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Sludge dewatering with cyclodextrins

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ABSTRACT

Cyclodextrins (CDs) increase the cake solids and drainage rate of belt-pressed biological or primary sludge when added to the sludge slurry along with conventional conditioning chemicals. These benefits are obtained at very low CD dosage. A 2.8 percentage point increase in cake solids was obtained in a full-scale trial with mixed primary and biological sludge from a paper mill. CDs also decrease the specific resistance to filtration and increase the capture rate of solids during belt pressing. Mechanistic studies showed that CDs increase the surface tension of c-PAM polymers in water and reduce the turbidity, indicating that they are able to aggregate the charged polymers, and, by inference, sludge particles treated with the polymer. A mechanism is proposed where CDs reduce excessively charged regions of the polymer-treated surface of the sludge, thereby facilitating its flocculation.

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1. Introduction

Cyclodextrins (CDs) are torus-like rings assembled from six, seven, or eight glucopyranose units: α-, β-, and γ-CD, respectively. The structure of β-CD is illustrated in Fig. 1. They are commodity chemicals, non-toxic, and are prepared by the action of bacteria on starch (Tonkova, 1998). The CD has a cylindrical structure with a hydrophobic cavity and a hydrophilic exterior. Hydrophobic compounds or functional groups can be accommodated inside the CD cavity to form inclusion complexes. The hydroxyl groups present on the exterior surface of the CD makes the entire structure hydrophilic. Thus, CDs offer a means to stabilize hydrophobic species in water (Szejtli, 1998). Practical applications (Hedges, 1998) include solubility enhancement of hydrophobic solutes such as pharmaceuticals (Charumanee et al., 2006), the stabilization of volatile compounds for odor control (Lo Nostro et al., 2003; Goubet et al., 2000), and the controlled release of pesticides (Szente, 1998).

We have recently found that β-CD can alter the surface properties of polymers commonly used as adhesives in the paper industry (Banerjee, 2006a). Polymers are important in sludge dewatering where cationic and anionic polymers are applied sequentially to coagulate and flocculate sludge particles. In this paper, we demonstrate through laboratory work and full-scale trials that very low doses of β-CD boost the performance of conventional sludge conditioning chemicals by increasing both the cake solids and the dewatering rate of biological or primary sludge (Banerjee, 2006b).

2. Methods and materials

Our major objective was to demonstrate that low doses of CD improve the aggregation of sludge. Visual evidence was first

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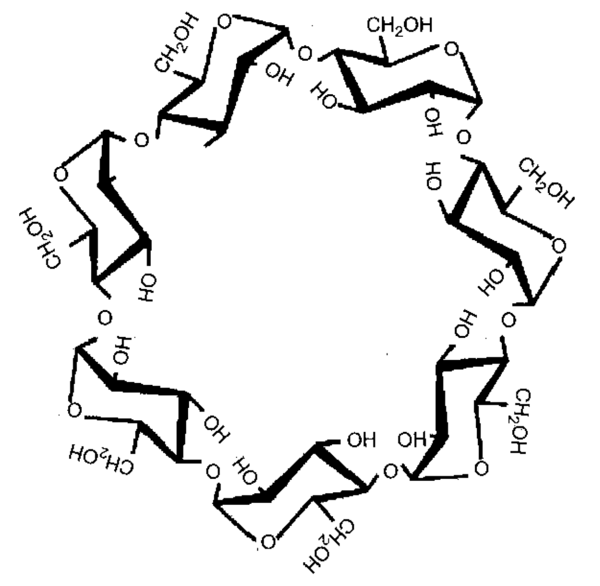

Fig. 1 – Structure of β-cyclodextrin.

obtained through microscopy where sludge particles were shown to agglomerate in the presence of β-CD. Next, the effect of CDs on drainage rate and cake solids was measured with a belt press simulator. The specific resistance to filtration (SRF) was also determined by the method of Vesilind (1974). The sludge used was biological and fibrous paper mill sludge. In some cases, pulp was used in place of fibrous sludge in order to minimize the inherent variability of sludge. A mill trial was then run to demonstrate full-scale benefits. Finally, the mechanism of the process was explored through surface tension and turbidity measurements.

