



Cationic proteins for enhancing biosludge dewaterability: A comparative assessment of surface and conditioning characteristics of synthetic polymers, surfactants and proteins



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ABSTRACT

Synthetic organic polymers are commonly used to facilitate challenging solid-liquid separations such as biosludge dewatering. However, there is interest in reducing the use of polymers due to their toxicity and synthetic sourcing. Surfactants and proteins have shown potential to enhance sludge dewaterability but little is known about the properties and/or mechanism(s) that promote this enhancement. In this study, synthetic polymers, surfactants and proteins were investigated to evaluate whether surface properties such as charge, surfactant activity and hydrophobicity, play a role in how these conditioners affect biosludge dewatering. Capillary suction time (CST), dry solids content, filtrate rate and filtrate solids content were used to assess dewaterability. Results show that surface charge determines the potential of conditioners. The effect of charge was greater for surfactants and proteins than for polymers. In contrast with previous reports, surfactant activity negatively affected the dewaterability of biosludge. Cationic conditioners, regardless of the group improved biosludge dewaterability. However, the dose of cationic proteins is still high compared to currently used synthetic polymers (e.g. protamine is 0.1 g/g TSS vs. synthetic polymer 0.03 g/g TSS). Our results suggest that there is potential for using proteins to improve biosludge dewaterability but a further reduction in protein dose and/or an increase in the protein's efficiency as a conditioner is needed.

1. Introduction

Biosludge dewatering is a challenge in wastewater treatment plants. Biosludge, also known as waste activated sludge, is a colloidal suspension of microbial aggregates with high moisture content (> 98%) and a gel-like matrix of extracellular polymeric substances that hinders the removal of water, making biosludge particularly difficult to dewater [18,11,20]. Several pretreatment and conditioning strategies are used to improve biosludge dewaterability.

Chemicals that improve biosludge dewaterability, also known as conditioners, are widely employed in wastewater treatment plants. Synthetic, water-soluble polymers are the most commonly used. Polymers are effective at low doses but there are some disadvantages associated with their use as conditioners. They represent a major portion of the overall cost of the treatment, are petroleum-derived, dose-sensitive and can be toxic to aquatic systems [9,4]. Moreover, high moisture content in the cake after dewatering has been associated with the hydration of high molecular weight polymers [9,2].

Cationic polymers are preferred for negatively-charged colloidal suspensions, such as biosludge. The cationic charge reduces the

repulsion between polymer molecules and biosludge particles which destabilizes the suspension and facilitates bridging of particles [12]. Bridging leads to large, strong flocs and is the main mechanism by which polymers improve biosludge dewaterability [17,4]. It has been reported that polymers that carry the same charge as the suspension can also lead to flocculation with bridging as the sole mechanism [30] and it is acknowledged that while charge neutralization aids particle bridging, it is not a requirement.

In addition to synthetic polymers, surfactants have also been proposed as potential conditioners of biosludge. Their use has been extensively reported for enhancing liquid-solid separations in the mineral industry. A review of studies in fine particle suspensions was prepared by Besra et al. [1]. Surfactant addition is thought to complement polymer conditioning when the end-goal is to reduce the moisture content in cakes after mechanical dewatering [25]. Reducing the surface tension of the suspension facilitates movement of water through cake pores [24]. Dual conditioning (i.e., surfactant-polymer) has been reported on various suspensions and improvements were found regardless of the ionicity (i.e. charge) of the surfactants studied [8,14,3]. However, when surfactants have been used on biosludge, and as a

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single conditioner step (in the absence of polymer), only cationic surfactants have shown improvements on biosludge dewaterability [29,25,28,27]. The effect of surfactant activity on biosludge dewaterability has yet to be explored.

Proteins have shown potential as a ‘greener’ alternative to enhance liquid-solid separations. Proteins can improve the dewaterability of biosludge and promote the solid-liquid separation of kaolin suspensions. Given the abundance of proteins in renewable materials and organic waste, it is conceivable that proteins could be a feasible alternative to chemical conditioners in the near future. However, a lack of understanding of the mechanisms and the key properties that affect the potential of proteins as conditioners hinders the development of protein-based conditioners and treatments. Previous studies of lysozyme on biosludge and kaolin suspensions suggest that charge neutralization is the main mechanism for such enhancement [6,5]. However, proteins have also been reported to have surfactant activity [21]. Thus, it is currently unknown if the protein’s cationic surface charge and/or its surfactant activity is responsible for the improvement of biosludge dewatering properties.

The aim of this study was to evaluate the effect of various conditioners representing the three chemical groups previously discussed, i.e., polymers, surfactants, and proteins, on biosludge dewaterability, to get a better understanding of their effect on dewatering properties. Surface charge, surface tension and contact angles of conditioners were evaluated to investigate the effect of surface properties on their potential to improve dewatering.

