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Magnetic field enhanced cake filtration of superparamagnetic PVAc-particles

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ABSTRACT

The combination of two classical separation methods, cake filtration and magnetic field driven separation, for superparamagnetic nanocomposites results in positive synergetic effects and in extension of the field of application of the cake filtration process. In inhomogeneous magnetic fields magnetic particles experience a magnetic force. Experimental results show that two different effects of the magnetic field influence the cake building process. A special configuration of the magnet system leads to a slow down of the cake built-up. Due to changes of the structure the cake itself has a higher permeability. The result is an increase of the overall filtrate mass flow and therefore an improvement of filtration kinetics.

This new process could be applied to the emerging field of biotechnology, especially in the so called downstream processing.

Since the different components (protein, DNA, etc.) of, e.g. a fermentation broth are very small in size and have similar physical properties, the extraction of the target component out of this mixture is achieved only with high effort and expenses in a multi-step process. With the use of tailor-made magnetic adsorbent particles this process chain can be reduced considerably. The surface of these magnetic beads is manipulated in a way that only the target component is adsorbed selectively. Therefore the surface functionalization has to be concerted with the target component as well as the other side components to avoid the adsorption of one of those. The following separation of the target bio-product out of the remaining mixture is then accomplished due to the magnetic properties of the adsorbent particles.

This paper discusses in detail the results of magnetic filtration experiments of non-functionalized particles. Such results are required for further development of this process for industrial scale bio-production. In this work the acceleration of cake filtration due to the above mentioned magnetic field effects is shown. Based on that a theoretical approach is suggested that describes both effects individually providing reference of their interaction.

1. Introduction

Economic studies claim the biotechnology to be a future key technology and anticipate vast finance interests and positive effects on the job market (PricewaterhouseCoopers, 2007; Nusser, 2007). In modern biotechnological processes the natural metabolism of an organism is used to produce complex molecules during fermentation. This enables the development of new products such as pharmaceuticals as well as the cost-effective production of known products. But beside the desired product a fermentation broth usually contains also several side products which have to be removed in cumbersome purification steps, the so called downstream processing. It mainly consists of unit operations such as chromatography, ultra-centrifugation, filtration, and many more. Up to 80% of the investment and operating costs originate from this downstream processing. Against the background of increasing demands on the efficiency of production processes this particular sector requires the improvement of separation devices or the development of new approaches. One attempt is to establish hybrid processes to benefit from synergetic effects that result from the combination of different techniques. For example such effects can be observed combining filtration and magnetic separation. In the past magnetic fields have been used mainly for selective sorting of strongly and weakly or non-magnetic products in minerals industry (Svoboda, 1987). Since several decades high gradient magnetic separation (HGMS) emerges into industrial scale for the separation of low concentrated suspensions, e.g. in the wastewater industry (Franzreb and Höll, 2000). Establishing this concept in bio-separation is also subject of current research (Franzreb et al., 2006). By using highly functionalized magnetic substrate particles, which adsorb the desired product like protein, enzyme, DNA, etc. selectively, bio-product can be separated out of a mixture of non-magnetic components, e.g. bio-broth

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(Safarik et al., 2001). A wide range of these surface ligands for different target products are already in application, e.g. in diagnostics or in adsorption chromatography. HGMS is a kind of deep bed filtration with a porous, non-remanent ferromagnetic matrix similar to a steel wool network with very low filter resistances. In an external magnetic field high field gradients around the wires of the matrix induce high magnetic forces in direction of the matrix wires upon approaching magnetic particles. Non-magnetic components pass the matrix with the liquid phase without being trapped. But limited capacity of the matrix makes HGMS applicable for low concentrated feed streams only.

To use the advantages of the magnetic field also for high concentrated slurries a new hybrid separation process, the magnetic field enhanced cake filtration, has been developed at the University of Karlsruhe (Fuchs, 2005). As a classical unit operation cake filtration is present in most industrial production processes for particulate products. The design ranges from lab-scale discontinuous nutsche filters to large-scale continuous filter apparatus. Experimental and theoretical investigations show that the combination of classical cake filtration and magnetic fields results in a reduction of the overall filtration resistance. In inhomogeneous magnetic fields magnetic particles experience a magnetic force. That gives the possibility to decouple solid and liquid phase motion to decrease the rate of cake formation. This implicates a reduction of the cake layer the liquid phase has to drain. Furthermore magnetic interparticle forces excite magnetic structuring and agglomeration effects, resulting in a higher permeability of the filter cake. The new hybrid process is not restricted to one procedural principle in the cake filtration. Till now the implementation in a filter press (Stolarski et al., 2006; Eichholz et al., 2007) and a nutsche filter (Fuchs et al., 2006) could be established. The new technology offers potential to increase process efficiency in the field of nano-scale magnetic particulate product systems and in bio-separation.

