

**MECHANISM AND NOVEL DEINKING METHODS FOR NON-IMPACT
PRINTED PAPER**

A Thesis
Presented to
The Academic Faculty

By

Daniel T. Lee

In Partial Fulfillment
Of the Requirements for the Degree
Master of Science in Chemical and Biomolecular Engineering

Georgia Institute of Technology

August 2014

Copyright © Daniel T. Lee 2014

**DEINKING OF HYDROPHILIC INKS BY DECREASED INK
REATTACHMENT DURING PULPING**

Dr. Jeffery S. Hsieh, Advisor
School of Chemical and Biomolecular Engineering
Georgia Institute of Technology

Dr. Martha A. Grover
School of Chemical and Biomolecular Engineering
Georgia Institute of Technology

Dr. Dennis W. Hess
School of Chemical and Biomolecular Engineering
Georgia Institute of Technology

Date Approved: June 12, 2014

ACKNOWLEDGMENTS

I would like to express my sincere thanks to my advisor Jeffery Hsieh for his support, advice, and significant time commitment to my research while at Georgia Tech. I would also like to thank Dr. Hsieh's research group for all of their assistance. Specifically, I would like to thank Xiaotang (Tony) Du for his thought provoking questions, expertise, and advice along the way. Also, I would like to thank Alex Jordan for introducing me to the lab and Mary Johnson for her patience while supporting our lab. Finally, I would like to thank my committee members, Dr. Grover and Dr. Hess, for committing their time to serve on my thesis committee as well as their insightful critiques of my work.

TABLE OF CONTENTS

ACKNOWLEDGMENTS	iii
LIST OF TABLES	vii
LIST OF FIGURES	viii
LIST OF ABBREVIATIONS AND TERMS.....	xi
SUMMARY	xii
CHAPTER 1: INTRODUCTION AND BACKGROUND	1
1.1 Paper Recycling and Deinking.....	1
1.2 Deinking of Hydrophilic Pigmented Printing Inks	2
1.2.1 Ink Formulation and Impact on Deinking	3
1.2.2 Ink Size Distribution.....	7
1.2.3 Hydrophilic Interactions of Ink	8
1.2.4 Redeposition of Ink	9
1.3 Deinking Methods for Hydrophilic Inks	10
1.3.1 Optimization and Fractional Pulping.....	10
1.3.2 Enzyme Deinking	12
1.3.3 Neutral Pulping and coagulation	14
1.3.4 Liquid Phase Plasma (LPP) Treatment.....	16
1.3.5 Adsorption Deinking	17
CHAPTER 2: EXPERIMENTAL PROCEDURES.....	19
2.1 Laboratory Scale Deinking and Sample Preparation for Paper Recycling	19
2.1.1 Standard and Reference Deinking Procedure.....	19

2.1.2 Standard Measurement Methods for Paper Recycling	19
2.1.3 Preparation of Inkjet and Flexographic Printed Newsprint	22
2.1.4 Hyperwashing of deinking pulp	22
2.1.5 Development of Model Hydrophilic Inks.....	22
CHAPTER 3: FUNDAMENTAL UNDERSTANDING OF BEHAVIOR AND EFFECT OF PROCESS PARAMETERS ON HYDROPHILIC INKS	24
3.1 Experimental Procedures.....	24
3.1.1 Evaluation of Pulping Chemicals for Deinking of Hydrophilic Inks	24
3.1.2 Evaluation of Pulping Consistency on Deinking of Hydrophilic Inks	25
3.1.3 Evaluation of Lignosulfonate Loading	25
3.1.4 Preparation of Dried Ink for Redeposition Experiments	25
3.1.5 Evaluation of Hydrophilic Ink Redeposition during Pulping Operations	26
3.1.6 Evaluation of Ink Behavior during Pulping Operations	26
3.1.7 Determination of Effect of Pulping Consistency on Bound and Redeposited Ink	27
3.1.8 Lignosulfonate Pulping with Mixed Inks	27
3.1.9 Evaluation of Flotation and Storage Process Variables for Hydrophilic Inks..	28
3.2 Effect of Pulping Chemicals on Pulping of Hydrophilic Inks	28
3.3 Evaluation of Flotation and Storage Process Variables for Hydrophilic Inks	32
3.4 Effect of Pulping Consistency on Deinking of Hydrophilic Inks	36
3.5 Behavior of Hydrophilic Ink during Pulping	39
3.6 Lignosulfonate Pulping with Hydrophilic and Mixed Inks.....	47
CHAPTER 4: LIQUID PLASMA TREATMENT (LPP) FOR IMPROVED SEPARATION OF HYDROPHILIC INKS	50
4.1 Experimental Procedures.....	51

4.1.1 Apparatus and Method for Treatment with LPP	51
4.1.2 Evaluation of Liquid Phase Plasma (LPP) for Deinking of Hydrophilic Inks .	51
4.1.3 Evaluation of LPP Treatment for Mixed Paper Grades.....	54
4.1.4 Effect of Electrode Material on LPP Treatment Efficacy	54
4.1.5 Determination of Importance of Secondary Parameters in LPP Treatment	55
4.2 Improved Separation of Hydrophilic Inks with LPP Treatment	55
4.3 Trial with Mixed Paper Sources.....	60
4.4 LPP Treatment Effect of Fiber Presence on Coagulation of Ink.....	66
CHAPTER 5: ADSORPTION DEINKING FOR DECREASED REDEPOSITION AND IMPROVED SEPARATION OF HYDROPHILIC INKS	70
5.1 Experimental Procedures.....	70
5.1.1 Pulping Operation for Hydrophilic Inks Experiments.....	70
5.1.2 Adsorption Deinking with Polyacrylate Adsorbent.....	71
5.1.3 Analysis of Multiple Adsorbents for Use in Adsorption Deinking Experiments	71
5.1.4 Thermodynamics of Ink Adsorption onto Chitosan and Cellulose Fiber	71
5.1.5 Adsorption Deinking Experiments for Improved Pulping of Hydrophilic Inks	73
5.1.6 Testing of Adsorbent Material for Hydrophilic Inks	73
5.1.7 Evaluation of Efficacy of Adsorption Deinking for Hydrophilic Inks	73
5.2 Selection of Adsorbent for Separation of Hydrophilic inks.....	74
5.3 Analysis of Adsorption Deinking for Deinking of Hydrophilic Inks.....	81
CHAPTER 6: CONCLUSIONS AND RECOMMENDATIONS	85
REFERENCES	91

LIST OF TABLES

Table 1. Detrimental effects of flotation on separation of pigmented inkjet inks from newsprint as shown through the ISO% Brightness and ERIC of the INGEDE Method 11 recycled newsprint.	35
Table 2. Average mass of pigmented inkjet ink per mass of unprinted paper as measured from 100 sheets of newsprint.....	42
Table 3. Deinking methods for determination of behavior of hydrophilic inks during paper recycling operations.	44
Table 4 Estimated mass percent of pigmented inkjet ink that is bound and redeposited during pulping or pad formation determined from Figure 15.	46
Table 5. Deinkability thresholds for ONP as defined by INGEDE[86]. The parameters measured by INGEDE include the luminosity (Y), Color a*, ink area (A), ink elimination, and filtrate darkening (ΔY) [93].....	55

LIST OF FIGURES

Figure 1. Example structure of Carbon Black pigment used in the majority of black printing inks.	5
Figure 2. Polyacrylic acid stabilizing polymer structure used for stabilization of hydrophobic in water for hydrophilic inks.	6
Figure 3. Illustration of ink pigment stabilization in hydrophilic inks.	6
Figure 4. Structure of Cellulose making up paper fibers.	18
Figure 5. Effect of INGEDE Method 11 deinking chemicals and interactions between each of the deinking chemicals on ISO% Brightness of newsprint printed with pigmented inkjet ink. The chemicals include sodium hydroxide (NaOH), oleic acid (OA), sodium silicate (Na ₂ SiO ₃), and calcium chloride (Ca).	31
Figure 6. Effect of INGEDE Method 11 deinking chemicals and interactions between each of the deinking chemicals on ERIC of newsprint printed with pigmented inkjet ink. The chemicals include sodium hydroxide (NaOH), oleic acid (OA), sodium silicate (Na ₂ SiO ₃), and calcium chloride (Ca).	31
Figure 7. Effect of heat bath time on the ERIC of recycled inkjet printed newsprint.	33
Figure 8. Effect of heat bath consistency on the ERIC of recycled inkjet printed newsprint.	33
Figure 9. Effect of storage temperature on pulping effectiveness with cold bath being conducted at room temperature and hot bath being conducted at 40°C.	34
Figure 10. Effect of pulping consistency on ISO% Brightness and ERIC of INGEDE Method 11 deinked newsprint printed with pigmented inkjet ink.	38
Figure 11. Lignosulfonate sample structure.	40
Figure 12. Determination of minimum Lignosulfonate loading (g/g dry fiber) using ERIC measurements after standard Method 11 pulping.	41
Figure 13. Effect of lignosulfonate on ISO% Brightness and ERIC measurements of unprinted newsprint pulped according to Method 11.	41
Figure 14. Evaluation of proportion of ink redeposited during paper recycling with and without Lignosulfonate using a variation of INGEDE Method 11.	44
Figure 15. ERIC measurements for various adaptations of INGEDE Method 11 for determination of the fate of pigmented inkjet ink during paper recycling.	45

Figure 16. Bound versus redeposited ink between 5 and 15% consistency.....	46
Figure 17. Effect of lignosulfonate pulping on filtrate darkening for mixed grades of paper ranging from 100% hydrophobic ONP to 100% hydrophilic inkjet ink.	49
Figure 18. Effect of lignosulfonate pulping on filtrate darkening for mixed grades of paper ranging from 100% hydrophobic ONP to 100% hydrophilic inkjet ink.	49
Figure 19. Picture of each LPP treatment method used in the improved deinking experiments including from left to right direct treatment, indirect treatment, and filtrate treatment.	53
Figure 20. The ink elimination was measured for each of the treatment methods (the reference method (M), direct (D), indirect (I), filtrate (F), and combined treatment (C)). The red arrow indicates the threshold ink elimination value[93].	56
Figure 21. The luminosity was measured for each of the treatment methods (the reference method (M), direct (D), indirect (I), filtrate (F), and combined treatment (C)). The red arrow indicates the optimal luminosity value as shown in Table 4[93].	56
Figure 22. The ink area was measured for each of the treatment methods (the reference method (M), direct (D), indirect (I), filtrate (F), and combined treatment (C)). The red arrow indicates the optimal ink area value[93].	58
Figure 23. Effect of LPP on optical properties and mechanical strength of unprinted paper fiber.	59
Figure 24. Effectiveness of deinking combined with LPP direct treatment on improving ISO% Brightness and ERIC for a mixed source of paper containing 35% inkjet printed newsprint and 65% offset printed newsprint.	61
Figure 25. Effect of deinking combined with LPP direct treatment on hydrophobic offset newsprint compared to deinking with standard Method 11 deinking.	61
Figure 26. Effect of LPP direct treatment on the particle size of inkjet ink with and without the presence of fibers at a consistency of 0.5% measured by dynamic light scattering.	62
Figure 27. The ISO Brightness and ERIC of the reject from flotation are shown for untreated and direct treatment of 100% inkjet printed paper.	64
Figure 28. The filtrate darkening was compared for the reference Method 11 and filtrate treatment methods[93].	64
Figure 29. Effect of copper chloride concentration (g/L) on stability of pigmented inkjet ink at a concentration of 0.5 g/L.....	67
Figure 30. The effect of solution temperature on the coagulation of pigmented inkjet ink at a concentration of 0.5 g/L measured by UV/Vis absorbance and DLS particle size analysis.	67

Figure 31. Data comparing the performance of copper and steel electrodes for direct LPP treatment.	68
Figure 32. Polyacrylate chemical structure.	74
Figure 33. ISO% Brightness and ERIC measurements for adsorption with hydrophilic polymers with standard Method 11 Pulping.	75
Figure 34. Adsorption performance of Talc and Chitosan analyzed using UV/Vis absorbance at 300 nm without the presence of fibers. The adsorbents were compared to a control of diluted ink without an adsorbent present.	75
Figure 35. Structure of talc with a magnesium hydroxide layer between two silicate layers having an overall composition of $Mg_3Si_4O_{10}(OH)_2$	76
Figure 36. Chitosan chemical structure.	77
Figure 37. Time dependent adsorption of pigmented inkjet ink using chitosan.	77
Figure 38. Deposition of hydrophilic ink onto cellulose fiber during the paper formation process as a function of solution ink concentration.	79
Figure 39. Equilibrium adsorption isotherm of inkjet ink onto chitosan.	79
Figure 40. Effect of chitosan on filter pad ISO% Brightness over the range of 0-10 mass%.	82
Figure 41. Impact of chitosan adsorption deinking on the ISO% Brightness and ERIC of pigmented inks pulped at 15% consistency.	82
Figure 42. Impact of chitosan adsorption deinking on the ISO% Brightness and ERIC of pigmented inks pulped at 10% consistency.	83
Figure 43. Filtrate darkening of pigmented inks when using chitosan for adsorption deinking at 10% consistency.	83

LIST OF ABBREVIATIONS AND TERMS

Pulping:	Method of breaking down paper
Pulp:	Mixture of broken down paper, chemicals, and water
Deinking:	Separation of ink from pulp through various separation methods
ERIC:	Effective Residual Ink Concentration is an optical measurement method used to approximate the concentration of ink on the paper surface
ISO% Brightness:	Optical measurement method for reflectance of light in the blue spectrum, which approximates how white a sheet of paper will appear
Luminosity:	Optical measurement method similar to ISO% Brightness with full spectrum of light
Ink area:	Optical measurement method looking at the size distribution of visible specs on a paper sheet such as large ink particles or dirt
Color a*:	Optical measurement method looking at the hue of a paper sheet in the red-green spectrum. Shifts in this spectrum cause darkening of the paper decreasing the quality
Ink Elimination:	Comparison of ERIC before and after deinking operations given as a percent removed
Filtrate Darkening:	Optical measurement method used to relate the amount of ink present in the filtrate after forming paper. It is important to prevent ink from going to the filtrate due to recycling of process water
Tear index:	Mechanical strength measurement of the resistance of a sheet of paper from tearing
Flotation:	Deinking method involving separation of ink through
INGEDE:	International Association of the Deinking Industry
ONP:	Old newsprint paper
Consistency:	Mass percent of fiber in the pulp

SUMMARY

Separation of hydrophilic inks such as pigmented inkjet and flexographic inks has been an issue in paper recycling since the beginning of their use. Since these inks use water as a solvent rather than organic solvents like traditional inks, the particle size has been decreased to the range of 40 nm - 2 μ m and the surface of the ink particles has been made more hydrophilic to improve dispersion. These properties are necessary for the ink before printing, but both of these properties make separation of these inks during paper recycling significantly more difficult. Additionally, the use of inkjet printing is continuing to increase due to improved print quality, reduced rub off, and on-demand printing capabilities, and it does not appear that this increase will slow down anytime soon.

Because of this, it is essential to find an adequate method of deinking these inks for the recycling of paper products. There has been a significant amount of research on methods of improving deinking of hydrophilic inks including the use of enzymes, changing the pulping conditions and chemistry, and using a hybrid deinking method with an improved separation method for hydrophilic inks. However, enzyme deinking has not been shown to have significant deinking improvements for hydrophilic inks, and using optimized pulping chemistry and conditions for hydrophilic inks causes significant issues with deinking traditional hydrophobic inks. Although these methods have shown some improvement in deinking of hydrophilic inks, further improvements are necessary in order to effectively recycle paper printed with these inks.

One of the major problems with the deinking of hydrophilic inks is that there is not a complete understanding of the behavior of the ink during deinking operations. To overcome these difficulties, a thorough investigation of deinking chemicals and parameters was conducted in this research along with an investigation of the behavior of the hydrophilic inks during the paper recycling, such as the detachment and reattachment of the ink. From previous research, it has been shown that hydrophilic ink is easily dispersed under alkaline conditions but also redeposit onto the broken down paper. This led researchers to assume that all of the hydrophilic ink is detached from the fiber during deinking and all ink remaining on the paper after deinking was due to redeposition. However, it was observed in this study that around one third of the remaining ink was likely due to ink that was not detached during deinking. In the future, this may be a useful topic to investigate. However, two thirds of the remaining ink was from redeposition, so the proposed deinking methods focused on mitigating this.

Through the investigation of fundamental knowledge, it was determined that lignosulfonate (a byproduct of the paper making process) could completely prevent redeposition of hydrophilic inks, so an improved deinking method using lignosulfonate was tested. However, when using lignosulfonate with a mixed grade of paper containing both hydrophilic and hydrophobic inks, it was clearly shown that using a dispersant such as lignosulfonate causes significant negative results for hydrophobic inks. From this experiment, the complexity of the deinking process is shown, and future deinking methods must account for any negative effects that might occur for traditional inks, which currently make up more than 90% of the printing market.

The previous results led to a novel deinking method that was developed through previous experiments called Liquid Plasma Treatment. In this treatment, a plasma region is generated under atmospheric pressure within a solution containing the recycled paper. Previous research has shown that this treatment method is able to dramatically increase the particle size of hydrophilic inks in an ink/water system, so it was proposed that this could improve the separation of hydrophilic inks, it was shown that deinking improvements were seen with this method. However, it was also shown that the treatment was not effective when used with a mixed grade of paper containing hydrophobic and hydrophilic inks due to the particle size of the ink increasing negligibly in the presence of paper fibers. It is likely that this treatment is instead improving the removal of hydrophilic inks into the filtrate similar to what was seen with the use of lignosulfonate, which causes major problems due to recycling of process water as well as significant negative effects on hydrophobic inks.

Since both previous methods have been shown to have significant negative effects on hydrophobic inks, a new method was developed for hydrophilic inks based on a deinking method that has been previously shown to be effective for hydrophobic inks. This method is adsorption deinking. Chitosan was used as an adsorbent for this method due to its potential to hydrogen bond with the ink, and it was shown that significant improvements in deinking of hydrophilic inks can be achieved by using adsorption deinking.

CHAPTER 1: INTRODUCTION AND BACKGROUND

1.1 Paper Recycling and Deinking

Paper has been used for many applications over the millennia, and recycling of paper has been feasible for over a century. However, paper recycling only really began becoming prevalent in the past decades. It is well known that paper production has enormous effects on the environment both in raw material as well as energy usage[1-3]. Paper and paperboard represented almost 32% of the discarded municipal waste in 1992[2], and it is estimated that each ton of recycled paper products saves 2.4 cubic meters of landfill space[4]. Because of this as well as lower energy requirements, paper recycling has become more and more prevalent around the world[3]. By 2011, over 70% of the paper produced in Europe was recycled, and over 50% of the paper making fibers used worldwide come from recycled paper[5, 6]. Additionally, paper production has grown by 3% since 2000 and is expected to grow by 2.5% per year in the future, so paper recycling will continue to be an issue in the years to come[7].

There are several steps involved in the paper recycling process including defibering, deinking, and reforming. Defibering involves breaking down recycled material into the individual wood fibers that make up a sheet of paper, and reforming involves production of the final product from the wood fiber similar to how virgin paper products are produced. Both defibering and reforming are relatively straightforward operations, but some recycled paper products, such as printing paper and some components of paper board, require deinking. Deinking is the process of removing

printed inks from the paper products, and is required in order to improve the optical properties of the recycled paper product for either functional or aesthetic reasons.

There are two main deinking operations that have been used in the paper industry: flotation and wash deinking. Wash deinking is a filtration separation process, and uses a screen to retain wood fiber and allow the unwanted ink to pass through. Wash deinking has many advantages when separating inks with large ranges in chemical properties since separation is dependent only on size. However, this also leads significant decrease in yield (as low as 70% yield) due to the loss of paper fines and ash[8]. Flotation deinking on the other hand selectively removes hydrophobic particles from solution using surfactants and air bubbles allowing yields of over 90%[8]. However, flexographic and other hydrophilic inks are not able to be removed by flotation leading to many recyclability issues if the proportion of hydrophilic inks is large[8].

1.2 Deinking of Hydrophilic Pigmented Printing Inks

Hydrophilic printing inks have been gaining popularity due to environmental and health concerns from the volatile organic compounds present in the solvent of traditional inks[9, 10]. This started with flexographic ink for newsprint applications but more recently includes digital non-impact printing inks such as inkjet ink[11]. However, there have been many concerns about the recyclability of flexographic inks such as unacceptable optical properties with as little as 10% hydrophilic ink, which has resulted in limited adoption of flexographic printing[10-14]. However, concerns about poor deinkability of these inks have not discouraged the adoption of inkjet printing, which has been gaining popularity in recent years for newsprint and other publication applications

due to the fast turnaround, on-demand printing capabilities, and exceptional print quality[11-17]. There have been efforts to improve the deinkability of these inks through ink chemistry and process conditions, but so far, there has not been a suitable method of deinking hydrophilic inks[17]. Because of this, deinking of hydrophilic inks will continue to be an issue in coming years, and a solution is required in order to maintain and grow the current recycling levels as is desired.

1.2.1 Ink Formulation and Impact on Deinking

The main difference between the hydrophilic inks and traditional printing inks is the solvent of the ink material. In traditional printing such as offset printing for newsprint, the ink was composed of pigments, hydrocarbon solvents, and resins[18]. The pigments give the ink a visible color while the resin stabilizes the pigment and the hydrocarbon solvent allows for adequate flow and drying of the ink after printing[18]. There are numerous pigments used for printing applications, but carbon black is used for almost all black printing applications since it is inexpensive and resists fading when exposed to light[19]. Because of this, it is important to know the structure of carbon black in order to understand the deinking of these inks. A sample structure of carbon black is shown in Figure 1, but the chemical structure and especially the surface groups can vary through modification of the surface[19]. For use in traditional, hydrophobic inks, the carbon black is left unmodified allowing the surface to be relatively hydrophobic[18]. The use of hydrocarbon solvents was a standard in ink formulation for many years, but there has recently been a transition away from the use of hydrocarbons as a solvent, which has led to the use of vegetable oils such as tall oil for the solvent of offset and similar printing inks[18-20]. Additionally, a complete transition to the use of water as a

solvent has also taken place leading to new requirements for stabilization of the pigment. These inks are generally referred to as hydrophilic inks due to the fact that the hydrophobic pigment particles are made to be more hydrophilic through surface modification and the adsorption of polymers, such as an acrylic resin, to stabilize the pigment in water[21, 22]. Polyacrylic acid is used extensively for printing inks for the purpose of stabilizing the hydrophobic pigment in water, the chemical structure of which is shown in Figure 2[23]. For the surface, the surface groups of the carbon black are modified for use in hydrophilic inks in order to make the ink more hydrophilic by oxidizing the surface leading to acid groups such as hydroxyl, carboxyl, carbonyl, etc.[23]. Overall, this results in a stable dispersion of the pigment particles in water as shown in Figure 3. Additionally, the resins used in the printing inks have more functions than just stabilization including forming a film when printing, adhesion to the printing substrate, and specific properties such as gloss to the print requiring multiple resins for a given ink[24]. In addition to changing the resins and solvents, the additives required vary widely in order to form an ink with the correct viscosity and other properties for a printing technology[25]. In addition to the three solvents mentioned, ethyl acetate, isopropanol, cyclohexanone, and aromatic distillates have been used for the solvent depending on the printing technology[24]. Despite the large variety of additives and pigments used for hydrophilic inks, the surface charge is almost always negative at alkaline pH due to the addition of acid groups as well as the presence of carboxyl groups on the polyacrylic acid, which is similar to the charge of the cellulose fibers. This can affect the rate of adsorption of hydrophilic inks during deinking, but the salt

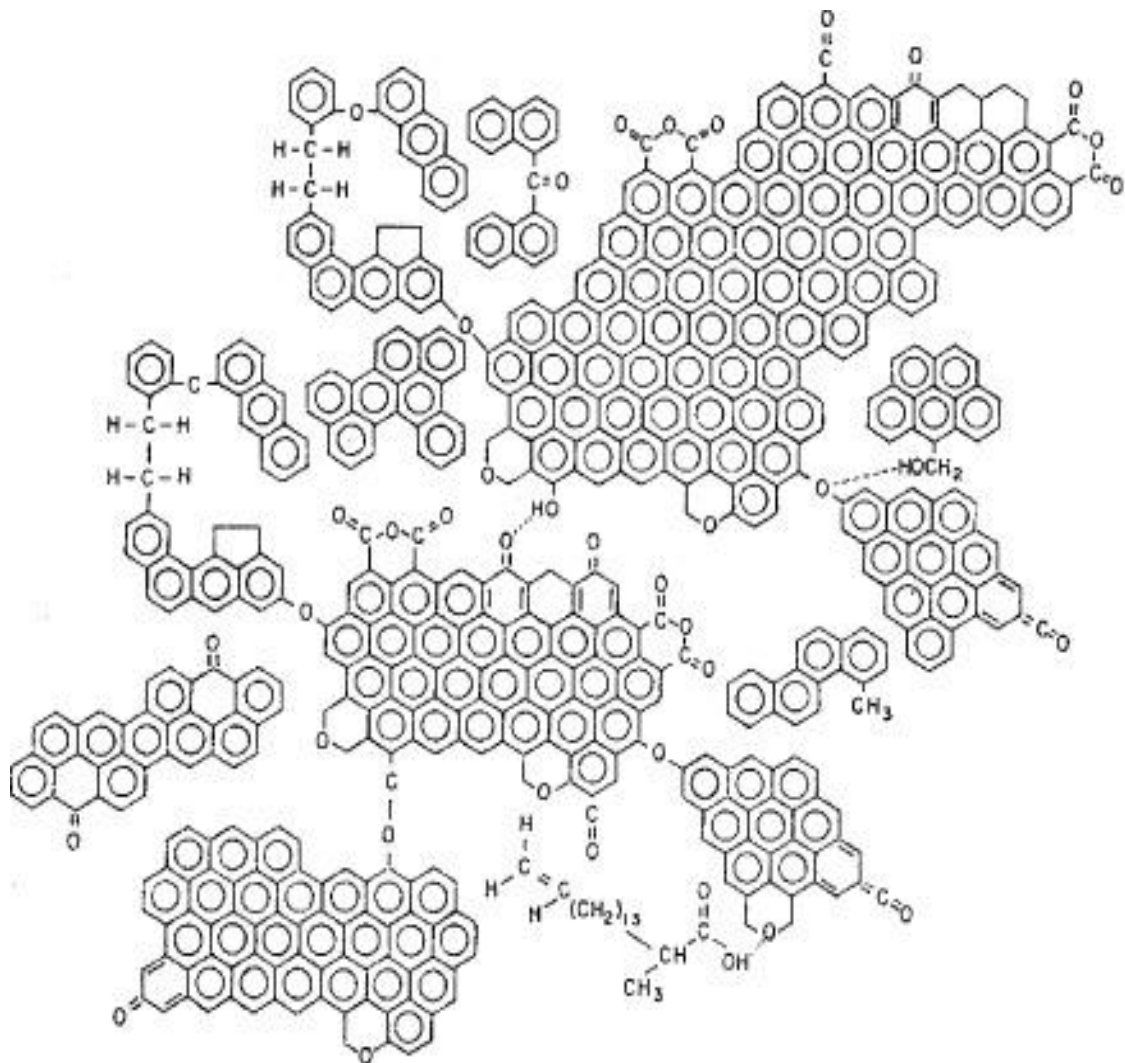


Figure 1. Example structure of Carbon Black pigment used in the majority of black printing inks.

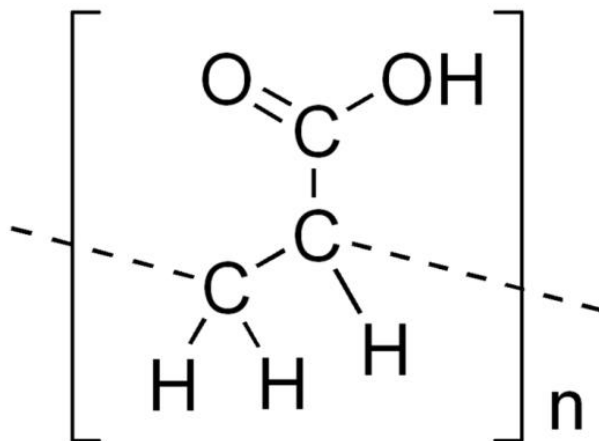


Figure 2. Polyacrylic acid stabilizing polymer structure used for stabilization of hydrophobic in water for hydrophilic inks.

