

FILTECH 2011

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FILTER CAKE WASHING OF MESOPOROUS PARTICLES

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ABSTRACT

Characteristic properties of mesoporous particles such as a high specific surface area are important for their application in chromatographic and catalytic processes. However, these advantageous properties impede a probably required purification of the particles. Impurities, located in areas of low accessibility to the wash liquor, are removed mainly by a slow diffusive mechanism. Moreover adsorption of the impurities may hinder the impurity removal. In the present study the effect of the intraparticle pore space and the specific surface area, and therefore of adsorption and diffusion, on purification of mesoporous particles using filter cake washing is examined.

KEYWORDS

Mesoporous Particles, Filter Cake Wash, Adsorption, Dyes

1 Introduction

A wide range of particulate systems is synthesized in the liquid phase. Undesired impurities such as educts and byproducts can be dissolved in the liquid phase. Depending on the amount of impurities and the desired purification grade of the final particulate product, washing is applied additionally to the required solid/liquid separation. Washing is defined as the replacement of a liquid (mother liquor, with or without dissolved impurities) from particles by another liquid (wash liquor) [1]. Many washing processes can be assigned to filter cake washing. Cake washing is characterized by a fixed bed of particles, which is penetrated by a wash liquid. Hence, displacement mechanism is the dominating purifying effect [1]. The required wash liquor flow through the cake can be either driven by pressure (differential pressure field) or mass/volumetric forces (gravitational/centrifugal field). Due to the rigid structure of the particle cake, some stagnant areas, like areas close to particle-particle contacts, exist. Impurities in those areas are mainly removed by diffusion, since the accessibility of the wash liquid is limited. In case of mesoporous particles this challenge may be even intensified. While impurities in the interpore space are rinsed easily by convectional transport, the mesopores are not flowed through at all. Hence, nearly half of the total porous volume may consist of stagnant areas. Additionally to diffusional effects slow desorption kinetics decelerate the wash process.

2 Theoretical background

A wash performance is usually characterized by the wash curve. To obtain a wash curve for a specific particle/impurity system and specific process parameters the concentration ratio c^* is plotted against the wash ratio W . Hereby the wash ratio W and the concentration ratio c^* are defined as

$$W = \frac{V_{WL}}{V_{Pore}} \quad (1)$$

$$c^* = \frac{c}{c_0} \quad (2)$$

in which V_{WL} is the added wash liquid volume, V_{Pore} the total pore volume (inter- and intraparticle void volume), c the remaining impurity concentration and c_0 the initial impurity concentration in the filter cake. However, an accurate description of the wash results demands the consideration of the adsorbed impurity fraction. The amount of adsorbed molecules for a known impurity concentration in the surrounding fluid can be determined from the sorption isotherm for the present particle/impurity system. A common model for sorption isotherms is the Freundlich model, which is based on the following relation between the particle loading Q and the impurity concentration c_{eq} in a state of equilibrium [2].

$$Q = f c_{eq}^n \quad (3)$$

with the two constants f and n for a given particle/impurity system.

3 Materials and Methods

The apparatus used for the experimental studies is a compression-permeability cell (CP-cell, Fig. 3.1).

