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Highly permeable twinned alumina nanoparticles for the precoat filtration of fine colloids

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ABSTRACT

Pretreatment is key to the success of any fine filtration process. Precoat filtration is a common method to reduce fine particulate matter in feed streams. In this study, precoat filters were formed by the deposition of the diatomaceous earth (DE) or twinned alumina nanosheets (TAN) particles on a substrate. The TAN particles were produced via metal salt hydrolysis. The performance of the precoat filters was investigated during the constant-pressure filtration of a bentonite solution. The results showed that the TAN precoat exhibited enhanced flow properties and reduced the turbidity of the filtrate more rapidly than either of the DE precoats. The TAN precoat reached the required turbidity level of $\leq$0.10 NTU at a flux that was up to 28 times higher than the fluxes obtained by the DE precoats. The superior performance of the TAN precoat was explained by (1) the ability of the TAN precoat to resist compaction during filtration due to the unique twinning of the alumina nanosheets forming the TAN particles, (2) the strong attractive forces between the bentonite and TAN particles based on their opposite surface charges, and (3) the isotropic permeability of the TAN aggregates.

1. Introduction

Membrane fouling due to finely suspended solids and colloids continue to be problematic in the long term operation of nanofiltration (NF), reverse osmosis (RO) and electrodialysis (ED) water treatment systems. Excessive particulates can also block spacers in NF/RO and ED membrane modules. These fine suspended solids are increasingly being removed by precoat filtration [1,2].

The operating lifetime of membranes can be increased by adopting methods that reduce fouling [3,4]. In addition, these methods have the potential to decrease maintenance time [5,6], plant operating costs [4–6], and overall energy consumption [3–6]. They also play a pivotal role in the operation of desalination plants. In 2007, the largest desalination plant in North America, located in Tampa, Florida, could be reopened by the addition of a diatomaceous earth (DE) precoat filtration system [7].

Precoat filtration is a common method to reduce fouling and flux decline during treatment, whereby large particles and debris are removed by a thin, dense, and highly permeable layer of particles. Foulants are separated during prefiltration primarily by sieving. Common filter aids include diatomaceous earth (DE), perlite, cellulose and activated carbon [8–10].

Prefilters and filter aids have been studied extensively in the literature. Lihong et al. compared the compressibility of DE and cellulose filter aids during the filtration of highly viscous gels [9]; Michen et al. fabricated a depth filter from DE and investigated its ability to remove colloidal latex particles from solution [11]; Valderamma-Bravo et al. explored the effect of DE precoat thickness on filtration rate during constant pressure filtration of corn liquor [12]; Farag and El-Anany explored the effect of different filter aids (Magnesol XL, DE, and kaolin) on the removal of secondary oxidation products from used fryer oils [13].

Filter aids find great applicability in drinking water filtration [14], as they can be used to reduce parameters like turbidity to acceptable levels. High turbidity can be an indication of contaminated water [15], therefore it is desirable to minimize turbidity values. Turbidity targets for drinking water are shown in Table 1.

With common filter aids like diatomaceous earth and perlite, there is a tradeoff between permeability and achievable turbidity reduction during filtration. In the studies on precoat filtration cited above, it was found that the effectiveness of the filter aids was reduced due to either the low porosity, low hydraulic permeability or compaction of the precoat. There is a need for filter aids with enhanced flow properties, whereby a rapid decrease in turbidity can be achieved at high filtrate throughput. The fabrication of such a filter aid is therefore of great interest.

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Table 1
Turbidity regulations for drinking water.

Regulatory agency	Turbidity target	References
World Health Organization	Median turbidity $\leq$ 0.1 NTU	[16]
Health Canada	Conventional and direct filtration: $\leq$ 0.3 NTU Slow sand and diatomaceous earth filtration: $\leq$ 1.0 NTU Membrane filtration: $\leq$ 0.1 NTU	[15]
United States Environmental Protection Agency	$\leq$0.3 NTU in 95% of tests	[17]

In a previous work, low density, high porosity alumina filter aids were manufactured under hydrothermal conditions at three ethanol-water concentrations (0 vol%, 25 vol%, and 50 vol%) [18]. The filter aid synthesized at 50 vol% ethanol-water had the highest hydraulic permeability, and was therefore selected for use in this study. However, the performance of the alumina filter aids in comparison to widely-used industrial filter aids is unknown.

In this study, twinned alumina nanosheets were hydrothermally synthesized in a 50 vol% ethanol-water mixture. Then, the TAN and diatomaceous earth precoats were formed *in situ* by the deposition of the materials on a substrate. The precoats were challenged with sonicated bentonite to compare the filtration performances of the TAN and diatomaceous earth filter aids.

