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FLOTATION DEINKING OF OLD NEWSPRINT USING POLY(DIALLYLMETHYLAMMONIUM CHLORIDE) AS A SINGLE DEINKING AGENT

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ABSTRACT

Flotation deinking of old newsprint (ONP) using polydiallyldimethylammonium chloride (polyDADMAC) as the only deinking agent was studied. The results demonstrate that polyDADMAC can neutralize dissolved anionics to form small particles. These small particles, together with ink, filler, and fines, strongly adsorbed onto air bubble surfaces and functioned as particle foaming agents. Therefore, no conventional surfactant was needed during flotation. An unexpected benefit using polyDADMAC as a single flotation agent was much higher ink, ash, and anionic trash removal during flotation than that achieved with traditional fatty acid/calcium systems. This single flotation agent can be used in acidic, neutral, and alkaline deinking processes.

Keywords

Flotation deinking, cationic polymers, polyDADMAC, brightness, charge neutralization, old newsprint.

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INTRODUCTION

A number of processes including screening, cleaning, washing, and flotation (1-6) are currently used for ink removal from waste papers. Flotation has been used for over 100 years in mineral separation and has been successfully employed in deinking for several decades (7). Collector and foaming agents are two important chemicals among other chemicals used in flotation deinking. The collector can adsorb preferentially to the surface of the solid to render it hydrophobic or aggregate the small particles to reasonable sizes for flotation, and foaming agents can adsorb on air bubble surfaces to stabilize foam for ink removal.

Many different surfactants and collectors have been developed or studied for flotation deinking of old newsprint (3, 4, 8-10). The most common chemical commercially used in current flotation deinking of ONP is calcium soap of fatty acid. One of the problems associated with fatty acid/calcium systems is the deposition and scaling of calcium on deinking equipment and paper machines. To overcome the disadvantages of calcium soap of fatty acid, many different nonionic surfactants have been developed. However, some problems, such as surfactant carry over to a paper machine, water pollution by using surfactant, and fiber-fiber bonding reduction are also associated with these surfactant systems.

Cationic polymers as coagulants for treating wastewater from deinking plants have been utilized to assist in the solid/liquid separation, providing charge neutralization and efficient solids removal. The use of hydrophilic dispersion polymers for the clarification of deinking process waters was disclosed in U.S. Patents 5,750,034 and 6,019,904, respectively (11,12). However, no report that uses a cationic polymer or copolymer as a single flotation deinking agent can be found in the literature. This study presents some results using polyDADMAC as a single flotation deinking agent for ONP at different conditions. It was found that a cationic polymer, particularly polyDADMAC, is a very effective flotation agent for ONP deinking. Possible mechanisms for the ink and trash removal are discussed.

EXPERIMENTAL

Materials

Low-molecular-weight polydiallyldimethylammonium chloride (polyDADMAC, 20% solid, Aldrich) was used as the deinking agent. Low-charge-density and medium-high-molecular-weight cationic polyacrylamide (Perol® 175, Allieds Colloid) and polyemine-P (Aldrich) were used as received.

The Wall Street Journal and *The Atlanta Journal Constitution* were used as ONPs in this study. Both newspapers were two to three months old. Some local advertisement flyers, such as The Chronicle of Higher Education and Atlanta's Creative Loafing were also used as comparisons. *The Wall Street Journal* is one of the most widely circulated newspapers in the United States, with production of approximately 200,000 tons per year. Ash level of this newspaper is usually quite low (less than 5%), and it is usually printed by the offset process (6). The papers were first cut into 0.5 cm slips in width by a paper shredder and then pulped at a pH of 10 and a consistency of 8% (on an o.d. paper basis) without adding any chemicals except sodium hydroxide. Repulping of the newspapers was carried out in the LAMORT Repulper (made in France) under temperatures of 40-50°C for 25 min.