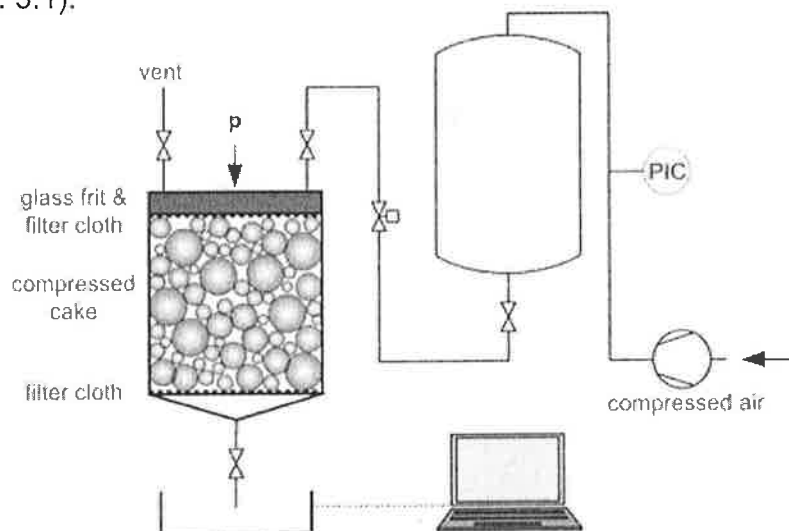


Fig. 3.1: Apparatus set-up of compression-permeability cell

Due to its small filtration area of 9 cm^2 the maximum cake volume is limited to about 34 cm^3 . But the dead volume, which is filled with demineralised water previously to the washing experiment, is minimized. During an experiment the wash liquor is added either by a pump or pressure vessel depending on the magnitude of the wash liquor

flow rate. Hence, a pressure force drives the wash liquor transport in the CP-cell. Before entering the filter cake, the wash liquor is distributed by a sintered glass frit and a filter cloth. Therefore the influence of wash liquid maldistribution on the wash performance can be avoided as far as possible. The displaced mother and wash liquor leave the apparatus via a filter cloth, a perforated plate and a funnel-shaped drain. The outgoing filtrate flow is collected and detected online on a balance. Acrylic glass inserts sidewise the apparatus allow a good, direct observation of the washing process.

Two types of silica gel particles for the wash experiments were purchased from Merck KGaA and used without further purification. The particle size of both silica gels ranges from 200-500 μm (and 63-200 μm , respectively), but vary in average pore size d_{Pore} , specific surface S_{BET} and pore volume V_{Pore} as listed in Table 3.1.

Table 3.1: List of silica gel particles used for the wash experiments

| Type of silica gel | Average pore size d_{Pore} [nm] | Specific surface S_{BET} [m^2/g] | Pore volume V_{Pore} [ml/g] |
|--------------------|---|--|---|
| Silica gel 40 | 4 | 600 | 0.6 |
| Silica gel 100 | 10 | 360 | 0.8 |

Riboflavin, a fluorescent dye, was chosen as impurity. A low detection limit and an accurate concentration determination of fluorescent dyes are beneficial to the reproducibility of the wash experiments. The riboflavin concentration is detected with a fluorescence photospectrometer (Cary Eclipse, Varian). Demineralized water was used as wash liquor.

As first step in the experimental procedure a specific amount of silica gel particles was suspended in a riboflavin solution of a defined dye concentration (0.05 g/l). The suspension was stirred and left in an air-conditioned room for two hours to assure that the particles were wetted completely by the mother liquor (dye solution). Secondary the impurity molecules could adsorb on the particles surface until adsorption equilibrium. The suspended particles were spooned into the apparatus. The remaining mother liquor supernatant drains into the sintered glass drip, when the chop is pressed on the cake surface with approximately 5 bar. For all experiments the initial conditions were kept the same as listed in Table 3.2.

Table 3.2: List of initial operating conditions for the wash experiments

| Parameter | Value | Unit |
|---------------------------------|-------|------|
| Cake height h | 34 | mm |
| Initial dye concentration c_0 | 0.05 | g/l |

Prior to the wash liquor flow through, the feed line is vented. Embedding air in the filter cake and thus the influence of washing a two phase system (solid and air) is avoided. In Table 3.3 the parameters changed for the set of experiments are given.

Table 3.3: List of varied parameters

| Parameter | Value | Unit |
|-----------------------|--------|------|
| Wash liquor flow rate | 0,26-7 | g/l |
| Wash ratio W | 0-20 | - |