2. Experimental

2.1. Materials

Cetyl trimethylammonium bromide (CTAB), sodium hydroxide pellets, anhydrous ethanol, isopropanol, diatomaceous earth (medium grade DE-512 and fine-grade DE-577), and bentonite (montmorillonite) were purchased from Sigma-Aldrich (Canada). Aluminum chloride hexahydrate (99%, nitrogen flushed) was purchased from Acros Organics. Cellulose filter paper (Whatman #4) was purchased from Fisher Scientific (Canada). All materials were used as purchased.

2.2. Methods

2.2.1. Alumina synthesis

Boehmite nanosheets were synthesized by metal salt hydrolysis. A precursor solution was formed by the dissolution of a known quantity of aluminum chloride hexahydrate in distilled, deionized water under vigorous stirring. The pH of the solution was raised to 14 using sodium hydroxide pellets. A surfactant solution was formed by the dissolution of CTAB in anhydrous ethanol. The surfactant solution was added to the precursor solution to form a 50 vol% ethanol-water mixture. The final mixture was left to stir at room temperature in a fume hood. After 24 h of stirring, the solution was poured into a Teflon-lined stainless steel autoclave (Parr Instrument Company, Illinois), sealed, and placed in a 165 °C oven for 12 h under autogenous pressure. The precipitate formed under crystallization accumulated at the bottom of the autoclave in the form of a disk. The disk of particles was placed in a fume hood to dry. The particles were calcined at 600 °C for 4 h in a muffle furnace to produce twinned alumina nanosheets (TAN).

2.2.2. Precoat filtration

A typical filtration experiment was as follows: a clean 5.5 cm diameter filter paper was placed in a filtration cell. Initially, 500 g of distilled water was passed through the filter paper to determine its hydraulic permeability. Two hundred and fifty milligrams of alumina or diatomaceous earth particles were suspended in 2500 g of distilled water and deposited as a filter cake at an applied pressure of 6.89 kPa. Five hundred grams of distilled water was passed through the filter cake at 6.89 kPa to determine the hydraulic permeability of the cake. One hundred and twenty-five milligrams of bentonite was ultrasonicated using a Fisher Scientific Sonic Dismembranator 550 in 80 g of distilled water for 60 s at 50% power and added to 4020 g of distilled water. The turbidity of this mixture was measured three times using an HF Scientific Inc. Micro 100 Turbidimeter (Fort Myers, Florida); it was then filtered through the cake at 34.47 kPa. The mass of filtrate leaving the flow cell was continuously monitored by a balance using LabVIEW software (National Instruments, Québec). The permeate flow was redirected manually into a sample vial at 250 g intervals to allow for the immediate measurement of the turbidity. A 30 mL vial was used to collect these samples.

2.2.3. Particle characterization

SEM imaging was performed using a Phenom Pro Desktop SEM (Nanoscience Instruments, Virginia) at an accelerating voltage of 10 kV.

The particle size distribution of the bentonite particles was determined with dynamic light scattering using a Zetasizer ZS90 (Malvern Instruments, Worcestershire, UK).

The particle size distributions of the DE and TAN particles were determined by dynamic particle size analysis. A typical procedure was as follows: a capillary flow cell was cleaned using isopropanol and deionized (DI) water. A 1-mL aliquot from a 0.01 M of DE or TAN stock solution was diluted to 100 mL with DI water. The solution was pumped through the flow cell at 0.1 mL/min using a peristaltic pump and analyzed using a DPA-4100 dynamic particle analyzer at high magnification (Brightwell Technologies Inc., Ottawa).

The bulk density of the DE and TAN samples were determined by measuring the volume of known masses of these samples after settling in water. The porosities of the samples were determined using the water evaporation method [19,20].

The hydraulic permeabilities of the filter aids were measured during filtration by the application of Darcy's law:

$$\lambda = \frac{\Delta P}{\mu}\left(\frac{1}{J_{total}} - \frac{1}{J_0}\right) \tag{1}$$

where λ is the resistance of the precoat (m^{-1}), ΔP is the pressure difference across the precoat and filter paper (Pa), μ is the viscosity of the fluid (Pa s), J_0 is the average flux across the filter paper (m/s), and J_{total} is the average flux across the precoat and filter paper, as determined in separate experiments [21].

The hydraulic permeability of the precoat is then

$$\kappa = \frac{x}{\lambda} \tag{2}$$

where κ is the hydraulic permeability (m^2), and x is the thickness of the precoat (m) [21]. The value of κ is converted to millidarcies with the following conversion factor: 1 mDa = 9.869×10^{-16} m^2.

Given the bulk density of the particles, the thickness of the precoat was estimated by

$$x = \frac{m}{\rho_b A} \tag{3}$$

where m is the mass of the sample (kg), ρ_b is the bulk density of the sample (kg/m^3), and A is the area of the filter paper available for filtration (m^2). The thickness of the precoat was also measured manually using a Mitutoyo digital caliper.

A bentonite turbidity calibration curve was prepared in the range of 0–10 NTU. A plot of concentration versus turbidity was