Flotation

The flotation of the pulp was performed in the WEMCO Laboratory Flotation cell (Sacramento, California, U.S.A.). The cell uses a motor to drive a variable-speed rotor between 300 to 3300 rpm. The pulp consistency for flotation deinking was 1%, and the pH was adjusted by sodium hydroxide or diluted sulfuric acid. Air was injected through the rotor at an airflow rate of 15 standard liters per minute (SLPM) and was mixed with diluted pulp slurry to generate air bubbles. As the foam reached the top of the 4.0 L flotation cell, it was removed with a flat metal plate. Flotation continued for 10 minutes at a rotor speed of 900 rpm under room temperature. Different amounts of polyDADMAC were added either in a single step prior to flotation or continuously during a flotation run using a metering pump.

Preparation of handsheets

Pulp samples were taken before and after flotation for sheetmaking. The handsheets were formed from 300 mL samples of the flotation feed and accept using a 15cm Büchner funnel according to TAPPI Standard Method T 218 om-91. The handsheets were pressed and dried according to TAPPI Standard Method T 218 om-91.

Brightness Measurement

Brightness of the handsheets was measured according to TAPPI Standard Method T 452 om-92 using a Shimadzu UV-VIS spectrophotometer (UV-160A). Five replicate brightness measurements on both sides of the standard handsheet were made for each sample. Only the mean value of top-bottom brightness of handsheets will be reported as an average.

Zeta Potential Measurement

Zeta potential of fiber slurry was measured by the Magendans SZP 04 Zeta Potential (MUTEK, Germany), and the zeta potential of fines was measured by a Malvern Zetasizer 3000 at a stationary position. The pH for all samples was adjusted by sodium hydroxide and diluted sulfuric acid. The zeta potentials of both pulp fibers and filtrated fines before the flotation deinking process were measured under room temperature.

RESULTS AND DISCUSSION

1. Effectiveness of polyDADMAC

The effectiveness of polyDADMAC as a single deinking agent in the flotation deinking process of ONP at pH 8.7 at room temperature is shown in Fig. 1. The brightness gain after flotation was in the range of 10 to 15% ISO (International Organization for Standardization) for all samples. Fig. 2 shows the effect of polyDADMAC concentration on the brightness gain of the handsheets.

It was observed that adding 10-20 ppm polyDADMAC in the flotation slurry caused significant foaming and the foam was stable during the flotation deinking process. Forming ability tests indicated that foam stability was affected by the concentration of polyDADMAC under both alkaline and weak acidic conditions. It was found that the froth stability increased with the increase in polyDADMAC concentration. An excessive dosage above 20 ppm had no addition effect on the ink-removal efficiency, but higher concentrations of polyDADMAC generated too much foam, resulting in higher water and fiber losses. The higher water and fiber losses caused by increased foam have been studied (13,14), and it is believed that physical entrapment of water and fibers in the froth is the major reason for the high fiber loss.

2. Comparison with fatty acid calcium system

To compare the results obtained using a polyDADMAC single system with other commercially avaliable systems, flotation deinking with fatty acid calcium salt was carried out under the condition of pH 10 at room temperature. Fig. 3 shows that the brightness of handsheets increases as the total amount of calcium soap of fatty acid (the weight ratio of sodium oleate to calcium chloride was 1:2) is increased. The maximum value was obtained in the vicinity of 150 ppm of sodium oleate. Fig. 4 presents the comparison of brightness of the handsheets prepared using a polyDADMAC system and fatty acid/calcium system under the conditions of pH 10 and pH 5, respectively. Under both alkaline and weak acidic conditions, the brightness of handsheets from polyDADMAC system is a little higher than that from fatty acid/calcium system. The amount of polyDADMAC added was much lower than that of fatty acid/calcium. It should also be noted that, for polyDADMAC system, no additional chemicals were added except sodium hydroxide or sulfuric acid, which were used to adjust pH. These results suggest that flotation deinking of ONP using polyDADMAC as a single flotation agent can provide many unique advantages, such as saving chemicals and reducing deposition on the machine. The results also indicate that similar to the fatty acid/calcium system, polyDADMAC is effective for all old newspapers tested in this study. We are now applying polyDADMAC in flotation deinking of mixed office in our laboratory.

