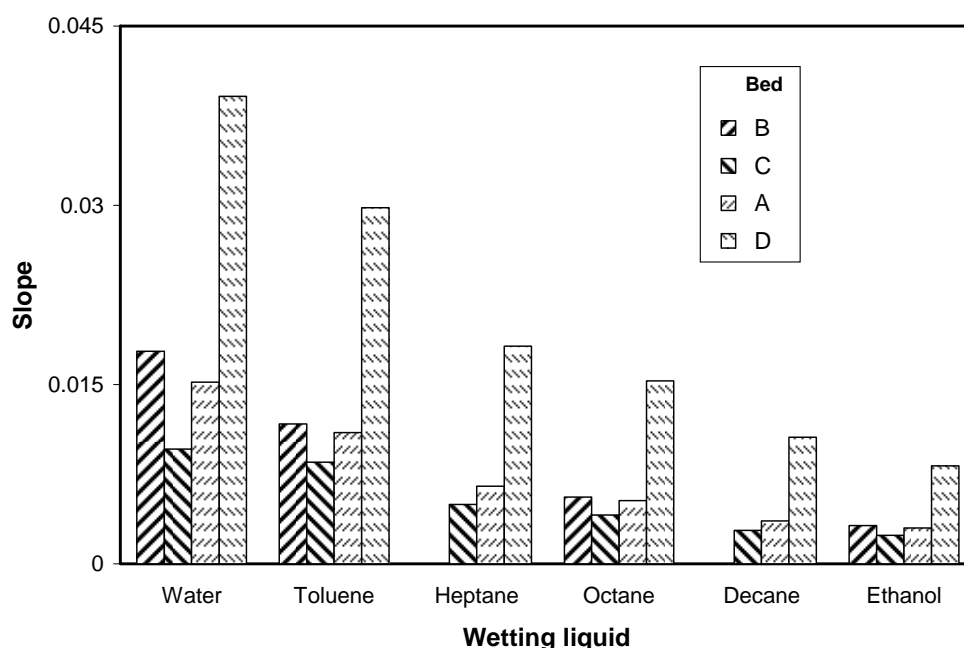


Fig. 4. The slope of m^2 vs. t curve for glass beads: A - unmodified small particles with pore size of 60 – 110 μm ; B - unmodified large particles with pore size of 150 – 250 μm , C - unmodified particles with pores size of 60 – 250 μm ; and D - large particles with pore size of 150 – 250 μm and modified surface (rough)

Table 3. Slope and contact angles for bed D

Wetting liquid	Slope of m^2 vs. t curve	Contact angle [deg]
Water	0.039	47
Toluene	0.030	* (0)
Heptane	0.018	13
Octane	0.015	15
Decane	0.011	18
Ethanol	0.008	26

* Toluene was assumed to be the reference wetting liquid

As shown in Table 3, for alkane hydrocarbon the contact angle decreases with the chain length. Similar result has been reported in literature (Dang-Vu *et al.*, 2002; Gonzalez-Martin *et al.*, 2001; Prestidge and Tsatouhas, 2000).

Similarly to the penetration kinetics study, in order to observe the effect of surface roughness on the contact angle, the calculated contact angle for bed D was plotted together with that for bed A, B, and C in Fig. 5. As can be seen there, the relative contact angle of liquids on the modified rough surface is comparable to that of unmodified particles. In contrary to penetration kinetics, the effect of surface roughness on the contact angle is insignificant.

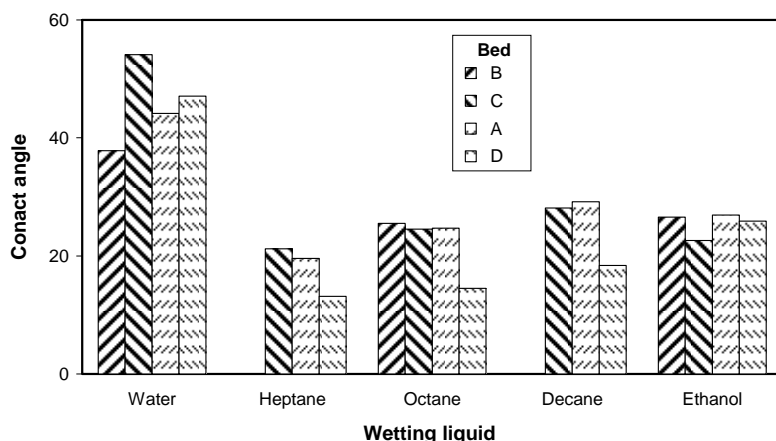


Fig. 5. Contact angle for beds A, B, C, D. A - unmodified small particles with pore size of 60 – 110 μm ; B - unmodified large particles with pore size of 150 – 250 μm , C - unmodified particles with pores size of 60 – 250 μm ; and D - large particles with pore size of 150 – 250 μm and modified surface (rough)

In the capillary rise (Washburn) method, the contact angles are calculated from the ratio of penetration rate of the reference wetting liquid and the studied liquid (Dang-Vu, 2005). The surface roughness of the particles increases the penetration rate of all liquids, i.e. the studied and reference liquid. Therefore, the variation in the penetration rate of the reference wetting and studied liquid is small, resulting in small variation in contact angle value of both liquids.

