Electric treatment for hydrophilic ink deinking
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ABSTRACT
Hydrophilic inks have been widely used due to higher printing speed, competitive cost and being healthy non-organic solvents. However, they cause problems in both product quality and process runnability due to their hydrophilic surface wettability, strong negative surface charge and sub-micron size. Electric treatment was shown to be able to increase the ink sizes from 60 nm to 700 nm through electrocoagulation and electrophoresis. In addition, electric treatment assisted flotation could reduce effective residual ink concentration (ERIC) by 90 ppm, compared with only 20 ppm by traditional flotation. Furthermore, the effect of electric treatment alone on ink separation was investigated by two anode materials, graphite and stainless steel. Both of them could remove hydrophilic inks with less than 1% yield loss via electrofloation and electrophoresis. But graphite is a better material as the anode because graphite reduced ERIC by an additional 100 ppm. The yield loss of flotation following electric treatment was also lower by 17% if graphite was the anode material. The difference between the two electrode materials resulted from electrocoagulation and ink redeposition during electric treatment. An electric pretreatment-flotation-hyperwashing process was conducted to understand the deinking performance in conditions similar to a paper mill, and the ERIC was reduced from 950 ppm to less than 400 ppm.

Key words | agglomeration, deinking, electrocoagulation, electrofloation, electrophoresis, hydrophilic ink

INTRODUCTION
Each year, there are 250 million tons of municipal solid waste generated in the USA, and paper related waste is the largest source of municipal solid waste source, accounting for 27%. In the USA alone, the overall recovery of paper and paperboard was 66.8%. It is forecasted that in the future, the trend for recycling and recovery will significantly increase (Dorris et al. 2011). Paper recycling has a profound impact on the environment as producing recycled paper requires about 60% of the energy used to make paper from virgin wood pulp. To be more specific, recycling 1 ton of paper could save 7,000 gallons of water, 17 mature trees, 3 cubic yards of land filling space and 4,100 kilowatt hours of electricity. Recycled paper is further used to produce different paper grades such as cardboard, packaging grades, office paper, newsprint and hygiene paper. In order to recycle used paper, any contaminants, like inks, adhesives, dusts have to be removed during the recycling process, and flotation is the key process in paper recycling for contaminants removal, where hydrophobic (water-repellent) particles are separated from hydrophilic (water-wettable) fibers based on their strong interaction with air bubbles. This process has been developed to remove hydrophobic inks like offset and gravure inks, which are roughly more than 95% in the current recovered paper mixture.

The advance in the printing industry moving from offset printing into hydrophilic ink has an adverse effect on the performance of the deinking industry. Hydrophilic inks have several advantages over inks used in offset printing, one of which is that they do not contain volatile organic compounds that cause environmental and health issues (Aksoy et al. 2006). Hydrophilic inks are also superior compared to traditional inks because of the higher stability of the colloidal dispersion and smaller particle size, which are essential for high quality printing (0.1 μm compared to 5–20 μm). However, the small particle size and colloidal stability by high surface charge density are the two factors that inflict a detrimental impact on the deinking capability. The performance of the flotation deinking process relies
on a large enough particle size and a hydrophobic particle surface, thus new hydrophilic inks render the flotation process ineffective (Ben & Dorris 2011). The negatively charged particles also have to overcome a high energy barrier before attaching to air bubbles, because bubbles are also negatively charged. Furthermore, it has been well known that hydrophilic inks would irreversibly redeposit onto the fiber surfaces, or inside the fiber lumen due to their small size (Ben et al. 1996; Ben & Dorris 2000; Galland et al. 2000, 2001; Ben & Dorris 2011). The ink redeposition and the inefficacy of flotation deinking cause only a small amount of hydrophilic inks to be removed through the current deinking operations in recycling mills (Yarnell 2011), reducing the quality of the final paper product due to decreased optical properties. In addition to the paper quality problem, the hydrophilic inks also create process problems. Residual hydrophilic inks could contaminate the water in paper mills and further increase the burden for wastewater treatment. Furthermore, the contaminated water could be transferred and applied to other paper machines in the same mill because paper industries close water loops, which will reduce the paper quality of other product lines. Due to these concerns, recycling plants generally only accept recycled paper sources that contain little to no hydrophilic ink printed paper products (Yarnell 2011).