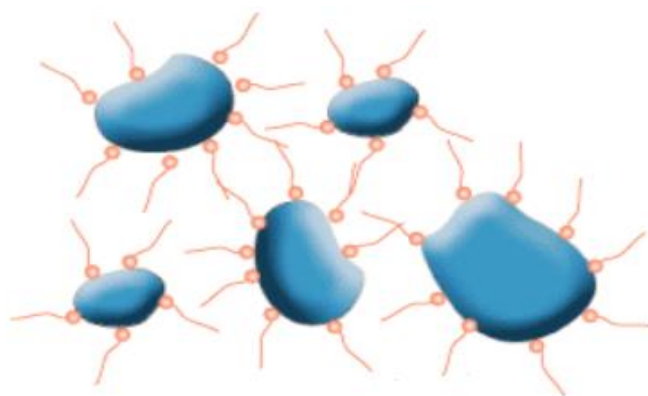


Figure 3. Illustration of ink pigment stabilization in hydrophilic inks.

concentration during deinking is often high, which causes the screening of the electrostatic interactions[26].

With all of this variation, deinking of recycled paper can be a difficult task. In general, changes in any of the specific additives can affect the deinking operations, but changes in the solvent tend to have the largest effect on deinking. For example, the use of water as a solvent for flexographic and inkjet inks results in a fine dispersion of ink during the paper recycling operations, which makes deinking more difficult as outlined later in this paper[27, 28]. In contrast, offset printing inks dispersed in mineral oil are generally more easily deinked during recycling operations[27]. There are also many more printing technologies including rotogravure and Xerox printing as well as UV, UV coated, and dye-based inks causing additional complexity to the deinking operations. Finally, the efficacy of the deinking operations is dependent not only on the composition of the ink but also on the drying and aging of the printed product as well as the composition of the printing paper[29].

1.2.2 Ink Size Distribution

The first major issue with hydrophilic pigmented inks, which was referenced above, is that these inks have been found to have submicron pigment particles (ranging from 0.04 - 2 μm) after pulping in alkaline conditions compared to 10-250 μm for traditional offset pigments after pulping in similar conditions[15, 16, 25, 30]. This is mainly due to the requirement of stabilization of the pigmented ink in water before printing, which causes the pigments to have hydrophilic polymers adsorbed to the pigment surfaces[25, 30-32]. The stabilizing polymers allow the dried pigmented ink to

easily disperse into solution during deinking operations resulting in the submicron particle size inks seen in the dispersions mentioned[25, 30-32].

The dispersion of the hydrophilic inks into submicron particles has been shown to result in drastically reduced separation of the ink by flotation as well as redeposition of the ink onto the fiber, which will be discussed later[15, 17, 25, 33]. Traditional flotation is currently the dominant separation method for inks during paper recycling, and this type of flotation has an optimal particle size range of about 30-250 microns. As mentioned, this is ideal for the inks used for offset printing, but is not suitable for submicron hydrophilic ink particles. Other forms of flotation for the removal of smaller particles are significantly more expensive and tend to drastically reduce the loss of paper fiber during the separation. Additionally, previous research has shown improved deinking of hydrophilic inks through destabilization of the inks without the presence of paper fibers, but this has not been able to be effectively implemented in the presence of paper fibers[34-37].

1.2.3 Hydrophilic Interactions of Ink

The next issue with these inks is that both inkjet and flexographic pigments are dispersed in water to reduce the use of VOC's, which increases the hydrophilicity of the pigments[16]. The hydrophilic nature of the pigments prevents the flotation bubbles from effectively removing the ink particles and causes a buildup of ink in the filtrate[17, 38]. Additionally, pulp fibers interfere with the agglomeration of the ink particles, which prevents the ink particles from agglomerating to an optimal size for flotation[37, 39]. This has led to a limited percentage of flexographic and inkjet printed paper to be used in deinking mills[12].

Another negative consequence of the hydrophilic nature of the pigments used in hydrophilic inks is the fate of the ink after deinking operations. Since the ink is finely dispersed, a portion of the hydrophilic inks is removed in the filtrate of the paper[12]. This would not be an issue except that a large portion of the process water is recycled in a deinking plant to reduce water usage. Due to recycling of the process water, hydrophilic inks build up in the system causing significant reduction in paper quality as time goes on[12].

1.2.4 Redeposition of Ink

The final issue with hydrophilic inks is the reattachment of ink during the recycling process. It has previously been determined that hydrophilic inks can be easily formed into flocs and removed by flotation when fibers are not present in solution[39]. However, it was also determined that a similar deinking chemistry is not effective in the presence of paper fibers[37]. This suggests that flocculants tend to cause redeposition of the flexographic ink on the fiber surface rather than formation of flocs which can be removed by flotation[37]. Additionally, the hydrophilic ink tends to redeposit on the surface of the paper fibers during paper formation, where the consistency of the fibers increases dramatically[40]. There have been effort to reduce redeposition of hydrophilic inks, but there has not been a good solution for hydrophilic inks up to this point[41, 42].

There have been several studies to get a better understanding of ink redeposition phenomena[33, 38, 42]. It has been determined that there are many factors that have been found to affect redeposition of ink such as salt concentration and consistency[33, 38, 42]. Additionally, previous studies have shown that ink redeposition is likely due to adsorption during paper formation and entrapment during pulping[38]. First, for

redeposition during paper formation, it was determined that redeposition could be eliminated by removing metal ions from solution[40]. This suggests that the electrostatic repulsion is able to prevent redeposition and adsorption of the ink is occurring[40]. In contrast, during pulping, it was determined that ink redeposition occurs solely in the “lumen” of the paper fibers, which is a cavity in the center of the fiber[38].

1.3 Deinking Methods for Hydrophilic Inks

Because of the limit on flexographic and inkjet printed paper for recycling, there has been a large amount of research to mitigate these issues in order to increase the amount of paper printed with pigmented ink that can be recycled. Some of the more successful efforts have been optimization of pulping conditions[43, 44], using enzymes such as laccase, cellulase, xylanase, and amylase[45], and using coagulants, flocculants or an electric field technology to increase the particle size of the inkjet ink particles[46, 47]. However, these technologies have not been able to fully reduce the negative impact of pigmented inks on deinking of recycled paper.

1.3.1 Optimization and Fractional Pulping

The most obvious modification that could be made for deinking of hydrophilic pigmented inks is the optimization of the deinking parameters for these inks. There have been quite a few studies investigating the effect of process parameters both in pulping and flotation on the deinking of these inks both to optimize the pulping conditions as well as to get a better understanding of deinking of hydrophilic inks[47-49]. Many researchers have found that after the first few minutes of pulping, an increase in pulping time had a negative effect on optical properties of deinking hydrophilic pigmented inks[12, 21, 38,

42, 48, 50, 51]. Additionally, it has been shown that decreased mixing and alkaline pulping conditions are required for optimal pulping of hydrophilic pigmented inks[38, 42, 50, 51]. Specifically, it was found that friction between fibers resulted in increased redeposition of flexographic ink either by increased consistency or viscosity of the pulp as well as increased mechanical energy from mixing[38, 42, 50, 51]. Similarly, Ciampa has previously shown that a decrease in pH had a significant negative effect on repulping of flexographic ink with temperature having an almost negligible effect[48].

All of these findings suggest that the optimal pulping conditions for hydrophilic pigmented inks are at a low consistency, mixing energy, and pulping time for optimal pulping with the effect of the pH showing conflicting results. However, each of these criteria is the opposite of the optimal conditions for deinking of traditional offset printing inks. Specifically, the quality of deinked pulp for offset printing inks continues to increase as the pulping energy and time increase with the optimal consistency being at a fairly high 15-18%[21, 48]. Optimization of the pulping conditions by reducing pulping time and decreasing agitation was able to decrease redeposition of ink in the fiber lumen, but the optimal conditions would only apply to 100% hydrophilic ink stocks because the optimal conditions for these inks are inadequate for traditional inks[44]. To incorporate this with traditional inks, the operating conditions would have to be compromised between the two, which would greatly reduce effectiveness of the technique on improving pigmented ink removal during paper recycling. Because of this, it is not feasible to solely optimize the pulping conditions for hydrophilic pigmented inks because this will result in drastically reduced quality for traditional inks, which currently make up the bulk of the printing market[12].

An extension of this that could be useful for the mixed recycled paper found at an industrial paper recycling mill is fractional pulping. Fractional pulping has been shown to remove the hydrophilic inks at the beginning of the pulping stage while also allowing pulping to continue to remove offset and other printing inks[31, 52-54]. The basic idea behind this is a hybrid deinking system that allows hydrophilic pigmented inks to be removed by washing at shorter pulping times with the hydrophobic inks being removed by flotation as normal with longer pulping times. In order to do this, the pulping stage is stopped at specific time intervals such as every 2 minutes and a mini-washing stage is performed before pulping is continued[31, 52, 53]. Although this has been shown to be effective, there are several drawbacks that have prevented widespread use. First, the separation relies on wash deinking, which has been almost completely replaced for industrial scale paper recycling due to unacceptable yield losses[8, 32, 46, 55]. Second, due to environmental regulations, water usage in the paper industry has been drastically reduced in recent decades, which requires recycling of a large portion of the process water. One of the major issues of deinking of hydrophilic inks is that it remains dispersed in the process water causing it to build up in the deinking mill[12]. Fractional pulping has no way of mitigating this issue for deinking operations, and there is currently not a practical method to do this on an industrial scale[12].

1.3.2 Enzyme Deinking

Next, there have also been many efforts on using enzymes for deinking of many types of inks such as toner, offset, flexographic, and inkjet inks[56-58]. There are several theories about how to effectively deink a paper sample using enzymes, but in general, enzymes are used to hydrolyze cellulose or hemicellulose[59]. For example,

endoglucanase, cellulase, and hemicellulose cleave either random interior cellulose bonds, end cellulose units, or solubilizes parts of the cellulose structure[59]. This can be used useful for deinking for several reasons. First, a portion of any type of ink can be irreversibly deposited on the surface of a paper fiber[38, 60]. By using enzymes to cleave portions of the fiber, it is possible to separate the ink without detaching the ink from the fiber surface[60]. Additionally, much of this ink is mechanically trapped in the lumen or pores of paper fibers, so cleavage of cellulose bonds may allow for this ink to escape. Next, a major problem with some inks is the redeposition of the ink[33, 42]. By removing the ink through cleavage of the cellulose, a portion of the cellulose will remain with the ink preventing reattachment through electrostatic and steric forces. A final method that is sometimes employed is cleavage of bonds in the ink itself. For example, with toner inks, the ink pigment is generally attached to the paper fiber by melted polymers[58]. By using lipase, these polymers can be hydrolyzed allowing the colored pigment to detach from the paper fiber as well make the pigment more hydrophobic and decrease the particle size, which is useful for separation of toner inks[58]. In addition to the benefits seen in deinking, enzymes have been used for almost every conceivable application in the paper industry including fibrillation, debarking, pitch and slime removal, production of dissolving pulp, and bleaching[57, 61-70]. These applications use many of the same enzymes that have been investigated for deinking, so it is possible that enzymes will be used for an all in one solution sometime in the future[57].

It has been shown that the efficacy of enzyme deinking depends on several factors including ink type and paper substrate[71]. In the case of toners, it has been shown that enzyme deinking can improve the ISO% Brightness of a recycled paper by up to 5

points[57]. Others have found similar results for toner inks in that over 85% of the ink was removed during deinking operations when using enzymes compared to less than 50% without enzymes[71]. However, it was also shown that a similar deinking procedure for deinking of offset prints, such as those used for newsprint, showed less than 15% removal of the ink when standard deinking procedures are generally able to remove close to 50% of these types of inks with similar results seen for hydrophilic inks[71].

Although there have been some success using enzymes for deinking, there are several difficulties that currently prevent adequate deinking through enzymes. First, in the case of cleavage of specific bonds in ink or ink binders, there are countless pigments and binders used for various types of ink, so this is not feasible for an industrial scale where a large number of unknown inks need to be removed[12]. Next, in the case of cleavage of the cellulose, enzymes have been shown to be effective for toner based inks. However, enzymes have not been shown to remove hydrophilic inks such as inkjet and flexographic inks to an acceptable degree[71].

1.3.3 Neutral Pulping and coagulation

Neutral pulping conditions have been investigated for hydrophilic inks due to the nature of the stabilizers uses in these inks[41, 55, 72, 73]. The ink is often solubilized using polyacrylic acids which provide a good print quality with limited bleeding[55]. However, this allows the ink to be readily dispersed in alkaline conditions such as those generally used for deinking[38, 55, 72]. As discussed previously, dispersion leads to a significant portion of the ink redepositing on the paper surface and prevents separation of the ink using flotation. Because of this, using neutral pulping conditions has been proposed as a method of improving deinking of hydrophilic inks by limiting dispersion.

First, neutral deinking was used in combination with alkaline deinking practices. For example, a two stage deinking process was conducted to remove the hydrophilic inkjet or flexographic ink followed by an alkaline deinking process to remove offset ink[55, 74]. This is necessary as offset ink tends to be difficult deink at neutral pH, especially when it has been aged[55].

The use of neutral deinking has improved in recent years for use with deinking of hydrophilic inks, and in fact there are some mills that have converted to neutral deinking operations[75, 76]. For hydrophilic inks, it has been shown that neutral deinking can dramatically improve filtrate darkening as well as decrease redeposition of the hydrophilic inks during the deinking process[73]. Although this is a major improvement, there are still limitations to neutral deinking. First, in many studies, the final properties of the recycled paper do not meet the deinkability requirements for use in industrial deinking operations. Additionally, it was determined that to get sufficient deinking of hydrophilic inks, the surfactant used must be optimized for the ink, but this method is likely to have a significant negative effect on deinking of ONP[41].

A similar method of increasing the particle size of detached hydrophilic inks is the use of coagulants. There are several techniques that have been tested to increase the particle size of the inkjet ink particles. A variety of coagulants and flocculants have been tested to increase the particle size of the ink after detachment. However, research has shown that the addition of a coagulant or flocculant results in redeposition of the hydrophilic inks onto the cellulose fiber rather than an increase in particle size[33, 38, 47]. Another method that has been tested for this idea is electric field treatment. In electric field treatment, a voltage is applied to the pulp solution in order to produce an

electric field[46]. This voltage causes migration of the ink particles improving detachment as well as increasing the particle size of the ink[46]. However, this method resulted in a limited increase the brightness of recycled inkjet printed paper by 2 points[46].

1.3.4 Liquid Phase Plasma (LPP) Treatment

Because of the insufficient removal of inkjet and flexographic inks with these methods, a new method of assisting in the deinking of pigmented inkjet ink has been developed and investigated. This method is called liquid phase plasma polymerization (LPP), and uses an applied voltage across two submerged electrodes to generate a plasma region within the pulp slurry. Previously, LPP treatment has been used for water decontamination and decoloration, polymerization, breakdown of organic molecules (such as phenol to CO₂ and H₂O), and agglomeration of polymer suspensions[77-79].

Research from the pulp and paper industry has shown that LPP treatment can be used to drastically increase the particle size of pigmented inks in solution[80]. This research extensively analyzed the use of LPP treatment under various conditions and found that the coagulation of ink particles occurred regardless of many operating conditions, such as pH, concentration of ink, and power usage[80]. Additionally, this research proposed a polymerization mechanism for the coagulation phenomenon based on radical reactions with carbon double bonds in the ink concluding that the active species from the plasma region initiate polymerization of the inkjet ink particles, which greatly increases the size of the ink particles. When used to treat recycled pulp before flotation, it is hypothesized that the increase in particle size will allow for reduced

redeposition of ink and improved ink removal through flotation without negatively affecting other parts of the deinking process.

1.3.5 Adsorption Deinking

Adsorption has been used for countless purposes for industrial separation. However, it has not been investigated thoroughly for use in deinking operations. Recent studies have applied the idea of adsorption deinking for deinking of traditional hydrophobic inks by using nylon beads with a relatively low water content required[81]. They have shown that traditional inks can be deinked during paper recycling operations as effectively using the adsorption deinking method as using the standard flotation method[81]. Additionally, this idea was based on a recent invention in detergency for a nearly waterless washing machine that can remove stains using the same nylon beads[82]. However, this deinking method has not been extended to the removal of hydrophilic inks.

Although the adsorption deinking method has been shown to be effective for hydrophobic inks, it is unknown if it can be applied to the removal of inkjet inks. Due to the hydrophilic nature of these inks, the chemical structure of the adsorbent is critically important for the success of adsorption deinking. To overcome this, the adsorbent material could be selected based on the theory for adsorption between ink and paper during printing. Previous research has shown that the main forces responsible for adsorption between hydrophilic inks and paper fiber are due to hydrogen bonding. The cellulose fibers that make up paper have hydroxyl groups covering their surface allowing for significant hydrogen bonding. Because of this, inks are formulated to take advantage of this to create strong bonds between the two. Chitosan and polyacrylate are both

hydrophilic polymers that fit the criteria selected, chitosan being a biopolymer with a similar chemical structure to cellulose.

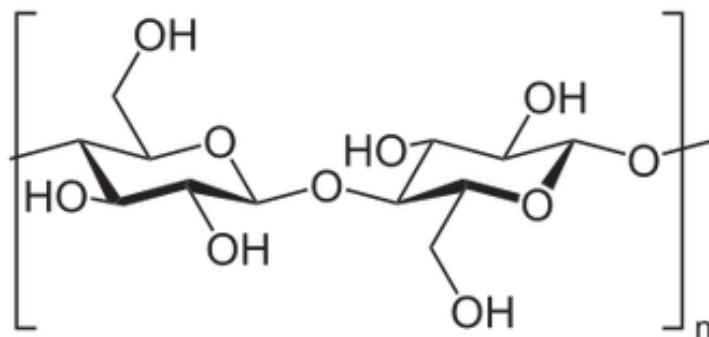


Figure 4. Structure of Cellulose making up paper fibers.

CHAPTER 2: EXPERIMENTAL PROCEDURES

2.1 Laboratory Scale Deinking and Sample Preparation for Paper Recycling

2.1.1 Standard and Reference Deinking Procedure

International Association of the Deinking Industry (INGEDE) Method 11 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. INGEDE Method 11 has 3 general steps: pulping, storage, and flotation. The pulping step uses mechanical force to break down paper into individual wood fibers and also detaches ink from the fiber surface. The storage step uses a heat bath at 40°C to allow for increased ink detachment. Finally, the flotation step actually removes the ink through interactions between the ink, a surfactant, and bubbles that are pumped to the bottom of the flotation cell. This allows the ink to be easily removed at the surface of the solution. A Kitchen Aid mixer and Denver flotation device with a five liter flotation cell were used for the pulping and flotation steps, respectively. All deinking samples followed the INGEDE Method 11 procedure unless specified otherwise.

2.1.2 Standard Measurement Methods for Paper Recycling

There are multiple measurement methods that were used in these experiments including ISO% Brightness, effective residual ink concentration (ERIC), filtrate darkening, ink elimination, luminosity (Y), and Total Dirt particle area. The ISO% Brightness, ERIC, ink elimination, and luminosity all give information about the ink removal efficacy of the paper recycling operation and were measured using a Color

Touch 2 Model ISO (Technidyne Corporation, New Albany, IN) according to INGEDE Method 2[83]. Each of these measurements relies on optical measurement techniques in order to take the measurements. The ERIC approximates the concentration of ink on the cellulose surface due to the difference between the adsorption of light at a wavelength of 950 nm for cellulose and carbon black[84]. Similarly, the ISO% Brightness measures the reflectance of light at a wavelength of 457 nm, which closely approximates the whiteness of the paper when observed. Finally, the filtrate darkening is used to approximate the concentration of ink in the filtrate after forming the final paper product. This is useful because the paper industry recycles a large portion of its process water, so ink will build up in the system if it is being removed in the filtrate rather than by flotation or washing[84]. The luminosity is closely related to the ISO% Brightness at varying wavelengths. The samples for these measurements were prepared using the procedure described in INGEDE Method 1, and consisted of at least three “filter pads” for each sample[85]. The filter pad has a basis weight of 225 g/m² and was formed using a vacuum filtration system along with a 25-30 micron filter paper (Fisherbrand Q8 filter paper, Fisher-Scientific, Pittsburg, PA).

The filtrate darkening was also measured using the ColorTouch 2 Model ISO (Technidyne Corporation, New Albany, IN), but the sample preparation differed from the previous measurements. For the filtrate darkening, the samples were prepared according to INGEDE Method 1, and one “filtrate sample” was made for each trial in the experiments where this was used. The filtrate sample was prepared using a vacuum filtration system along with a cellulose nitrate membrane filter (Whatman 7184-004, Fisher-Scientific, Pittsburg, PA) with a pore size of 0.45 microns. The luminosity of the

filtrate sample is measured using the ColorTouch 2 Model ISO (Technidyne Corporation, New Albany, IN) and compared to a “blank” filtrate sample which is made by filtering the same amount of water without the presence of fibers or inks through the cellulose nitrate membrane filter. The filtrate darkening is then given as the difference between the filtrate sample and blank filtrate sample.

The Total Dirt particle area also measures the optical properties of the recycled paper but is looking at large colored particles such as ink and dirt remaining with the recycled paper fibers rather than invisible micron sized contaminants like ERIC. The Total Dirt particle area was measured using SpecScan 2000 software (Apogee Systems, Panama City Beach, FL) along with an Epson V500 scanner (Epson, Long Beach, CA) according to INGEDE Method 2[83]. Additionally, the samples for the Total Dirt particle area were prepared according to INGEDE Method 1 with two samples made for each trial in the experiments where this was used[85]. The samples were prepared using a standard sheet former (Testing Machines Inc., New Castle, DE) with a basis weight of 42.6 g/m².

Finally, ink elimination is a comparison between the ERIC of a recycled paper sample after pulping and after flotation. It is used as a standard so that the efficacy of flotation can be compared across labs and paper samples. The ink elimination is calculated using the following equation where E_{UP} is the ERIC of the recycled paper after pulping, E_{DP} is the ERIC of the recycled paper after flotation, and $E_{unprinted}$ is the ERIC of an unprinted sample[86].

$$Ink\ Elimination\% = \frac{E_{UP} - E_{DP}}{E_{UP} - E_{unprinted}} * 100$$

2.1.3 Preparation of Inkjet and Flexographic Printed Newsprint

These deinking experiments looked specifically at newspapers printed with hydrophilic ink. The use of flexographic inks has been limited for paper recycling because of the difficulties with recyclability as discussed previously. However, a commercial newspaper printed with flexographic ink was used for these experiments. The newspaper is The Macon Telegraph (Macon, GA), and newspaper was collected and artificial aged at 60°C in an oven for three days as described in INGEDE Method 11[87].

However, it is more difficult to find and obtain inkjet printed newsprint, so the newsprint was printed at Georgia Institute of Technology. A commercial pigment-based 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 Prairies, WI) using an inkjet printer (Deskjet 1000, HP, Palo Alto, CA). The newsprint was then stored at room temperature in a dark cabinet for one year before being used in the deinking experiments.

2.1.4 Hyperwashing of deinking pulp

Hyperwashing can be performed after the pulping or flotation 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 ERIC, ISO% Brightness, or color measurements as described previously.

2.1.5 Development of Model Hydrophilic Inks

The deinking of hydrophilic inks is a complex procedure with many unknowns, so it was desired to make a set of model inkjet inks that could be printed. This would be

helpful because commercial inks have unknown pigment, stabilizing polymers, and additives making it very difficult to develop a theory for treatment methods. To develop a model ink, two commonly used pigments were obtained (Pigment Red 4 and Pigment Blue 15, Fisher-Scientific, Pittsburg, PA). The pigments are mostly hydrophobic, so they could not be readily dispersed in water. Because of this, a surfactant (90% oleic acid, VWR, Suwanee, GA) was dissolved in water before adding each of the pigments, which allowed for the dispersion of the pigments. After analysis, it was found the particle size of the dispersed pigments was 3-4 μm , which was much larger than the commercial ink used in these studies with a particle size of 114 nm. This may have been due to incomplete dispersion of the pigment.

CHAPTER 3: FUNDAMENTAL UNDERSTANDING OF BEHAVIOR AND EFFECT OF PROCESS PARAMETERS ON HYDROPHILIC INKS

The increased use of hydrophilic inks such as inkjet and flexographic inks has already started causing problems in paper recycling operations. Many of these issues occur because of the fact that paper recycling mills are currently optimized for the removal of hydrophobic inks such as those used for offset printing. These inks have been and continue to be the main printing inks used for industrial scale printing, which has required mills to optimize for these inks. However, as hydrophilic inks continue to increase in industrial printing, it is necessary to investigate how these optimal deinking conditions affect the deinking of hydrophilic inks. Although there has been significant efforts in understanding the behavior of these inks during the paper recycling process, there are several gaps in this knowledge that need to be investigated further. The following experiments will improve this fundamental understanding of the behavior of ink allowing for improved understanding of what can be done to improve deinking of hydrophilic inks.

3.1 Experimental Procedures

3.1.1 Evaluation of Pulping Chemicals for Deinking of Hydrophilic Inks

The deinking was performed according to the INGEDE Method 11 as described with variations on the loading of each chemical to determine the effect of each chemical and the interaction between each of the chemicals. In order to do this, a factorial design of experiments was performed with the concentration of each chemical being 0 (absence

of the chemical in the deinking experiment) or 1 (normal loading of chemical based on Method 11). Each deinking trial was performed once. Using this method, the primary, secondary, tertiary, and quaternary effects were evaluated.

3.1.2 Evaluation of Pulping Consistency on Deinking of Hydrophilic Inks

The pulping consistency was evaluated in order to test the effect of consistency on deinking of hydrophilic inks. To do this, INGEDE Method 11 was used as a reference method, and the consistency of the pulp was varied from 5-20% during the pulping. Three samples were made for each trial, and the results were compared to other parameters evaluated in previous research.

3.1.3 Evaluation of Lignosulfonate Loading

The loading of lignosulfonate necessary to stabilize the ink in solution must be determined in order to ensure redeposition is optimally reduced. To do this, the loading of lignosulfonate was varied from 1-4 mass% on fiber. Then, Method 11 pulping was performed with 100% inkjet printed newsprint and hyperwashed after flotation to remove all of the detached ink from the paper fibers.

3.1.4 Preparation of Dried Ink for Redeposition Experiments

Dried inkjet ink was prepared for the following procedure in order to estimate the amount of ink that is redeposited on the fiber surface. The inkjet ink used for this experiment was a commercial pigmented inkjet ink (HP 60, LD Products, Long Beach, CA). The ink was dried in an oven at 125°C for 4 hours. After drying, the ink was crushed using a mortar and pestle and stored at room temperature until used.

3.1.5 Evaluation of Hydrophilic Ink Redeposition during Pulping Operations

The redeposition of hydrophilic ink was evaluated using a variation of Method 11 as described previously. In the modified method, unprinted newsprint was used instead of inkjet or flexographic printed newsprint. Additionally, after 2 minutes of the pulping stage, dried ink was added to the pulp slurry and pulping was continued for a total of 22 minutes. The mass of ink added was approximately the amount of ink that would be present in the liquid phase during pulping, which was determined by finding the average mass of ink per mass of paper for the inkjet printed newsprint. To do this, 100 pages of inkjet printed newsprint were printed, and the mass of ink used was determined by weighing the ink cartridge before and after printing. Additionally, the moisture content of the ink was determined by comparing the mass of the ink before and after drying. Using this information along with the mass of the 100 pages of unprinted newsprint, the average mass of ink per mass of paper was found. Three runs of each trial were performed for each experiment.