The CDs and the c-PAMs were provided by Wacker Chemicals, Eka Chemicals, and Hercules Chemicals, respectively. Surface tension was measured with a Dynamic Contact Angle Analyzer (Model DCA-312, Cahn Instruments, Inc., Cerritos, CA). Turbidity was determined with an Orbeco-Hellige digital turbidimeter (Orbeco Analytical Systems, Farmingdale, NY). In both cases, the polymer suspension was mechanically stirred for at least 30 min to invert the polymer before the CD was then added.

The belt press simulator was a Crown press obtained from Phipps and Bird, Richmond, VA. A sludge slurry (200 ml) was drained through a screen and the volume collected after 1 or 2 min was measured. The solids remaining on the screen were then pressed and the final cake solids determined. Measurements were made in triplicate for the experiments with sludge collected from paper mills. The conditioning chemicals and their dosage were identical to those used at the mills.

The biological sludge used in the laboratory experiments was waste activated sludge (TSS: 0.97%) collected from a linerboard mill in the Southeastern US. The pH of the sludge as collected was 7.8. It was dosed sequentially with alum at 0.9 kg/dry tonne, a c-PAM (Eka 2560) at 4.5 or 6.8 kg/dry tonne, and various amounts of β-CD. The suspension was stirred for a few minutes before dewatering. The mixed sludge (40% primary and 60% biological) was obtained at a TSS of 2.5% from another mill in the Southeastern US, which makes bleached market pulp and uses an activated sludge treatment system. Here, ferric sulfate (1.5 ml of a 60% solution) was added to 1 l of sludge, followed by 34 ml of Axchem AF-9520 polymer at 0.36% solids The mixture was stirred for 30 s, the β-CD was added, and the suspension stirred for an additional 5 min. The sludge was then dewatered in the Crown press.

SRF measurements were made on softwood pulp (100 kappa) as a substitute for fibrous paper mill sludge. The TSS of the pulp suspension was 1.1%. Different c-PAMs at 1.8 kg/dry tonne followed by β-CD at 0.09 kg/dry tonne were added to the pulp.

The mill trial was run during May 2005 at the Stora Enso wastewater center at Wisconsin Rapids, WI. The center collects effluent from three paper mills. The effluent is routed through a primary clarifier and the overflow treated in an activated sludge treatment system. The primary and secondary sludge is mixed in a 6.8 m^3 gal blend tank from which the sludge is pumped at 3000 l/min to four belt presses. Flow from the primary and secondary thickeners is 1000 and 1900 l/min, respectively. Ferric chloride (38% active) was added to the blend tank at 600 ml/min. A coagulant, Stockhausen 187 KH at 6.8 kg/tonne, and a flocculant, Stockhausen K133L at 73.4 kg/tonne, were added to each individual press. A β-CD solution was pumped into the sludge slurry along with the polymer. An Andritz belt press was used in this study.

3. Results and discussion

3.1. *Studies on biosludge*

The effect of β-CD on the drainage of biosludge in a Crown press was measured. Fig. 2 shows that the presence of the CD sharply improves the drainage rate up to a dosage of 0.045 kg/dry ton of sludge, beyond which the drainage deteriorates. In order to isolate the effect of the CD on the polymer alone a drainage measurement was made without