There has been a large amount of research done in an attempt to mitigate these issues in order to increase the amount of paper printed with hydrophilic inks that can be recycled. Some of the more successful efforts have been optimization of pulping conditions for hydrophilic ink printed paper (Ben et al. 2000; Bennington & Wang 2001; Fabry et al. 2001; Miller 2009; Kemppainen et al. 2011), deinking at a neutral pH condition (Galland et al. 1997, 2000, 2001; Morrow et al. 2005; Bhattacharyya et al. 2012; Korkko et al. 2012), adsorption deinking (Wasmund & Pelton 1994; Muvundamina & Liu 1997; Petzold & Schwarz 2015; Du et al. 2016; Ravi et al. 2016) and enzyme assisted deinking by laccase, cellulase, xylanase, and amylase to decolor chromophore groups (Heise et al. 1996; Nyman & Hakala 2011; Das et al. 2013; Lee et al. 2015).

However, these technologies have not been able to fully solve the problems from hydrophilic inks during paper recycling. Optimization of the pulping conditions was able to decrease redeposition of ink in the fiber lumen by reducing pulping time and agitation. However, the optimal conditions for hydrophilic ink are inadequate for traditional inks (Ben et al. 2000; Bennington & Wang 2001; Fabry et al. 2001; Ben & Dorris 2011). Thus the operating conditions would have to be compromised between hydrophilic inks and traditional inks, which would greatly reduce the effectiveness of the technique in improving the ink removal efficiency. Additionally, fractional pulping also showed potential to remove mixed offset inks and hydrophilic inks (Kemppainen et al. 2010, 2011), but the deinking process requires extensive washing, leading to unacceptable yield loss (Galland et al. 1997; Josephson & Krishnanagopal 2005; Dumea et al. 2009; Hsieh 2012). Next, neutral deinking could prevent the redeposition of ink into the fiber lumen. However, this method could not remove traditional offset ink, and more ink particles would deposit onto the fiber surfaces (Galland et al. 2000). Thus, it is necessary to have another alkaline dispersion and flotation to remove offset ink (Galland et al. 1997; Galland et al. 2001). Adsorption deinking has also been shown to be successful for both traditional offset inks and hydrophilic inks by different adsorbents (Wasmund & Pelton 1994; Muvundamina & Liu 1997; Petzold & Schwarz 2015; Du et al. 2016; Ravi et al. 2016). This technique can also dramatically reduce the water consumption by 90% and energy consumption by 20% (Schrinner & Grossmann 2012). However, multiple different adsorbents have to be chosen to remove different kinds of inks, and the adsorbent separation from fiber and adsorbent recovery has not been well studied. At last, there has been some success by using enzymes, but the enzyme-ink interactions are very specific and enzymes are selective for the type of ink that can be treated. Although very high ink removal efficiencies can be achieved in laboratory conditions, it would be impractical to apply enzyme deinking because the ink composition is unknown in industrial applications (Ben & Dorris 2011; Lee et al. 2015).

Electric treatment has been applied in wastewater treatment (Soloman et al. 2009; Mu et al. 2014; Ashrafi et al. 2015; Mahesh et al. 2016), sludge dewatering (Mahmoud et al. 2010; Citeau et al. 2011; Mahmoud et al. 2011; Fernandez & Hodgson 2013; Rahmani et al. 2013; Olivier et al. 2015), algae harvesting (Gao et al. 2010; Mascia et al. 2013; Zhang et al. 2015), mineral recovery (Casqueira et al. 2006; Sarkar et al. 2011) and particle agglomeration (Hsieh 2012; Du & Hsieh 2014, 2016) through three different mechanisms, including electrocoagulation, electroflocculation and electrophoresis. Both electrocoagulation and electrophoresis could agglomerate particles in water, while electroflocculation generates fine bubbles with greater surface area. As a result, bubbles are more likely to catch larger particles in water and float to the water surface. Based on this theory, the current work focuses on the impact of electric treatment on hydrophilic ink agglomeration and on deinking efficiency. The effects of anode material and electric treatment time
on deinking performance were also investigated to under-
stand the electric treatment mechanism and optimize the
electric treatment process. Finally, a combined treatment
was established to recycle hydrophilic ink printed paper.

