Sugar surfactants in paper recycling

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SUMMARY: The objective of this research was to evaluate surfactants based on renewable materials (sugars and proteins) for use in ink removal from recycled paper via flotation deinking. By applying green chemistry approaches we aim to minimize the environmental impact of deinking agents and to open an avenue for a number of products that are being produced from natural resources. Foamability by the respective surfactants was considered and detergency experiments via piezoelectric sensing were used to reveal fundamental differences in terms of surfactant activity. Lab scale flotation deinking efficiency was measured primarily by image analysis and flotation yield determined gravimetrically. Based on deinking efficiency versus yield results, it was demonstrated that sugar-based surfactants are viable replacements to petroleum-based surfactants in flotation.

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In paper recycling, deinking operations are used to remove the ink from recovered paper by washing and flotation processes. The flotation process separates ink from the fibers by the injection of air in the presence of a foaming agent (McCull 1993). Rising bubbles carry away the ink particles and are then separated from the top of the flotation vat. It is beneficial to minimize fibers lost in the reject stream. Likewise, some ink particles remain in the fiber accepts and therefore the final paper quality depends on the selectivity of the separation process. The key operational steps in flotation involve the use of surfactants to ensure the detachment of the ink from the fibers (detergency) and the formation of a stable foam that can be separated from the pulp during the flotation stage. In a typical process the amount of surfactant used is approximately 0.025-0.25% based on oven-dry fiber mass.

The effect of the surfactant on the attachment of ink and other hydrophobic particles to the air bubbles is complex. The surfactant can exist at the ink-water interface, the ink-air interface, and the air-water interface, changing the surface characteristics.

Foaming is a key performance attribute of flotation surfactants. It has been found that surfactants have the ability to promote foaming above and below their critical micelle concentration (Borchardt 1992). For linear alkyl benzene sulfonates, it has been found that the foaming activity of the surfactant increases with length of the alkyl chain and that anionic surfactants tend to foam more readily than non-ionic ones with the same hydrophobe.

Two of the most common types of surfactants used for deinking are fatty acid soaps and polyethyleneoxide alkyl ethers, which are classified as anionic and non-ionic surfactants, respectively. The case of nonylphenol ethoxylates is particularly significant. Nonylphenols used as a nonionic surfactant could potentially result in its release to the environment through various waste streams in paper recycling operations. Furthermore, nonylphenols are suspected to be endocrine disruptors (Ren et al. 1997) and are severely irritating to eyes and skin in high concentrations (NIOSH 1983). Therefore, our research objective was to evaluate natural surfactants and understand their behavior in flotation deinking with respect to foaming, detergency and separation effectiveness.

Experimental

Materials

The main deinking agents discussed in this study were received as donations from chemical suppliers and included an alkyl phenol ethoxylates (APE), sugar-based surfactant, protein-based surfactant, and a commercial surfactant mixture. The ethoxylated surfactant consisted of octylphenol ethoxylate with an average of 9.5 ethylene oxide units per molecule. The sugar-based surfactant was an alkyl (C10-C16) mono and oligomeric D-glucopyranose. The protein-based surfactant was derived from soybean with a base (amphoteric) polymer composed of approximately 25 different types of amino acids linked with amide bonds with a weight averaged molecular weight of around 100-300 kDa. Only at pH values above 7 is the polymer fully soluble. A proprietary commercial flotation deinking aid intended for mixed office paper based on a non-ionic surfactant blend was also investigated.

Commercial copy paper with calcium carbonate as a filler with a recycled fiber content of 30% was printed on both sides with 12 point font, single spacing, and one inch margins using xerographic toner (Konica Minolta MT Toner 303A). Sheets were shredded and pulped at 3% consistency for ten minutes in a TAPPI British disintegrator.

Model ink films

In order to conduct detergency studies in controlled conditions, model films were used. An oil-based ink film was produced by using tripalmitin, a fatty acid, via vacuum sublimation. Reflux condensation using acetic acid was used to keep the surface at 75°C (Weerawardena et al. 1999). Model toner films were also manufactured. This involved spin coating (Laurrell Technologies model WS-400A-6NPP: North Wales, USA) poly(methyl methacrylate) (Sigma-Aldrich CAS 9011-14-7) in THF (1% solution) on gold surfaces at 5000 rpm for 40 seconds followed by air drying.
Methods

Surface tension and foamability
Surface tension was measured using a Du Noüy Ring (Fisher Scientific Model 20) to determine the critical micelle concentration and minimum surface tension (surfactant effectiveness). Static foamability was performed using the Ross-Miles Test (ASTM 2001) whereby foam height was recorded five minutes after impact of surfactant solution on the same solution in a thermostated column. A dynamic method to measure foamability and foam stability was also used. In this case 185 ml/min air was bubbled through 400 ml surfactant solution (0.025 g/L) with a diffusing stone while recording the foam height.