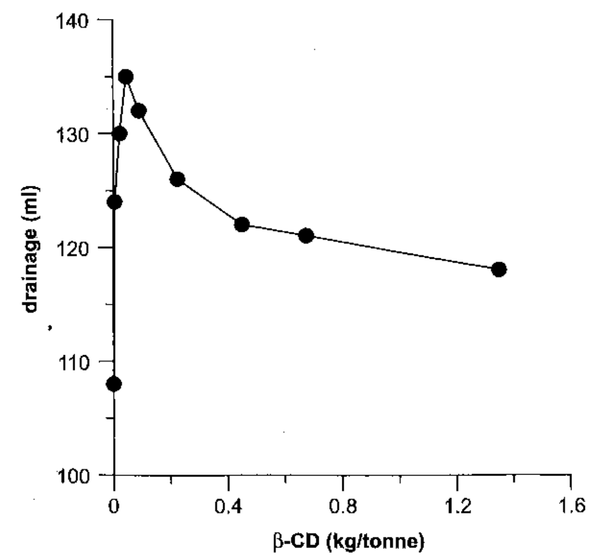

Fig. 2 – Effect of β-CD on the drainage of biological sludge dosed with 0.9 kg/dry tonne alum and 6.8 kg/dry tonne c-PAM.

the alum and at two different c-PAM concentrations. The results are illustrated in Fig. 3. The increase in the drainage rate caused by the CD remains the same at both polymer levels demonstrating that the benefit provided by the CD is insensitive to small changes in polymer dose.

Addition of β-CD alone to the sludge did not change the particle size as seen under a microscope. However, adding β-CD along with c-PAM appeared to lead to denser flocs. In order to obtain floc sizes small enough to fit into the field of vision, about one-tenth of the polymer dose used in Fig. 2 was applied (0.5 kg/dry ton). As shown in Fig. 3, the flocs appeared to densify at 0.045 kg/dry ton β-CD. Higher β-CD dosages did not show further consolidation. A remarkable attribute of Figs. 2 and 4 is that the CD exerts its effect at very low dosage.

3.2. *Studies on pulp*

Primary sludge in the paper industry mainly consists of short fiber. Various inorganic components used in fillers are also usually present (Koshikawa and Isogai, 2004). The proportion of these components can be variable in sludge, and measurements were made on pulp, which served as a well-characterized surrogate. The effect of β-CD on the SRF of the sludge was measured. The results in Table 1 demonstrate that the CD reduces the SRF quite substantially, which would arise from improved floc formation. The pulp was also used in several experiments where it was pressed in the presence of various c-PAMs and CDs, and the cake solids measured. The results, illustrated in Fig. 5, show that all the CDs considered increased cake solids by 0.5–2.6 percentage points. Although the differences are small, the larger CDs and the hydroxylated derivatives consistently performed better across all the polymers considered.

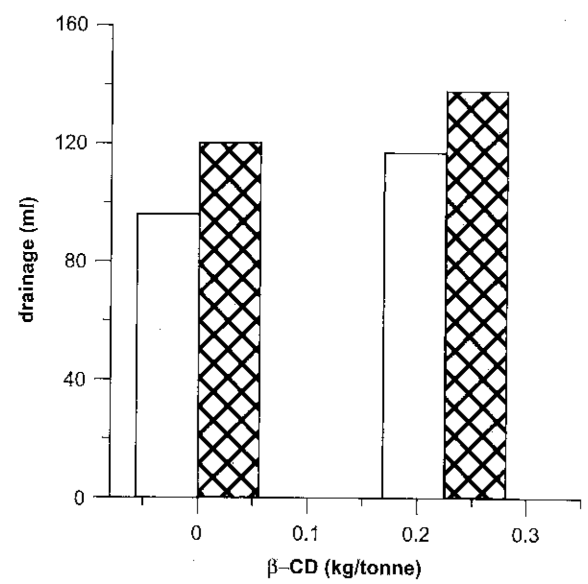

Fig. 3 – Effect of β-CD on the drainage of biological sludge dosed with c-PAM. The clear and hatched bars represent c-PAM doses of 4.5 and 6.8 kg/tonne, respectively.

Table 1 – Effect of β-CD on the filterability of pulp

CD (kg/tonne)	SRF (in 10^9 m/kg)[a]
0	0.92
0.05	1.1
0.23	0.41
0.45	0.40
0.90	0.36

[a] Average of 2 determinations, avg deviation ~20%.