EXPERIMENTAL PROCEDURE

Materials

Deionized (DI) water from an ion-exchange system with a
resistivity of greater than 18 MΩ cm was used in all
described experiments. All the deinking chemicals, includ-
ing NaOH (AR), CaCl₂ (AR), Na₂SiO₃ (AR), and H₂O₂
(AR), were obtained from VWR International. Oleic acid
used in deinking experiments was 80% (w/w). The printing
substrate, blank newsprint, was purchased from Uline and
the product code is S-19325. The basis weight is 30 lbs. and
the ISO brightness is 58%. A commercial pigment-based
hydrophilic inkjet ink (HP 60, LD Products, Long Beach,
CA) was purchased to prepare model hydrophilic ink printed
newspaper. Stainless steel and graphite electrode were
purchased from McMaster-Carr.

Methods

Electric treatment of ink suspension in DI water

0.5 mL ink was dispersed in 1 L DI water to prepare 0.5 g/L ink
suspension. The suspension was treated with 3.6 kV and
200 mA with stainless steel or graphite as the anode, and a stain-
less steel container as the cathode for 30 min. The container
was 13 cm in length and width, and 19 cm in height. The
lower end of the anode was 3 cm below the surface of the water.

Preparation of model hydrophilic ink printed newspaper

A commercial pigment-based hydrophilic inkjet ink (HP 60, LD
Products, Long Beach, CA), was used to print a black and white
image of the INGEDE gray deinking test page on one side of
virgin newspaper (30 lbs newsprint sheets, Uline, Pleasant Prai-
ries, WI) using an inkjet printer (Deskjet 1000, HP, Palo Alto,
CA). The INGEDE deinking test page was chosen to ensure the
reproducibility of printed newspaper samples.

Standard deinking procedure INGEDE Method 11

The International Association of the Deinking Industry
(INGEDE) Method 11 (2002) was used for the deinking
method in many of the following experiments. INGEDE
Method 11 is a laboratory scale deinking procedure that
was developed to approximate the deinking performance
of a given sample for industrial deinking operations. The
printed samples in the laboratory were shredded to the
size of 2 cm × 2 cm. After that, the small pieces of samples
were immersed in deinking solution with sodium hydroxide
(0.6%), sodium silicate (1.8%), oleic acid (0.8%) and water
with a hardness of 128 mg Ca²⁺/L and pulped with mechan-
ical force for 20 min. The pulp was stored at 40 °C for 1 hour
to allow for increased ink detachment, and floated in a 5 L
flotation cell by a Denver flotation device to remove the
inks. All deinking samples followed the INGEDE Method
11 procedure unless specified otherwise.

Electric treatment and flotation simultaneously

The flotation procedure is the same with INGEDE Method
11, except that DI water was applied to dilute the pulp slurry
after pulping. Either a stainless steel or graphite electrode
was applied as the anode, and the stainless steel flotation
cell was connected to the cathode. The treatment voltage
is 1 kV and current is 250 mA. The treatment was conducted
with flotation simultaneously for 10 min as in Figure 1(a).

Electric treatment of pulp slurry

Pulp slurry was diluted to 1% solid by water with a hardness
of 128 mg Ca²⁺/L and treated with an electric charge for
0.5 h, 1 h, or 2 h, with 0.06 kV and 400 mA as shown in
Figure 1(b). The pulp slurry was agitated by an impeller at
500 rpm.