3.1.6 Evaluation of Ink Behavior during Pulping Operations

The behavior of hydrophilic ink during pulping was determined using three independent modifications to the Method 11 deinking procedure with the ink removal efficiency of each modification compared to unmodified Method 11. The three modifications were lignosulfonate stabilization, hyperwashing after flotation, and the use of a flocculent after pulping.

For lignosulfonate stabilization, lignosulfonate was added to the pulp in addition to the other deinking chemicals at the beginning of pulping with all other parameters unchanged. The required concentration of Lignosulfonate was determined using the

previously described method and found to be 3%, which was used for these experiments. In the next modification, hyperwashing was performed on the pulp at the completion of the standard Method 11 deinking procedure. Finally, the undeinked pulping method only used a portion of the Method 11 procedure and used a flocculent to retain the entire sample of ink. Specifically, the inkjet printed paper underwent the pulping step of Method 11, and then, 2 grams of Nalco® 74508 was added as a flocculent for the ink. The flocculent is necessary as a portion of the ink will be removed in the liquid phase during the sample formation without the flocculent.

3.1.7 Determination of Effect of Pulping Consistency on Bound and Redeposited Ink

The proportion of ink that was “bound” and the total “redeposited” ink as defined previously were investigated using the same modifications used in 3.1.6. To do this, the exact same procedures were used for the use of lignosulfonate with hyperwashing as well as Method 11. However, the consistency during pulping was made to be 5%, 10%, and 15% rather than only 15% as in the previous section. This allowed the determination of the total bound and redeposited ink for each consistency similar to what was done in the previous section (3.1.6). The total redeposited ink was defined as the combination of the ink redeposited during pulping and the ink redeposited during paper formation, and 1 trial was performed at each consistency.

3.1.8 Lignosulfonate Pulping with Mixed Inks

These experiments followed the standard Method 11 deinking method with the sole modification being the use of lignosulfonate as a deinking chemical. Lignosulfonate was added to the pulp at the beginning of pulping along with the other deinking chemicals at a loading of 3 mass% lignosulfonate based on the mass of fiber. The

deinking procedure was performed on 0%, 50%, and 100% inkjet printed paper (printed at Georgia Tech with a HP 1000 printer) with the balance being hydrophobic offset newsprint (The Atlanta Journal Constitution) After completing the deinking procedure, three filter pads made for each run and three runs were performed for each of the ink samples. Additionally, one filtrate darkening pad was formed for each run.

3.1.9 Evaluation of Flotation and Storage Process Variables for Hydrophilic Inks

Several of the Method 11 process variables were evaluated in this study including the consistency of the pulp and length of pulping and storage. This was done to test the dependence of each process parameter on deinking of hydrophilic ink. To do this, INGEDE Method 11 was used as a reference, and the consistency of the pulp was varied from 5-20% for pulping and 1-15% for storage. Additionally, the storage time was varied between 0 and 90 minutes. Three samples were made for each set of process parameters, and ISO% Brightness and ERIC measurements were taken for each sample.

3.2 Effect of Pulping Chemicals on Pulping of Hydrophilic Inks

There are two aspects of pulping that are important in determining the behavior of hydrophilic ink: mechanical energy applied to the paper and pulping chemicals. As stated previously, the pulping chemicals used in industry have been optimized for the deinking of hydrophobic inks, and the standard chemicals used to emulate these systems for laboratory scale deinking are oleic acid, sodium silicate, hydrogen peroxide, sodium hydroxide, and calcium chloride. Each of the chemicals used in Method 11 have a specific function for hydrophobic inks. Sodium hydroxide raises the pH of the solution to near 11, which causes swelling of the paper fibers and improved detachment of

hydrophobic ink. Oleic acid complexes with calcium as a coagulant, which assists in forming microparticles suitable for separation by flotation. Finally, sodium silicate acts as a dispersant, which improves detachment of the ink from the paper fiber. However, it is unclear if these functions carry over for hydrophilic inks. Previous researchers have shown that concentration of calcium has a positive correlation with the redeposition of hydrophilic inks on the cellulose fiber surface[40]. Additionally, previous researchers have found that the pH of the pulping operation has a significant effect on the deinking of hydrophilic inks and that a lower pH (around pH 8 compared to pH 11) had a positive effect on hydrophilic ink deinking[40, 41, 73]. Finally, a significant amount of previous research has been performed on the effect of the surfactant used during pulping, and it was found that ionic surfactants improve the deinking of hydrophilic inks more than nonionic surfactants such as oleic acid[8]. However, the effect of sodium silicate and the interaction between each of these chemicals has not been clearly investigated previously. To do this, a factorial design of experiments was used to show the effect of each chemical as well as the interaction between the chemicals. All of the chemicals used for INGEDE Method 11 except hydrogen peroxide were evaluated. Hydrogen peroxide was excluded from this analysis because it has been shown that pigmented inks are not able to be decolorized by bleaching chemicals.

From Figure 5 and Figure 6, there are several interesting observations that can be seen. First, it is apparent that the individual effects of each of the deinking chemicals are as follows: sodium hydroxide, oleic acid, and sodium silicate have a positive effect and calcium chloride has a negative effect on deinking of hydrophilic inks during pulping. As stated above, previous researchers have shown that calcium chloride causes deposition

of flexographic inks during the formation of paper, so this is consistent with the results[40]. Additionally, sodium silicate causes dispersion, which has previously been shown to improve detachment of hydrophilic ink during pulping[38]. However, recent research has shown that neutral pH pulping has a positive impact on the deinking of hydrophilic inks when using flotation, which seems inconsistent with these results[48, 55]. However, previous researchers have also shown that neutral pulping conditions have a negative effect on the optical properties of hydrophilic inks after pulping[48]. Because of this, it appears that the conditions necessary for improvement in the optical properties of hydrophilic ink after pulping is the opposite of that required for improvement after flotation. In fact, it has previously been seen that the conditions that improve the optical properties after pulping tend to have a negative effect after flotation and vice versa for other treatments as well such as temperature[48]. A likely explanation of this is the requirements for removal of the ink during pulping and flotation. In pulping, it is advantageous to have ink that is finely dispersed, but in flotation, it is necessary for the ink to have a particle size at least above 10 microns to be removed. This is consistent with previous results showing that deinking chemicals that had a positive effect during pulping had a negative effect after flotation but a positive effect if wash deinking was used instead of flotation[48].

The interaction between the deinking chemicals can also be seen from the results. For hydrophobic inks, there are several second order interactions that are expected. First, the interaction between oleic acid and calcium is thought to act as a coagulant. Next, sodium hydroxide and sodium silicate have similar functions in detaching ink, which may have a synergistic effect. From Figure 5 and Figure 6, it is apparent that there are no

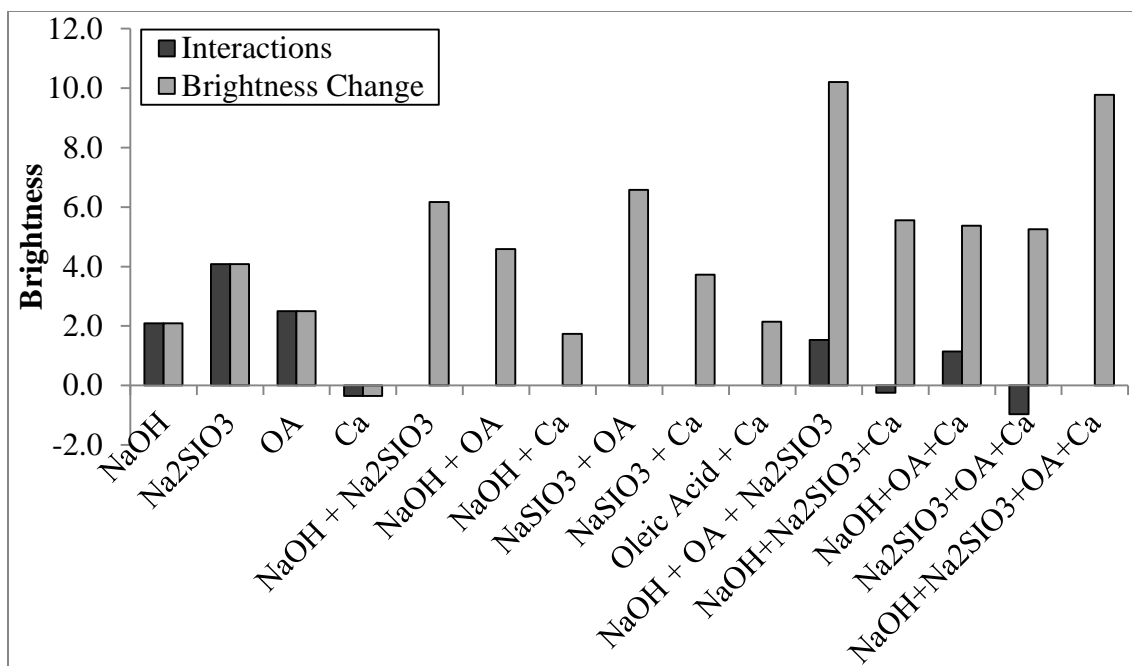


Figure 5. Effect of INGEDE Method 11 deinking chemicals and interactions between each of the deinking chemicals on ISO% Brightness of newsprint printed with pigmented inkjet ink. The chemicals include sodium hydroxide (NaOH), oleic acid (OA), sodium silicate (Na₂SiO₃), and calcium chloride (Ca).

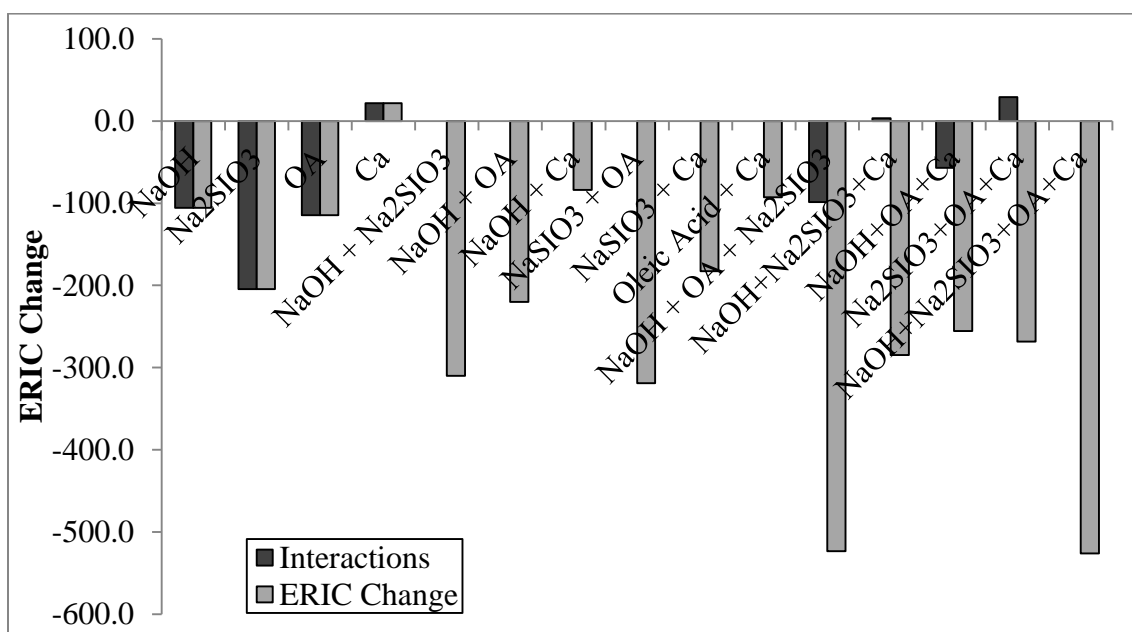


Figure 6. Effect of INGEDE Method 11 deinking chemicals and interactions between each of the deinking chemicals on ERIC of newsprint printed with pigmented inkjet ink. The chemicals include sodium hydroxide (NaOH), oleic acid (OA), sodium silicate (Na₂SiO₃), and calcium chloride (Ca).

secondary interactions for the hydrophilic ink. This is interesting as it has previously been shown that oleic acid and calcium led to redeposition of hydrophilic inks during pulping[40]. However, it can also be seen that there is a tertiary effect between sodium hydroxide, oleic acid, and calcium, which suggests that the negative impact of the oleic acid/calcium complex is only present with alkaline pulping conditions. Despite previous research suggesting that the deinking chemistry has a significant impact on hydrophilic inks, it was shown that using the standard deinking chemicals used for traditional inks was insignificantly different from the maximum deinking properties.

3.3 Evaluation of Flotation and Storage Process Variables for Hydrophilic Inks

Finally, the process variables used for storage and flotation were reviewed and investigated. Previous research has shown the effect time, temperature, and consistency of flotation on the separation of hydrophilic inks, but the effect of the temperature and length of storage between pulping and flotation has not been investigated previously. As a summary, Ciampa found that the temperature of flotation had a slight positive effect on the deinkability of hydrophilic inks, but increased time of flotation had a significant negative effect on the deinkability of hydrophilic inks[48]. It is expected that the flotation time would have a negative effect on the deinking of hydrophilic ink since previous research has shown that redeposition of these inks occurs throughout the deinking process[88]. Additionally, it was previously shown that up to 90% of these inks cannot be removed by flotation[88]. It has also been shown previously that the deinking chemistry has a significant impact on the deinking of both hydrophobic and hydrophilic inks[41, 73, 74].

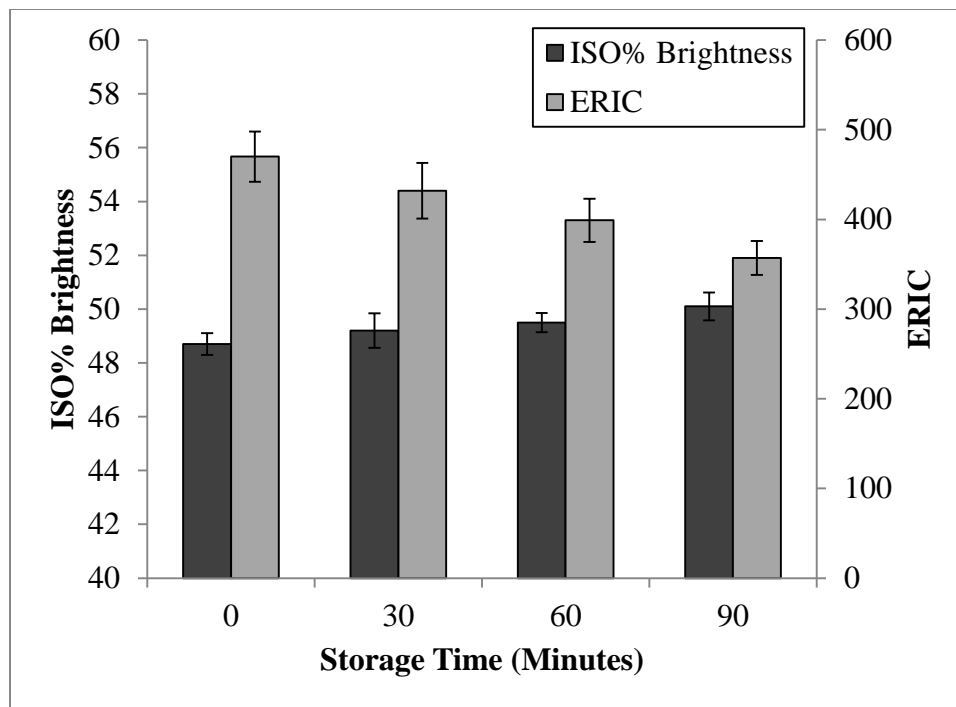


Figure 7. Effect of heat bath time on the ERIC of recycled inkjet printed newsprint.

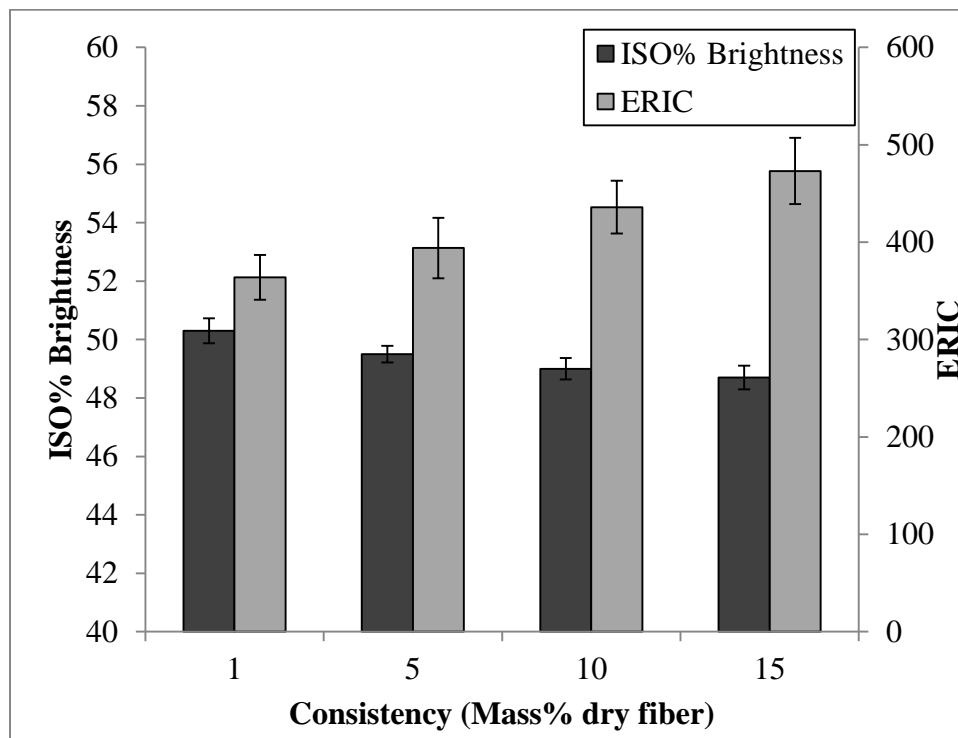


Figure 8. Effect of heat bath consistency on the ERIC of recycled inkjet printed newsprint.

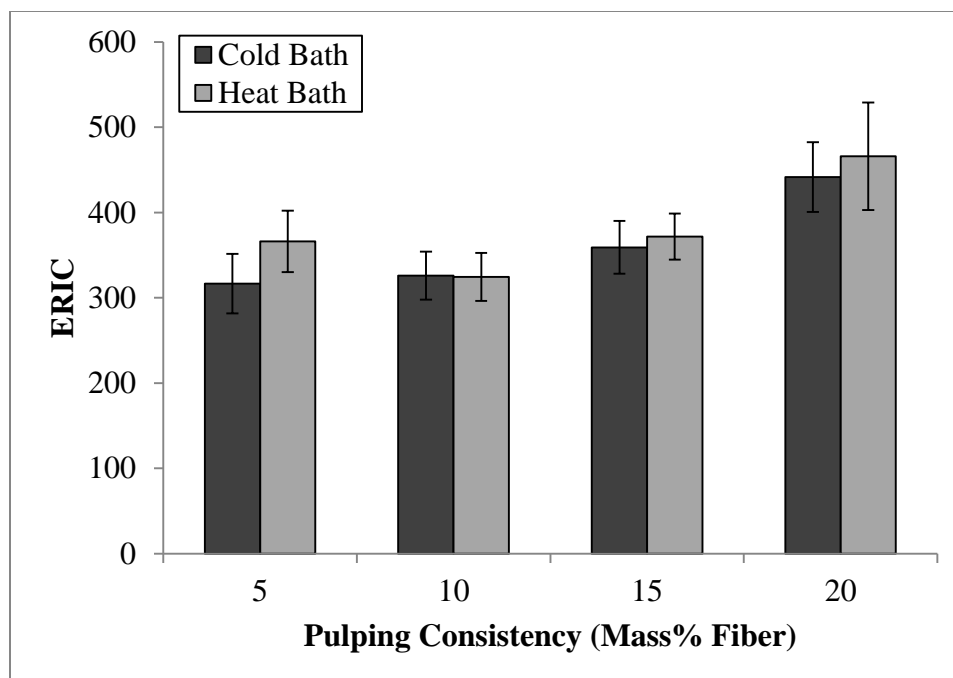


Figure 9. Effect of storage temperature on pulping effectiveness with cold bath being conducted at room temperature and hot bath being conducted at 40°C.

This study looked to increase the understanding of this phenomenon by looking at the effect of length, temperature, and consistency of storage in order to test these variables as well as the effect of flotation on the removal of hydrophilic inks. It is apparent from Figure 7 and Figure 8 that the storage time and consistency had a significant effect on both the ISO% Brightness and ERIC of the recycled paper.

Additionally, it is apparent from Figure 9 that the storage temperature did not have a significant effect on deinking. This is interesting because it suggests that the hydrophilic inks disperse into solution during the storage period. Previously, it was thought that any ink that was redeposited during pulping was irreversibly deposited, but this suggests that the ink can still be dispersed into solution. Another interesting result of this research is the difference between the optical properties of the recycled paper before and after flotation, which can be seen in Table 1.

Table 1. Detrimental effects of flotation on separation of pigmented inkjet inks from newsprint as shown through the ISO% Brightness and ERIC of the INGEDE Method 11 recycled newsprint.

	Brightness	ERIC
Heat Bath	49.4	406
Flotation	48.7	476

Previously, the optical properties of recycled paper were compared for after pulping and after flotation, which showed a significant but small improvement after flotation. However, when comparing the recycled paper directly before and after flotation, it is clear that flotation actually has a significant negative impact on the optical properties of the recycled paper. This means that flotation either causes increased redeposition of the ink or removes a larger portion of paper fibers than ink. Finally, it is curious that temperature does not affect the dispersion of ink in the storage step of paper recycling as it would generally be assumed that an increase in temperature would increase the rate of deposition due to increased energy. However, it may be the case that an increase in temperature increases both the dispersion and redeposition of ink similar to what was seen for increased fiber-fiber interaction during pulping.

The result from the analysis of the storage and flotation of hydrophilic inks provided some interesting insights showing how ineffective flotation is for these inks. Additionally, the complexity of the deinking process is evident. However, this is similar to what was found by previous researchers, so the focus of the subsequent experiments was on prevention of redeposition and improved separation as was found from the previous section.

3.4 Effect of Pulping Consistency on Deinking of Hydrophilic Inks

In addition to the chemical interactions, there are also several non-chemical pulping factors that are not completely understood from previous research. One of these factors is the effect of fiber-fiber interactions on redeposition of hydrophilic inks. It has previously been shown that an increase in mechanical force during pulping has a positive effect on deinking hydrophobic inks, but has a negative effect on hydrophilic inks[48]. The mechanical force on the paper fibers is affected by the length of pulping, fiber-fiber interaction, the mixing speed, and the type of pulper that is used. However, previous research has only investigated the effect of mixing speed and pulping time on redeposition of hydrophilic inks. Specifically, an increase in pulping time of flexographic ink from 15 minutes to 25 minutes showed a decrease in ISO% Brightness by 5 points with similar results for an increase in mixing speed[48]. This is likely due to redeposition of the ink during pulping, which has been shown to be one of the main issues with deinking of hydrophilic inks[37, 48].

Although other sources of mechanical energy have been studied, the effect of fiber-fiber interactions on the deinkability of hydrophilic inks has not been evaluated previously. This is interesting as significant research has been performed in the past on optimizing the fiber-fiber interactions for hydrophobic ink, and it has been shown that the fiber-fiber interaction is important for detaching hydrophobic inks[89]. However, redeposition is not an issue for hydrophobic inks, so it was interesting to see if this may have an effect on redeposition of hydrophilic inks[89]. Additionally, previous researchers have theorized that hydrophilic inks are almost instantaneously dispersed during pulping operations, which means that decreasing fiber-fiber interactions should have no effect on

the deinking efficiency[12, 38, 53]. In order to determine the effect of fiber-fiber interactions, the consistency of the pulp was varied during the pulping operation, which has been shown previously to decrease fiber-fiber interactions. Since previous researchers concluded that hydrophilic ink is completely dispersed without the need for mechanical energy, it was expected that decreasing the consistency would continue to improve the deinkability of hydrophilic inks. Because of this, the effect of pulping consistency was investigated.

Additionally, at higher consistencies, the majority of the mechanical force comes from fiber-fiber interactions[89]. Because of this, it is likely that hydrophilic ink transfers directly between the paper fibers rather than being dispersed in solution. In the case of hydrophobic inks, fiber-fiber interactions improve the detachment of ink from the fiber surface[89]. However, with hydrophilic inks, redeposition is likely to occur when ink comes into contact with the fiber surface[38].

From Figure 6, it is apparent that decreasing the consistency during pulping from 20% to 10% had a significant positive effect on the deinkability of hydrophilic inks as was expected from the hypothesis. However, when the consistency is decreased further to 5%, the optical properties return to those seen at 15% consistency disproving the hypothesis that decreasing the consistency will have a continuing positive effect as the consistency decreases. This result may be perplexing at first, but by reassessing the assumptions, there is a plausible explanation for this observation. As the consistency during pulping is decreased, the mechanical energy applied to the paper through fiber-fiber interactions is also decreased. Although it has previously been shown that mechanical energy causes redeposition of hydrophilic inks, fiber-fiber interactions are

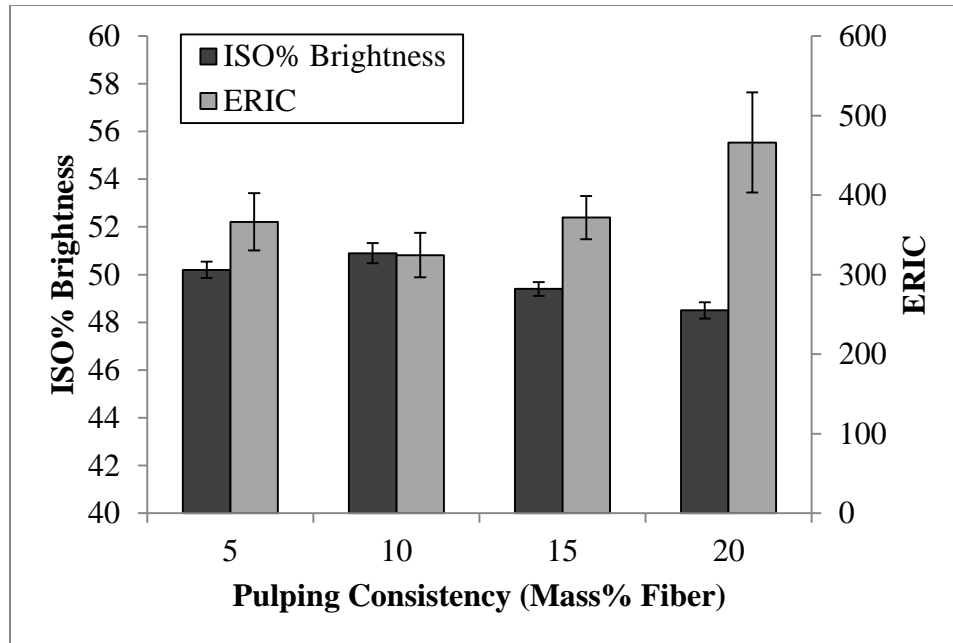


Figure 10. Effect of pulping consistency on ISO% Brightness and ERIC of INGEDE Method 11 deinked newsprint printed with pigmented inkjet ink.

also necessary to detach traditional inks from the recycle paper fibers[89]. If the hydrophilic ink is not instantaneously dispersed in solution during pulping as previously theorized, fiber-fiber interactions could be required to effectively detach the hydrophilic ink as well. In fact, a previous study has shown that up to three minutes of pulping under standard conditions, the amount of hydrophilic ink is decreased by increasing mechanical energy[12], and when this theory was tested, it was shown that there is a trend similar to this for the hydrophilic ink as can be seen later in Figure 16. This led to the hypothesis that hydrophilic ink does not completely disperse into solution during pulping operations, which could have a significant impact on future research into deinking and recycling of paper printed with these inks.

