The effect of particle surface charge density on filter cake properties during dead-end filtration

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HIGHLIGHTS

- Model particles with variable surface charge were used in dead-end filtration.
- Specific resistance and compressibility increase with particle charge.
- Porosity increase with particle charge and decrease with applied pressure.
- Existing models fail to predict specific cake resistance for charged particles.
- Osmotic pressure in the filter cake proposed as a possible explanation.

ABSTRACT

During the filtration of suspended organic material, filter cakes with high specific resistances are often formed. The properties of these filter cakes differ markedly from the classical filtration properties derived from inorganic suspensions, not only by having a higher specific resistance but also by being highly compressible. These organic substances typically have a high surface charge density, due to the different functional groups on their surfaces, so a set of model particles was synthesized in which the surface charge density can be varied while keeping all other properties constant. The synthesized monodisperse particles all have a polystyrene core and varying ratios of charged (*i.e.* polyacrylic acid) and uncharged (*i.e.* hydroxypropyl cellulose) stabilizing polymers covalently grafted to the surface. All used particles have proven to be stable against aggregation during storage and are easily redispersed upon agitation. Aqueous suspensions of the particles were filtered in a dead-end setup at constant pressure to determine the filter cake properties. Results indicate that the specific cake resistance, cake compressibility, and cake porosity increase with the particle surface charge. Comparison with two empirical models of filter cake resistance demonstrates that particle charge is more important than is porosity, as highly charged filter cakes have resistances orders of magnitude higher than calculated, which is not the case for filter cakes of uncharged particles. DLVO theory suggests that the results cannot be explained in terms of classical double-layer effects, even in the extreme case of very small interparticle distances. Deviations from this classical behavior, arising from the confinement of charged particles by charged walls or pores, are a possible explanation, allowing the high resistances to be interpreted as increased osmotic pressure due to the distribution of counterions in the pores. Calculations indicate that osmotic pressure increases with particle charge and with decreasing porosity, but remains close to zero for uncharged particles.

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1. Introduction

Dewatering filtration is a common unit operation whenever suspended solids must be separated from a liquid. In almost all applications, the properties of the filter cake deposited on the filter medium govern the process. The liquid flow through the porous filter cake will thus be a limiting factor for the filtration, and efforts to reduce the hydraulic resistance account for a significant part of the operational costs of a filtration unit. The liquid flux through porous media (*e.g.* filter cakes) is often interpreted using Darcy's law, in which the flux is expressed as the pressure drop across the cake divided by the hydraulic resistance. Properly dimensioning the equipment used for dewatering calls for knowledge of the expected properties of the filter cake formed. For this purpose, semi-empirical models exist for predicting the hydraulic resistance

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from the cake thickness, cake porosity, liquid viscosity, and solid–liquid contact area in the cake (which can be calculated from particle size and shape). One often-used model is the Kozeny–Carman model (Eq. (1)), giving the specific resistance, α, *i.e.* hydraulic resistance per cake mass deposited. In it, k is the Kozeny constant (with a value of 5 ± 0.5 for spherical particles; Carman, 1937), S_0 the volume-specific surface of a particle, ρ_s the solid density, and ε the filter cake porosity. This model also serves as the basis of some other models (Xu and Yu, 2008).

$$\alpha_{KC} = k \frac{S_0^2 \cdot (1 - \varepsilon)}{\rho_s \cdot \varepsilon^3} \tag{1}$$

Although this and some derived models are extensively used, they have several limitations. Indeed, the Kozeny–Carman model has been found to give satisfactory predictions of the filtration of simple inorganic suspensions or suspensions of uncharged latex particles (Ogden and Davis, 1990). However, the model is very poor at dealing with suspensions of biological origin, such as microbial cell suspensions (Foley, 2006) or activated sludge (Mikkelsen and Keiding, 2002), and application of the model is complicated by the difficulty of determining S_0 and ε, especially for activated sludge.

Previous work on the filtration of wastewater sludge has found very high specific filter cake resistances, typically several hundred times higher than would be expected from the Kozeny–Carman model, *i.e.* 10–100 Tm kg^{-1} (Bugge et al., 2012; Chu and Li, 2005; Mikkelsen and Keiding, 2002; Wu et al., 2001). Among the suggested explanations of this difference are (1) blinding effects within the cake itself, which occur when the filter cake acts as a secondary membrane, capturing smaller particles within the pores (Sørensen et al., 1997; Novak et al., 1988), and (2) skin formation, leading to reduced filter cake porosity, especially in layers near the membrane where the solid stress is the highest, caused by the high degree of compressibility typical of wastewater sludge (Tiller and Kwon, 1998). Both these effects are possible in systems in which the suspended solids have a broad range of characteristics, further complicating the prediction and modeling of cake resistance. As sludge is a very complex matrix (Le-Clech et al., 2006), it is difficult to isolate and vary only one property of a sludge floc without affecting several others, all of which can affect filterability.