3. Zeta potential measurement

The polymer polyDADMAC has a high cationic charge density, and fibers, fillers, and trash mainly have anionic charge in aqueous solution. To understand the interaction of electrostatic character for the polyDADMAC system, the zeta potential of the fibers and fines particles in the pulp slurry before flotation was investigated. The effect of polyDADMAC concentration on zeta potential is shown in Fig. 5. The zeta potentials of both fibers and filtrate particles are going toward positive linearly and reach the isoelectric point at approximately 40 and 80 ppm polyDADMAC, respectively.

Compared to the results in Fig. 2, it can be seen that the effective flotation deinking occurred when the zeta potential of both fibers and fines was still negative (about 10 ppm of polyDADMAC). Further increase in the zeta potential of fines and fibers to positive by adding more polyDADMAC significantly affected flotation deinking efficiency. Even at 100 ppm of polyDADMAC, at which the zeta potential of fibers is +20 mV, the deinking efficiency was almost identical with that obtained by 15 ppm of polyDADMAC (zeta potential of fibers is -7 mV). At very low polyDADMAC concentration (<6 ppm), the ink and other contaminants could still float on the top of pulp slurry during flotation. However, because there was no stable foam at this low polyDADMAC concentration, the ink could not be removed effectively.

Fig. 6 shows the effect of pH on zeta potentials. Negative zeta potential values over the entire pH range studied were obtained. When flotation deinking was carried out under these pH conditions, the cationic promoter could easily attach to ink and trash particles to form large aggregates that were suitable for flotation. All these phenomena indicated that flotation deinking using polyDADMAC involves the neutralization of anionic substances (dissolved and dispersed) to form particles with a certain particle sizes and surface chemistries. Once these particles are formed, further increasing the concentration of polyDADMAC or changing the charge density of particles will not significantly affect flotation efficiency. This was supported by results that concentration change of polyDADMAC above 15 ppm did not significantly affect the flotation deinking efficiency.

4. Effect of flotation pH on handsheet brightness

The effect of flotation pH on handsheet brightness is presented in Fig. 6. The maximum value of brightness of handsheets was obtained at pH 5. A significant foaming occurred at this pH. Because the charge density of fines, fibers, and ink particles in water usually increases (less negative) as pH decreases, the anionic charge of fines, fibers, inks, and dissolved materials are less negative and easier to neutralize by polyDADMC at low pH. Therefore, the ink-removal efficiency is expected to be more effective at low pH than high pH. This agrees with experimental results that handsheet brightness is higher at pH 5 than pH 10. However, when pH was lower than 5, the ink removal efficiency slightly decreased as shown in Fig. 6. The reason for this decrease is not clear, and more study is needed.

5. Effect of other cationic polymers and alum on the handsheet brightness

To see if other positively charged materials have a similar effect on ink removal, some cationic polymers and inorganics and their combination were also tested in this study. The cationic polymers tested include polyemine and cationic polyacrylamide (high-molecular-weight and low-charge-density flocculant), and inorganic cationic material of alum.

It was found that polyemine (PEM) was only effective under acidic conditions, and the effectiveness was lower than polyDADMAC at the same mass concentration. This is not surprising because PEM is positively charged only at low pH. The addition of a very high-molecular-weight and low-charge-density polyacrylamide did improve the ink removal. When this polymer was used, large fiber flocs formed and flotation could not be processed.

To compare it with cationic polymer systems, alum was selected as an inorganic cationic agent. Traditionally, alum has been used as a coagulant in many areas such as water treatment. The mechanism for removing suspended particles using alum is positively charged Al^{3+}, $Al(OH)^{2+}$, and $Al(OH)_2^{+}$, as well as the polymeric aluminum hydroxide neutralize and flocculate the suspensions. Similar to pulp furnish, it is expected that the addition of alum in waste pulp furnish will neutralize the anionics and cause them to form large particles. How this neutralization interaction affects ink removal was studied. Fig. 8 shows the effect of alum, polyDADMAC, and fatty acid calcium on the brightness of handsheets. Although alum itself in the pulp slurry could also generate reasonable foam, the ink removal using alum as a single flotation deinking agent was much less effective than when polyDADMAC was used. This is not surprising because alum consists of small ions while polyDADMAC is a polymer. The coagulating effect of a polymer usually is higher than that of small ions.