3.5 Behavior of Hydrophilic Ink during Pulping

From the investigation of the effect of pulping concentration on deinking of hydrophilic inks, it is apparent that there may be a portion of the ink that is not easily detached from the cellulose fiber during deinking operations, so the behavior of hydrophilic inks was investigated further in this study as described to test the hypothesis that there is a portion of the hydrophilic inks which requires mechanical energy to detach. For the purposes of this study, the ink proportion was determined for four predefined categories: bound, redeposited during deinking, redeposited during paper formation, and separated ink. The bound ink is the portion of the hydrophilic ink that cannot be easily detached from the cellulose fiber during standard pulping, the redeposited ink is ink that can be detached from cellulose but is caused to reattach during either deinking or formation, and separated ink is the portion of ink that is removed either by flotation or in the filtrate.

In order to investigate each of these categories of ink, modifications to Method 11 must be defined and performed. Method 11 without modification is the standard method that can be modified to distinguish each of these inks types. Method 11 without modification will show the “bound” and both types of redeposited ink. Next, each of the types of redeposition must be prevented. In the case of redeposited ink during paper formation, there is a common method in the paper industry that is used to do this. The deinking method is not changed, so Method 11 is again followed. However, when forming the paper, a method called hyperwashing is performed. In hyperwashing, the pulp is diluted “infinitely” to decrease the ink concentration and prevent redeposition during paper formation. By comparing the difference between Method 11 and Method 11

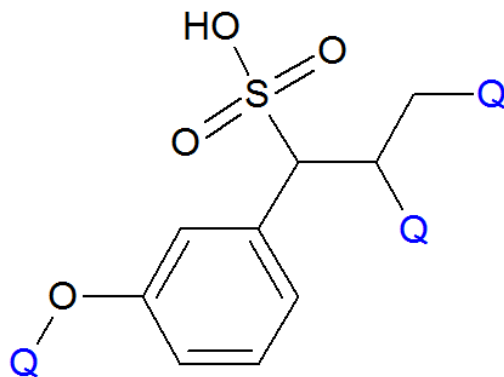


Figure 11. Lignosulfonate sample structure.

with hyperwashing, it is then possible to determine the amount of ink that is redeposited during paper formation. Similarly, it is desired to determine the amount of ink that is separated during deinking. To do this, another modification was made for Method 11 which involved only performing pulping and using a flocculent to prevent separation of the ink into the filtrate. The final modification that was necessary was completely preventing redeposition of hydrophilic ink during the deinking operation. Hyperwashing was again used during the paper formation to prevent redeposition at that stage, but there is not a method that has been used to completely prevent redeposition of ink during deinking operations, so defining a method to do this was the next step to study the behavior of hydrophilic ink during deinking operations.

In order to prevent redeposition, it is necessary to stabilize the ink in solution. To do this, lignosulfonate was used as a dispersant to prevent redeposition. A sample chemical structure for lignosulfonate is shown in Figure 11, and it has previously been shown that lignosulfonate adsorbs to cellulose fibers and pigments through hydrophobic interactions, which would allow the lignosulfonate to prevent redeposition of hydrophilic ink either through electrostatic or steric interactions[26]. It was necessary to determine

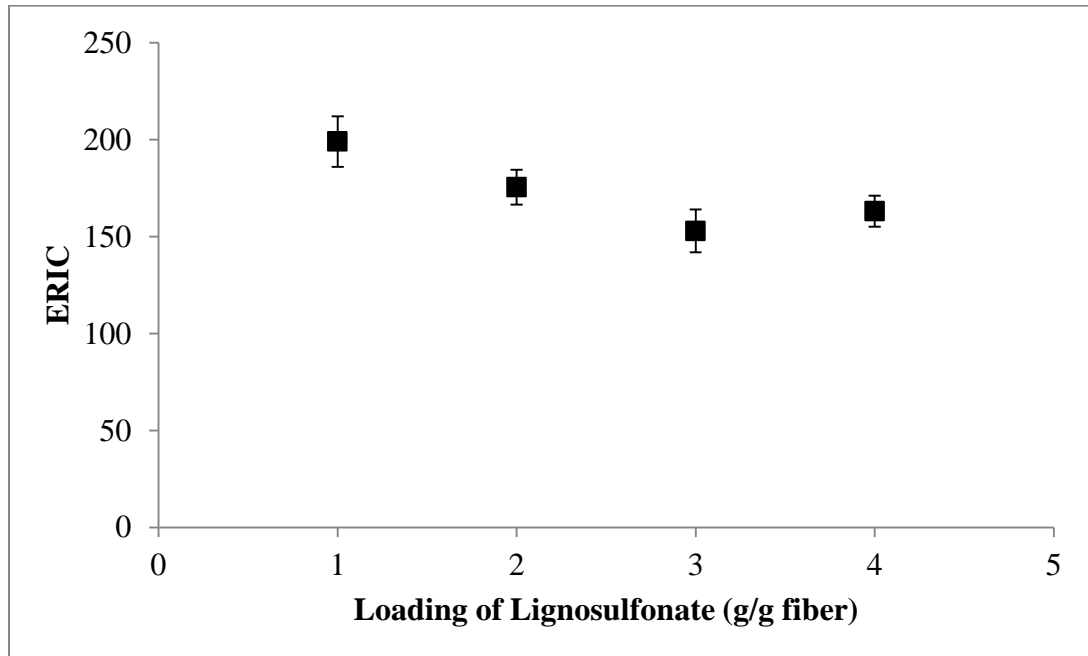


Figure 12. Determination of minimum Lignosulfonate loading (g/g dry fiber) using ERIC measurements after standard Method 11 pulping.

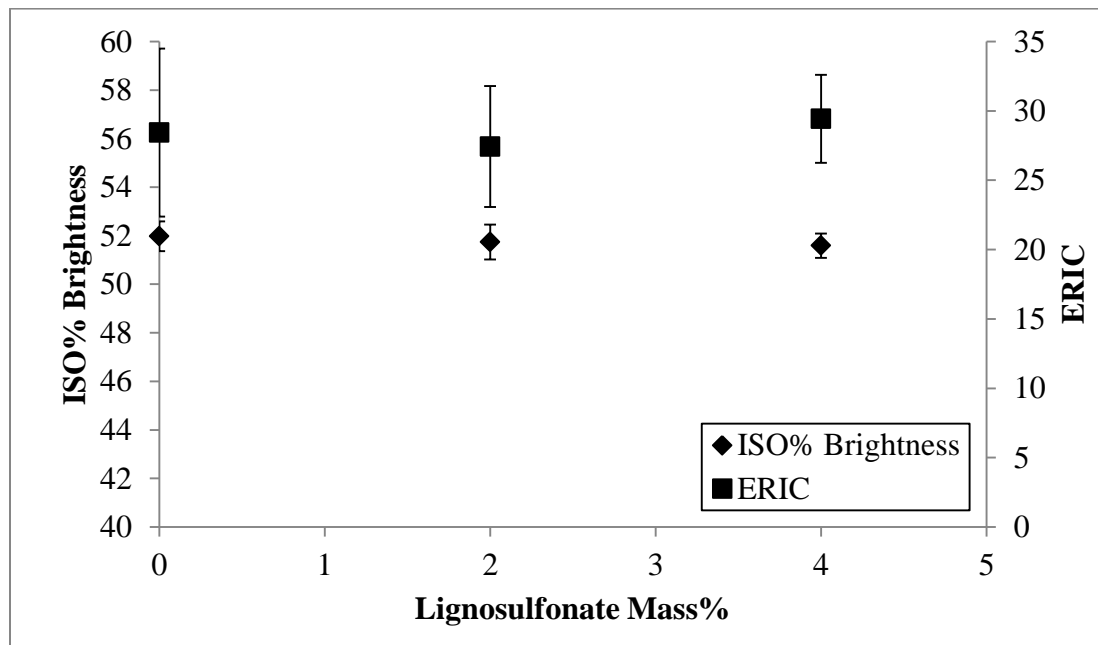


Figure 13. Effect of lignosulfonate on ISO% Brightness and ERIC measurements of unprinted newsprint pulped according to Method 11.

the effect of Lignosulfonate on the optical measurements as well as to determine the optimal loading of Lignosulfonate. To determine the optimal Lignosulfonate loading, the loading of lignosulfonate was varied. As can be seen in Figure 12, ink removal was significantly increased by increasing the loading of lignosulfonate from 1% to 3%, but there was an insignificant difference when increasing the loading to 4% consistency. Because of this, it was assumed that lignosulfonate completely stabilizes inkjet ink when the loading is 3 mass% on fiber for the purposes of this study, and this loading was used for each of the subsequent experiments.

Next, the effect of lignosulfonate on the measurement methods used in these experiments was determined. To do this, unprinted paper was pulped with lignosulfonate at 0 - 4 mass% on fiber. From Figure 13, it is apparent that lignosulfonate did not have a significant effect on the ISO% Brightness or ERIC measurements of recycled paper when no ink was present, which suggests that the lignosulfonate will not interfere with the optical measurements during these experiments.

After determining the optimal loading for Lignosulfonate and verifying that Lignosulfonate will not interfere with the optical measurements, it is still unknown if lignosulfonate can completely prevent redeposition of the hydrophilic ink during pulping, which is necessary to study the behavior of the ink. To do this, redeposition of dried pigmented inkjet ink onto unprinted newsprint was evaluated during the deinking

Table 2. Average mass of pigmented inkjet ink per mass of unprinted paper as measured from 100 sheets of newsprint.

	Paper Fiber	Inkjet Ink
Mass per Newsprint Sheet (g)	2.928	0.0031

operations with and without lignosulfonate. The amount of dried ink required was determined using the average mass of inkjet ink per mass of paper fiber, shown in Table 2. From Figure 14, it is apparent that Lignosulfonate is able to prevent the majority of the redeposition of hydrophilic inks during pulping operations.

Now that there is a method of prevent redeposition of hydrophilic ink during paper recycling, it is possible to determine the proportion of each of the ink types defined earlier. The results of these pulping methods are shown in Figure 15, and as expected, there is a portion of ink that is redeposited during both pulping and pad formation. Additionally it can be seen that there is a significant portion of the hydrophilic ink that remains attached to the paper fiber during standard pulping. Additionally, by comparing all of these method, the amount of ink that is bound, detached, reattached during pulping, and reattached during paper formation can be estimated, which is summarized in Table 2. There are two significant aspects of this data. First, the proportion of bound ink is significant, which is contrary to previous theories that assume that hydrophilic ink is quickly and completely dispersed in solution during pulping[12, 38, 40, 73, 90, 91]. Second, the proportion of hydrophilic ink that is redeposited is about twice as much as the bound ink. Because of this, the major concern for improving the deinkability of hydrophilic inks will be to prevent redeposition of the inks. Another interesting note is that when you compare the redeposition of ink from Figure 14 and Figure 15, the estimation of redeposition of ink during pulping is similar in magnitude, which supports each of the analyses.

After performing this analysis, it was desired to test the previous hypothesis that the proportion of bound ink on the fiber increases as the consistency decreases

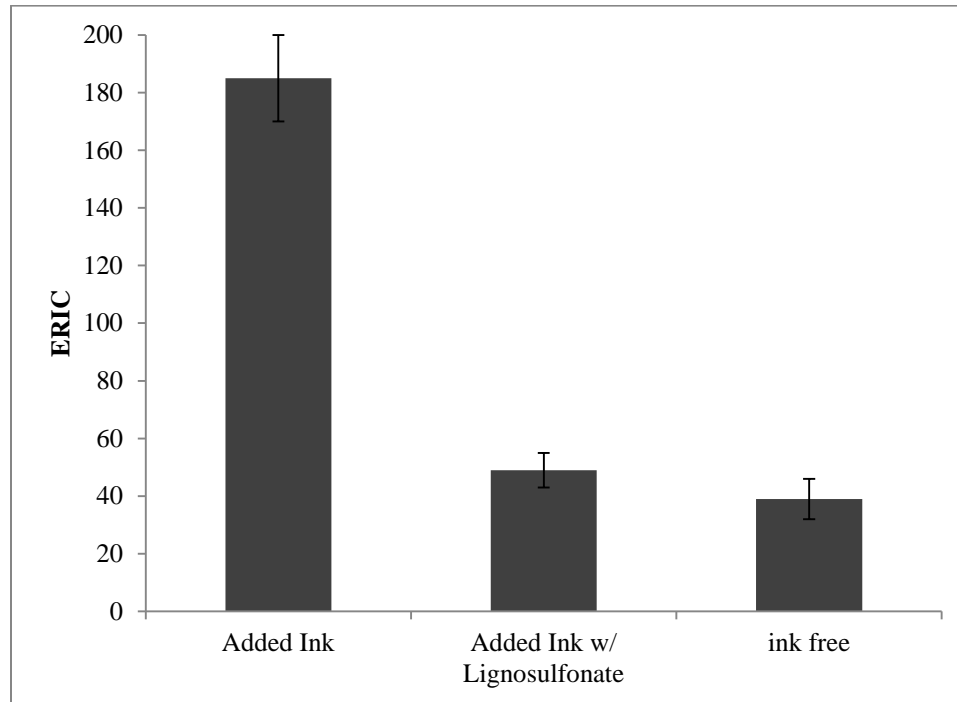


Figure 14. Evaluation of proportion of ink redeposited during paper recycling with and without Lignosulfonate using a variation of INGEDE Method 11.

Table 3. Deinking methods for determination of behavior of hydrophilic inks during paper recycling operations.

	Bound Ink	Redeposited Ink (Pulping)	Redeposited Ink (Paper Formation)	Separated Ink (Flotation & Filtrate)
Lignosulfonate, Method 11, and Hyperwashing	X			
Method 11 & Hyperwashing	X	X		
Method 11	X	X	X	
Method 11 & Flocculent	X	X	X	X

based on the inconsistency seen in Figure 10. In order to do this, the same procedure used to measure the “bound” and “redeposited ink from the above data was used expect that the pulping consistency was changed to 5% and 10% in order to determine the change in these values as the consistency changed. For this purposes of this data, the redeposited during pulping and redeposited were combined to measure the total amount of ink redeposited during these experiments. As can be seen from Figure 16, it is apparent that the proportion of redeposited ink decreases as the consistency decreases, which was what was hypothesized at the beginning of the experiment. However, when looking at the portion of bound ink, it is apparent that the bound ink increases as the consistency increases from 5-15%. This explains the inconsistency seen earlier that the deinking efficiency declines at 5% pulping consistency rather than continuing to improve deinking by reducing the liquid phase ink concentration.

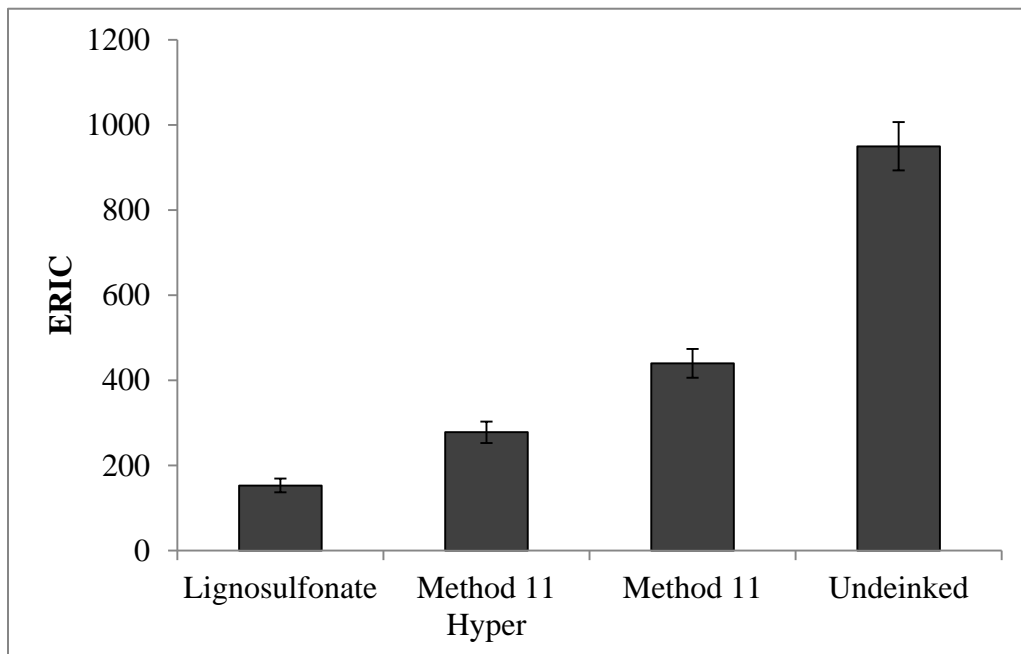


Figure 15. ERIC measurements for various adaptations of INGEDE Method 11 for determination of the fate of pigmented inkjet ink during paper recycling.

Table 4 Estimated mass percent of pigmented inkjet ink that is bound and redeposited during pulping or pad formation determined from Figure 15.

	Bound Ink	Redeposited (pulping)	Redeposited (pad formation)	Separated Ink (Flotation & Filtrate)
Mass% Ink	15.8	13.7	17.9	52.6

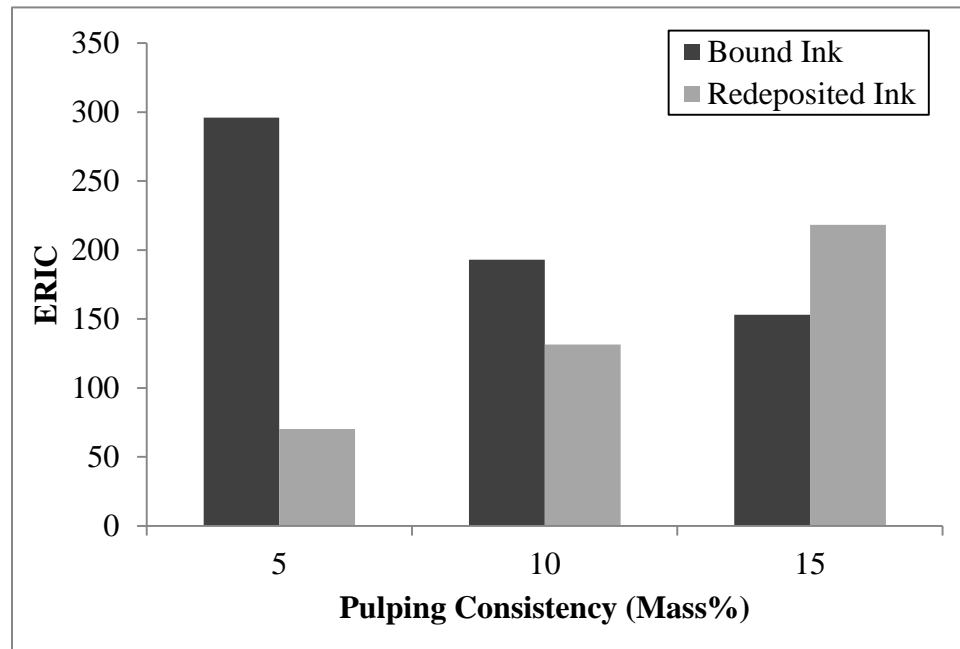


Figure 16. Bound versus redeposited ink between 5 and 15% consistency.

3.6 Lignosulfonate Pulping with Hydrophilic and Mixed Inks

After showing that lignosulfonate could adequately prevent redeposition of hydrophilic ink, it was hypothesized that lignosulfonate may be able to be used as a deinking chemical to improve deinking of hydrophilic inks. It has already been shown that lignosulfonate can prevent redeposition of hydrophilic inks, which is one of the goals of this research. However, it was also necessary to lignosulfonate for mixed sources of paper containing both hydrophilic and hydrophobic inks, which is much closer to what would be seen in industrial settings. Although this would likely cause issues with the ink being separated into the filtrate rather than by flotation due to dispersion, a method of improving separation of hydrophilic inks in mixed grades of paper is still an attractive goal. To test deinking of mixed grades of paper with lignosulfonate, trials were run on 100% hydrophilic inkjet ink, 100% hydrophobic offset ink, and a mixed trial of 50% inkjet ink and 50% offset ink. As can be seen in Figure 17, it is apparent that lignosulfonate has a positive effect on the deinking of 100% inkjet ink, and a negative effect when hydrophobic offset ink is present increasing with the proportion of offset ink. Similarly, it can be seen in Figure 18, that the filtrate darkening is negatively affected when using lignosulfonate regardless of the ink type as expected. However, it was unexpected to see that lignosulfonate would cause increased redeposition of the hydrophobic offset inks during the deinking operation since it would be expected that the dispersant would not have an effect on offset inks which do not tend to redeposit onto the cellulose fibers during deinking. However, previous researchers have seen similar effects showing that as the average particle size of any ink is decreased, the redeposition of the ink is increased[92]. Although it may be expected that smaller particles would be less

likely to redeposit due to increased electrostatic force to mass ratios, the adsorption of these inks has been found to be physical adsorption rather than chemical adsorption[92]. Because of this, the smaller particle size allows a higher portion of the ink to enter the pores of the cellulose fiber causing adsorption. Additionally, hydrophobic inks have a stronger attractive force with the cellulose fibers due to hydrophobic interactions which likely increases redeposition of these inks when the particle size is decreased[26].

Another interesting observation that can be made from Figure 17 and Figure 18 is that for the lignosulfonate deinking method, there is more ink present on the recycled paper as well as in the filtrate when hydrophobic ink is present. Due to material balances, it is necessary that this ink is coming from somewhere, and can be explained by looking at the flotation efficiency. Lignosulfonate is expected to stabilize both hydrophobic and hydrophilic ink in solution, which would prevent removal of the ink by flotation. Since hydrophilic ink is already poorly removed during flotation, there is little difference because of this. However, hydrophobic inks are readily removed by flotation, so the increase in ink in both the recycled paper as well as the filtrate can be explained by the lower removal of ink by flotation. Essentially, the hydrophobic ink that would have been removed by flotation is transferred to the paper surface or into the filtrate instead with the use of lignosulfonate. Due to this, it is apparent that any new treatment method used for hydrophilic ink could have significant, unexpected effects on the deinking of traditional hydrophobic inks, and that lignosulfonate as a deinking chemical is not suitable due to this.

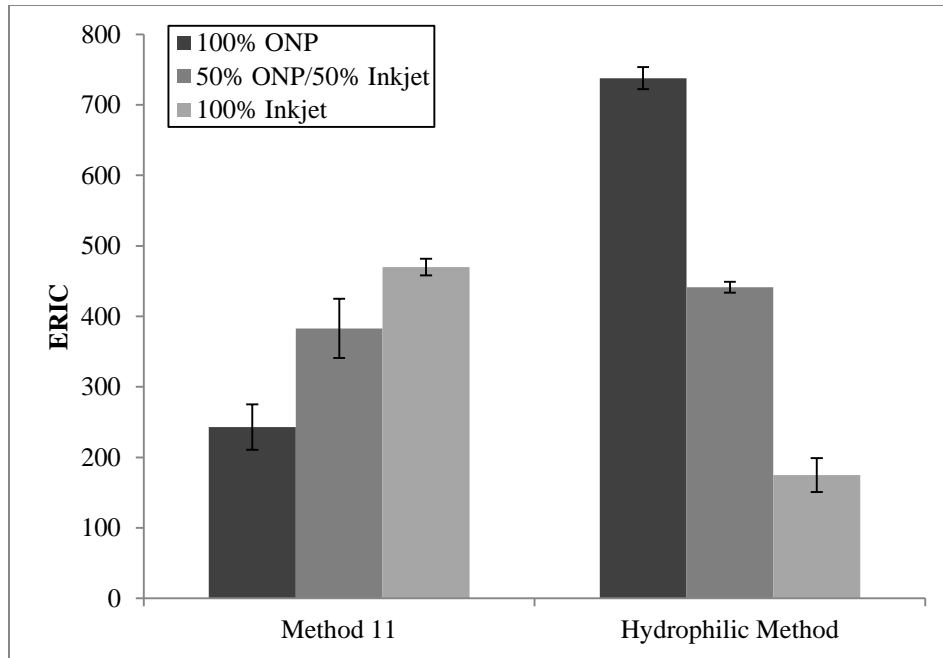


Figure 17. Effect of liginosulfonate pulping on filtrate darkening for mixed grades of paper ranging from 100% hydrophobic ONP to 100% hydrophilic inkjet ink.

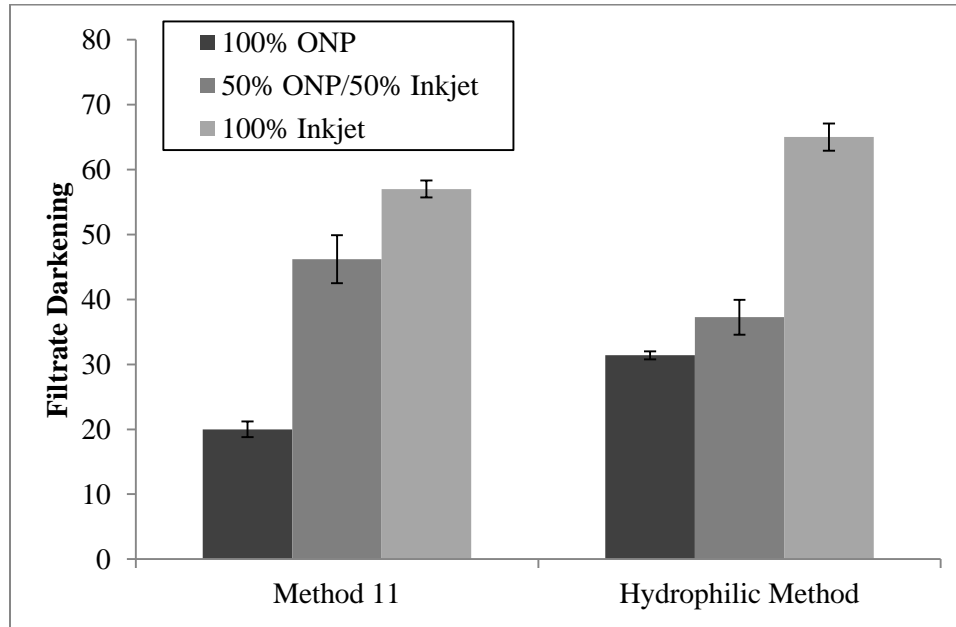


Figure 18. Effect of liginosulfonate pulping on filtrate darkening for mixed grades of paper ranging from 100% hydrophobic ONP to 100% hydrophilic inkjet ink.

CHAPTER 4: LIQUID PLASMA TREATMENT (LPP) FOR IMPROVED SEPARATION OF HYDROPHILIC INKS

It was already shown that dispersion of the hydrophilic ink can cause severe negative effects on the hydrophobic inks that make up the majority of the current printing inks, so the next method that was looked at for improving deinking of hydrophilic inks was a method of increasing the particle size of the ink. As stated previously, one of the major issues with hydrophilic inks is the submicron average particle size of the ink preventing removal of the ink through flotation. This causes issues because the remaining ink will continue to redeposit during the deinking process and also redeposit during the paper formation process. Because of this, increasing the particle size may improve deinking of hydrophilic inks. Additionally, increasing the particle size of hydrophobic inks should not have a significant effect on deinking since there is a large size range that flotation is effective for. However, it has been previously shown that using coagulants or flocculants with hydrophilic inks causes redeposition of the ink onto cellulose rather than increases in particle size. Because of this, a new method was evaluated for increasing the particle size of hydrophilic inks as well as making them more hydrophobic before and during flotation. This new method is called liquid phase plasma (LPP) treatment, and uses an applied voltage to generate a plasma region in solution. This treatment method has previously been shown to cause coagulation of hydrophilic ink particles in solution when no paper fibers were present. However, it has not been tested for applications with paper fibers until this research.

4.1 Experimental Procedures

4.1.1 Apparatus and Method for Treatment with LPP

LPP treatment was used to improve the deinkability of these hydrophilic inks. The apparatus shown in **Error! Reference source not found.** was used to generate the LPP. The apparatus has a volume of 1 liter and is stirred vigorously during the treatment process. In order to induce the LPP, two electrodes, separated by 4 cm, are submerged in the solution. The electrodes are identical to each other and were made by inserting a PVC insulated 14 gauge copper wire into a ceramic tube with inner diameter of 0.156 inches (McMaster-Carr, Aurora, OH). The copper wires were inserted into the ceramic tube so that 4 cm of the insulated wire was exposed in the solution. The copper wire was replaced after each use. A DC voltage of 2.5 kV and amperage of 650 mA was applied across the electrodes to form the LPP in solution for a discharge time of 2 minutes. The ISO% Brightness and ERIC of the reject from flotation was also measured in order to evaluate the efficacy of flotation. This was done by making a filter pad following INGEDE Method 1 and measured using a Technidyne ColorTouch 2 Model ISO (Technidyne Corporation, New Albany, IN)[85].