Detergency via contact angle and Quartz Crystal Microbalance measurements
The evaluation of detergency was performed by measuring the contact angles with water on the ink and toner films before and after surfactant treatment. Each film was incubated with 0.25% surfactant solution by suspending the substrate in a beaker immersed in surfactant with continuous stirring. At each time interval, the film was removed, dried with compressed air, and the contact angle measured. Thereafter, the film was dried with air and placed back in the beaker with the solution. Surfactant treatment was carried out until the contact angle with a water drop probe reached a constant value. A rinsing sequence was performed by suspending the film in a beaker of deionized water and the procedure repeated until the contact angle reached a constant value.

A Quartz Crystal Microbalance with Dissipation monitoring, QCM-D (Q-sense D-300, Sweden) was also used to study surfactant adsorption and activity on films deposited (via vacuum sublimation or spin coating) on coated quartz/gold electrodes (with surface area of 0.2 cm²). The monitored change in frequency was related to the mass adsorbed and released (after rinsing) for each surfactant using the Sauerbrey relation (Rodahl, et al. 1995). As stated by the Sauerbrey equation, if a thin and rigid film is adsorbed on the sensor, the change in frequency ∆f (relative to the bare surface) is proportional to the change in mass ∆m (added or released):

\[ \Delta m = -CAf / n, \]

where \( C = 17.7 \) ng Hz⁻¹ cm² for a 5 MHz quartz crystal and \( n = 1,3,5,7 \) is the overtone number. In this investigation, the QCM third overtone frequency was used to calculate the change in model ink mass (Sauerbrey 1959). It is noted that the mass detected by the QCM-D includes any change in the amount of solvent that oscillates with the surface.

Flotation deinking
Flotation deinking was performed in a Wemco Laboratory Flotation Unit (EIMCO Process Equipment, Salt Lake City, UT) equipped with the Wemco 1+1 rotor disperser with 2000 gram cell tank. Surfactant was added either prior to pulping or in the flotation cell. Different surfactant concentrations (0.1-0.75% on OD solids) were evaluated. Handsheets were made in a standard Tappi handsheet mold and pressed using a standard Tappi press. The ink content and hand sheets brightness were measured after conditioning at 50% relative humidity and 23°C using a Spec*Scan 2000 (Apogee Systems Inc.) and a Color Touch 2 spectrophotometer (Technidyne Corporation), respectively.

Results

Surface tension and foamability
The surface activity of the different surfactants is important in detergency, foamability and foam stability in flotation deinking (Table 1). It is noted that the protein solution did not exhibit a critical micelle concentration (cmc) while the sugar-based surfactant had the lowest surface tension at the cmc (effectiveness).

<table>
<thead>
<tr>
<th>Material</th>
<th>cmc (mg/l)</th>
<th>Minimum Surface Tension (mN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Protein solution</td>
<td>NA</td>
<td>43</td>
</tr>
<tr>
<td>Commercial blend</td>
<td>222</td>
<td>34</td>
</tr>
<tr>
<td>Sugar-based</td>
<td>112</td>
<td>31</td>
</tr>
<tr>
<td>Alkyl phenol ethoxylates</td>
<td>743</td>
<td>37</td>
</tr>
</tbody>
</table>

Foam behavior, including foamability and stability produced from each surfactant type, is important in deinking operations. The foam generated must be strong enough to be mechanically removed from the system but have low time persistence to facilitate disposal. Dynamic foam tests showed that the protein-based surfactant produced no foam while the sugar and commercial surfactants exhibited similar behaviors (Fig 1). The static Ross Miles foam height for sugar-based surfactant was higher than those of APE and commercial mixtures (Fig 1).
Detergency by contact angle measurements

Surfactants assist in detergency (separation of ink from fiber) in a positive way but can negatively impact flotation by adsorbing to ink particles, producing a more hydrophilic surface. In flotation, it is desirable for the contaminant to be hydrophobic (i.e., have a very high contact angle with water). If the adsorption of surfactant to the ink is an important factor to determine flotation efficiency, then surfactants that promote a high contact angle would be expected to have higher efficiency.