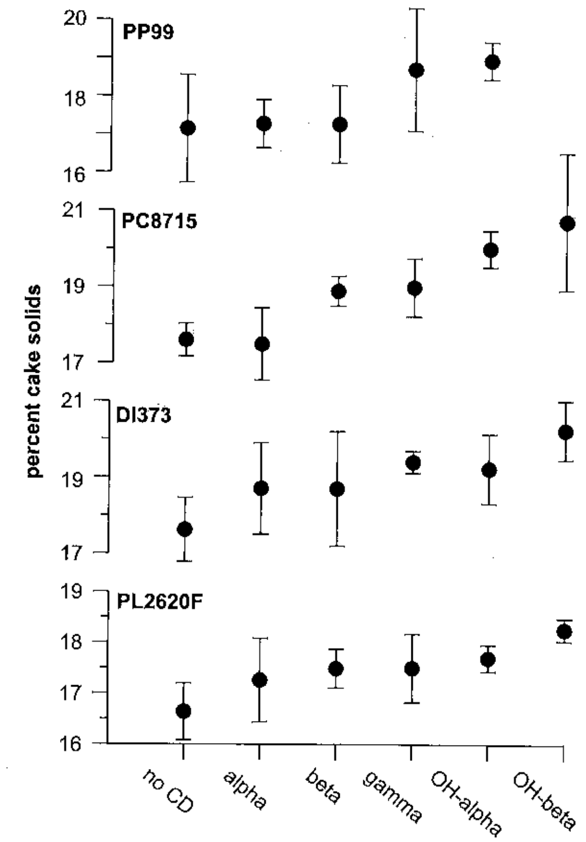

Fig. 5 – Dewatering of pulp with various cyclodextrins.

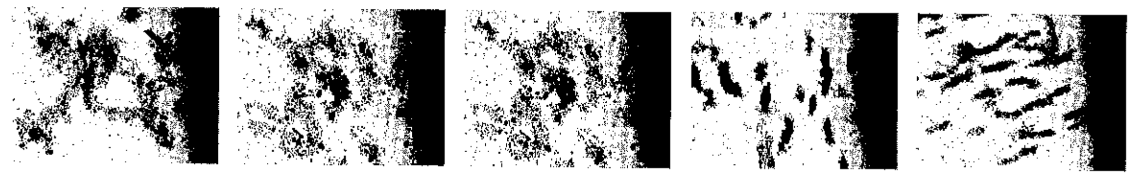

Fig. 4 – Micrographs of biological sludge with 0.5 kg/tonne c-PAM and increasing dosages of β-CD (from left to right: 0, 0.0045, 0.023, 0.045, 0.09 kg of β-CD/dry tonne).

3.3. Studies on mixed sludge

Mixed biological and secondary sludge collected from a paper mill was dewatered in the Crown Press, and both cake solids and filtrate TSS was measured. The results, provided in Table 2, show that the CD provides a marginal increase in solids at best. However, there is a significant decrease in filtrate TSS, and the difference in filtrate clarity was evident. This is a direct outcome of the better flocculation caused by the CD; the smaller particles are agglomerated and filtered out. The lower TSS reflects an increase in the capture rate, which is important because the filtrate is directed back to the treatment system and the solids released with the filtrate will eventually need to be reprocessed.

3.4. Mill trial at Wisconsin rapids

Biological sludge collected from the Stora Enso facility was evaluated in our laboratory Crown press as a prelude to a trial at the Stora Enso Wisconsin Rapids mill. Polymers were added at the same dosage used at the mill to a sludge sample collected from the mill at about 2% solids. Three CDs were evaluated, and the results, provided in Table 3, show that all of them increased cake solids at a t-test confidence level of >98%. There was no significant change in the drainage rate. The polymers used for the biosludge were also added at the same dosage to primary sludge obtained from the mill at 4.7% solids. β-CD was added at 0, 0.09 and 0.23 kg/dry tonne of sludge and the material was processed through a Crown Press. The results, listed in Table 4, show a small improvement in both drainage rate and cake solids. The benefit levels off at a CD concentration of about 0.09 kg/tonne.