4.1.2 Evaluation of Liquid Phase Plasma (LPP) for Deinking of Hydrophilic Inks

Samples of hydrophilic ink were coagulated using LPP treatment. The ink that was used was a commercial pigment-based inkjet inks (HP 60 Black) and was dissolved in distilled water for the coagulation tests. The ink also had 356.3 mg/L of calcium chloride added to solution to approximate the conductivity of tap water. The samples had varying concentrations from 0.1-0.8 g/L and were treated with the LPP for 2 minutes.

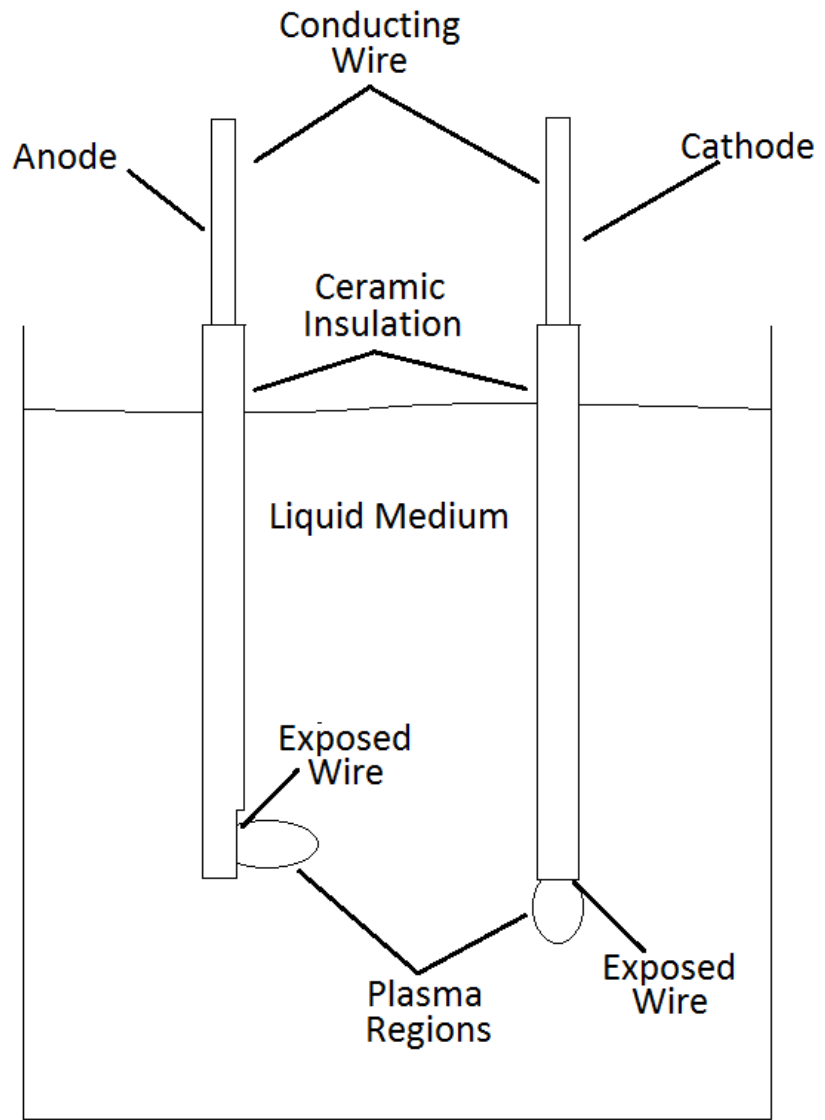


Figure 1. Diagram of apparatus for liquid plasma treatment[93].

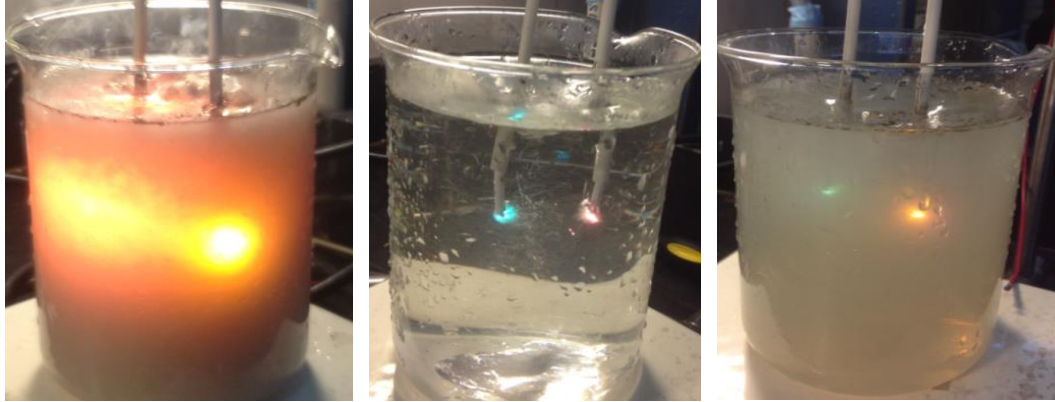


Figure 19. Picture of each LPP treatment method used in the improved deinking experiments including from left to right direct treatment, indirect treatment, and filtrate treatment.

The samples were then measured using UV/Vis spectroscopy using a spectrophotometer (Spectronic 601, Milton Roy, Ivyland, PA). The measurement was taken at a wavelength of 500 nm, using distilled water as a reference. A calibration curve was made for the ink over a concentration range of 0.02-0.6 g/L.

The efficacy of the LPP treatment was evaluated using three independent modifications to INGEDE Method 11. These modifications will subsequently be referred to as “direct”, “indirect”, and “filtrate” treatment and pictures of each are shown as a reference in Figure 19. Each of these modifications uses the LPP method described above but the LPP is used to treat varying solutions throughout the deinking process. The solution used in the LPP generation apparatus was either pulp at 1% consistency, DI water with calcium chloride, or the filtrate from 1% consistency pulp dewatered to 5% consistency.

In the direct treatment method, pulp at 1% consistency was treated directly before flotation. In the indirect treatment method, dilution water was treated directly before diluting the pulp during pulping, storage, and flotation. Finally, in the filtrate treatment

method, the 1% consistency pulp was dewatered to 5% consistency. The filtrate was then treated with LPP and then mixed with the 5% consistency dewatered pulp. In addition to testing each of these treatment methods individually, the direct and indirect treatment methods were also combined to determine if the two methods used different mechanisms to improve the deinkability of the pulp, which is referred to as combined treatment.

4.1.3 Evaluation of LPP Treatment for Mixed Paper Grades

It was necessary to test the LPP treatment method for mixed paper grades to ensure that the treatment did not have a negative effect on hydrophobic inks. To do this, the LPP direct treatment method as described previously was compared to standard Method 11 deinking for a 35% hydrophilic and 65% hydrophobic ink printed paper.

4.1.4 Effect of Electrode Material on LPP Treatment Efficacy

The electrode material was evaluated to determine if there was a significant effect on the efficacy of the LPP treatment. To do this, deinkability tests were carried out with 100% flexographic newsprint (The Telegraph, Macon, GA) with the same modifications to Method 11. However, the electrode material used was iron instead of copper. Using each of the modifications, a filter pad was made after pulping and flotation according to INGEDE Method 2 in order to compare to the treatment with a copper electrode. Additionally, a filtrate darkening filter pad was made according to INGEDE Method 1. The ISO% Brightness, ERIC, and Filtrate darkening were measured using a Technidyne Color Touch 2 Model ISO (Technidyne, New Albany, IN).

4.1.5 Determination of Importance of Secondary Parameters in LPP Treatment

In order to test various process variables that may have had an effect on the recycled paper during the deinking operation, the temperature and ion concentration were evaluated independently of the LPP treatment. To do this, the coagulation tendency of the hydrophilic ink was evaluated in solution at varying temperatures and concentrations of copper ions. The ink was a commercial pigment-based inkjet ink (HP 60, LD Products, Long Beach, CA). The temperature was controlled between 40 and 90°C, and the copper concentration was varied between 0.0372-0.186 g/L using copper chloride (Fisher-Scientific, Pittsburg, PA). The samples were then measured using UV/Vis spectroscopy at 300 nm using distilled water as a reference and also using dynamic light scattering to determine the particle size distribution.

4.2 Improved Separation of Hydrophilic Inks with LPP Treatment

LPP treatment has previously been shown to increase the particle size of hydrophilic inks in ink/water solutions by up to 100 times, and the mechanism was proposed to be through polymerization of the ink particles. Because of this, it was assumed that LPP treatment could be used to increase the particle size of hydrophilic inks into the size range necessary to be removed by flotation without causing redeposition of the ink as was seen in previous studies on increasing the ink particle size[33, 38, 47]. In

Table 5. Deinkability thresholds for ONP as defined by INGEDE[86]. The parameters measured by INGEDE include the luminosity (Y), Color a*, ink area (A), ink elimination, and filtrate darkening (ΔY) [93].

Parameter	Y (Points)	Color a*	A (mm ² /m ²)	Ink Elimination (%)	ΔY
Lower Threshold	47	-3.0		40	
Upper Threshold		2.0	2,000		18

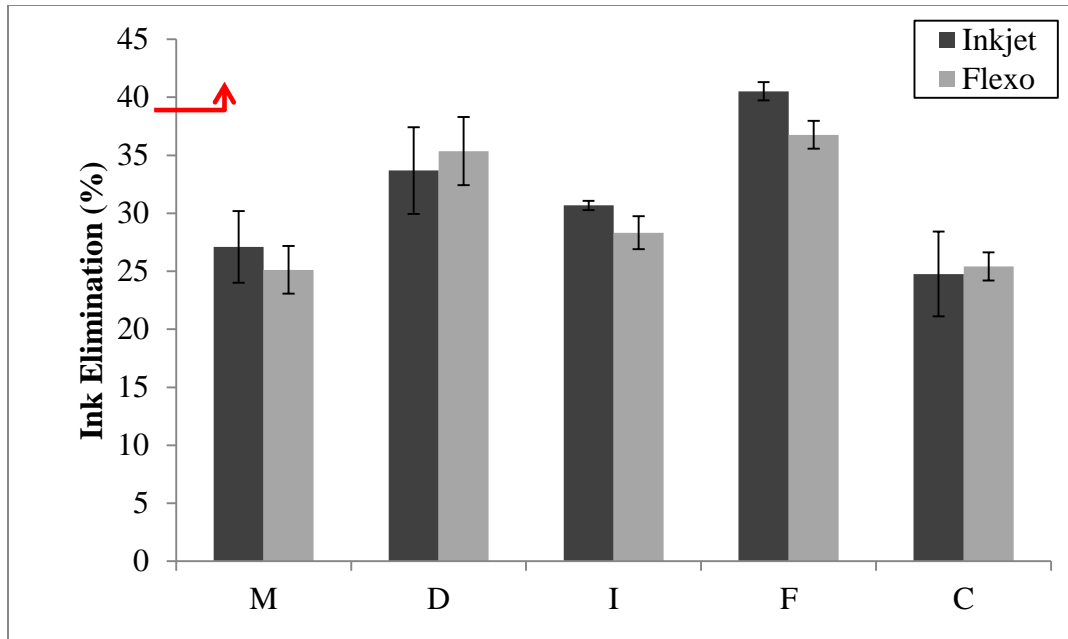


Figure 20. The ink elimination was measured for each of the treatment methods (the reference method (M), direct (D), indirect (I), filtrate (F), and combined treatment (C)). The red arrow indicates the threshold ink elimination value[93].

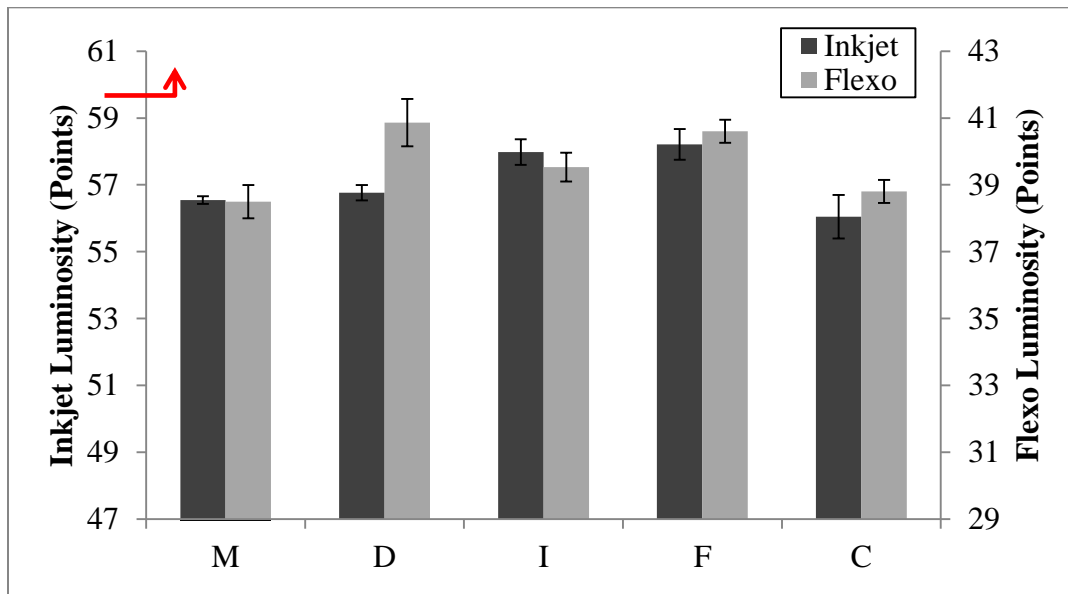


Figure 21. The luminosity was measured for each of the treatment methods (the reference method (M), direct (D), indirect (I), filtrate (F), and combined treatment (C)). The red arrow indicates the optimal luminosity value as shown in Table 4[93].

order to test the deinkability of inkjet and flexographic printed newsprint with LPP treatment, the ink area, ink elimination, luminosity, brightness, and filtrate darkening were compared to the deinkability standards developed by INGEDE for old newsprint (ONP) as shown in Table 4[86].

The treatment method was also varied in order to test the mechanism of the LPP treatment. INGEDE Method 11 was used as a reference method for these pulping experiments as well as the four LPP variations. As stated previously, two major problems with deinking of hydrophilic inks is the reattachment of ink and the inability to separate the ink with flotation. The LPP treatment methods were selected to determine if LPP could effectively mitigate these issues. Adding LPP treated water at an early stage could allow for decreased ink reattachment by an increase in particle size of the ink, which was the goal of the indirect treatment method. Additionally, larger increases in particle size have been found at lower concentrations of paper fiber, so treating the pulp before flotation may allow for improved increase in particle size, which was the goal of direct LPP treatment[93].

Additionally, treatment of the ink in the filtrate treatment method allows for an ink solution without the presence of fibers. Finally, it would be ideal if reattachment and flotation of hydrophilic inks could be removed, so combined treatment was evaluated to see if a combination of these methods could enhance the deinking of hydrophilic inks. When comparing the LPP treatment to the reference method, there are clear improvements in ink elimination and luminosity for both inkjet and flexographic printing as can be seen from Figure 20. The indirect and direct treatment methods were able to improve the ink elimination to some extent, but the filtrate treatment was able to increase

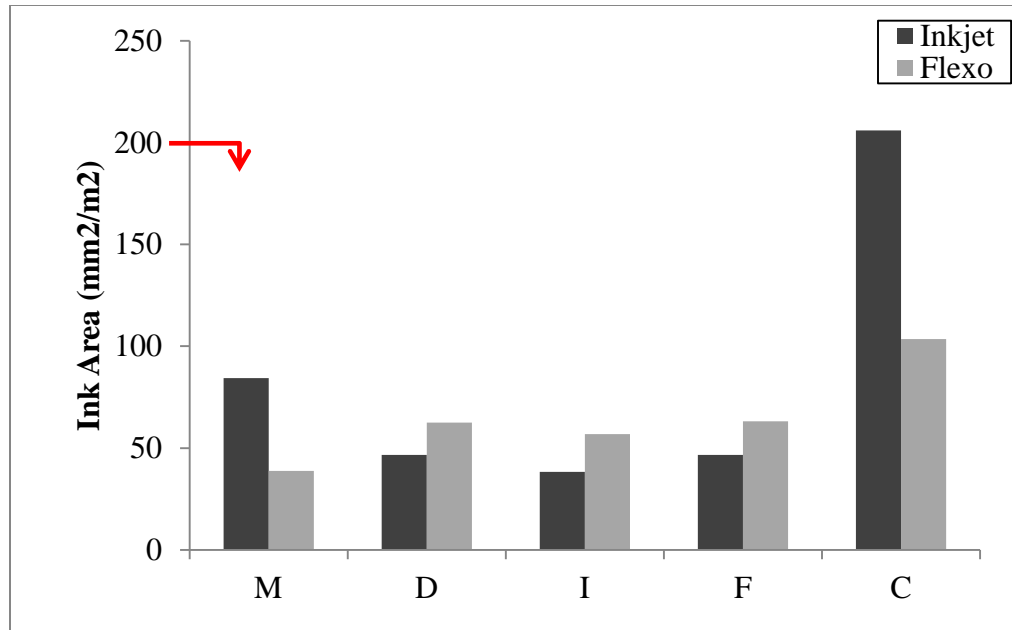


Figure 22. The ink area was measured for each of the treatment methods (the reference method (M), direct (D), indirect (I), filtrate (F), and combined treatment (C)). The red arrow indicates the optimal ink area value[93].

the ink elimination above the threshold to 40.5% for inkjet and 36.8% for flexographic ink. Similar results were seen when looking at the luminosity, as can be seen in Figure 21. Additionally, each of the treatment methods except the combined treatment improved the Total Dirt particle area of the inkjet and flexographic printed paper. A reduction in all of these measurements indicates that a greater amount of ink is being removed from the paper fibers when treated with the liquid plasma except when the combined treatment is used. Additionally, the Color a^* was in the optimal range for each treatment method including the reference method showing that the LPP treatment is not causing discoloring of the paper fiber in the red-green spectrum. . Similarly, the Total Dirt particle area was in the optimal range as defined by INGEDE for each treatment method showing that there was not increased visible contamination in the formed paper. However, it is clear that

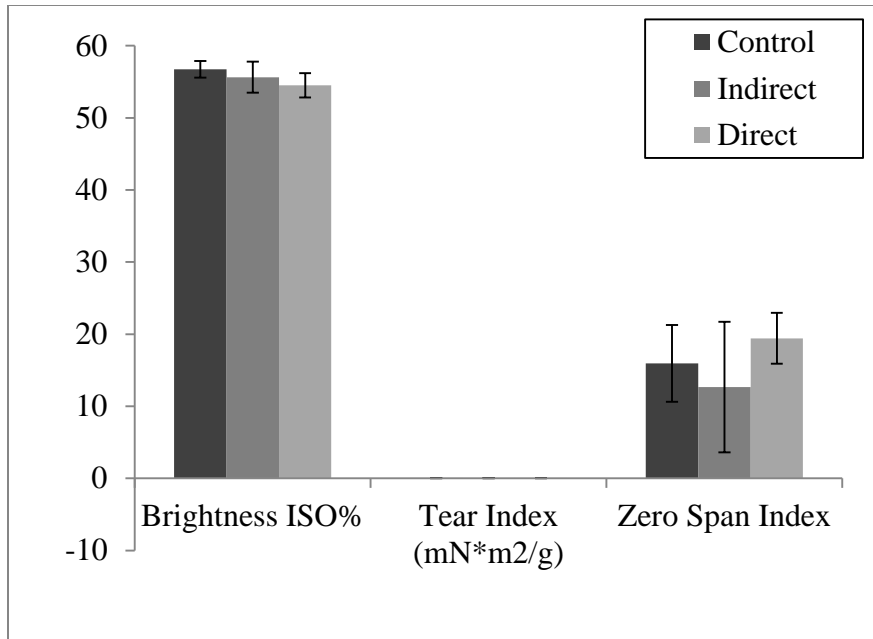


Figure 23. Effect of LPP on optical properties and mechanical strength of unprinted paper fiber.

there is a significant increase in the Total Dirt particle area when using the combined treatment method, as can be seen in Figure 22.

After analysis of the effect of LPP treatment on the optical properties of recycled paper, it was desired to analyze the effect on the strength properties as well. The LPP treatment has the potential to have a negative impact on the properties of the cellulose fibers independent of the deinking of the recycled paper. For example, oxidation of the paper fibers can cause yellowing and darkening of the recycled paper product. Additionally, the mechanical properties of the recycled paper are very important for many of the applications recycled paper is used for, so the effect of LPP treatment on the tear index and zero span index was evaluated for the recycled paper. From

Figure 23, it is apparent that there is an insignificant effect on the ISO% Brightness, tear index, and zero span index for the recycled paper, which suggests that

the LPP treatment does not have a significant effect on the macroscopic optical or mechanical properties of unprinted paper fibers.

4.3 Trial with Mixed Paper Sources

After showing that deinking of 100% hydrophilic inkjet ink could be improved through LPP treatment, it was desired to test the LPP treatment method for a mixed source of paper including both hydrophilic and hydrophobic inks. This was shown to be a very important step in the previous chapter, but it was not expected that the LPP treatment would have a negative affect hydrophobic inks since the mechanism is assumed to be coagulation of the hydrophilic inks through polymerization as theorized in previous work[80]. Because of this, the LPP treatment was used for a mixed source of paper that included 35% hydrophilic inkjet printed newsprint and 65% hydrophobic offset printed newsprint. From Figure 24, it is apparent that with mixed sources of paper the LPP treatment does not have a positive impact like what was seen with 100% hydrophilic inks. As was stated, this was an unexpected result based on the proposed mechanism. Due to these results, it was hypothesized that the LPP treatment has a negative effect on hydrophobic inks similar to what was seen with the lignosulfonate deinking experiments. To test this hypothesis, the LPP treatment was used for 100% hydrophobic offset ink, and as can be seen from Figure 25, it is apparent that the LPP treatment has a significant negative effect on hydrophobic inks. This is clearly the reason that the LPP treatment did not show an improvement in deinking with the mixed pulp. However, it was still not clear the reason why this was occurring. The original experiments with LPP treatment focused on ink and water systems without the presence of paper fibers, so it was hypothesized that the fiber system interfered with the coagulation mechanism seen in

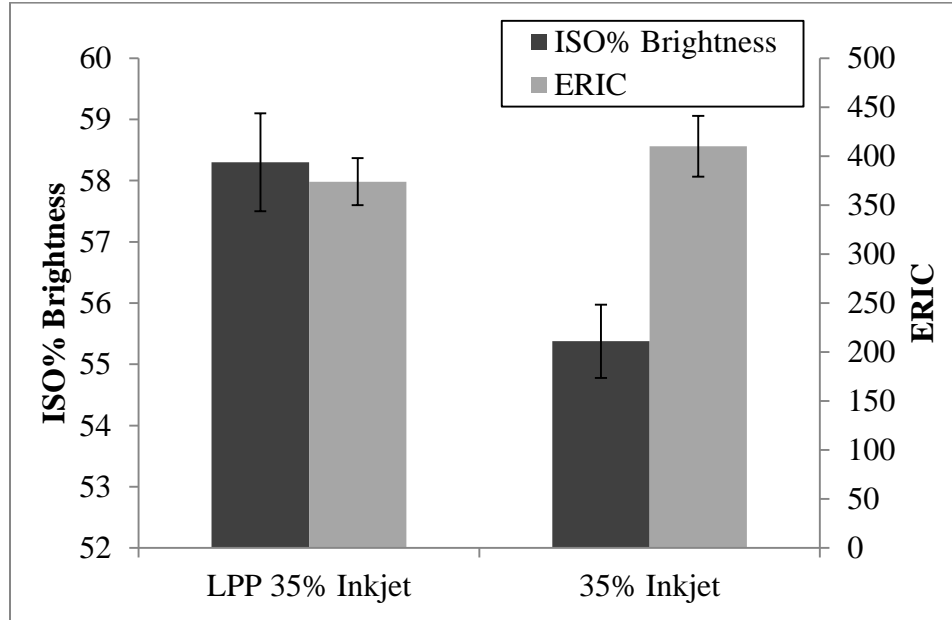


Figure 24. Effectiveness of deinking combined with LPP direct treatment on improving ISO% Brightness and ERIC for a mixed source of paper containing 35% inkjet printed newsprint and 65% offset printed newsprint.

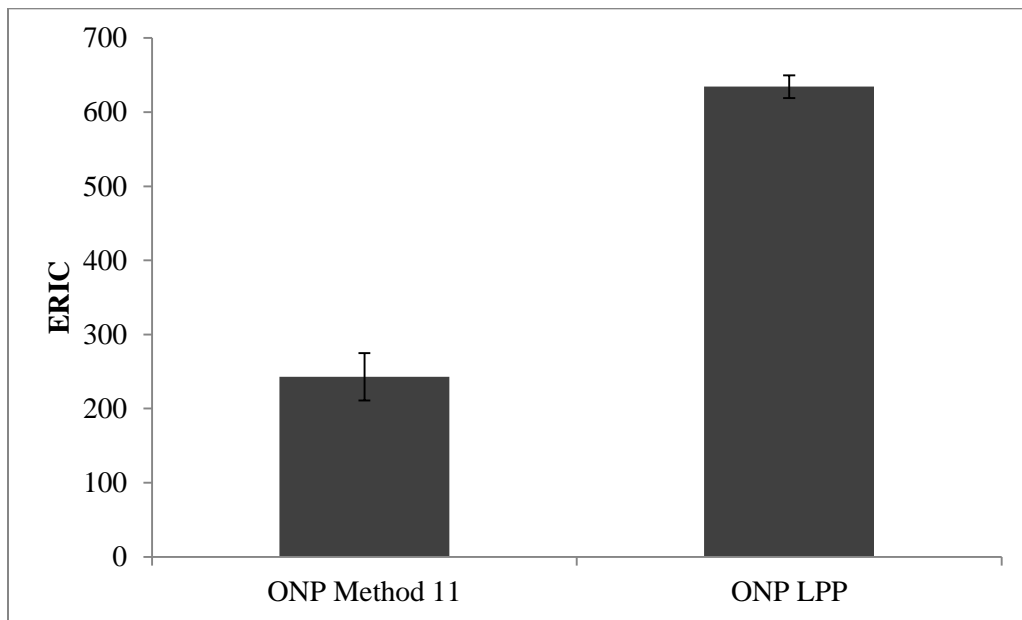


Figure 25. Effect of deinking combined with LPP direct treatment on hydrophobic offset newsprint compared to deinking with standard Method 11 deinking.

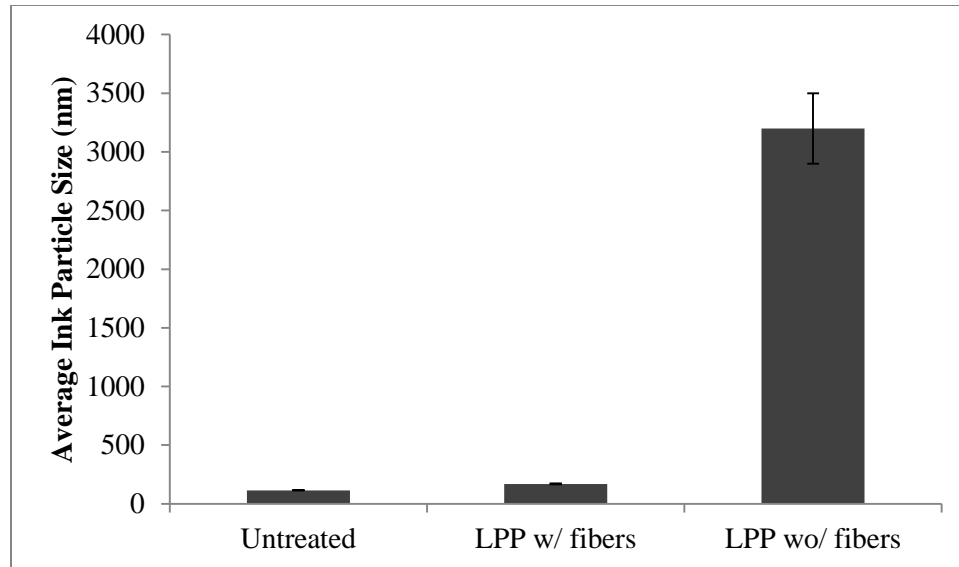


Figure 26. Effect of LPP direct treatment on the particle size of inkjet ink with and without the presence of fibers at a consistency of 0.5% measured by dynamic light scattering.

pure ink systems. To test this, the particle size of the ink was measured after LPP treatment with and without the presence of fibers. From Figure 26, it is apparent that the particle size increase with fibers present is negligible in comparison to the particle size increase in the pure ink system.