6. Possible mechanism

Several have been offered in the past in an attempt to explain the flotation mechanism among the oil-based calcium soap of fatty acid, ink particles, and the air bubbles for calcium soap of fatty acid (15-16). In this system, fatty acid molecules form hydrophobic complex particles with calcium then strongly adsorb on ink particle surfaces, making ink more hydrophobic and attachable to air bubbles.

In contrast with calcium soap of fatty acid, the polyDADMAC is hydrophilic in nature. The adsorption of polyDADMAC on ink particles should not significantly improve the hydrophobicity of ink particles. It was believed that the addition of polyDADMAC has two major functions, i.e., as a coagulant for dispersed particles and as a charge neutralizer for dissolved anionics. As a coagulant, the charge density of ink particles can be neutralized and the particles coagulated into required particle size for flotation. As a charge neutralizer for dissolved anionics, the solubility of dissolved anionics will be significantly reduced when they are neutralized by oppositely charged polymers. As a result, insoluble particles between dissolved anionics and polyDADMAC are formed. These particles further adsorb onto air bubble surfaces to function as a particle stabilizer or adsorb on ink particle surfaces as a collector (similar to calcium soap of fatty-acid particles).

To verify the above assumption, the foaming ability of polyDADMAC in different fractions of pulp filtrates was tested. Two different filtrates, filtrate-1 (a clear filtrate from a 5-μm filter paper) and filtrate-2 (a fines-containing filtrate from a dynamic drainage jar, 65-μm screen) were obtained from 1% ONP slurry. No stable foam could be generated for either filtrates or original ONP slurry if no chemical was added, and the addition of polyDADMAC in pure water could not generate foam. However, if 10 ppm polyDADMAC was added to filtrate-1 (containing dissolved materials only), a foam layer could be generated when air was blown into the system, although this foam was not stable enough for flotation. When the same amount of polyDADMAC was added to filtrate-2 (containing dissolved organics, ink, contaminants, and wood fines), relative stable foam was observed. If the same amount of polyDADMAC was added to the original pulp slurry, very stable foam could be generated. However, if the ONP was washed, the addition of polyDADMAC could not produce any foam. These results suggest that the foam generated in this particular system strongly depends on the presence of small suspended particles. These particles may include ink, colloidal contaminants, and newly formed colloids between polyDADMAC and dissolved organics. Although the contribution of different particles on foaming ability is complicated, both the contaminants in pulp slurry and the addition of polyDADMAC play a very important role in forming. After the ink and contaminats were removed by flotation, further addition of polyDADMAC could not create more foam. Further work is needed to fully understand the foaming mechanism in this system.

CONCLUSION

The polymer of polyDADMAC was first evaluated as a single deinking agent for flotation deinking of ONP under laboratory conditions. The results demonstrate that some cationic polymers such as polyDADMAC can be used as a single flotation deinking agent for ONP. The efficiency of polyDADMAC single systems is higher than commercial fatty acid/calcium systems. An unexpected benefit observed in these particular trials was a much higher ash removal across flotation than that achieved with conventional calcium soap of fatty acid/systems.

The advantage of using cationic polymeric coagulants as an ONP flotation deinking agent is that both ink and dissolved anionic trash and pitch are removed from the system in the form of macroscopic particles. Alum also shows some degree of ink-removal improvement because of its high cationic charge characteristics. However, the efficiency of alum is much lower than polyDADMAC. Unlike alum, the cationic charge of a polymer is not necessarily dependent on the pH of the system, thus cationic polymers can be used in acidic, neutral, and alkaline paper machines. In addition, cationic polymers remain soluble under normal alkaline papermaking conditions while alum can form insoluble aluminum hydroxide, which may result in unwanted deposits.

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FIGURE CAPTION

Fig. 1. Flotation Deinking. Newspaper samples: 1, *The Wall Street Journal*; 2, *The Chronicle of Higher Education*; 3, *Atlanta's Creative Loafing*; 4, Kroger coupons; 1% Pulp consistency, pH 8.7, 20 ppm polyDADMAC, flotation under room temperature for 10 min.