To overcome this, model particles can be used to simulate real-world suspensions, with the added benefit of ruling out effects caused by blinding and skin formation. A key factor in sludge filtration is thought to be related to the primarily negatively charged groups on the surfaces of the sludge flocs, single cells, and exopolymers, in line with the findings of Hodgson et al. (1993) and Ohmori and Iritani (Ohmori and Glatz, 1999; Ohmori and Iritani, 2004). It has been found that reducing the surface density of these charges positively affects the filterability (Mikkelsen and Keiding, 2002). This positive effect is thought to be caused mainly by increased flocculation (Bugge et al., 2013), as the low surface charge cannot provide the interparticle repulsion necessary to keep the sludge flocs apart, while a more direct influence of particle charge also have been proven to be of importance (Lorenzen et al., 2014). In contrast, Mukai et al. found that increasing protein surface charge would decrease cake resistance during ultrafiltration, due to a higher porosity resulting from increased electrostatic repulsion (Mukai et al., 1997). Thus, conflicting results from different systems have been reported, which only serves to increase the importance of further research in this area.

Some researchers have also discussed a more direct influence of charge, exerted mainly through increased osmotic pressure in the filter cake caused by the colligative properties of the counterions associated with the charged groups. This osmotic pressure counteracts the applied pressure and is therefore perceived as increased

resistance (Keiding and Rasmussen, 2003; Wijmans et al., 1984). This effect has only recently been quantified in MBR systems (Chen et al., 2012; Curvers et al., 2009; Zhang et al., 2013, 2014), while earlier work has found osmotic pressure to be negligible in cross-flow microfiltration (Davis, 1992). The complexity and diversity of sludge, however, will make it difficult to compare results and might even lead to contradictory conclusions, as the effects of charge are impossible to isolate due to the adverse secondary effects occurring when attempting to increase or decrease the charge density, such as changes in floc strength and particle size distribution.

Although several attempts have been made to modify the Kozeny–Carman equation (Valdes-Parada et al., 2009; Xu and Yu, 2008), none of these models accounts for variations in particle surface charge and, to the authors' best knowledge, no such model exists. As shown, charged surfaces have been found to have a significant impact on filter cake resistance in applications containing organic material (Foley, 2006; Hodgson et al., 1993; Ohmori and Glatz, 1999; Ohmori and Iritani, 2004). The ability to isolate the effects of charge in such a system is therefore necessary in order to develop and test new models. A set of novel monodisperse model particles, with a core/shell structure and in which the surface charge can be varied without compromising stability against aggregation, was used to mimic suspensions of biological origin and thus can be used in filtration experiments to gain knowledge of the influence of charge in such systems.

2. Materials and methods

2.1. Particle synthesis

Micrometer-sized core/shell particles were synthesized by the dispersion polymerization of styrene (Sigma-Aldrich, CAS: 100-42-5, 99%) in methanol (Sigma-Aldrich, CAS: 67-56-1, 99.8%), with the use of benzoyl peroxide (BPO) (Acros Organics, CAS: 94-36-0, 75%, remainder water) as initiator. Poly(acrylic acid) (PAA) (Sigma-Aldrich, CAS: 9003-01-4, 35 wt.% in water) and hydroxypropyl cellulose (HPC) (Sigma-Aldrich, CAS: 9004-64-2, $\geqslant$95%) were used as graftable polymeric stabilizers. Before the synthesis, benzoyl peroxide was recrystallized in methanol to remove any water and impurities, while all other chemicals were used as received. The synthesis was performed in 250-mL round-bottomed two-necked flasks with reflux and magnetic stirring and under nitrogen atmosphere. The stirring was kept constant at 300 RPM throughout the synthesis.

To obtain particles with varying surface charge densities, different weight ratios of HPC to PAA were used as stabilizers in the synthesis. The batches of particles are named using the letters A–E, and the amounts of stabilizers (dry weight) can be found in Table 1.

The corresponding amounts of PAA and/or HPC were dissolved in methanol in the reaction flask, then preheated and degassed by being bubbled with nitrogen for 10 min. BPO was dissolved in styrene, degassed in a similar manner as was the polymer solution, and kept at a temperature under 5 °C for no longer than 1 h until use. The BPO/styrene solution was then added to the preheated polymer solution and left under nitrogen at a reaction temperature of 70 °C for 24 h. The produced particle suspension was filtered through a filter cloth with an average pore size of 45 μm to remove any coagulated material, and then cleaned by repeated sedimentation/resuspension in methanol five times. The cleaned particles were all stored in methanol and then rinsed and resuspended in an aqueous 1 mM NaOH solution before use.

The monomer contained a small amount of inhibitor (4-*tert*-butylcatechol). It was deliberately not removed as it slows the onset of polymerization, allowing the temperature of the reaction