With this new information, it is apparent that the LPP treatment does not increase the particle size of the hydrophilic ink to an extent that could be removed with flotation as previously thought. This was perplexing because the LPP treatment was shown to significantly improve deinking of 100% hydrophilic ink trials. Since the particle size of the ink was not being increased, it was hypothesized that the LPP treatment was not improving the separation of hydrophilic inks. To test this hypothesis, the ISO brightness and ERIC of the rejects from flotation were evaluated for untreated and LPP filtrate treated pulps to determine if the amount of ink removed by flotation was increased

through treatment. As can be seen in Figure 27, there is not a significant difference in either the brightness or ERIC value for the reject of untreated and filtrate treated samples. Although there was not an improvement in the flotation separation of hydrophilic ink through LPP treatment, it is still unclear how the optical properties of the recycled paper could be improved through this treatment. Since the ink is not being removed by floatation, it must be removed in the filtrate of the pulp instead. Because of this, it was hypothesized that the LPP treatment improved detachment of ink or prevents redeposition similar to what was seen with the use of lignosulfonate during the deinking process. There are several possible reasons that this would occur. For example, the treatment method also results in dissolved copper, which has been shown in previous studies to compress the stabilizing polymer layer on the pigment surfaces[94]. This polymer layer is responsible for the hydrophilic nature of the ink, and it has been shown that the ink will reattach to the fiber surface during dewatering[37, 40]. A compressed polymer layer would minimize reattachment of the ink by making the ink particle less hydrophilic[94]. To test this hypothesis, the filtrate darkening for a 100% inkjet sample was analyzed with and without LPP direct treatment.

As can be seen in Figure 28, the filtrate darkening was increased by each of the treatment methods in this study showing that any ink that is removed from the paper surface by LPP treatment is transferred to the filtrate rather than removed by flotation. This may seem counterintuitive since it was shown that there was a slight increase in the particle size of the ink. However, the particle size increase of the ink was negligible in the presence of fibers and previous researchers have shown that the redeposition of ink during paper formation is due to adsorption rather than entrapment[38]. Because of this,

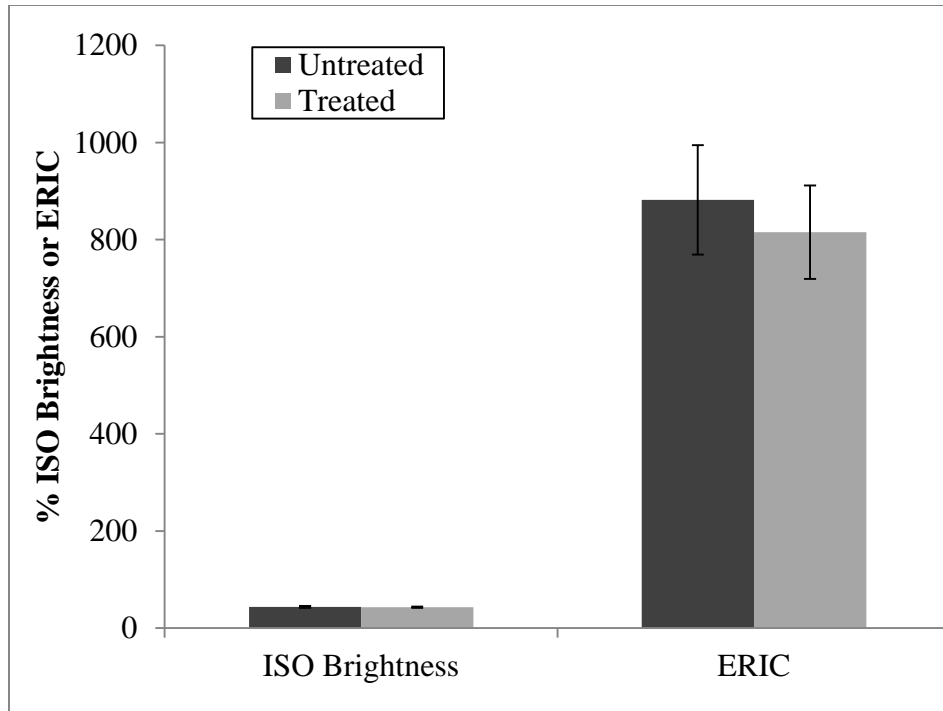


Figure 27. The ISO Brightness and ERIC of the reject from flotation are shown for untreated and direct treatment of 100% inkjet printed paper.

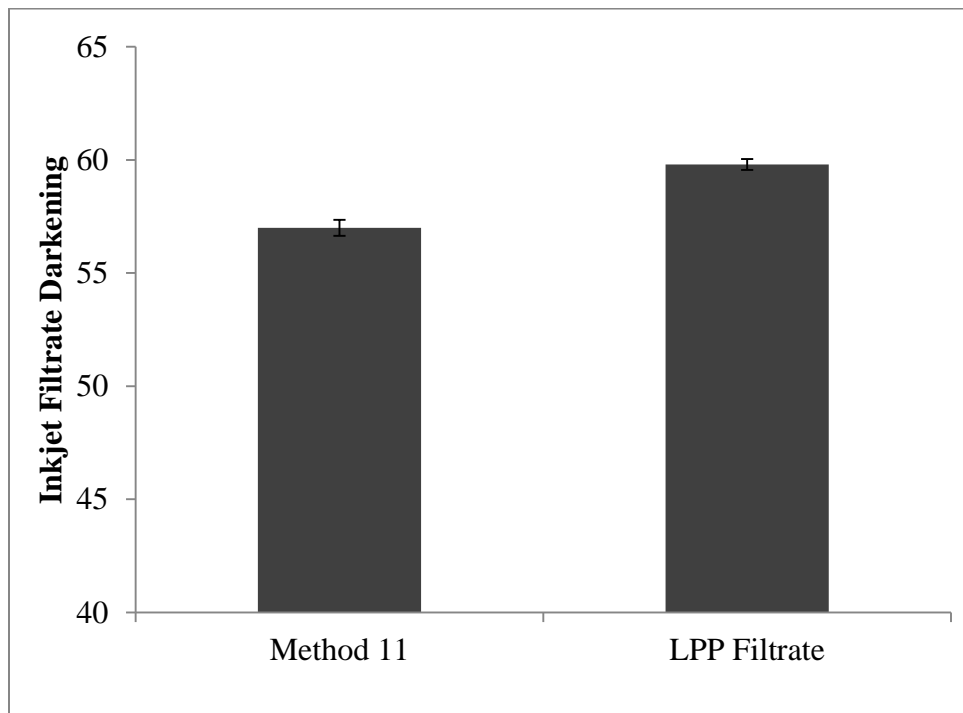


Figure 28. The filtrate darkening was compared for the reference Method 11 and filtrate treatment methods[93].

the small particle size increase would not be expected to influence the redeposition of the ink during formation, so it was concluded that the LPP treatment is able to increase the detachment or prevent redeposition of the ink in the system. There are several possible mechanisms that could be responsible for this observation. First, previous researchers have shown that the pressure waves caused by the treatment of pulp with a LPP treatment can cause ink particles to disperse[95]. Although this was shown to be positive in the previous research for detaching the ink, it is also likely that these pressure waves would cause ink particles to break up. Since hydrophobic inks are in the optimal size range for flotation, the reduction of particle size of these inks that could be caused by LPP would cause reduced removal by flotation resulting in more ink on both the recycled paper and in the filtrate. The second mechanism is preventing redeposition of the ink. A possible reason behind this improvement is the oxidation of the pigment surface by the LPP treatment. It has been previously shown that carbon black is readily oxidized through treatment with plasma producing surface groups such as hydroxyl, carboxylic, and carbonyl groups[96]. This oxidation will cause the pigment to become more hydrophilic and also significantly increase the surface charge of the ink in alkaline conditions. Both of these outcomes would explain the increase separation of hydrophilic inks in the filtrate as well as the negative effect on hydrophobic inks.

In previous research, it was found that the inclusion of 10% inkjet printed paper in the wastepaper stream was the upper limit for deinking mills due to an increase in filtrate darkening when deinking inkjet-printed paper[12]. Because of this, filtrate darkening is an important property for the deinkability of both flexographic and inkjet printed paper because increased filtrate darkening results in the recycling of higher concentrations of

ink in the recycling plant. If the ink is not removed by flotation, it will build up in the system and reduce the optical properties of the pulp as run time increases. The negative effect on filtrate darkening again shows that the treated inkjet and flexographic inks are not being removed by the flotation process even though there is a significant improvement in ink elimination and luminosity of the paper.

4.4 LPP Treatment Effect of Fiber Presence on Coagulation of Ink

It was shown in the previous section that the LPP treatment was not able to increase the particle size of hydrophilic ink when fibers were present. It is unclear why the presence of fibers would prevent the coagulation of the ink, but there are several possible explanations. First, it is possible that the coagulation seen in previous work is due to the dissolution of copper destabilizing the ink rather than polymerization, which has been shown to occur in previous research[94]. Additionally, previous researchers have shown that cellulose fibers are able to prevent coagulation of colloidal particles through electrostatic and steric interactions, which could be similar for inks[97]. In order to test if copper is responsible for the coagulation of the ink, the concentrations of metal ions commonly used for coagulation were investigated. From Figure 29, it is apparent that copper ions in the range of 0.0372-0.186 g/L also did not have a significant effect on the coagulation of hydrophilic pigmented ink. Finally, it was seen that increasing the temperature of the solution did not have a significant effect on the coagulation of hydrophilic ink.

From this analysis, it appears that increase in temperature was not the cause of increase in particle size seen in previous research as well as the improvements from LPP seen in the previous section. However, the effect of metal ion concentration was also

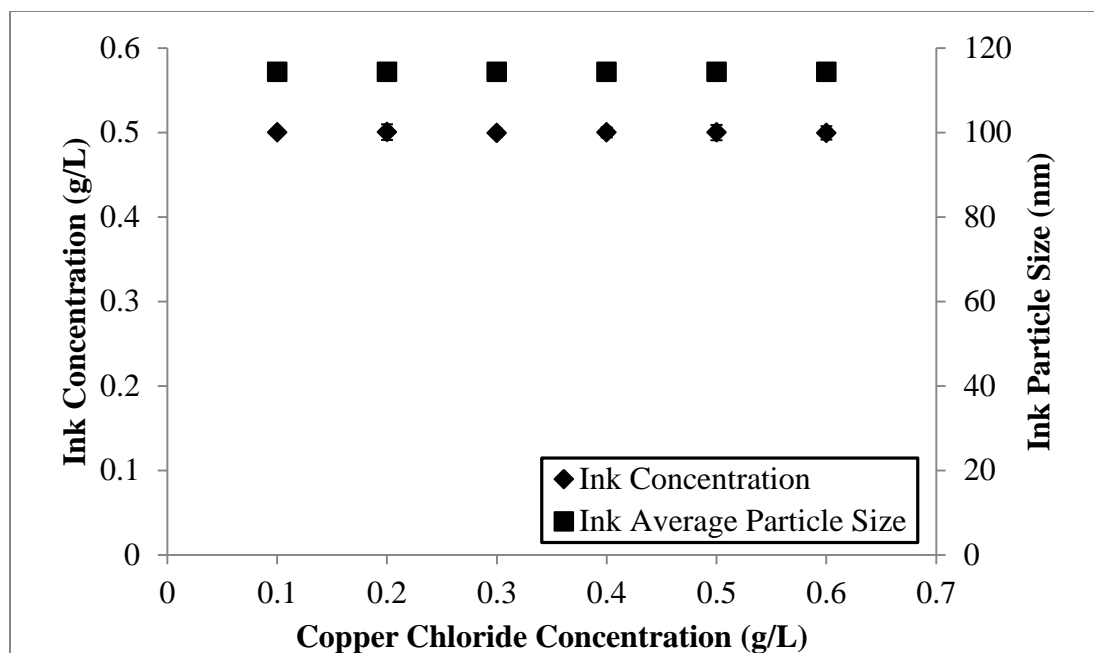


Figure 29. Effect of copper chloride concentration (g/L) on stability of pigmented inkjet ink at a concentration of 0.5 g/L.

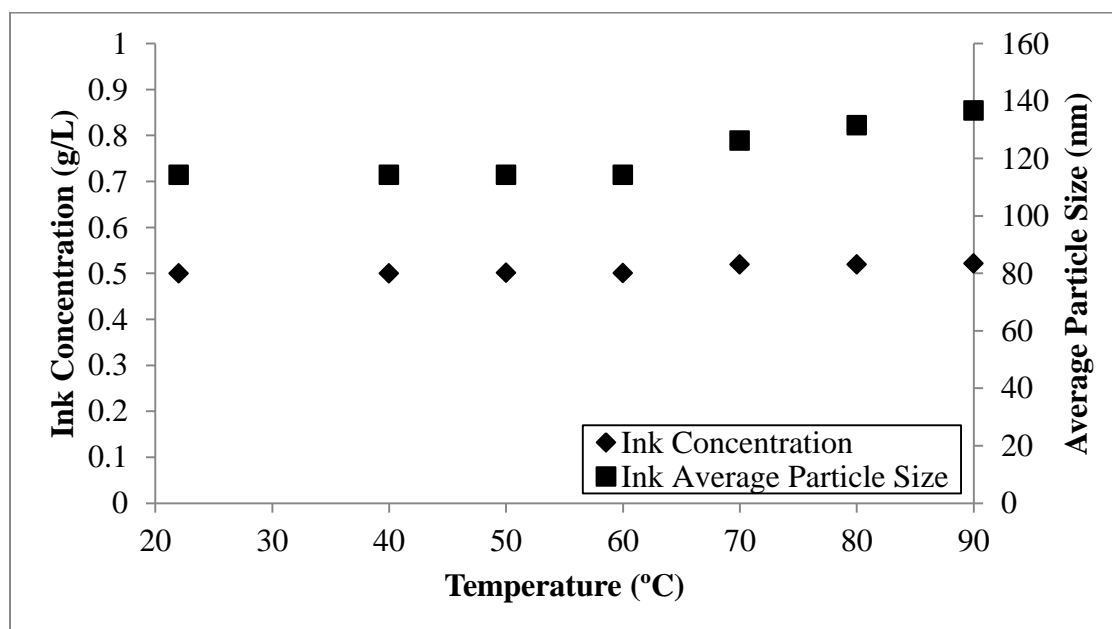


Figure 30. The effect of solution temperature on the coagulation of pigmented inkjet ink at a concentration of 0.5 g/L measured by UV/Vis absorbance and DLS particle size analysis.

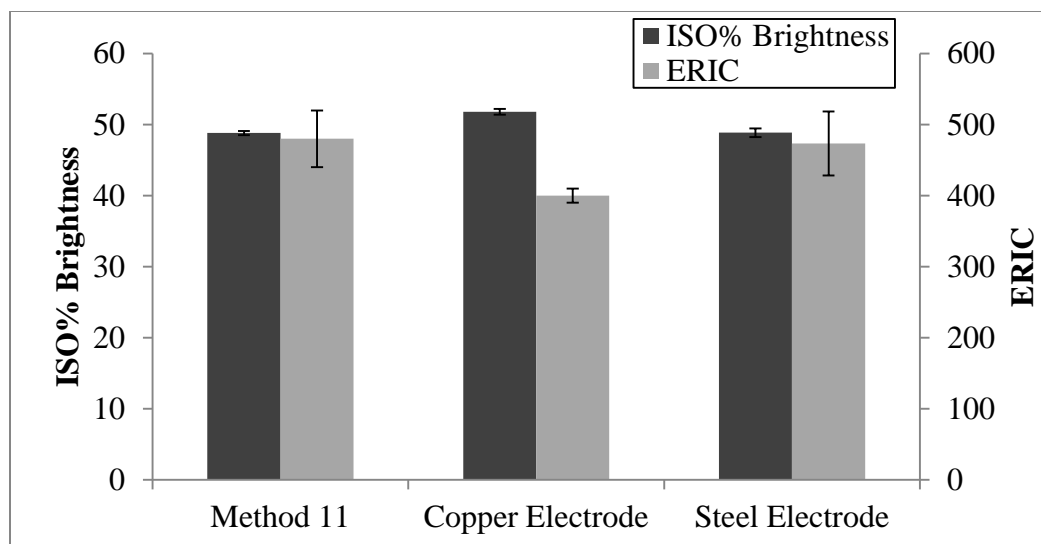


Figure 31. Data comparing the performance of copper and steel electrodes for direct LPP treatment.

evaluated in conjunction with temperature increases as would occur in LPP treatment, and it can be seen from Figure 30 that the combination of temperature increase and copper ion concentration has a significant effect on the coagulation of ink. Because of this, it is likely that the destabilization mechanism of LPP is increase in temperature and dissolution of copper ions of the solution, and that the destabilization also results in more hydrophobic ink particles, which are less likely to redeposit onto the hydrophilic paper fiber surface.

Additionally, the LPP parameters were investigated in the presence of fibers. A comparison between a copper and steel electrode was performed, and the results can be seen in Figure 31. From the data, it is apparent that copper electrodes have a significant improvement in the optical properties of the recycled inkjet paper. However, the steel electrodes had an insignificant impact on the optical properties of recycled inkjet paper. This reinforces the theory that the improvement in optical properties is due to dissolution

of copper and temperature increase causing the ink particles to become larger and more hydrophobic. A major issue with this method is the dissolution of copper ions and precipitates[98]. Through this treatment, dissolution of copper is inevitable due to the use of an electrochemical cell, and the copper electrode has been shown to be an important factor in these studies. There are many industries that use and discharge copper, but there are some significant environmental and health related concerns from these metals[99-102]. In general, it is necessary to remove heavy metal ions from the waste, which will dramatically increase cost requirements for this and similar methods[99-102].

From this analysis, it appears that copper has a significant role in the destabilization of ink as well as the increased removal of ink in the filtrate. This suggests that the coagulation of ink could be reduced by adding fibers due to the competitive adsorption of copper. Previous research on the destabilization of ink with copper ions showed that the dissolved copper precipitates on the ink surface reducing the stabilizing polymer layer and coagulating the ink[94]. If a large concentration of fiber is present along with the ink, the copper will deposit on both the fiber and ink reducing the coagulation of the ink significantly. Additionally, it is likely that the fiber will interfere with coagulation of colloidal particles similar to what was seen for microstickies in the paper industry[91].

CHAPTER 5: ADSORPTION DEINKING FOR DECREASED REDEPOSITION AND IMPROVED SEPARATION OF HYDROPHILIC INKS

The previous attempts in this research have both proven to be ineffective for hydrophobic inks, so it was desired to develop a method of separating hydrophilic ink without having a negative effect on deinking of hydrophobic ink. This led to the investigation of adsorption deinking for improved deinking of hydrophilic inks. Adsorption deinking uses adsorbent material to collect the ink during the deinking process, which would assist in both preventing redeposition as well as separating the ink. In adsorption deinking, the ink is removed by an adsorbent present in the pulping stage. This allows the ink to be removed during pulping to prevent redeposition of the ink. Additionally, the size and chemical nature of the adsorbent can be controlled to allow for improved separation after pulping either by flotation or screening. Additionally, adsorption deinking has previously been shown to be as effective as flotation for hydrophobic inks, so both hydrophilic and hydrophobic inks could be removed with the same separation process.

5.1 Experimental Procedures

5.1.1 Pulping Operation for Hydrophilic Inks Experiments

Inkjet printed newsprint was used in these experiments, which was printed at Georgia Tech using the procedure described previously. Additionally, three runs of each trial were performed for each experiment. A set of three filter pads was made from the pulp after each trial and ISO% Brightness and ERIC measurements were taken.

5.1.2 Adsorption Deinking with Polyacrylate Adsorbent

It was desired to do a proof of concept for adsorption deinking of hydrophilic inks, so a polymer adsorbent was selected to test the theory. The adsorbent that was tested was polyacrylate beads, and adsorption deinking was performed according to the procedure described in 5.1.1. Filter pads were produced after the adsorption deinking experiments, and the ERIC was measured for each of the sample runs.

5.1.3 Analysis of Multiple Adsorbents for Use in Adsorption Deinking Experiments

Adsorption deinking has not been performed on hydrophilic inks previously, so several adsorbents were selected. The adsorbents that were chosen to be analyzed were chitosan and talc. These adsorbents were analyzed to determine the adsorption capacity of hydrophilic inks. To do this, 0.5 grams of the ink solution (HP 60) was added to 1 liter of water. Then, 1 gram of the adsorbent material was added to the solution and continuously mixed in a closed container for 48 hours. The concentration of ink remaining in solution was measured using UV/Vis spectroscopy (Spectronic 601, Milton Roy, Ivyland, PA) at 300nm using a calibration curve for the ink. The adsorption capacity of polyacrylate was also analyzed in this experiment to clarify the results of the previous experiment.

5.1.4 Thermodynamics of Ink Adsorption onto Chitosan and Cellulose Fiber

The thermodynamic equilibrium isotherm and kinetics of adsorption were performed for both hydrophilic and hydrophobic inks in order to get a better understanding of the adsorption deinking process. For kinetics of adsorption for the hydrophilic ink (HP 60), 0.5 grams of ink was dissolved in 1 liter of water along with 1 grams of chitosan. The solution concentration was then measured every 30 minutes by

filtering a 3 mL aliquot of the solution through a 1 micron filter paper and analyzing the filtrate with UV/Vis. This was performed until the solution concentration was constant.

For the equilibrium isotherm of hydrophilic ink onto chitosan, the chitosan concentration was kept constant at 0.275 g/L, and the initial solution concentration was varied from 0.35 g/L to 0.5 g/L. Then, the solution was well mixed for 24 hours, filtered through a 1 micron filter paper, and the filtrate concentration was measured using UV/Vis at 300nm. Similarly, for the equilibrium isotherm for hydrophilic ink onto cellulose fiber, a pulp was prepared from unprinted newsprint at a consistency of 0.5%, and an ink solution was made with 1 mass% ink. Then, various ratios of these solutions were mixed ranging from 100-200 grams of pulp and 15-200 grams of ink. The samples were well mixed for 24 hours, and then, the solution concentration was then measured by centrifuging a sample from each trial for 2 hours at 2000 g's. The concentration of ink in the supernatant was measured using UV/Vis at 300nm.

Finally, the equilibrium isotherms of hydrophobic ink were determined for both chitosan and fiber. The hydrophobic ink was obtained from the Atlanta Journal Constitution. In order to disperse the ink into water, the ink was dried at 110°C and then ground to approximate the ink that would be in solution during deinking. The dried hydrophobic ink particles were then mixed in solution ranging from 0.001-0.011 g along with 0.01-0.1 g of chitosan and 200 mL of DI water or 200 g of 0.25% consistency, hyperwashed unprinted newsprint. The chitosan and fiber were screened out with a 1 mm screen and the solution concentration was measured using UV/Vis at 300nm.

5.1.5 Adsorption Deinking Experiments for Improved Pulping of Hydrophilic Inks

Pigment-based inkjet ink was used as the ink in this experiment and is the same as the ink used previously and was printed onto virgin newsprint at Georgia Tech. Pulp samples were taken after pulping as well as after flotation. An undeinked filter pad was made from the pulp taken after pulping, and a deinked filter pad, hand sheet, and filtrate darkening filter pad were made from the pulp sample taken after flotation. The filter pads and hand sheets were made according to INGEDE Method 1. Brightness, luminosity, color a^* , ink elimination, and filtrate darkening were measured for each of these samples using a Technidyne ColorTouch ISO (Technidyne; New Albany, IN, USA), and the total ink area for the hand sheets was measured using SpecScan 2002.

5.1.6 Testing of Adsorbent Material for Hydrophilic Inks

For this evaluation, 0.5 g of ink was added to 1 L of DI water. Chitosan was then added to this system at 1 g/L. The removal of ink over time was measured using UV/Vis Spectroscopy at a wavelength of 300 nm on 3 mL aliquots of the ink solution every 30 minutes.

5.1.7 Evaluation of Efficacy of Adsorption Deinking for Hydrophilic Inks

Deinkability tests were carried out with 100% pigmented inkjet printed newsprint. Deinking of each of the 100% inkjet-printed newsprint was performed by following INGEDE Method 11 as a standard. For the adsorption deinking experiments, chitosan was used as the adsorbent and was added at the beginning of pulping. The chitosan was attached to the surface of a polymer bead by heating. Then, 20% chitosan by fiber mass was added with the inkjet printed paper during the pulping step following the same procedure as Method 11. However, the chitosan was separated from the fibers after

pulping using a screen with openings of size 0.203 inches and no flotation was performed.

5.2 Selection of Adsorbent for Separation of Hydrophilic inks

Adsorption deinking is an interesting concept that has been investigated with significant success for hydrophobic inks, but has not been tested for use with hydrophilic inks[81]. The first and most important objective is to identify an adequate adsorbent for deinking. For the removal of hydrophobic inks, a nylon bead was used as an adsorbent[81]. Since nylon is relatively hydrophobic, the first attempt at adsorption deinking for hydrophilic inks was to select a hydrophilic polymer. The polymer that was selected was a polyacrylate resin as it was relatively easy to obtain in the size range desired for separation after adsorption deinking. The chemical structure of the polyacrylate is shown in Figure 32, and it is apparent that the structure is fairly hydrophilic which should allow for interactions between the ink and polymer. When looking at the results of the adsorption deinking experiments in Figure 33, it is apparent that the polymer beads led to only a slight increase in the removal of ink. However, it did not appear that the polymer was adsorbing any ink from visual inspection, so the adsorption

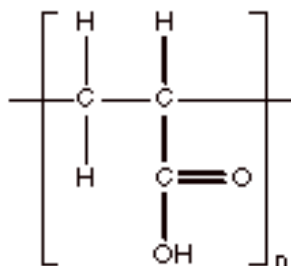


Figure 32. Polyacrylate chemical structure.

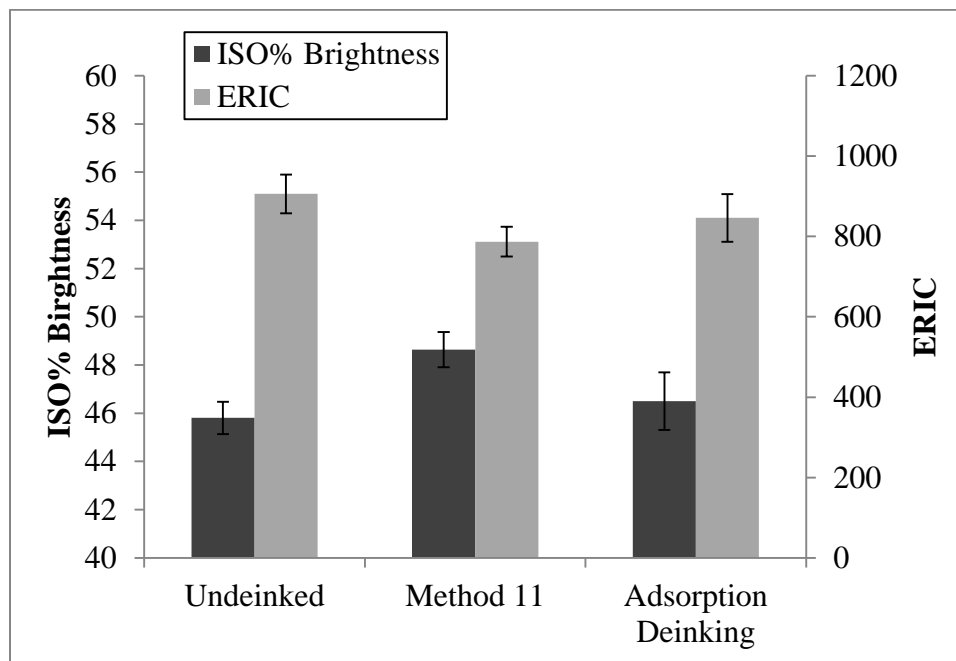


Figure 33. ISO% Brightness and ERIC measurements for adsorption with hydrophilic polymers with standard Method 11 Pulping.