Fig. 2. Effect of the polyDADMAC amount on the brightness of handsheets. 1% Pulp consistency, pH 5.0, flotation under room temperature for 10 min.

Fig. 3. Effect of fatty acid calcium amount on brightness of handsheets. The ratio of oleate to calcium was 1:2. 1% pulp consistency, pH 10.0, flotation under room temperature for 10 min.

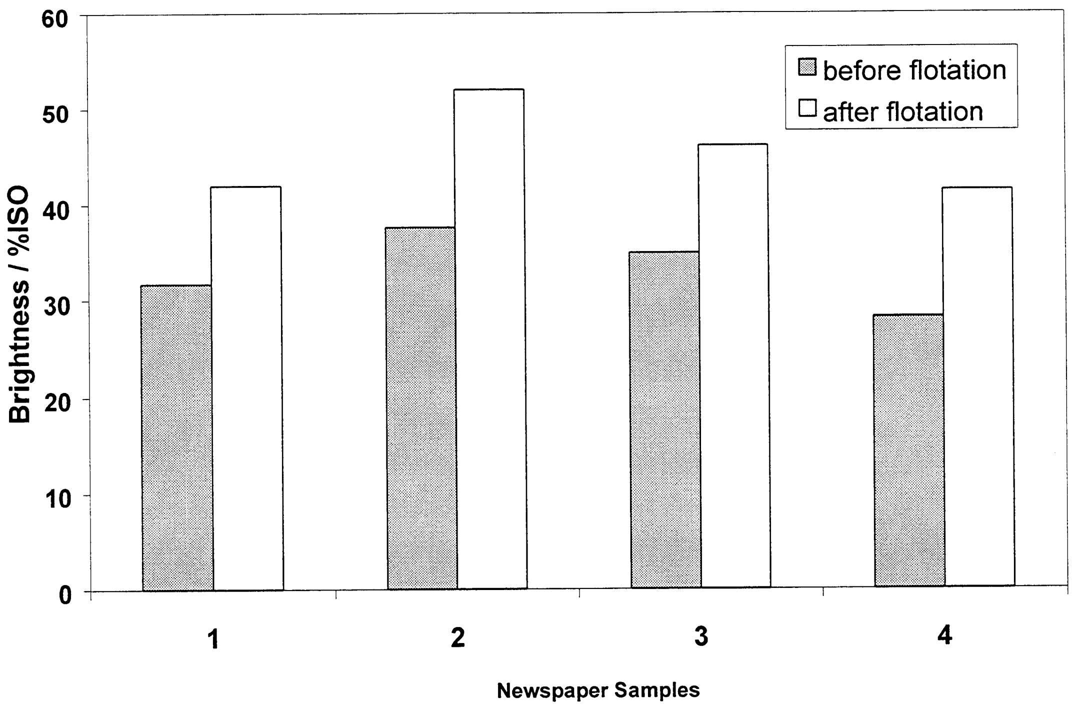
Fig. 4. The comparison of brightness of handsheets prepared from polyDADMAC system and fatty acid calcium system. Sample 1: pH 10, 150 ppm fatty acid calcium; Sample 2: pH 10, 15 ppm polyDADMAC; Sample 3: pH 5, 150 ppm fatty acid calcium; Sample 4: pH 5, 15 ppm polyDADMAC. For all samples, the flotation was carried out with 1% pulp consistency, under room temperature for 10 min.

Fig. 5. Effect of polyDADMAC amount on zeta potentials of both fibers and filtrated fines. 1% pulp consistency, pH 5.1.

Fig. 6. Effect of pH on zeta potentials of filtrated fines. 15 ppm polyDADMAC.

Fig. 7. Effect of flotation pH on the brightness of handsheets. For all samples, the flotation was carried out with 1% pulp consistency, 20 ppm polyDADMAC, under room temperature for 10 min.

Fig. 8. The comparison of brightness of handsheets prepared using a polyDADMAC system, fatty acid calcium system, and alum system. Sample 1, 15 ppm polyDADMAC, pH 5.0; Sample 2, 150 ppm oleate and 300 ppm calcium, pH 10; Sample 3, 1.0 g/L alum, pH 5.0. For all samples, the flotation was carried out with 1% pulp consistency, at room temperature for 10 min.



