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Dewatering fibrous sludge with soy protein

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ABSTRACT

Sludge is typically conditioned with petroleum-based polymers such as cationic polyacrylamides (c-PAMs) prior to dewatering. It is shown that soy and whey proteins can function as sludge conditioners. High cake solids are obtained when fiber or fibrous sludge is dewatered after treatment with a crude soy flour hydrolysate. Filtrate turbidity is not reduced by the soy alone, but it can be significantly lowered with a small c-PAM supplement. The approach is demonstrated with wood pulp fiber and several paper mill sludges. The binding of soy protein to sludge solids is much weaker than that of c-PAM, but it still produces a denser cake because charge reversal is reduced. Although soy protein and sludge particles are both negatively charged overall they both contain positively charged groups that facilitate bonding. The cost:benefits of c-PAM supplemented soy protein are attractive when compared to a full c-PAM dose. In addition, the soy product has a green value.

1. Introduction

Approximately 4% of the feedstock that enters a paper mill is discarded as sludge, which translates to several million tons worldwide on an annual basis [1]. Sludge is typical disposed of through landfilling, land spreading or burning [1]. Increasing the solids content of sludge reduces transportation costs and decreases the landfill space used. If the sludge is burned, fuel costs decrease with increasing solids because of the lower water content. Cake solids can be increased by more intensive pressing [2] and/or by using agglomerants and flocculants that promote dewatering [3,4]. Agglomerants neutralize the negative charge on the sludge particles, thereby reducing their mutual repulsion and allowing them to aggregate. Flocculants of higher molecular weight and of negative charge then consolidate the aggregates into flocs through bridging [5–7]. However, flocculants are not always necessary. Both agglomeration and flocculation promote dewatering by consolidating the solids and opening up channels in the sludge matrix. Cationic polyacrylamide (c-PAM) is a typical polymer used for conditioning sludge. It is also used for agglomeration during papermaking and in the mineral processing industry [8–10].

Soy derivatives have been used to partially or completely replace petroleum-based products in several applications. For example, soy proteins are found in adhesives and plastics [11–15]. Nguyen and Gu [16] have utilized soy and other proteins as components in formulations that detackify adhesives that enter recycle paper mills with wastepaper. c-PAMs are manufactured from petroleum feedstocks and their cost fluctuates with the price of oil. This paper demonstrates that c-PAMs can be mostly substituted with soy protein for conditioning paper mill sludge prior to dewatering. The soy/c-PAM combination is cheaper and greener than c-PAMs when used alone at their conventional dose.

2. Materials and methods

Defatted soy flour (50 μm) was obtained from Archer Daniels Midland Co. Pro-Cote 4200 (a soy isolate) was provided by Solae; the average molecular weight of this protein is 300,000 Da [17]. Whey protein (42% protein content) was purchased from Unjury.com. The c-PAM was a gift from Eka Chemicals; it had a molecular weight of 6.7 MDa and a nominal charge substitution of 20%. Bleached hardwood fiber was provided by the Alabama River Pulp Co. Sludge was obtained from several paper mills; their properties are listed in Table 1. The high ash content of some of the sludges (especially sludge B) was due to the presence of boiler ash and paper filler. Turbidity was measured with an Orbeco-Hellige turbidimeter. Zeta potential was determined at pH 7.0 with a 90 Plus particle size analyzer from Brookhaven Instruments. Sludge and fiber suspensions prepared at 2% solids were dewatered in a Crown press, which is known to predict the performance of a belt filter press [18]. Because the varying fines content of fiber and sludge can affect dewaterability, sub-samples taken for comparative measurements were drawn from the same fiber or sludge suspension. Where c-PAM and soy protein were both added, the c-PAM concentration was first optimized to the minimum dose necessary for the formation of a compressible cake.

Pro-Cote 4200 was cationized by Quat 188 (a solution of 3-chloro-2-hydroxypropyl-trimethylammonium chloride, 65% active), obtained from Dow Chemical. The Pro-Cote (50 g) was mixed with 150 ml deionized water and 106 g Quat 188 solution at 700 rpm at 60 °C for 30 h. The pH was maintained at 8.5–10.0 with NaOH. The final mixture contained 41.2% solids. Cationization increased the zeta potential (measured at pH 7.0) of the Procote from −24.5 mV to 14.5 mV. The cationized protein was used as is, *i.e.* it was not isolated from solution.

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Table 1
Properties of paper mill sludge.

Sludge	Source	Ash content (%)
C	Recycled bleached kraft pulp	25
B	Bleached kraft pulp	48
P	Bleached kraft pulp	23
W	Bleached kraft pulp	11

The Pro-Cote isolate is relatively expensive and cationization increases cost. The performance of (uncationized) soy protein isolated from soy flour was also evaluated because it is much cheaper. A 20% suspension of the flour in pH 10.0 water was stirred for 2 h at 55 °C. The solids were removed through centrifugation and the filtrate adjusted to pH 4.5 with HCl. The precipitated solids were washed three times with water and collected through centrifugation between each washing. The yield of the soy protein was 51%, which is consistent with literature values [19]. This material is referred to in the discussion as isolated soy protein and was used without drying to conserve cost. Finally, crude soy protein was prepared as above by stirring soy flour at pH 10 and omitting all the succeeding steps. The suspension formed a paste which was added directly to the sludge.