Hyperwashing of deinking pulp

Hyperwashing can be performed after the pulping or flota-
tion step described in any deinking procedure. In order
to hyperwash the pulp, it was diluted to 0.02% consistency. The paper fibers were then screened out of solution using a 100 micron screen (McMaster-Carr, Atlanta, GA). The pulp was then used to make filter pad samples for effective residual ink concentration (ERIC), ISO% Brightness. Hyperwash could remove all the inks in liquid phase to avoid ink redeposition during pad formation.

**Characterization**

**Particle size and zeta-potential of hydrophilic ink**

The particle size and zeta potential of hydrophilic ink was analyzed using a zetasizer (Malvern Zetasizer Nano ZS90, Malvern Instruments Co. Ltd, UK). The particle size was measured 10 times with 50 scans in each cycle. The zeta potential was measured in DI water, 50 mM NaCl and 100 mM NaCl solutions, with an ink concentration of 0.2 g/L. The pH of the suspension was then adjusted to several values by adding HCl or NaOH solution.

**Chemical structure of hydrophilic ink**

Silicon wafers were spin-coated with ink suspension prior to X-ray photoelectron spectroscopy (XPS) measurement. XPS analysis was performed with Thermo K-Alpha XPS. The XPS spectra of the cellulose films were obtained using a monochromatic Al Kα X-ray source (1,486.6 eV) at a voltage of 15 kV and a current of 10 mA. The vacuum level of the analyzing chamber was maintained below 5E-7 Pa during the measurements. The pass energy and step width during the survey scan were set at 200 and 1 eV, respectively. In the element narrow scan mode, these scan parameters were set at 50 and 0.1 eV, respectively. The binding energies for all spectra were determined with respect to the C 1 s reference signal (unoxidized C–C band) at 285.0 eV.

**Fiber sample preparation and measurement**

Pulp samples were taken after pulping, after electric treatment, after flotation and after washing. An undeinked filter pad was made from the pulp taken after pulping, and deinked filter pads were made from pulp samples after either electric treatment, flotation or hyperwash. The filter pads were made according to INGEDE Method 1. Brightness and ERIC were measured for each of these samples using a Technidyne ColorTouch ISO (Technidyne; New Albany, IN, USA).

**RESULTS AND DISCUSSION**

**Hydrophilic ink property and the effect of electric treatment on ink size**

Before studying the deinking process of ink printed paper, it is necessary to have a basic understanding of the ink structure and property. Based on dynamic light scattering and zeta potential measurement shown in Figure 2, the size of the ink is 60 nm and ink particles are highly negatively charged with an isoelectric point of pH ≈ 4. The ink particles also showed an electric double layer screening effect when additional electrolytes were introduced. In addition, the XPS spectrum in Figure 3 showed that ink only contains carbon and oxygen; that oxygen element rendered the carbon black hydrophilic. As described previously in the paper, the submicron size, high surface charge density and hydrophilic surface are the major reasons why hydrophilic ink is not compatible with flotation deinking. Thus, the hydrophilic ink in our study is a good representative for inks that have caused problems in paper mills.

The electric treatment has multiple effects simultaneously, including electroflotation, electrocoagulation and electrophoresis. The graphite anode is very stable, while a stainless steel electrode would release metal ions, causing electrocoagulation. Electrocoagulation could be very beneficial for hydrophilic ink removal because it can agglomerate ink particles. In order to verify this hypothesis, ink particles were dispersed in DI water to suppress current density and inhibit the electrofloation effect. The ink particle after electric treatment is shown in Figure 4. It was very clear that both graphite and stainless steel electrodes could agglomerate ink particles to 400 nm and 700 nm,
respectively. The agglomeration with the graphite electrode is mainly driven by electrophoresis. Since the ink particles are highly charged in water, they have a tendency to migrate under an electric field and increase the local particle concentration (Wakamatsu 2015; Zhou et al. 2015; Du & Hsieh 2016; Wu et al. 2016). As a result, particles are more likely to collide in a high concentration region, increasing particle size. However, stainless steel further increased particles to 700 nm because the process was driven by both electrophoresis and electrocoagulation. Besides electrophoresis, the metal ions from the stainless steel anode could increase ionic strength, screen the electrostatic repulsion between particles and agglomerate ink particles.