For the model oil-based ink, the results from the surfactant treatment and rinsing experiments are shown in Fig 2. The protein solution produced a significant decrease in contact angle even after rinsing, suggesting that the relatively hydrophilic protein had a strong affinity for the surface. On the other hand, the commercial surfactant mixture showed the smallest change in contact angle, both before and after rinsing.

For model toner, the protein solution also produced a significant decrease in contact angle, suggesting a strong affinity for the toner surface. Similar to the model ink, the commercial mixture had the smallest change in contact angle before and after rinsing.

The contact angle change (% change) after surfactant treatment and after washing with water (rinsing) sequence is shown for the model ink and toner surfaces in Table 2. The initial percent change was calculated using the initial contact angle and the equilibrium contact angle after surfactant treatment. The washing percent change was calculated using the initial contact angle and the equilibrium contact angle after the rinsing sequence. The protein solution produced the highest percent change after rinsing. The sugar and commercial based surfactants behaved similarly for the model ink. As for the model toner, the sugar-based performed more similarly to the APE.

Detergency by Quartz Crystal Microbalance

Quartz Crystal Microbalance (QCM) experiments were performed by monitoring the vibration frequency of the model ink- or toner-coated sensor as a function of time. These measurements allowed the elucidation of (a) the extent of adsorption and adsorption kinetics for the respective surfactant in contact with the model film and, (b) the affinity between surfactant with the substrate. This last parameter was accessed by monitoring the mass of surfactant released upon rinsing.

Fig 3 shows the sensor’s frequency during equilibrium in water, after injection of surfactant solution at about 500 s and following rinsing at 2500 s. An increase in \( -\Delta f \) indicates mass uptake by the sensor, i.e., adsorption of surfactant, while a decrease in \( -\Delta f \) value is related to the release of mass (surfactant desorption).

In all cases, adsorption to the ink surface follows a fast adsorption dynamics. In the case of the commercial surfactant mixture, the signal returns to near the original level after washing. In the case of the other surfactants the signal does not return to the original value after washing, indicating a larger degree of binding. The mass released after rinsing is related to the amount of surfactant that desorbs from the interface or, if film is removed from the interface, to the amount of ink that is released. A higher affinity (lower surfactant release) is a favorable situation in terms of the detachment of ink from fiber process because in this case a better wetting of the substrate occurs. However, for the attachment of ink to air bubbles, this is unfavorable.

The QCM results are summarized in Table 3. All surfactants adsorbed to a similar extent on the model ink surface. However, the degree of binding was significantly lower for the commercial surfactant blend. It is well known that proteins adsorb strongly and irreversibly to a variety of surfaces in agreement with results herein.

<table>
<thead>
<tr>
<th>Surfactant Type</th>
<th>Model Ink Initial % change</th>
<th>Washing % change</th>
<th>Model Toner Initial % change</th>
<th>Washing % change</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commercial blend</td>
<td>30.4</td>
<td>15.9</td>
<td>24.6</td>
<td>6.7</td>
</tr>
<tr>
<td>Alkyl phenol ethoxylates</td>
<td>50.0</td>
<td>30.0</td>
<td>50.0</td>
<td>33.3</td>
</tr>
<tr>
<td>Protein-based</td>
<td>40.3</td>
<td>41.7</td>
<td>61.3</td>
<td>52.9</td>
</tr>
<tr>
<td>Sugar-based</td>
<td>34.7</td>
<td>16.7</td>
<td>43.7</td>
<td>27.5</td>
</tr>
</tbody>
</table>

Fig 2. Changes in contact angle after treatment of model ink surfaces with surfactants 0.25% surfactant solution, before (solid symbol) and after rinsing with water (washing, open symbols).

Fig 3. QCM frequency change after exposing model ink coated sensors to different surfactant solutions of 0.25% concentration at about 500 s and after rinsing with water at about 2500 s.
showing the protein-based surfactant with largest degree of binding. The QCM signal for the commercial surfactant mixture, after rinsing, is lower than the baseline, which indicates that a portion of the ink substrate may have been removed from the interface. In the case of the model toner, the protein had the least adsorption, but the adsorption was irreversible. All of the surfactants adsorbed more readily to the model toner surface than the oil-based ink surface.