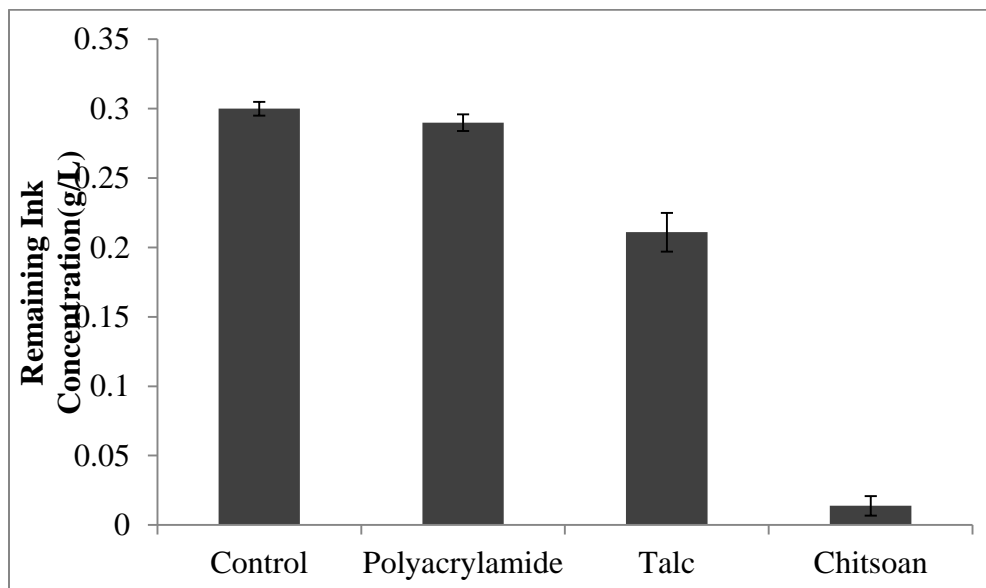


Figure 34. Adsorption performance of Talc and Chitsoan analyzed using UV/Vis absorbance at 300 nm without the presence of fibers. The adsorbents were compared to a control of diluted ink without an adsorbent present.

capacity of the polyacrylate was analyzed in an ink/water mixture. It is apparent from Figure 34 that there is an insignificant amount of ink being removed from the solution through adsorption. However, there was an improvement seen when using the polymer beads during pulping, which is perplexing given that adsorption of the ink is not occurring. A possible explanation of this comes from the results presented previously in this thesis. It was shown that the fiber-fiber interactions were necessary in order to detach the hydrophilic ink from the paper surface but also caused redeposition to occur for hydrophilic inks. Because of this, the use of the polymer beads could improve the detachment of the ink by introducing fiber-polymer interactions without increasing redeposition of the ink as well.

Because the initial trial selecting a hydrophilic adsorbent without using any theory did not show adsorption of the hydrophilic ink as was expected, the theory of adhesion between ink and cellulose fiber during the printing process was used to select additional adsorbents to test. It has been previously shown that the attractive forces between hydrophilic inks and the cellulose fiber are hydrogen bonding, which has led to ink

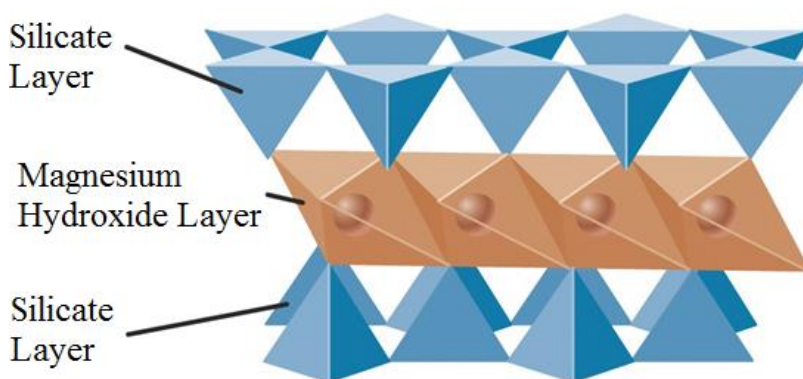


Figure 35. Structure of talc with a magnesium hydroxide layer between two silicate layers having an overall composition of $Mg_3Si_4O_{10}(OH)_2$.

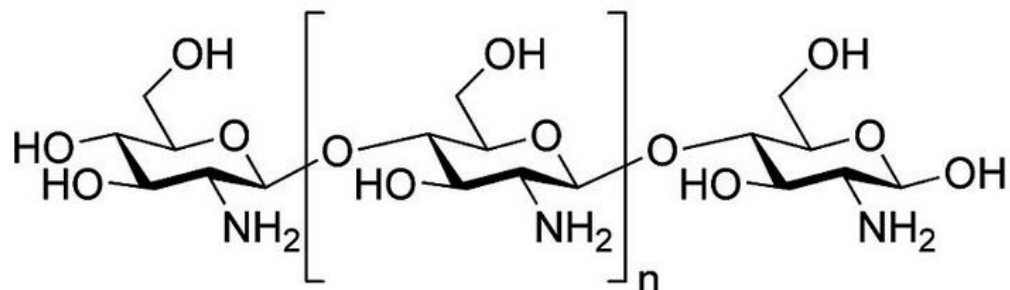


Figure 36. Chitosan chemical structure

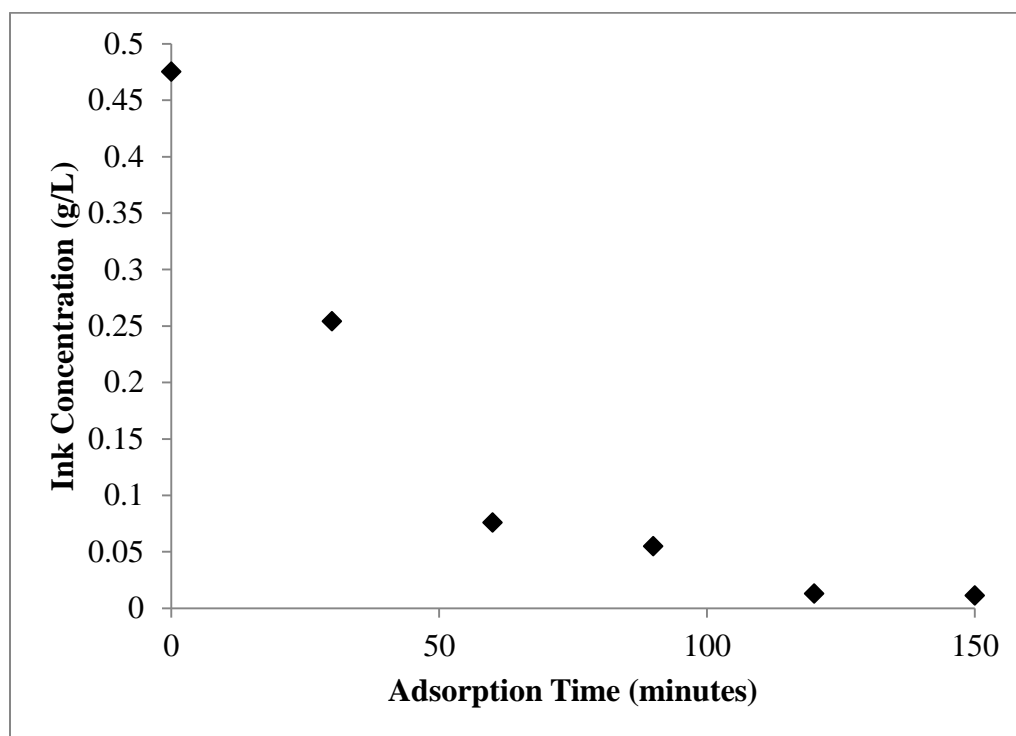


Figure 37. Time dependent adsorption of pigmented inkjet ink using chitosan.

manufacturers formulating ink to further take advantage of hydrogen bonding for improved print quality. Because of this, the next adsorbents were selected based on their potential to hydrogen bond with the hydrophilic ink during the deinking process. This led to the investigation of talc and chitosan as possible adsorbents for the hydrophilic inks.

Talc is a mineral that is commonly used in the pulp and paper industry to adsorb other contaminants. It has both hydrophobic and hydrophilic sites including hydrogen bonding hydroxyl sites as can be seen in the talc structure shown in Figure 35. Similarly, chitosan is a common industrial adsorbent material and has multiple hydroxyl as well as methylamine groups as can be seen in the chemical structure shown in Figure 36. In order to test these adsorbent materials for the removal of hydrophilic inks, the adsorption capacity was determined for each of the adsorbents in an ink/water solution before adding cellulose fibers. The results of this analysis are shown in Figure 34, and it is apparent that talc was able to adsorb a small amount of ink and chitosan was able to significantly reduce the concentration of ink in solution by adsorption. It is interesting to consider why chitosan would perform significantly better than both talc and the hydrophilic polymer previously tested. A very likely theory is the dissociation of the hydroxyl and carboxyl groups due to pH of the solution. The deinking procedures are performed at alkaline pH (~10-11), so it is likely that the hydroxyl and carboxyl groups would be dissociate preventing hydrogen bonding. However, chitosan as an amine group that is also able to hydrogen bond but will not dissociate allowing for attraction between the adsorbent and ink at any pH. Additionally, the pKa of hydroxyl and carboxyl groups are ~16 and ~7, respectively, so it would be expected that at the same pH the carboxylic acid

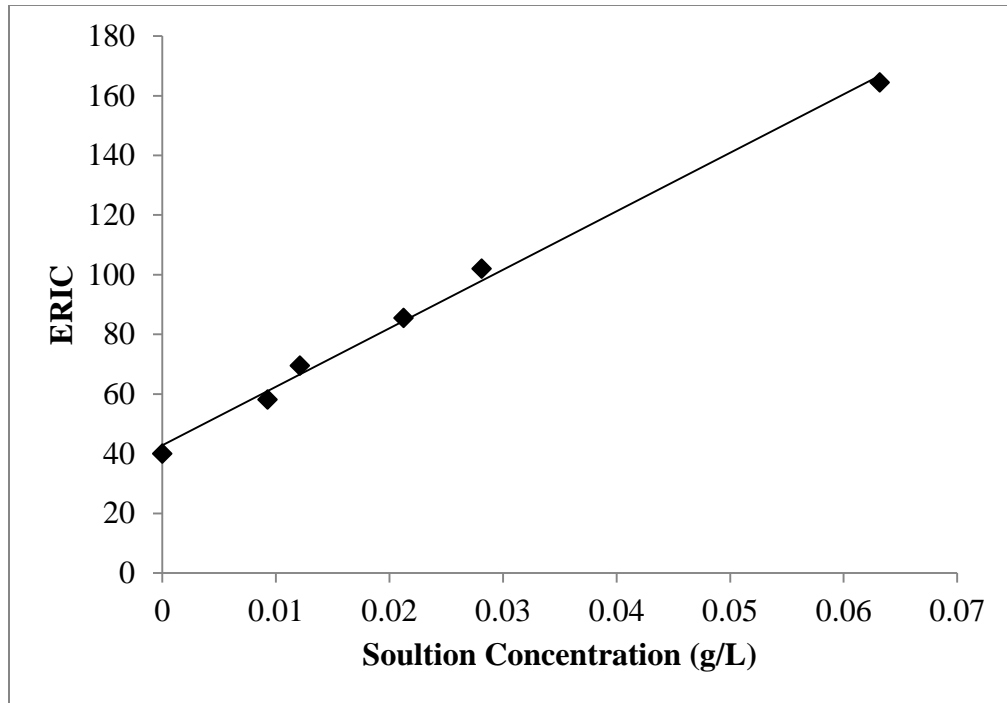


Figure 38. Deposition of hydrophilic ink onto cellulose fiber during the paper formation process as a function of solution ink concentration.

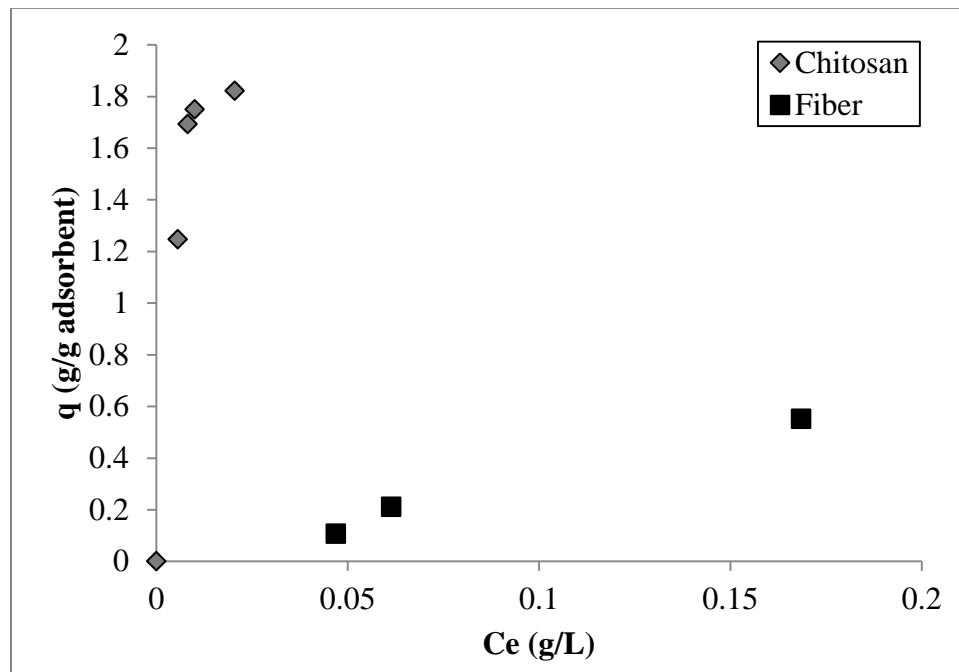


Figure 39. Equilibrium adsorption isotherm of inkjet ink onto chitosan.

groups in the hydrophilic polymer would be significantly more dissociated than the hydroxyl groups in the talc allowing for a larger adsorption capacity for talc. This led to the selection of chitosan as the adsorbent for the deinking studies. Before performing deinking with the chitosan, the time scale of adsorption, adsorption equilibrium isotherm, and relationship between solution concentration and redeposition during paper formation were analyzed.

First, as can be seen in Figure 37, chitosan is able to adsorb pigmented inkjet inks and can remove a significant portion of the ink from solution in the time frame of pulping. However, the ink removal was only about 50% for pigmented inks during the time frame of deinking, which suggests adsorption deinking can be improved if an adsorbent with faster kinetics is used. When looking at Figure 38, it is apparent that the redeposition of ink during paper formation is linearly related to the amount of ink redeposited, so any reduction in the solution ink concentration will have a positive effect on decreasing redeposition of ink during paper formation. Additionally, it can be seen in Figure 39 that adsorption of inkjet ink onto chitosan and fiber displays an isotherm similar to the Langmuir isotherm with a maximum adsorption of around 1.7 g/g chitosan and 0.8 g/g fiber. When compared to the equilibrium adsorption onto paper fiber, it is apparent that the capacity of chitosan is significantly greater than the capacity of fiber, which is a positive quality for the adsorption deinking study as at any solution concentration it would be expected that the portion of ink on the chitosan would be greater than the portion of ink on the fiber. It was shown previously that, if all of the ink is detached from the cellulose, the solution concentration would be 0.02 g/L. When looking at Figure 39, it is apparent that this is in region of saturated adsorption for

chitosan but not for the cellulose fiber. Because of this, decreasing the solution concentration in the region will allow for improved selectivity for adsorption of ink onto chitosan over fiber.

5.3 Analysis of Adsorption Deinking for Deinking of Hydrophilic Inks

After selection of chitosan as a reasonable adsorbent to test adsorption deinking of hydrophilic inks, it was necessary to test the efficacy of adsorption deinking in the presence of paper fibers. Although positive results were seen for the ink/water system, it cannot be assumed that ink removal from solution will behave the same as ink removal during pulping in the presence of paper fiber. However, the chitosan was first tested to ensure that it would not affect the optical measurement methods used in these experiments as a small portion of the chitosan could remain in the pulp. From Figure 40, it is apparent that chitosan has an insignificant effect on the ISO% Brightness and ERIC readings over the range of 0-10% chitosan by mass.

Next, deinking was performed with a variation of INGEDE Method 11. As can be seen in Figure 41, chitosan was not able to effectively remove pigmented from the pulp during pulping when following the pulping procedure for Method 11. In fact, the ISO brightness and ERIC for the pulp deinked with chitosan was not significantly different from undeinked pulp from Method 11. This suggests that there is not sufficient interaction between the detached ink and the chitosan. A possible reason for this is that a consistency of 15% is used for pulping. At 15% consistency, the majority of the water in the system is bound to the fiber surfaces, which may prevent the attachment of ink to the chitosan surface. Because of this, the consistency of the pulp was reduced to 10% to facilitate transfer of the ink into the liquid phase, which will more closely approximate

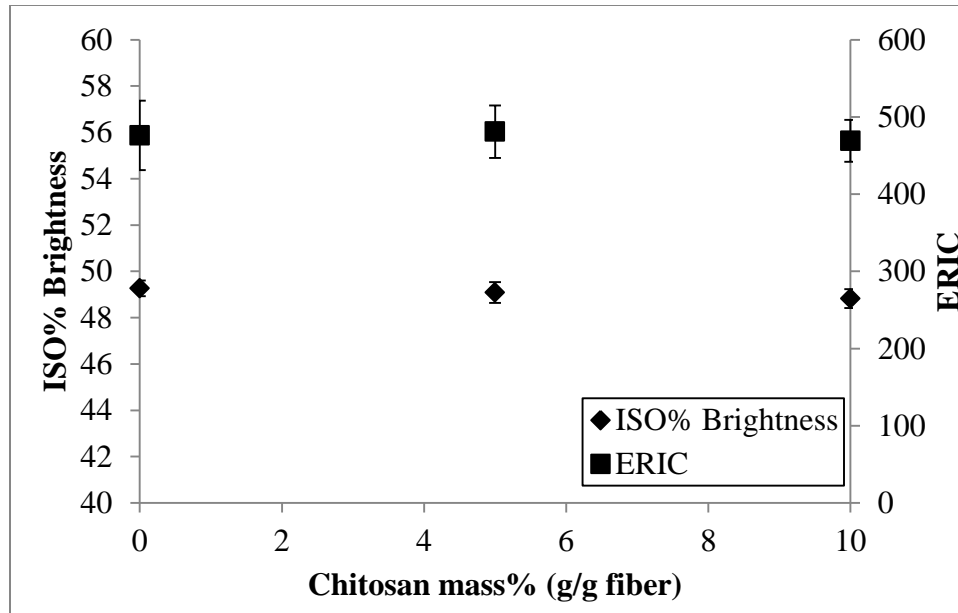


Figure 40. Effect of chitosan on filter pad ISO% Brightness over the range of 0-10 mass%.

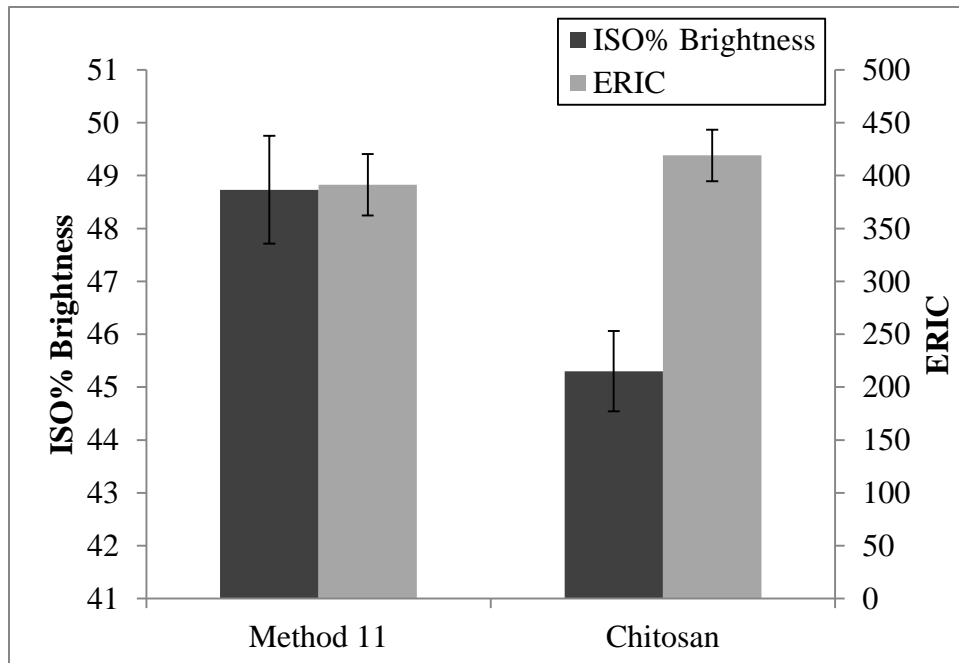


Figure 41. Impact of chitosan adsorption deinking on the ISO% Brightness and ERIC of pigmented inks pulped at 15% consistency.

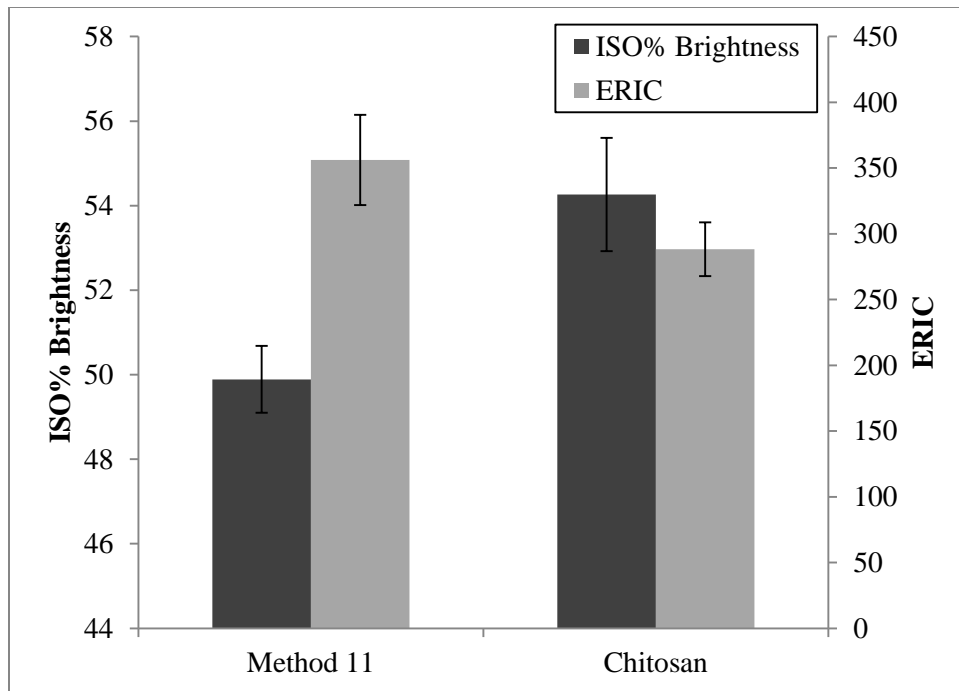


Figure 42. Impact of chitosan adsorption deinking on the ISO% Brightness and ERIC of pigmented inks pulped at 10% consistency.

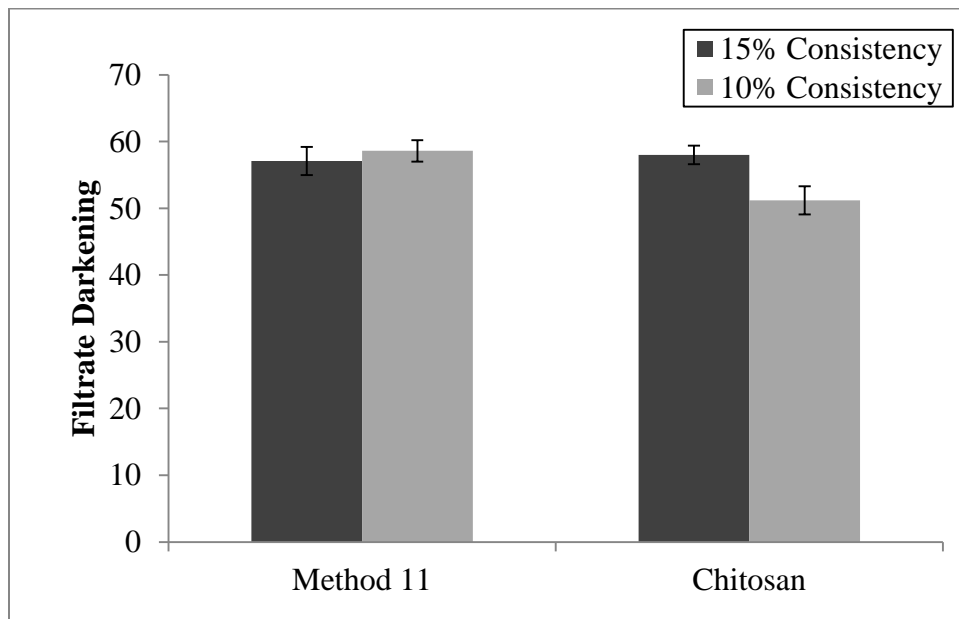


Figure 43. Filtrate darkening of pigmented inks when using chitosan for adsorption deinking at 10% consistency.

the removal of ink from an ink/water solution. From Figure 42, it is evident that at 10% consistency, the adsorption deinking has a much higher efficacy.

It is also important to look at the filtrate darkening to get an indication if ink is being removed by adsorption deinking. For inkjet and flexographic inks, the filtrate darkening is the most important issue in improving deinkability[12]. From Figure 43, it is apparent that the filtrate darkening is improved when using adsorption deinking at 10% consistency for pigmented inks. However, when compared to the filtrate darkening for hydrophobic inks, there is still a significant amount of ink remaining in the pulp. For hydrophobic inks, the filtrate darkening is less than 18 compared to around 50 for the adsorption deinking. Although this illustrates that there is a long way to go in using adsorption deinking to remove hydrophilic inks, it also shows that there is significant room for improvement since the remaining ink can be prevented from redeposition on to the paper. This could likely be done by improving the adsorption deinking parameters as the current study only did a proof of study. Also, it was shown that the kinetics of chitosan took significantly longer than the time used for deinking, so using an adsorbent with faster kinetics may be able to improve adsorption deinking. Additionally, although the filtrate darkening was not improved to the threshold range as defined by INGEDE (<18 points), the improvement is still useful because in industrial settings there will not be 100% inkjet and flexographic printed paper.

CHAPTER 6: CONCLUSIONS AND RECOMMENDATIONS

The deinking of hydrophilic inks has been studied for several decades now, but there is yet to be a complete solution for deinking of these inks. This study has provided some insights into the path that needs to be taken in order to effectively recycling paper printed with hydrophilic inks such as those used for flexographic and inkjet printing. First, fundamental understanding of the ink behavior during pulping was improved through the use of modified deinking methods. It was shown that there is a portion of hydrophilic ink that remains attached to the recycle paper fiber during standard deinking conditions, which is contrary to previous theories[12, 38, 40, 91]. Through these methods, it was shown that almost half of the ink present at the beginning of deinking operations was still present at the completion of the deinking process due to redeposition and bounded ink. Additionally, it was shown that about 1/3 of the remaining ink came from “bound” ink that could not be detached during the recycling operations with the remaining 2/3 coming from redeposited ink. Due to the high percentage of ink that is redeposited, subsequent studies focused on preventing redeposition of the hydrophilic inks as well as improving the separation process.