The effect of electric treatment on flotation deinking

Although ink particles increased dramatically after electric treatment, it is still a question whether ink can be removed by electric treatment assisted flotation. However, the effect of electric treatment on cellulose fiber had to be investigated because the change in fiber color would interfere with the
ERIC measurement. The influence of flotation, and flotation with electric treatment simultaneously to fiber ISO% brightness and ERIC was studied and is shown in Figure 5. Due to the fact that there were no ink particles on the fiber, the ISO% brightness was around 60 and ERIC was lower than 30 ppm. And there was no significant difference between the samples with and without electric treatment.

Since electric treatment did not change fiber brightness, the electric treatment assisted flotation was studied. Standard sheet samples were printed in order to make reproducible samples. The INGEDE Method 11, an optimized standardized method for offset deinking, was followed to deink hydrophilic ink printed paper. The ISO% Brightness and ERIC of fiber pads after pulping, flotation and flotation with electric treatment are shown in Figure 6. Traditional flotation could only remove a very small amount of inks and ERIC dropped 20 ppm. This phenomenon was consistent with the ink property in the first section. However, electric treatment with flotation simultaneously both decreased ERIC and increased the ISO% brightness. The ISO% brightness was increased by almost 2 points and ERIC was reduced by another 70 ppm when the pulp was electrically treated with graphite as the anode. The reduction in ERIC could be explained by the electroflootation and electrophoresis mechanism. It has been shown that electrophoresis increases ink size and electroflootation generates bubbles with fine size through water electrolysis, which greatly increases the surface area of air bubbles. This combinational effect accounted for the reduction in ERIC, because air bubbles are more likely to catch ink particles with greater size.

When the anode was stainless steel, the ERIC reduction was similar to graphite while the improvement in ISO% brightness was only 0.5 point. A stainless steel electrode can increase ink particle size even more with electroeosugulation, which should further improve flotation efficiency compared with graphite. However, this was not observed from the experiment results, so a series of experiments with electric treatment alone was conducted to understand the mechanism.

The effect of electric treatment on ink removal

The pulp was diluted to 1% consistency and electrically treated by graphite or stainless steel anode for 0.5 h, 1 h and 2 h under 0.06 kV and 400 mA. A thin layer of ink particles was observed on the water surface through electroflootation, and skimmed off. The yield can reach 99% because electroflootation has a very high selectivity and only ink particles were floated to the water surface. As a result, ERIC went down after electric treatment from 950 ppm to 850 ppm in the case of stainless steel, and to 700 ppm when graphite was the anode. And the graphite electrode always showed a better removal performance compared with the stainless steel electrode in all the three different lengths of treatment time based on Figure 7. There are two possible reasons for this phenomenon. The first is the redeposition of ink during electric treatment. As discussed previously, metal ions from electric treatment could reduce the electrostatic repulsion through a charge screening effect. Thus not only the particle-particle repulsion, but also the particle-fiber repulsion was reduced, leading to the redeposition of ink particles onto the fiber surface. The other reason is ink entrapment in the fiber network during sample preparation. Since the ink particle size was greatly increased after treatment, they were more easily entrapped into the fiber network, resulting in a higher residual ink value.
In order to understand which of the two is the major driver, the pulp was hyperwashed after electric treatment before sample preparation. Hyperwashing could remove ink particles in the water phase, preventing ink entrapment during sample preparation (Ben & Dorris 2011). If redeposition is the major reason for the high ERIC value, pulp samples treated by the stainless steel anode should have a higher ERIC compared with graphite after hyperwashing. However, if entrapment is the major driver, ERIC values of graphite treated samples and stainless steel treated samples should be very close because entrapment was prevented through hyperwashing. As shown in Figure 8, samples with electric treatment by stainless steel electrode showed a much higher ERIC value than the graphite electrode even after hyperwashing. This proved that ink redeposition during electric treatment is the reason for high ERIC value in samples with the stainless steel anode. This mechanism also explained why stainless steel has a similar flotation efficiency to graphite when electric treatment was conducted simultaneously with flotation in the previous section. Although ink particle sizes were greater with the stainless steel anode, they also redeposited onto fiber during the flotation process. Thus the benefits from larger ink particle size cancelled out with the ink redeposition, and this is why additional benefits were not observed.