2. Materials and methods

2.1. Biosludge

Biosludge from a secondary clarifier was obtained from a Canadian pulp and paper mill which produces a variety of pulp, paper and specialty products using sulfite pulping and mechanical pulping (bleached chemi-thermomechanical pulp- BCTMP). Biosludge is the by-product of the aeration stage in the wastewater treatment plant treating mill effluents. Samples were kept at 4 °C in the laboratory prior to the experiments and for a maximum of three weeks. All the experiments were carried out with the same batch of biosludge which had a total suspended solids (TSS) content of 12.4 (± 0.3) g/L and volatile suspended solids (VSS) content of 10.5 (± 0.3) g/L and pH 6.9.

2.2. Conditioners

2.2.1. Synthetic organic polymers

Different cationic polymers were used to evaluate their surface properties and compare their effect on dewaterability with surfactants and proteins. Polymers represent the benchmark as conditioners for improving biosludge dewaterability since they are used in virtually all wastewater treatment plants. A stock solution (0.5% w/v) of each polymer was prepared a day in advance of the experiment with pure deionized water. Polymers were added to water while vortexing to facilitate dispersion. The suspension was further mixed for 1 h and allowed to sit undisturbed until the next day when the experiments were conducted. Four polymers with different characteristics were used in this study (Table 1). Dewaterability assessment was conducted as described in Section 2.4.

2.2.2. Surfactants

To test the effect of surfactants on the dewaterability of biosludge and investigate the effect of surfactant activity on the potential of conditioners, three surfactants with different ionicity were selected. Triton X-100, CTAB and SDS represent non-ionic, cationic and anionic surfactants, respectively, and have been previously studied for enhancing biosludge dewaterability [8,14,3]. See Table 1 for more information on the surfactants used in this study.

Table 1

Conditioners used in this study to compare their surface properties and effect on biosludge dewaterability.

Conditioners	Supplier	Charge ^a
Polymers		
Zetag 8165 (Polyacrylamide)	BASF	Cationic (Medium-high)
Zetag 8185 (Polyacrylamide)	BASF	Cationic (high)
Organopol 5400 (Polyacrylamide)	BASF	Cationic (low)
AF 9645 (Polyacrylamide)	AXCHEM	Cationic (high)
Surfactants		
Triton X-100	Sigma	Non-ionic
Sodium dodecyl sulfate (SDS)	Sigma	Anionic
Cetyltrimethylammonium bromide (CTAB)	Sigma	Cationic
Proteins		
Lysozyme	Bioshop	pI ^b –10.7
Protamine	Sigma	pI ^b –12.5
Bovine Albumin Serum (BSA)	Sigma	pI ^b –4.8

^a Information provided by vendor.

^b pI : Isoelectric point.

A stock solution of 8 g/L was prepared for each of the surfactants in deionized water. In each of the experiments, the surfactants were added, mixed three times by inversion and left for 60 min before CST measurements. Dewaterability assessment was conducted as described in Section 2.4.

2.2.3. Proteins

Cationic proteins (active and inactive lysozyme, and protamine) were selected to investigate their surface properties and their effect on dewaterability. In addition to cationic proteins, bovine albumin serum (BSA) was added as a control since it does not carry a net cationic charge at the close-to-neutral pH values of biosludge (Table 1). Active and inactive stock solutions of lysozyme (50 g/L) were prepared as previously described in [5]. Stock solutions of protamine (20 g/L) and BSA (65 g/L) were prepared in deionized water and mixed using a vortex until dissolved. Proteins were added to biosludge and samples were mixed three times (by inversion) and left for 60 min before CST measurements. Dewaterability assessment was conducted as described in Section 2.4.

2.3. Surface properties analyses

2.3.1. Surface charge

Surface charge measurements were conducted with colloidal titration using the principles reported by Kawamura et al. [16]. In a 50 ml beaker, 5 ml of conditioner sample, 2 ml of poly (diallyldimethylammonium chloride) solution (3% w/w) and 2 drops of 0.1% (w/v) toluidine blue were added and gently mixed. The mixture was then back-titrated by adding potassium salt of polyvinyl sulfate (PVSK) (0.0025 N) until the neutral endpoint, indicated by a change of color from blue to purple, was maintained for at least 10 s. The milliequivalent charge of the samples was then compared to that of pure water to find out the surface charge of conditioners.

2.3.2. Surface tension

Surface tension of the conditioner and the conditioned sludge were measured with a Sigma 700 tensiometer (KSV Instruments, Helsinki, Finland) using the Wilhelmy plate method. Measurements were carried out at 22 (± 2) °C, using a stabilization time of 10 min. Before every experiment, and under the same conditions, the surface tension of deionized water was measured to confirm a value of 72 (± 1) mN/m for deionized water and ensure the accuracy of the instrument. Samples were measured at least 5 times and a maximum variability within replicates of ± 2 mN/m was observed.

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