**Flotation deinking**

Flotation deinking was performed on samples of copy paper, as explained in the Methods section. The detected toner particle count (PPM from optical scanning) was used to calculate the ink removal efficiency for the given sample compared to the control (a sample subjected to deinking operations in the absence of surfactant). The removal efficiency thus defined as:

$$RE\% = \frac{PPM_{control} - PPM_{sample}}{PPM_{control}} \times 100$$

The removal efficiency was plotted against the solids yield to determine surfactant overall performance when added to the flotation cell (Fig 4). Similar trends were obtained for the case of addition of the surfactant in the pulper. The alkyl phenol ethoxylate (APE) and sugar-based surfactants exhibited optimal removal efficiencies versus yield at both addition points. The commercial surfactant blend performed markedly better when added in the flotation cell rather than the pulper, in agreement with the intended addition point specified by the surfactant supplier. The protein-based surfactant had the least desirable removal efficiency versus yield performance when added to the pulper or the flotation cell.

The flotation results are plotted in terms of removal efficiency versus surfactant amount on oven dried (OD) fiber mass in Fig 5. The protein-based surfactant produced significantly lower removal efficiency versus surfactant charge than all of the others.

The effectiveness of the surfactants with respect to ash removal was also investigated. The sugar-based and the APE surfactants exhibited approximately the same ash removal if the surfactant was added in the pulper; however, if addition was in the flotation cell, the APE was slightly better. The protein is significantly less efficient at removing ash. When comparing multiple types of recycled fiber (newsprint, mixed office waste, and old magazine), the commercial mixture obtained the highest yield, removal efficiency, and brightness improvement (data not shown). The sugar and the APE surfactants were once again comparable for all grades except newspaper, in which case the sugar-based showed better yield but lower brightness improvement.

**Discussion**

The decreased performance of the protein-based surfactant in flotation deinking can be explained by the following two observations. The protein-based surfactant produced the lowest amount of foam. Further, the protein-based surfactant had the highest affinity/adsorption for the model ink and produced the lowest contact angle with water after adsorption to the model ink surfaces. This indicates that the protein-based surfactant is acting as a resistance to effective air bubble-toner contact that is required in flotation. A similar finding was reported for cationic starch and toner particle agglomeration by Venditti and coworkers (Zheng et al. 1999, 2001) and by Berg and coworkers (Snyder, Berg 1994). In these cases, starch adsorbed onto the surface of toner particles acted as a hindrance for toner-toner contact which is required in flotation. A similar finding was reported for cationic starch and toner particle agglomeration by Venditti and coworkers (Zheng et al. 1999, 2001) and by Berg and coworkers (Snyder, Berg 1994). In these cases, starch adsorbed onto the surface of toner particles acted as a hindrance for toner-toner contact which is required for agglomeration, similar to the air-toner contact required in flotation. Similar results were found for starch in water interfering with acrylic micro sphere-acrylic microsphere contact (Huo et al. 2001) and acrylate particle-polyester fiber contact (Huo et al. 1999).
There is a strong correlation between foamability and removal efficiency (Fig 6). Therefore, there is a strong correlation between foamability and removal efficiency, foambility and performance of a surfactant are closely related, and developing natural surfactants that create the correct quantity and quality of foam should also remove more ink from paper in recycling.

It has been found that the increase in contact angle between surfactant adsorption and rinsing can be related to the removal efficiency. In the case of protein surfactant, the contact angle did not increase between adsorption and rinsing but the other three surfactants all showed contact angles that increased by approximately 15 degrees on rinsing. This indicates that there is a correlation between affinity of the protein for the ink surfaces and flotation efficiency. As expected, the surfactant with the greatest change in water contact angle after treatment and rinsing had the lowest removal efficiency in flotation deinking.

Conclusions

The alteration of a model ink surface can be investigated by measuring contact angles of water on the model ink after exposure to different surfactant solutions. Adsorption of surfactant onto model ink film can be monitored using the QCM technique. The ability of the surfactants to produce foam was positively correlated to the flotation efficiency. The efficiency of a flotation cell (with respect to ink removal and process yield) was very sensitive to the surfactant chemistry utilized. It was demonstrated that a sugar-based surfactant produced flotation ink removal efficiency versus overall yield that was similar to conventional surfactants. A protein surfactant that had low foamability and adsorbed to the ink surface rendering the surface much more hydrophilic produced very low flotation ink removal efficiency versus overall yield, confirming that surfactant adsorption and foaming phenomena are important in the flotation deinking process.

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Literature


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