At any time during the wash experiment the filter cake is totally saturated. Therefore an inhomogeneous wash liquor distribution, which occurs in desaturated cakes, can be eliminated [3]. Since the purification grade of the filter cake is the main characteristic to evaluate the wash performance, the rest amount of impurities is

measured directly by resuspending the washed filter cake in a definite amount of demineralised water. Equivalent to the impurifying step, the resuspended filter cake is placed in an air-conditioned room for a certain time. Thus it is assured that the desorption process is completed before detecting the final dye concentration in the supernatant. The amount of dye molecules still adsorbed on the washed particles is not quantified directly, when analyzing the supernatant of the resuspended cake. For this purpose the correlation between particle impurity loading and the dye concentration in the supernatant, thus the sorption isotherm, was examined by batch sorption experiments. Therefore 0.2 mg silica gel particles and 1.5 ml riboflavin solution of different concentrations were mixed on a rotator for at least 1 h. The required time period of about 1 h was determined previously to sorption equilibrium experiments by sorption kinetic experiments. For these experiments silica particles were added to a 0.001 g/l riboflavin solution. The suspension was stirred and the riboflavin concentration of the supernatant was measured after certain time steps. The experiments showed (Fig. 3.2 a/b), that the adsorption and desorption equilibrium was reached after about 1800 s.

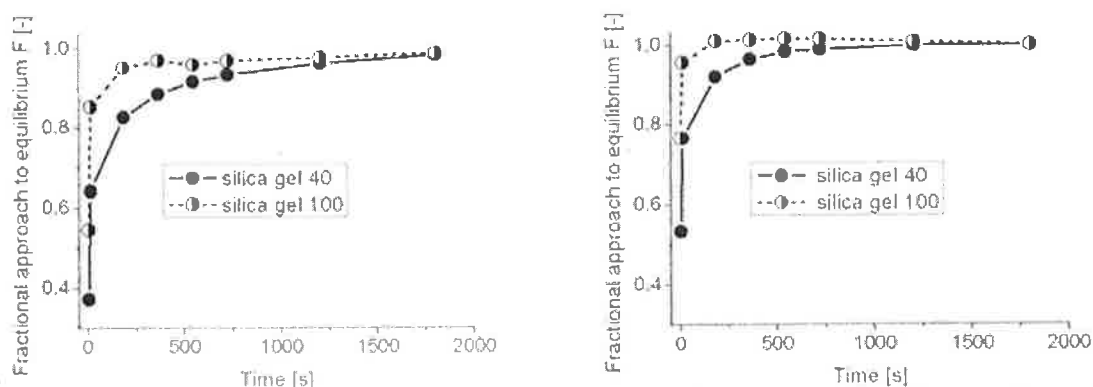


Fig. 3.2 a: Adsorption kinetics for silica gel 40 and 100 **b: Desorption kinetics for silica gel 40 and 100**

4 Results and Discussion

4.1 Sorption equilibrium

The determination of the concentration ratio c^* requires the total amount of impurities remaining in the filter cake after the washing experiment. The remaining impurities are either soluted or adsorbed on the particles surface. The adsorbed fraction has to be calculated from the accordant sorption isotherm (Fig. 4.1). Each point of the sorption isotherm represents a state of equilibrium between the particle loading Q and the equilibrium concentration c_{eq} in the supernatant. For both adsorption and desorption experiments the measured data is plotted together in Fig. 4.1. The good match between adsorption and desorption data indicates that the adsorption process is reversible. Reversibility of the adsorption process is a precondition for the removal of impurities in the washing process. As can be seen in Fig. 4.1 the riboflavin loading of silica gel 40 is considerably higher than the riboflavin loading of silica gel 100. Assuming equivalent sorption sites on both materials, this is expected, since the specific surface area of silica gel 40 is approximately twice as large as the specific surface area of silica gel 100 (Table 3.1). The experimental data can be described accurately with the Freundlich model. The following wash curves are corrected according to the sorption isotherms.