Table 2 – Effect of β-CD on the capture rate during belt filtration

	Percent cake solid (avg.)	Filtrate TSS (g/l)
Control	27.1, 27.7 (27.4)	1.60, 1.59
Control+0.2 lb CD	28.6, 28.0 (28.3)	1.32, 1.34

Table 3 – Crown press results for secondary sludge from Wisconsin Rapids

CD type	CD (kg/tonne)	Percent cake solids (avg)
β	0	15.4, 16.1, 16.8 (16.1)
	0.09	17.6, 17.9, 18.2 (17.9)
γ	0	16.2, 17.1, 16.2 (16.5)
	0.09	18.5, 18.1, 17.8 (18.1)
	0.23	17.6, 18.2, 19.2 (18.3)
α	0	16.2, 17.1, 16.2 (16.5)
	0.09	19.7, 17.6, 18.3 (19.0)
	0.23	18.3, 18.9, 18.7 (18.7)

Table 4 – Crown press results for primary sludge from Wisconsin Rapids

β-CD (kg/tonne)	Volume drained		Percent cake solids (avg.)
	1-min	2-min	
0	70, 70, 68	78, 78, 78	25.3, 24.9, 25.2 (25.1)
0.09	74, 74, 74	86, 86, 86	26.0, 26.4, 26.5 (26.3)
0.23	76, 76, 76	88, 88, 88	26.5, 25.9, 26.3 (26.2)
20% reduced polymer			
0	72, 72, 73	82, 83, 83	25.0, 26.0, 25.4 (25.5)
0.09	76, 76, 77	87, 86, 88	26.5, 26.0, 25.9 (26.1)

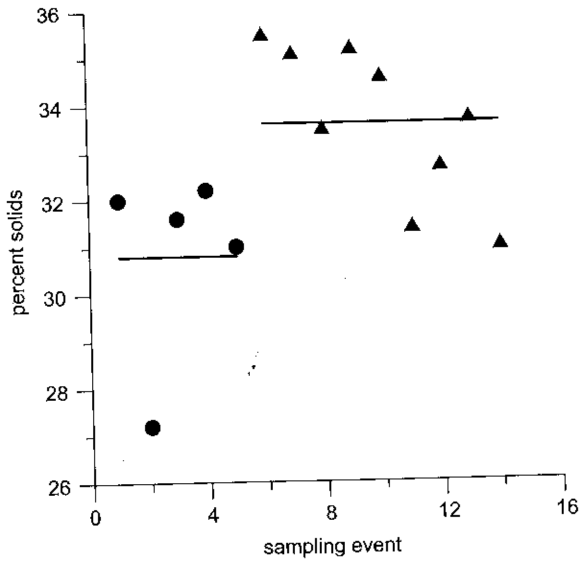

Fig. 6 – Cake solids with (triangles) and without (circles) β-CD for press 1. The lines are averages for each case.

The full-scale trial was run under normal mill operating conditions. The CD was added with the polymer at 0.045 and 0.09 kg/tonne, but the results from both applications were similar and the results are interpreted on an on/off basis for the CD. Fig. 6 summarizes the results with the CDs. The average pressed solids rose from a baseline value of 30.8–33.6%, an increase of 2.8 percentage points. A t-test shows the means to be different at a 99% confidence level. The mill reports a historical baseline of 28% solids. The increase in solids is slightly higher than the values obtained in the laboratory, but they are considered to be comparable given differences in the types of presses used.

Visually, the β-CDs caused a clear difference in the structure of the sludge. Much better flocs were obtained, and the dry line moved back on the belt indicating better drainage. The ash content was about 40% for both the secondary and primary sludges. It is unlikely that the β-CDs are effective on ash, and the results should be better for lower-ash sludge. Overall, the results from the mill are considered to be in general agreement with those obtained in the laboratory.