Such a bio-separation process consists of the following steps: fermentation, mixing, specific adsorption, magnetic separation, washing and elution. The product-specific functionalized particles are mixed with fermentation broth. The mixing provides intense contact of the particles with the bio-broth so that mass transfer limitations are negligible. The separation of the carrier particles with the attached product depends on the properties of the carrier particle rather than on the actual bio-product properties. The waste bio-broth can be recirculated into the fermentation process, if possible, or conveyed to waste treatment. After the first magnetic separation, the particles undergo several washing steps to reach the desired purity. During washing the external magnetic field is switched off and the particles are redispersed into washing liquor. To remove the contaminated washing liquor, further magnetic separation steps are performed. To retrieve a pure solution of the final product, it is removed from the particle surface in an elution step. Depending on the product and the binding properties, this elution is realized by change of pH, ionic strength, temperature or substitution reactions. The carrier particles are for disposal in the next separation cycle. The advantage of magnetic separation over classical chromatographic technologies is the higher capacity of the particles due to their smaller size and better product contact, maximal product recovery, minimal separation time and the reduction of unit operations at the same time. Compared with HGMS the magnetic field enhanced cake filtration features a higher cleanability of the nutsche filter and suspensions with higher solid concentrations can be handled.

The detailed understanding of the magnetic field enhanced cake filtration with superparamagnetic nanocomposites and approaches to describe the new process theoretically are necessary for an optimal design of the apparatus and the whole process. The present work contributes to this understanding to leverage the process idea to an industrial scale.

2. Theory

2.1. Magnetism

Materials can be classified into different types of magnetism. The three most important are dia-, para- and ferromagnetism (Bergmann and Schaefer, 2006). The classification is accomplished according to the susceptibility χ which describes the magnetic irritability of the substance exposed to a magnetic field. Out of these categories diamagnetism ($\chi < 0$) is the weakest phenomena. Thereby counter-directed magnetic moments in the material weaken the magnetic field in the immediate surrounding. In contrast paramagnetic ($\chi > 0$) and ferromagnetic ($\chi \gg 0$) materials intensify the magnetic field locally and experience a force in direction of increasing field gradients. Depending on susceptibility and magnetic field strength H the material is magnetized up to a certain magnetization M,

$$M = \chi \cdot H \tag{1}$$

While magnetization increases linear for paramagnetic materials for a wide range of magnetic field strengths, it reaches a maximum for ferromagnetic material. This maximum is referred to as saturation magnetization M_S. Another characteristic is the remaining magnetization M_r after disapplying the magnetic field. Of special importance to the proposed process is superparamagnetism. It is characterized by its ferromagnetic properties but without remanent magnetization. Therefore primary particles have to be composed of single magnetic domains in the range of 20–30 nm (Butler and Banerjee, 1975). In particle aggregates or composite particles with incorporated primary particles, as used in this work, the magnetic domains must not interact because this would abolish superparamagnetism.

For a magnetic field the following correlation of field strength H and magnetic flux density B can be obtained (Eq. (2)). In literature often both values are used interchangeable to describe the magnetic field strength,

$$B = \mu_0 \cdot \mu_r \cdot H \tag{2}$$

with μ_0 the magnetic vacuum permeability and μ_r the permeability number of the substance inside the field. In case of vacuum the magnetic permeability number is $\mu_r = 1$. For diamagnetics is $\mu_r < 1$, for para-, ferro- and superparamagnetics is $\mu_r > 1$. The magnetic volume susceptibility is equal to $\chi = \mu_r - 1$. The resulting force on a material, respectively, particle, in a magnetic field can be described by means of the magnetization of the particle M_p, the volume of the particle V_p and the gradient of the external field ∇H,

$$F_m = \mu_0 \cdot V_p \cdot M_p \cdot \nabla H = \frac{1}{\mu_0} \cdot \chi \cdot V_p \cdot B \cdot \nabla B \tag{3}$$

Transferring Eq. (3) to the induced magnetic field of magnetic particles, the magnetic interaction (magnetic potential E_m) between two neighboring particles with the distance r can be calculated (Lee et al., 1999). Eq. (4) describes the one-dimensional approach with the assumption of constant magnetization over the whole particle volume,

$$E_m = \frac{\pi}{144} \cdot \frac{\mu_0 \cdot M_p^2 \cdot \rho_p^2 \cdot d_p^6}{r^3} \tag{4}$$

with ρ_p the particle density and d_p the particle diameter.

Due to the magnetic potential aggregation effects free moving particles can be observed according to the modified DLVO-theory (Chin et al., 2000, 2001). Strength and geometry of the superposed magnetic field as well as shear stress on the aggregates determine essentially size and density of the formed agglomerates (Stolarski et al., 2007).