CONCLUSIONS

This investigation shows that the roughness of surface has a significant effect on the kinetics of liquid penetration of a collection of particles but not on the contact angle. The penetration rate of a liquid into porous material with a rough surface is over two-fold greater than that for smooth surfaces. This finding may have a significant importance in various phenomena, especially flotation of particles. The results of this investigation indicate that the hydrophobicity of flotation, in contrary to kinetics of flotation, should not be influenced by the roughness of particles.

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REFERENCES

- ADAMSON, A.W., (1967), *Physical Chemistry of surfaces*, Wiley.
- CRAWFORD R., KOOPAL L. K., RALSTON J., (1987), *Contact angles on particles and plates*, *Colloids Surf.* 27, 57-64.
- DANG-VU T., (2005), *PhD dissertation*, Gdansk University of Technology, Gdansk, Poland,
- DANG-VU T., HUPKA J., NALASKOWSKI J., (2002) *Important of time evaluation in capillary rise method*, *Proceedings of The Third International Conference Environmental Technology for Oil Pollution*, 08-11.09.2002, Gdańsk, 2, 139-145.
- DANG-VU T., HUPKA J., (2005), *Characterization of porous materials by capillary rise method*, *Physicochem. Problems Min. Process.* 39 47-65.
- DANG-VU T., HUPKA J., ARANOWSKI R., MISIUK S., (2005), *Analysis of different approaches of capillary rise method for characterization of porous materials*, *Proceedings of the 4th International Conference "Oils & Environment" AUZO 2005*, June 23-23, 2005, Gdansk, Poland, p. 184-191.
- DRELICH J., MILLER J. D., (1994), *The effect of solid surface heterogeneity and roughness on the contact angle/drop (bubble) size relationship*, *Colloid Interface Sci.*, 164, 252-259.
- GONZALEZ-MARTIN M. L., JANCZUK B., LABAJOS-BRONCANO L., BRUQUE J. M., GONZ C. M., (2001), *Analysis of the silica surface free energy by the imbibition*, *J. Colloid Interface Sci.*, 240, 467-472.
- HUPKA J., DANG-VU T., WERSOCKI S., (2003), *Badanie osadu czynnego jako sorbentu oleju*, *Inżynieria Ekologiczna*, 9, 145-153.
- KWOK D. Y., NEWMANN A. W., *Contact angle measurement and contact angle interpretation*, *Adv. Colloid Interface Sci.*, 81 (1999) 167-249.
- MILLER J. D., VEERAMASUNENI S., DRELICH J., YALAMANCHILI M. R., YAMAUCHI G., (1996), *Effect of roughness as determined by atomic force microscope on the wetting properties of PTFE thin films*, *Polym. Eng. Sci.*, 36, 1849-1855.
- PRESTIDGE C. A., TSATOUHAS G., (2000), *Wettability studies of morphine sulphate powders*, *Int. J. Pharm.*, 198, 201-212.

Trong Dan-Vu, J. Hupka, J. Drzymala, *Wpływ szorstkości powierzchni ziarn na ich hydrofobowość mierzona metodą Washburna*, *Physicochemical Problems of Mineral Processing*, 40 (2006), 45-52 (w jęz. ang.).

Badano zwilżalność oraz kinetyka penetracji cieczy w warstwie ziarn mineralnych metodą wzniesienia kapilarnego (metoda Washburna). Mierzono wzrost masy jako funkcję czasu dla układu w którym następowała penetracja cieczy w rurkę wypełnioną kulkami szklanymi. Użyto dwóch typów kulek szklanych: niemodyfikowanych o gładkiej powierzchni oraz modyfikowanych o szorstkiej powierzchni. Stwierdzono, że szorstkość powierzchni znacząco wpływa na szybkość penetracji cieczy w rurkach z ziarnami, ale nie wpływa na wyliczony kąt zwilżania, który jest miarą hydrofobowości układu. Szybkość penetracji cieczy w układ z kulkami o szorstkiej powierzchni był dwukrotnie większy niż z ziarnami w postaci niemodyfikowanych gładkich kulek. Wiadomo, że chropowatość powierzchni ma wpływ na makroskopowy kąt zwilżania płaskich powierzchni. Jednakże nasze eksperymenty wykazały, że dla materiałów ziarnistych tworzących warstwę kąt zwilżania nie zależy od porowatości ziarn. Może to sugerować, że mikroskopowy kąt zwilżania mało zależy od kształtu powierzchni.