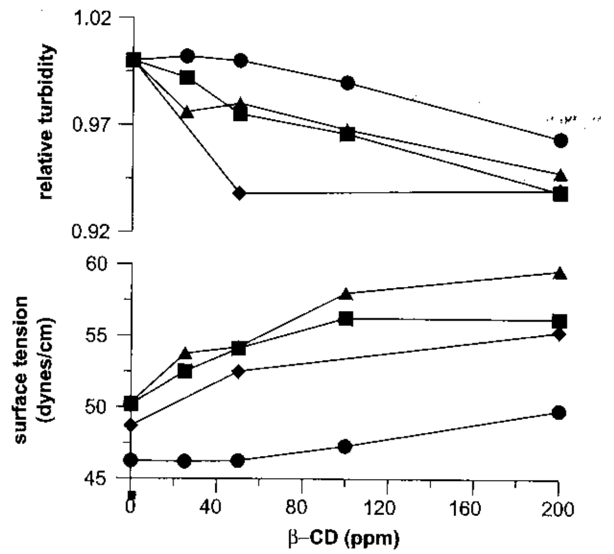

Fig. 7 – Effect of β-CD on the surface tension (dynes/cm) and relative turbidities of various c-PAMs: 2310 (triangles), 2320 (diamonds), 2610 (circles), 2620 (squares).

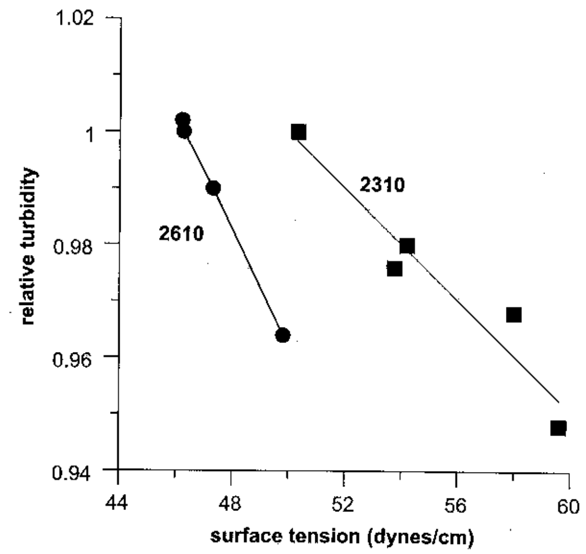

Fig. 8 – Relationship between turbidity and surface tension. The values in the plot refer to the polymers.

3.5. Mechanistic studies

We studied the interaction of polymer (without sludge) and β-CD through surface tension and turbidity measurements. Surface tension was measured by keeping the c-PAM concentration at 100 ppm and varying the concentration of the CD. The CD increased the surface tension in all cases, as shown in Fig. 7. Surface tension is caused by the attractive forces in liquids; the greater the attractive forces between the molecules the higher the surface tension. Organic liquids have surface tensions of between 25 and 40 dyn/cm, which reflect their low interaction; that of water is higher at 72 dyn/cm at 25 °C. The increase in surface tension caused by the CD indicates increased interaction among the polymer strands, which would result from agglomeration. Corresponding turbidity measurements are included in Fig. 7. The turbidity was normalized with respect to its starting value in each case so as to allow comparison of the effect of the CD on different c-PAMs. The surface tension and turbidity profiles illustrated in Fig. 7 bear a mirror-range relationship to each other, which is expected since they are both believed to originate from the agglomeration of the polymer. This is reinforced by the plot in Fig. 8 which relates surface tension with turbidity for two of the polymers used in Fig. 7. The other two polymers have fewer data points associated with them; their plots have more scatter, but the trend remains the same.

Changes in turbidity of a single c-PAM (Eka PL 2620F) at 100 ppm induced by various CDs are shown in Fig. 9. The CDs decrease the turbidity in almost all the cases, which is, again, a reflection of polymer agglomeration. Although β-CD has the greatest effect, the other CDs also lower turbidity to varying degrees. These results, taken in conjunction with those from Fig. 7 suggest that the interaction between the CD and the polymer is non-specific. A curious feature of Fig. 9 is that the lines are all roughly parallel above a threshold CD concentration of 100 ppm, but are unrelated at lower concentrations. We have seen a similar threshold in work on the effect of CDs on the tack of acrylate polymers (Banerjee, 2006a).