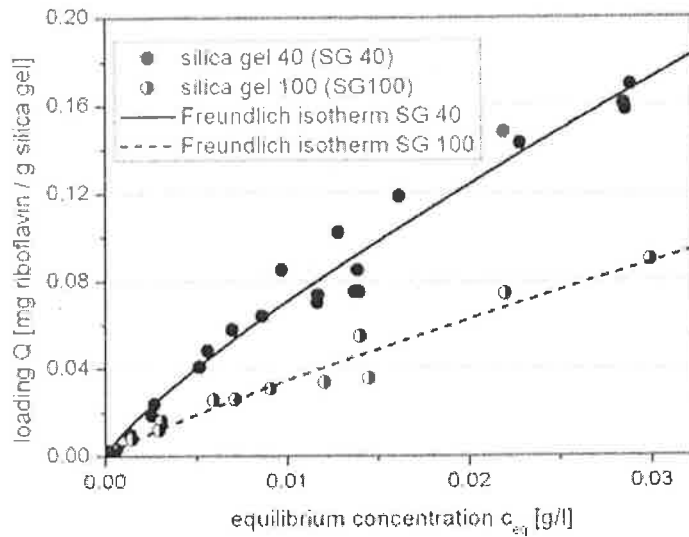


Fig. 4.1: Adsorption/desorption isotherm of riboflavin on silica gel 40 and 100, respectively

4.2 Wash results

The results of the wash experiments are shown in Fig. 4.2 to Fig. 4.4. For this purpose the concentration ratio c^* is plotted against the wash ratio W . Each data point represents one experiment, i.e. to obtain one data point a new, defined contaminated cake was built. In Fig. 4.2 the wash performance of the two different silica gel types 40 and 100 are compared to each other.

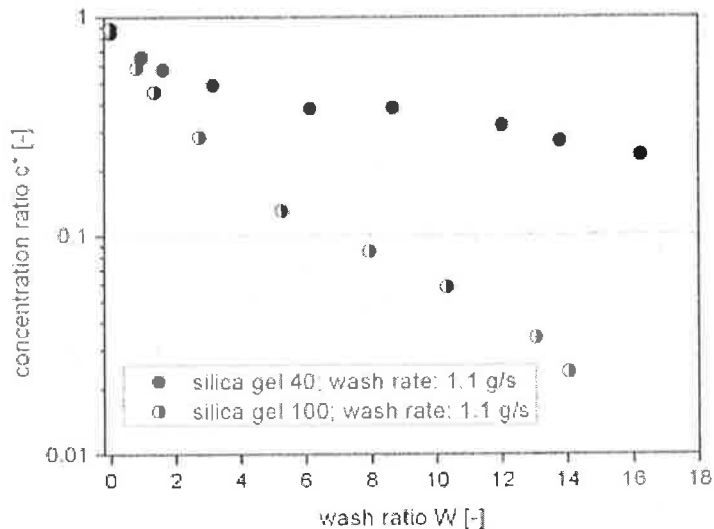


Fig. 4.2: wash curve of silica gel 40 and 100; wash rate: 1.1 g/s

As can be seen in the diagram the washability of silica gel 100 for the same wash rate is considerably better. Both silica gels are contaminated with a solution of a defined initial impurity concentration. In case of silica gel 40 the fraction of adsorbed impurities is higher as for silica gel 100 (Fig. 4.1). Moreover the wash curve of silica gel 100 declines more rapidly compared to the wash curve of silica gel 40. So either the desorption process itself or the smaller pore size in case of silica gel 40 hinders

the transport of the impurity molecules additionally. Results of wash experiments with silica gel 100 and various flow rates are plotted in Fig. 4.3 a.

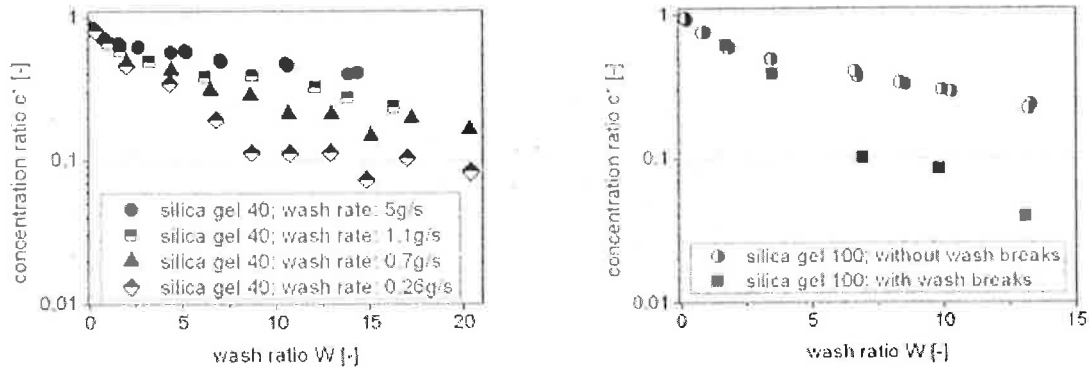


Fig. 4.3 a: wash curves of silica gel 100 with different wash rates **b:** wash curves of silica gel 100 with continuous and discontinuous wash liquor addition; wash rate: 7 g/s