Another interesting phenomenon from Figure 7 is the change in ERIC value with different lengths of electric treatment time. With the graphite anode, the residual ERIC value dropped steadily with an increase in treatment time through electroflotation and electrophoresis, while the ERIC value first increased and then decreased with treatment time if the stainless steel anode was chosen. This could also be explained by the counter effect between electroflotation and ink redeposition. Both of the two effects benefit from longer treatment time. However, the redeposition process is less sensitive to a high ionic strength; the energy barrier by electrostatic repulsion force cannot be reduced further if the ionic strength is already very high. On the other hand, the electroflotation effect benefits from longer treatment time continuously, and this explained why ERIC first increased and then decreased with treatment time when stainless steel was the anode.

In the previous section, electric treatment was conducted simultaneously with flotation. And with the understanding developed earlier in this section about electric treatment alone and electric treatment followed by hyperwashing, it would be interesting to study the flotation efficiency after electric pretreatment. Figure 9 showed that any differences in ERIC developed in electric pretreatment (Figure 7) disappeared after flotation and ERIC went down to 550 ppm in all conditions. However, the yield of flotation differed dramatically; the yield of the stainless steel treated sample was 80% while that of graphite was 97%, which was consistent with observation during flotation that stainless steel treated samples always had a thicker foam layer. It has been proved that salts are able to improve foam stability and removal of particles due to a weaker electrostatic repulsion force (Bournival et al. 2014; Duan et al. 2014; Firouzi et al. 2015). Thus, the metal ions from stainless steel contributed to a stable foam and higher yield loss. Although the fiber quality was the same after flotation, the graphite anode is still a better option due to its high yield.
The effect of electric treatment on ink removal followed by flotation and hyperwashing

In paper mills, fibers are extensively hyperwashed after flotation to remove fine particles. Thus pulp fibers were treated with flotation and hyperwashed after electric pretreatment to mimic the real recycling process. As shown in Figure 10, the fiber ERIC value further dropped to 400 ppm from 550 ppm (Figure 9) when graphite was chosen, which is very close to the 250 ppm recycling requirement. Thus, a combined electric pretreatment, flotation and hyperwash process is a promising recycling method for hydrophilic inks. Another important observation is for the samples with stainless steel treatment for 2 hr. The ERIC values were the same (550 ppm) before and after hyperwashing as in Figures 9 and 10, which further proved the redeposition mechanism of the stainless steel electrode. Although the stainless steel electrode is a widely applied anode in wastewater treatment (Casqueira et al. 2006; Senthil Kumar et al. 2010; Mansoorian et al. 2014), graphite is a better material as an anode in the deinking application due to the detrimental ink redeposition effect from metal ion induced electrocoagulation. At last, the non-sacrificial nature of graphite also ensures a longer application life time.

CONCLUSIONS

Electric treatment was selected to improve the recycling of hydrophilic ink printed paper. The electric treatment was able to agglomerate ink particles from 60 nm to 700 nm. In addition, electric treatment assisted flotation reduced ERIC by additional 70 ppm compared with traditional flotation. Furthermore, pulp samples were treated with electric treatment alone, electric treatment followed by hyperwashing, and electric treatment followed by flotation to understand the separation mechanism and optimize the process. Both electroflotation and electrophoresis mechanisms improved separation efficiency with less than 1% yield loss, while electrocoagulation led to ink redeposition onto fiber. Thus graphite is a better material candidate as an anode compared with stainless steel. Graphite also showed a 17% higher yield in flotation with electric pretreatment and longer application life time. Finally, a combined process similar to the paper mill recycling process was created and the ERIC value decreased to less than 400 ppm from the original 950 ppm. Electric treatment based on graphite showed great separation efficiency and high yield, and it is a promising technology to solve separation problems caused by sub-micron hydrophilic particles with a high negative surface charge.

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