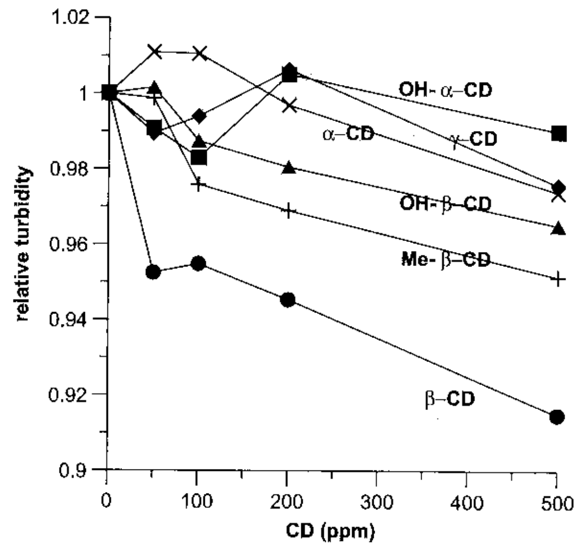

Fig. 9 – Effect of different CDs on the turbidity of 2620F c-PAM solution (100 ppm).

The most striking aspect of this study is that CDs are able to agglomerate the c-PAM polymers or the c-PAM-treated sludge when applied at very low doses. The patching and bridging mechanisms usually proposed to account for polymer induced agglomeration (Lee and Liu, 2000) are unlikely to apply here because the CDs are small uncharged molecules. The finding that CDs are effective at low dosage suggests that they are not acting on the entire surface of the sludge solids but only on a small part thereof. When a coagulant is added to sludge an overdose causes charge reversal. Even if the coagulant is added at a dose optimal for the entire sludge, some part of the sludge solids will be overdosed and bear excess charge. We propose that the CD neutralizes these "hot spots". The rigid CD frame carries several hydroxyl groups, which would be particularly effective as a charge sink. The ability of CDs to interact with cations has been previously noted by Eddaoudi et al. (1995) who found that calcium ions complexes with the hydroxyl groups of a derivatized CD at the air–water interface.

The actual mode of attachment of the CD to the polymer is not known, but it is unlikely that the inclusion mechanism proposed for most of the other CD applications applies here. Guo et al. (2005) have invoked inclusion in their work on polymer association, but in their case the CD was bonded to the polymer chain and was an integral part of it. Our CD is independent of the polymer and the inclusion mechanism would require the formation of a shear-resistant three-component system, which seems unlikely.

3.6. *Cost:benefits*

Derivatized CDs have been used to flocculate particles; e.g. clay suspensions have been flocculated with cationized CDs applied in conjunction with anionic polymers (Xiao and Cezar, 2005). Hashimoto et al. (2004) demonstrated that copolymerizing polyacrylamide with CD improves drainage when the product is added to pulp. However, sludge-treatment polymers are commodity chemicals, and derivatized CDs have not found commercial use possibly due to cost considerations.

The cost of β-CD is in the same range of a typical sludge conditioning polymer, but it is applied at very low doses so the increase in overall chemical cost is small. Its benefit is incremental; it essentially boosts the performance of the polymer(s) applied with regard to cake solids, drying rate, and capture efficiency. The cost:benefits are site-specific, but they are especially attractive at locations where sludge disposal costs are high.

4. Conclusions

Our major conclusions are as follows:

1. Laboratory work has shown that CDs are able to increase cake solids, and also, on occasion, the rate of dewatering of both biological and fibrous sludge when applied along with conventional coagulants and flocculants. The capture rate of solids during belt pressing is also increased. These results were confirmed in a full-scale trial at the Stora Enso Wisconsin Rapids wastewater facility.
2. CDs are able to destabilize cationic polymers in an aqueous suspension. The turbidity of these suspensions decrease and the surface tension of the solution increases, indicating the agglomeration of polymer chains. It is proposed that the CDs promote agglomeration by neutralizing excess charge on the polymer-conditioned sludge surface.
3. A key finding is that these benefits are obtained at very low CD dosages, which makes them attractive for commercial application.

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