The binding of protein to bleached hardwood fiber was determined by mixing Pro-Cote 4200 and/or c-PAM with 2% fiber in water for 1 h. The mixture was filtered through Whatman #4 filter paper and the total organic content (TOC) of the filtrate determined with a Shimadzu TOC-V_{CSH} instrument. Control experiments with only fiber and c-PAM showed that the c-PAM was completely taken up by the fiber and did not contribute to the TOC. The high affinity of c-PAM to fiber is well known [10].

3. Results and discussion

3.1. Dewatering measurements

Conventional sludge conditioners are typically cationic. Because soy proteins are isoelectric at pH ~4.5 [17] they would be negatively charged under typical dewatering conditions where the filtrate is essentially neutral. Hence, it seemed likely at the onset of the project that the protein would need to be cationized to be effective. Measurements were made with paper mill sludge as well as with hardwood fiber; the latter was included because of its greater uniformity. The solids (fiber or sludge) were dewatered after addition of cationized Pro-Cote. The results, shown in Fig. 1, demonstrate that higher cake solids are obtained with the soy than with the c-PAM. The soy does not reduce filtrate turbidity, but leaves it unchanged from the base case where the slurry is dewatered without any additive. Polymers reduce turbidity through bridging and a polymer chain has to be long enough to contact two or more particles. Accordingly, the molecular weights of bridging polymers are in the MDa range. The molecular weight of Procote is only about 300,000 Da [17], which is too low for it to reduce turbidity through bridging. The problem can be mitigated somewhat by supplementing the soy with a small amount of c-PAM. The turbidity is still higher than that obtained with the full c-PAM dose, but it should be acceptable in most cases. Similar results were obtained for sludge.

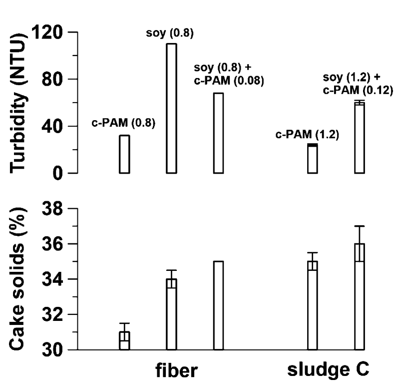

Fig. 1. Dewatering hardwood fiber and paper sludge conditioned with quaternized soy protein. The unit for the values in parentheses is g/kg dry solids. The results were averaged from two measurements.

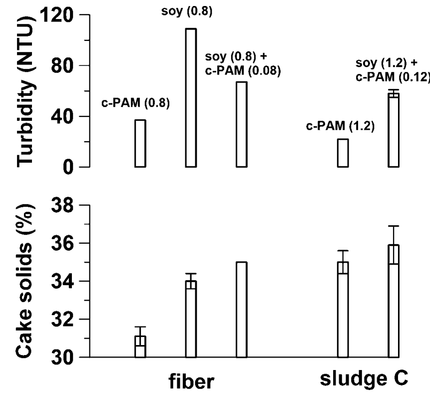

Fig. 2. Dewatering bleached hardwood fiber conditioned with isolated soy protein. The unit for the values in parentheses is g/kg fiber. The results were averaged from two measurements.

It is tempting to conclude that the Procote neutralizes negatively charged regions of the solids through a conventional patch mechanism [10]. However, high cakes solids are also obtained with native (uncationized) soy protein as shown below.

Because quaternizing the soy protein adds cost, the possibility of using extracted raw soy protein without derivatization was evaluated. Soy protein is anionic under neutral pH conditions and one would expect charge repulsion between sludge solids and protein to reduce binding. Nevertheless, Dentel [20] has shown that anionic polymers can bind to sludge, probably by associating with positively charged sites present in the sludge particles. In other words, although sludge particles are negatively charged overall, they contain a sufficient number of cationic sites to attract anionic polymers. Also, soy proteins are amphoteric and are known to carry cationic sites even at pH values above the isoelectric point [17]. Hence, binding occurs through a combination of cationic sites in soy associating with anionic regions in the sludge solids and by anionic sites in soy coupling to cationic regions in sludge. Hydrogen bonding of soy protein to the carboxylate groups in fiber may also contribute to binding.

Results from dewatering hardwood fiber with isolated soy protein are presented in Fig. 2. As before, the soy protein increases cake solids, but does not reduce filtrate turbidity. Again, a small c-PAM supplement lowers the turbidity significantly, although not to the levels achieved by the full c-PAM dose. Presumably, increasing the c-PAM dose would further reduce the total suspended solids (TSS); this is the case for another soy application discussed below. Overall, the Fig. 2 results reinforce those in Fig. 1 in that the soy provides higher cake solids but does not, by itself, reduce turbidity.

Isolation of the soy protein from soy flour requires suspension of the flour in alkali and acid precipitation of the protein followed by collection of the solids, all of which add to cost. Many of these costs were eliminated by adding the crude protein extract directly to the fiber slurry. The c-PAM supplement was added separately to the slurry in order to prevent exposure to the alkali present in the crude extract; otherwise, the polymer would lose charge through alkaline hydrolysis. The pulp was then dewatered in a Crown press. The results, provided in Table 2, demonstrate the success of the approach; the soy leads to a clear increase in cake solids. However, as before, the filtrate TSS (total suspended solids) is also high. Table 3 lists the effect of increasing the supplemental c-PAM dose while keeping the soy protein level constant on dewatering hardwood fiber. Although the cake solids are essentially unchanged, the TSS falls linearly with increasing c-PAM dose.

Results from dewatering three paper mill sludges with crude soy protein are compiled in Table 4. For mill B sludge the soy/c-PAM combination provides the same cake solids as the c-PAM alone, but