The modifications used to determine the proportion of ink that redeposit used a lignosulfonate as a dispersant to prevent redeposition of the ink, which is one of the goals of this study. Because of this, lignosulfonate was evaluated as a deinking chemical for these inks. The lignosulfonate works as expected with hydrophilic inks causing them to accumulate in the filtrate after formation of the paper product; however, when mixed sources of paper were used that included hydrophilic inks, it was clearly shown that

lignosulfonate was not effective at deinking these systems causing decreased removal of ink by flotation. It was later shown to be due to significantly declined deinking of hydrophobic inks with lignosulfonate, which could be due to either redeposition or decreased detachment of these inks.

Because of this, it was essential to investigate methods of increasing the particle size of hydrophilic inks while also improving separation of the ink by flotation or other methods. Liquid phase plasma treatment has been shown to effectively coagulate ink without fibers and was shown to significantly improve the optical properties of recycled inkjet printed paper, but it was also shown that this treatment is likely inducing coagulation through the dissolution of copper ions rather than the polymerization mechanism suggested previously.

The liquid phase plasma treatment process has been shown to improve the luminosity, and ink elimination of recycled 100% flexographic and inkjet newsprint while having a negligible effect on the color a^* , which was in the optimal range for ONP as defined by INGEDE. Additionally, the liquid plasma treatment improved the ink area for inkjet printed paper and had an insignificant effect on the ink area of flexographic printed paper. The filtrate treatment method was the most effective at improving these properties. However, the filtrate darkening for the pulp was increased by all of the liquid plasma treatment methods, and the brightness and ERIC of the reject from flotation was insignificantly different for untreated and filtrate treated inkjet pulps. Because of this result, it is unlikely that the increase in brightness, luminosity, ink elimination, and Total Dirt particle area is due to increased removal of ink by flotation after treatment. Instead, the ink detachment from the fiber surface was assisted by the plasma treatment, which

would end up in the filtrate of the paper making process. This may be due to the increase in particle size of the ink from the treatment or the increase in hydrophobicity of the ink particle from the addition of copper ions from the treatment.

It was shown that both lignosulfonate and LPP treatment cause significant negative effects on hydrophobic inks, and it is likely that this occurs due to dispersion of hydrophobic ink increasing redeposition and preventing separation by flotation. Because of this, a new deinking method was evaluated that has previously been shown to be effective for hydrophobic inks. The new method is called adsorption deinking and has been adapted to deink hydrophilic inks. Adsorption deinking was shown to improve the optical properties of inkjet printed paper without the use of flotation or storage. Preliminary results also suggest that this deinking method will be applicable for a wide range of ink. This may be an applicable technology in the future to mitigate the effect of ever increasing printing of hydrophilic inks on commercial scales.

Chitosan was selected as an adsorbent to show that pigmented inkjet and flexographic inks can be effectively adsorbed in the time frame of pulping due to the hydrogen bonding potential of chitosan. Chitosan was able to effectively remove pigmented inkjet ink from an ink/water solution, which should closely approximate the structure of ink during pulping. However, the ink removal after 30 minutes of adsorption was only about 50% for pigmented ink. Even though there was not complete removal of ink from an ink/water solution in the timeframe of pulping, it was still shown that using chitosan during pulping for adsorption deinking is able to improve ink removal for a 100% inkjet printed newsprint when the consistency is adjusted to 10%.

Similar to other researchers, the complexity of the problems caused by deinking of hydrophilic inks was seen in this study. However, a novel deinking method has been developed with that has the possibility of making a large impact on the paper recycling industry as the proportion of inkjet printing increases for industrial scale operations. A proof of concept was performed for adsorption deinking of hydrophilic inks. However, significant improvements may be made in regards to the adsorbent used as well as the separation method for the adsorbents. Ideally, adsorption deinking could be used as a deinking additive during pulping that could be removed through flotation to combine removal of both hydrophobic and hydrophilic ink.

There is a significant amount of work that could be done to improve the adsorption deinking process and deinking of hydrophilic inks in general. The most obvious improvement can be seen in the process parameters used for adsorption deinking. This study has shown a proof of concept that adsorption deinking can remove hydrophilic inks from pulp as well as hydrophobic inks. However, it was shown that there is a significant amount of ink remaining in solution at the end of the adsorption deinking with chitosan, which suggests that increasing the loading of chitosan would dramatically improve the deinkability of these inks both by preventing redeposition during the deinking process as well as preventing redeposition during formation and removing ink from the filtrate to stop build up in deinking mills. There are also likely other parts of the process that could be improved such as deinking time and temperature.

This leads to the second study that should be conducted regarding adsorption deinking. The proof of concept demonstrated that hydrophilic ink could be removed from pulp using adsorption deinking. However, it was not determined that adsorption

deinking could remove hydrophobic and hydrophilic ink simultaneously. This should be able to be done by using both nylon and chitosan as adsorbents to remove each respective ink, so it is not anticipated that chitosan adsorption would interfere with the nylon adsorption. However, throughout this study, there were examples of treatments that were not expected to interfere with the deinking of hydrophobic inks that actually had significant negative effects. Because of this, it will be necessary to do a combined deinking trial.

The third area of adsorption deinking that can be improved is the kinetics of the adsorbent. It was shown that the time required to reach equilibrium for chitosan was over double the time frame of deinking, so it is unlikely that equilibrium is reached during the deinking process. This would lead to significant waste if the adsorbent is not recyclable due to incomplete adsorption. This could be overcome by adding more adsorbent material, but again this would lead to waste. In order to improve the kinetics of the adsorbent, it would be necessary to look at the effect of surface chemistry on the adsorption kinetics. Although a thorough investigation was not conducted, it was shown that adsorbents with carboxyl and hydroxyl groups showed a lower adsorption capacity than chitosan with amine groups present. Printing inks are formulated to bond to cellulose fiber through hydrogen bonding, so it makes sense that adsorption of the ink to an adsorbent could be achieved in a similar manner. However, under alkaline conditions similar to those used in deinking, the carboxyl and hydroxyl groups will be dissociated whereas the amine group will still be able to hydrogen bond with the ink. Because of this, improving the adsorbent may rely on basic surface groups rather than acidic acid groups.

Finally, an interesting finding of this study was that hydrophilic ink is not completely dispersed into solution during deinking, which was previously assumed to be true. Although there is more ink present on the paper due to redeposition, there is a significant amount of ink that is not detached during standard deinking operations. Because of this, future research may focus on improving this detachment in addition to preventing redeposition of hydrophilic inks.

REFERENCES

- [1] A. Villanueva and H. Wenzel, "Paper waste - recycling, incineration or landfilling? A review of existing life cycle assessments," *Waste Manag*, vol. 27, pp. S29-46, 2007.
- [2] M. M. Nazhad and L. Paszner, "Fundamentals of strength loss in recycled paper," *Tappi J.*, vol. 77, pp. 171-9, 1994.
- [3] I. Cabalova, F. Kacik, A. Geffert, and D. Kacikova, "The Effects of Paper Recycling and its Environmental Impact," in *Environmental Management in Practice*, D. E. Broniewicz, Ed., ed InTech, 2011.
- [4] J. O'Brien, "U.S. Paper Industry Sets 50 Percent Recovered Goal for 2000," *PAPER AGE*, vol. 110, p. 30, 1994.
- [5] R. Miranda, E. Bobu, H. Grossmann, B. Stawicki, and A. Blanco, "Factors influencing a higher use of recovered paper in the European paper industry," *Cellul. Chem. Technol.*, vol. 44, pp. 419-430, 2010.
- [6] "CEPI Annual Statistics 2011," E. R. P. Association, Ed., ed. http://www.erpa.info/download/CEPI_annual_statistics_2011.pdf, 2012.
- [7] A. Blanco, C. Negro, C. Monte, E. Fuente, and J. Tijero, "The challenges of sustainable papermaking," *Environ. Sci. Technol.*, vol. 38, pp. 414A-420A, 2004.
- [8] W. E. Josephson and G. A. Krishnagopalan, "Deinking of furnishes containing flexographically printed old newsprint," *Appita J.*, vol. 58, pp. 470-474, 2005.
- [9] H. Aksoy, S. Yilmaz, M. Celik, D. Yuzbasioglu, and F. Unal, "Genotoxicity study in lymphocytes of offset printing workers," *J. Appl. Toxicol.*, vol. 26, pp. 10-15, 2006.
- [10] I. J. Philippe, "Effective flotation deinking of ONP with increasing levels of flexographic print," 1996, pp. 805-810.
- [11] A. Fischer, "Inkjet Heads Towards Ecological Dead End," *Recycling M@gazine*, pp. 8-15, 2008.
- [12] Y. Ben and G. Dorris, "Is deinkability of inkjet prints an issue?," *Tappi J.*, vol. 10, pp. 17-27, 2011.
- [13] C. P. Klass, "Will ink jet papers become a deinking nightmare?," *Paper360°*, vol. 4, pp. 10-13, 2009.

- [14] A. Fischer and Is, *What makes a digital print recyclable? Results of a European survey*, 2006.
- [15] B. Carre and L. Magnin, "Digital prints: a survey of the various deinkability behaviours," 2004, pp. 159-169.
- [16] K. T. Hodgson, "Deinking considerations with flexographic wastepaper," *Prog. Pap. Recycl.*, vol. 5, pp. 71-74, 1996.
- [17] G. M. Dorris and Y. Ben, "Is there an easy solution to the deinking of water-based inks?," *PTS-Symp.*, vol. PTS-SY 01/98, pp. 9E/1-9E/10, 1998.
- [18] P. Sabin, B. Benjelloun-Miayah, and M. Delmas, "Offset printing inks based on rapeseed oil and sunflower oil. Part II: varnish and ink formulation," *J. Am. Oil Chem. Soc.*, vol. 74, pp. 1227-1233, 1997.
- [19] J. Moynihan, "Offset Printing Inks," United States of America Patent, 1985.
- [20] J. Moynihan, "Printing Ink," United States of America Patent, 1983.
- [21] V. Husovska, "INVESTIGATION OF RECYCLED PAPER DEINKING MECHANISMS " Doctor of Philosophy, Paper Engineering, Chemical Engineering, and Imaging, West Michigan University, 2013.
- [22] E. O. Fernandez and K. T. Hodgson, "Stabilization mechanisms of water-based newsprint inks," *J. Pulp Pap. Sci.*, vol. 22, pp. J452-J456, 1996.
- [23] A. Shemi, "Flexographic Deinking with Electric Field Technology by Destabilization and Flotation," Master of Science, Chemical and Biomolecular Engineering, Georgia Institute of Technology, 2008.
- [24] S. Ahmed. (2007, *Technology of Printing Inks*.
- [25] B. Carre, L. Magnin, G. Galland, and Y. Vernac, "Deinking difficulties related to ink formulation, printing process, and type of paper," *Tappi J.*, vol. 83, p. 60, 2000.
- [26] T. Eriksson, J. Borjesson, and F. Tjerneld, "Mechanism of surfactant effect in enzymatic hydrolysis of lignocellulose," *Enzyme Microb. Technol.*, vol. 31, pp. 353-364, 2002.
- [27] B. Carre, L. Magnin, and G. Galland, "Printing processes and deinkability," 2004, pp. 28-44.
- [28] P. Oittinen and H. Saarelma, "Electronic Printing," in *Papermaking Science and Technology, Book 7: Recycled Fiber and Deinking*, F. Ltd., Ed., ed Helsinki, 2000, pp. 173-191.

- [29] A. M. Faul, "Quality requirements in graphic paper recycling," *Cellul. Chem. Technol.*, vol. 44, pp. 451-460, 2010.
- [30] A. Faul and J. Oberndorfer, "The challenge to deink inkjet prints together with recovered paper from households," presented at the TAPPI PEERS Conference, Norfolk, VA, 2010.
- [31] K. Kemppainen, M. Korkko, and J. Niinimäki, "Fractional pulping of toner and pigment-based inkjet ink printed papers - ink and dirt behavior," *BioResources*, vol. 6, pp. 2977-2989, 2011.
- [32] N. Dumea, Z. Lado, and E. Poppel, "Differences in the recycling behaviour of paper printed by various techniques," *Cellul. Chem. Technol.*, vol. 43, pp. 57-64, 2009.
- [33] G. Galland, B. Carre, X. Rousset, and Y. Vernac, "Deinking difficulties related to waterbased ink printed papers. Analysis of redeposition phenomena," 2000, pp. 503-516.
- [34] A. P. H. Davies and S. R. Duke, "Visualizations of offset and flexographic inks at bubble surfaces," *Tappi J.*, vol. 1, pp. 41-47, 2002.
- [35] A. P. H. Davies, "Visualizations of flexographic and offset ink at bubble surfaces", MS Thesis, Auburn University, 2000.
- [36] *Fundamentals and numerical modeling of unit operations in the forest products industries*. New York: American Institute of Chemical Engineers, 2000.
- [37] B. Chabot, C. Daneault, M. M. Sain, and G. M. Dorris, "The adverse role of fibers during the flotation of flexographic inks," *Pulp Pap. Can.*, vol. 98, pp. 115-118, 120-121, 1997.
- [38] Y. Ben and G. M. Dorris, "Irreversible ink redeposition during re-pulping. Part II. ONP/OMG furnishes," *J. Pulp Pap. Sci.*, vol. 26, pp. 289-293, 2000.
- [39] G. M. Dorris and N. Nguyen, "Flotation of model inks. Part II: Flexo ink dispersions without fibers," *J. Pulp Pap. Sci.*, vol. 21, pp. J55-J62, 1995.
- [40] Y. Ben and R. Pelton, "Retention and dislodgement of flexographic ink in a fibrous mat during thickening and displacement washing," *J. Pulp Pap. Sci.*, vol. 22, pp. J411-J419, 1996.
- [41] M. Bhattacharyya, H. T. Ng, L. Mittelstadt, and E. G. Hanson, "Neutral deinking chemistry for digital and offset prints," *Abstracts of Papers of the American Chemical Society*, vol. 241, Mar 27 2011.

- [42] G. Galland, Y. Vernac, B. Carre, and X. Rousset, "Effect of pulping conditions on ink redeposition and ink removal when recycling water-based ink printed papers," 2001, pp. 585-626.
- [43] N. Miller, "Sustainable Digital Print Solutions: Deinkable Inks, Papers, and Optimizes Deinking Processes," presented at the PaperCon, St. Louis, Missouri, 2009.
- [44] K. Kemppainen, M. Korkko, and J. Niinimaki, "Fractional pulping of toner and pigment-based inkjet ink printed papers - ink and dirt behavior," *BioResources*, vol. 6, pp. 2977-2989, 2011.
- [45] K. Nyman and T. Hakala, "Decolorization of inkjet ink and deinking of inkjet-printed paper with laccase-mediator system," *BioResources*, vol. 6, pp. 1336-1350, 2011.
- [46] J. S. Hsieh, "Deinking of inkjet digital nonimpact printing," *Tappi J.*, vol. 11, pp. 9-15, 2012.
- [47] H. T. Ng, M. K. Bhattacharyya, L. S. Mittelstadt, E. G. Hanson, and Sist, *Deinking of HP Digital Commercial Prints: Effect of Chemicals and Their Loadings on Deinkability*, 2009.
- [48] S. Ciampa, "The Effects of Repulping Variables on Deinking of Flexographic Inks," M.Sc. Thesis, Department of Paper and Printing Science and Engineering, Western Michigan University, Kalamazoo, Michigan, 1995.
- [49] L. S. Mittelstadt, H. T. Ng, M. K. Bhattacharyya, W. Zhang, and E. G. Hanson, "Alkaline deinking of digital prints with HEMA chemistry," 2011, pp. ENVR-144.
- [50] C. P. J. Bennington and M. H. Wang, "A kinetic model of ink detachment in the re-pulper," *J. Pulp Pap. Sci.*, vol. 27, pp. 347-352, 2001.
- [51] B. Fabry, B. Carre, and P. Cremon, "Pulping optimisation: effect of pulping parameters on defibering, ink detachment, and ink removal," presented at the 6th Research Forum on Recycling, Magog, Canada, 2001.
- [52] M. Korkko, D. Bussini, O. Laitinen, G. Elegir, and J. Niinimaki, "True-neutral fractional deinking for flexographic and offset newsprints," *Appita Annu. Conf. Exhib.*, vol. 65th, pp. 23-30, 2011.
- [53] K. Kemppainen, M. Korkko, A. Haapala, M. Illikainen, and J. Niinimaki, "BENEFITS OF FRACTIONATION DURING PULPING IN DEINKING," presented at the TAPPI PEERS, Norfolk, VA, 2010.
- [54] P. Tervola, J. Gullichsen, K. Henricson, P. Tech Assoc, and I. N. D. Paper, "A MATHEMATICAL-MODEL OF FRACTIONAL PULP WASHING AND

- APPLICATIONS IN A BLEACH PLANT," in *1993 Pulping Conference, Books 1-3*, ed Atlanta: Tappi Press, 1993, pp. 151-154.
- [55] G. Galland, Y. Vernac, and B. Carre, "The advantages of combining neutral and alkaline deinking. Part I. Comparison of deinking of offset and flexo printed paper," *Pulp Pap. Can.*, vol. 98, pp. 46-49, 1997.
- [56] O. U. Heise, J. P. Unwin, J. H. Klungness, W. G. Fineran, Jr., M. Sykes, and S. Abubakr, "Industrial scaleup of enzyme-enhanced deinking of nonimpact printed toners," *Tappi J.*, vol. 79, pp. 207-12, 1996.
- [57] P. Bajpai, "Application of Enzymes in the Pulp and Paper Industry," *Biotechnol. Prog.*, vol. 15, pp. 147-157, 1999.
- [58] T. W. Jeffries, J. H. Klungness, M. S. Sykes, and K. R. Rutledge-Cropsey, "Comparison of enzyme-enhanced with conventional deinking of xerographic and laser-printed paper," *Tappi J.*, vol. 77, pp. 173-9, 1994.
- [59] A. Das, T. Paul, S. K. Halder, A. Jana, C. Maity, P. K. Das Mohapatra, B. R. Pati, and K. C. Mondal, "Production of cellulolytic enzymes by *Aspergillus fumigatus* ABK9 in wheat bran-rice straw mixed substrate and use of cocktail enzymes for deinking of waste office paper pulp," *Bioresour. Technol.*, vol. 128, pp. 290-296, 2013.
- [60] T. W. Jeffries, R. N. Patel, M. S. Sykes, and J. Klungness, "Enzymic solutions to enhance bonding, bleaching and contaminant removal," *Mater. Res. Soc. Symp. Proc.*, vol. 266, pp. 277-87, 1992.
- [61] N. K. Bhardwaj, P. Bajpai, and P. K. Bajpai, "Use of enzymes in modification of fibers for improved beatability," *J. Biotechnol.*, vol. 51, pp. 21-26, 1996.
- [62] P. Bajpai and P. K. Bajpai, "Application of xylanases in prebleaching of bamboo kraft pulp," *Tappi J.*, vol. 79, pp. 225-30, 1996.
- [63] V. Piyush, N. K. Bhardwaj, and S. P. Singh, "Improvement in pulp dewatering through cellulases," *IPPTA*, vol. 25, pp. 105-108, 2013.
- [64] E. Bobu, T. Moraru, and V. I. Popa, "Papermaking potential improvement of secondary fibers by enzyme treatment," *Cellul. Chem. Technol.*, vol. 37, pp. 305-313, 2003.
- [65] N. K. Bhardwaj, P. Bajpai, and P. K. Bajpai, "Enhancement of strength and drainage of secondary fibers," *Appita J.*, vol. 50, pp. 230-232, 1997.
- [66] D. Y. Prasad, "enzymic deinking of laser and xerographic office wastes," *Appita J.*, vol. 46, pp. 289-92, 1993.

- [67] M. Ratto, A. Kantelinen, M. Bailey, and L. Viikari, "Potential of enzymes for wood debarking," *Tappi J.*, vol. 76, pp. 125-8, 1993.
- [68] K. Liu, G. Zhao, B. He, L. Chen, and L. Huang, "Immobilization of lipase on chitosan beads for removal of pitch particles from whitewater during papermaking," *BioResources*, vol. 7, pp. 5460-5468, 9 pp., 2012.
- [69] E. Dube, F. Shareck, Y. Hurtubise, M. Beauregard, and C. Daneault, "Enzyme-based approaches for pitch control in thermomechanical pulping of softwood and pitch removal in process water," *J. Chem. Technol. Biotechnol.*, vol. 83, pp. 1261-1266, 2008.
- [70] C. L. Wiatr, "Application of multiple enzyme blend to control industrial slime," CA2001540A1, 1990.
- [71] C. K. Lee, D. Ibrahim, and I. Che Omar, "Enzymatic deinking of various types of waste paper: Efficiency and characteristics," *Process Biochem. (Oxford, U. K.)*, vol. 48, pp. 299-305, 2013.
- [72] M. Korkko, D. Bussini, O. Laitinen, G. Elegir, and J. Niinimaki, "True-neutral fractional deinking for flexographic and offset newsprints," *Appita Journal*, vol. 65, pp. 71-77, Jan-Mar 2012.
- [73] M. K. Bhattacharyya, H. T. Ng, L. S. Mittelstadt, and E. G. Hanson, "Deinking of digital prints: effect of near-neutral deinking chemistry on deinkability," *J. Imaging Sci. Technol.*, vol. 56, pp. 060503/1-060503/5, 2012.
- [74] E. Bobu and F. Ciolacu, "EVALUATION OF NEUTRAL DEINKING METHODS IN PROCESSING DIFFERENT PRINTED PAPERS," *Cellulose Chemistry and Technology*, vol. 42, pp. 403-412, Jul-Aug 2008.
- [75] H. Morrow, B. Horacek, K. M. Hale, and S. Rosencrance, "True-Neutral Deinking," *PAPER AGE*, vol. 121, pp. 34-35, 2005.
- [76] E. Nicodimos and D. Haynes, "Introduction of Sodium Sulfite Free Neutral Deinking," presented at the PEERS 2011, Portland, OR, 2011.
- [77] J. Gao, "A novel technique for wastewater treatment by contact glow-discharge electrolysis," *Pak. J. Biol. Sci.*, vol. 9, pp. 323-329, 2006.
- [78] J. Gao, D. Ma, X. Guo, A. Wang, Y. Fu, J. Wu, and W. Yang, "Degradation of anionic dye eosin by glow discharge electrolysis plasma," *Plasma Sci. Technol. (Hefei, China)*, vol. 10, pp. 422-427, 2008.
- [79] Y.-g. He, G. Li, C. Yang, F. Yang, X.-q. Yu, and X. Bai, "The research of plasma induced polymerization of (2-methacryloyloxyethyl) trimethyl ammonium chloride," *Gaofenzi Cailiao Kexue Yu Gongcheng*, vol. 23, pp. 41-44, 2007.

- [80] A. T. Jordan, J. S. Hsieh, and D. T. Lee, "Purification of inkjet ink from water using liquid phase, electric discharge polymerization and cellulosic membrane filtration," *Water Science & Technology*, vol. 68, 2013.
- [81] T. Handke, T. Schrunner, and H. Grossmann, "Adsorption deinking: a new approach for higher energy efficiencies in paper recycling," *Prof. Papermaking*, vol. 9, pp. 32-37, 2012.
- [82] S. D. Jenkins and W. G. Westwater, "Cleaning Apparatus," United States Patent, 2011.
- [83] "INGEDE Method 2: Measurement of optical characteristics of pulps and filtrates from deinking processes," *International Association of the Deinking Industry*, 2011.
- [84] B. D. Jordan and S. J. Popson, "Measuring the concentration of residual ink in recycled newsprint," *Kami Parupu Gijutsu Taimusu*, vol. 42, pp. 13-19, 1999.
- [85] "INGEDE Method 1: Test Sheet Preparation of Pulps and Filtrates from Deinking Processes," *International Association of the Deinking Industry*, 2007.
- [86] A. Faul and H. J. Putz, "Scoring deinkability," *Prog. Pap. Recycl.*, vol. 18, pp. 17-23, 2009.
- [87] "INGEDE Method 11: Assessment of Print Product Recyclability," *International Association of the Deinking Industry*, 2012.
- [88] C. Ackermann, H. J. Putz, and L. Gottsching, "DEINKABILITY OF WATERBORNE FLEXO INKS BY FLOTATION," *Pulp & Paper-Canada*, vol. 95, pp. 28-33, Aug 1994.
- [89] B. D. Krafton, P. Tech Assoc, and I. N. D. Paper, "THE BENEFITS OF HIGH CONSISTENCY VS LOW CONSISTENCY PULPING OF OCC GRADE FURNISH FOR QUALITY, YIELD, AND OVERALL SYSTEM COSTS," in *1993 Pulping Conference, Books 1-3*, ed, 1993, pp. 223-231.
- [90] C. Ackermann, H. J. Putz, and L. Goettsching, "Deinkability of waterborne flexo inks by flotation," *Pulp Pap. Can.*, vol. 95, pp. 28-33, 1994.
- [91] V. Alesse, G. Belardi, C. Cozza, N. Shehu, and V. Koch, "Deinking recycled paper with a high flexographic ink content," *Tappi J.*, vol. 84, p. 44, 2001.
- [92] L. Gottsching, H. J. Putz, P. Tech Assoc, and I. N. D. Paper, "CURRENT RESEARCH ACTIVITIES ON WASTE PAPER RECYCLING AT THE IFP," in *1994 Recycling Symposium*, ed, 1994, pp. 207-224.
- [93] D. T. Lee and J. S. Hsieh, "Liquid phase plasma treatment for improved detachment of pigmented inkjet printed paper," *Tappi J.*, vol. 13, pp. 9-14, 2014.

- [94] E. O. Fernandez and K. T. Hodgson, "Deinking flexographic-printed papers: Destabilization of flexographic ink dispersions with copper compounds," *Prog. Pap. Recycl.*, vol. 12, pp. 9-15, 2013.
- [95] S. Banerjee, "Spark-induced agglomeration of aqueous polymeric suspensions," *J. Colloid Interface Sci.*, vol. 292, pp. 595-597, 2005.
- [96] M. S. Shafeeyan, W. M. A. W. Daud, A. Houshmand, and A. Shamiri, "A review on surface modification of activated carbon for carbon dioxide adsorption," *J. Anal. Appl. Pyrolysis*, vol. 89, pp. 143-151, 2010.
- [97] S. N. Patel and S. Banerjee, "Deposition of hot-melt and wax on surfaces," *Tappi J.*, vol. 82, pp. 99-103, 1999.
- [98] A. Shemi and J. S. Hsieh, "Electroflotation Combined with Flotation Deinking of Flexographic Newsprint," *Industrial & Engineering Chemistry Research*, vol. 49, pp. 2380-2387, 2010.
- [99] K. Dermentzis, A. Christoforidis, and E. Valsamidou, "Removal of nickel, copper, zinc and chromium from synthetic and industrial wastewater by electrocoagulation," *Int. J. Environ. Sci.*, vol. 1, pp. 697-710, 2011.
- [100] T. Javed, F. A. Awan, M. Arshad, A. Mashiatullah, F. J. Iftikhar, and S. N. Khan, "Removal of cadmium, copper, lead and zinc from simulated industrial effluents using silica powder," *Nucleus (Karachi, Pak.)*, vol. 50, pp. 135-140, 2013.
- [101] P. O. Fatoba, A. O. Adepoju, and G. A. Okewole, "Heavy metal accumulation in the fruits of Tomato and Okra irrigated with industrial waste effluents," *J. Ind. Pollut. Control*, vol. 28, pp. 103-107, 2012.
- [102] M. S. Sultana, U. Kulsum, A. Shakila, and M. S. Islam, "Toxic metal contamination on the river near industrial area of Dhaka," *Univers. J. Environ. Res. Technol.*, vol. 2, pp. 56-64, 2012.