The lower the wash rates, the smaller the concentration ratios. From a concentration ratio c^* of approximately 0.4 the wash curves show different gradients, whereas they match in case of concentration ratios higher than 0.4. From the adsorption experiments it is known, that about 58 % of the impurity molecules are adsorbed on the particles surface. Therefore the solved impurities are washed out independently of the wash rate, whereas the removal of adsorbed impurities is dominated by the limiting diffusion and desorption processes. However, to exclude possible different flow patterns in the apparatus as reason for the higher purification grades with decreasing flow rates, experiments with discontinuous wash liquor addition but same wash rate were conducted (Fig. 4.3 b). The results in Fig. 4.3 a and b show, that an improvement in the purification grade can be achieved simply by increasing the residence time of the wash liquor. Hence, the existing impurity concentration gradients between stagnant and accessible areas can be balanced.

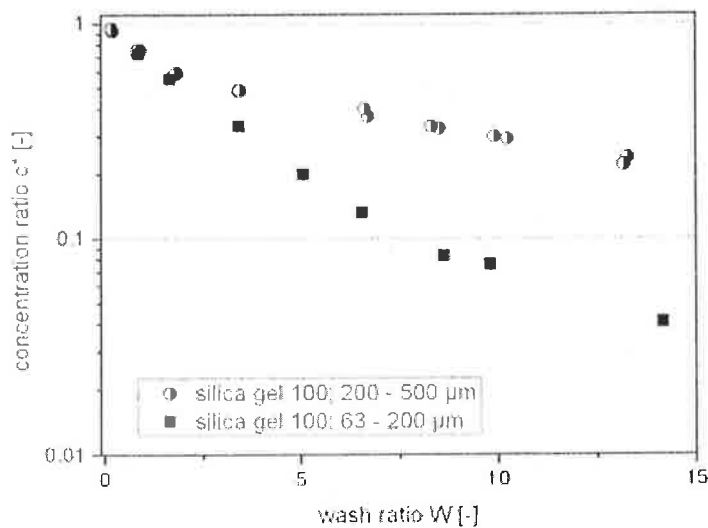


Fig. 4.4: wash curves of different fractions of silica gel 100; wash rate: 7 g/s

Further experiments were done with a smaller particle fraction. Both fractions of one specific silica gel type have the same specific surface area. For the smaller fraction the wash rate was adjusted to the previous experiments by increasing the differential pressure. As can be seen from Fig. 4.4 higher purification grades can be achieved for the smaller particle fraction. These results demonstrate that not the specific surface area and the total amount of absorbed impurities, but primarily diffusion and desorption processes influence the wash performance.

5 Conclusion and Outlook

If a high fraction of the impurities is adsorbed on the particles surface, the filter cake washing is clearly dominated by desorption and diffusion processes. The comparison of silica gel 40 and 100 as well as the comparison of two different fractions of silica gel 100 showed that the pore size and the particle size have a huge influence on the impurity removal. With decreasing pore size, the diffusion and desorption processes decelerate. In contrast the wash out proceeds faster for smaller particle fractions. Besides, the specific surface area plays a minor role for the removal of riboflavin from silica gel. By increasing the residence time of the wash liquor better wash results can be achieved for the same wash liquor consumption.

In further investigations the wash behavior of mesoporous particles in case of weak or no interaction between impurities and particles should be examined. It would be interesting to figure out, whether the particle geometry (pore size, particle size) still affects the wash results. For this either the interaction between fluorescent dyes and mesoporous particles could be minimized by chemical means or less complex molecules/ions should be chosen as impurities.

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