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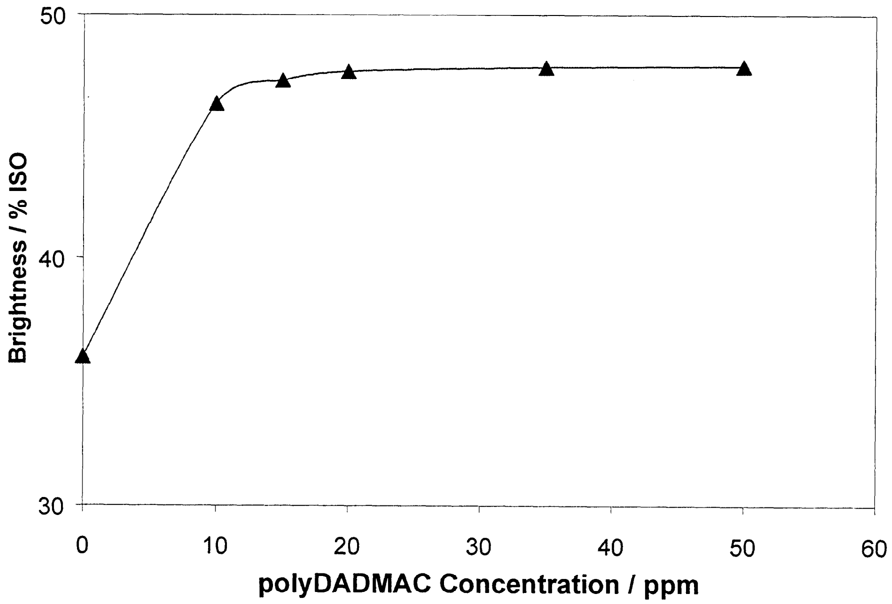
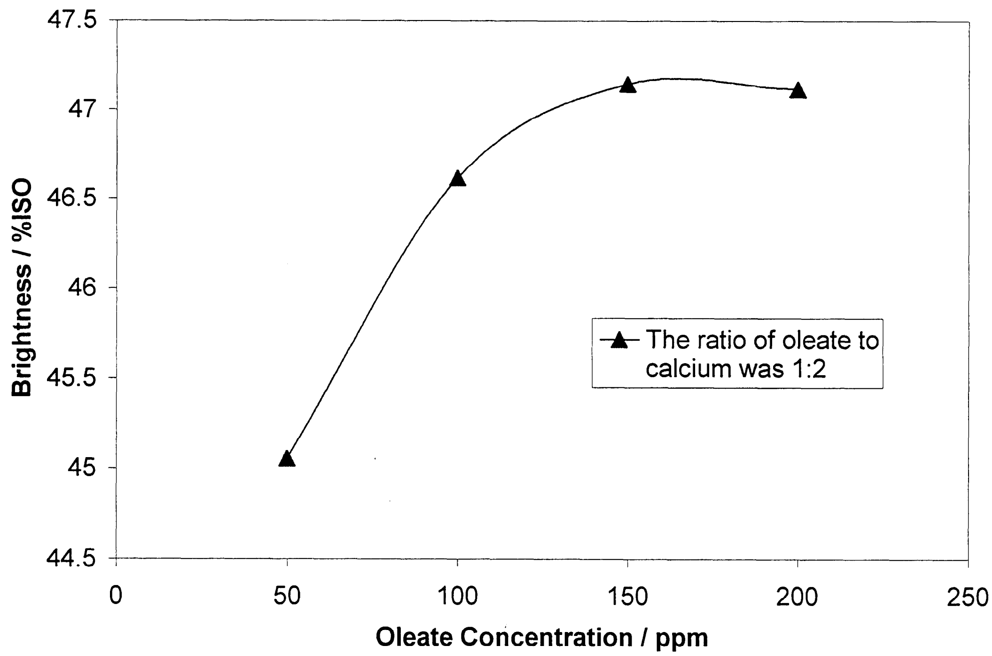


Fig. 2. Effect of the polyDADMAC amount on the brightness of handsheets. 1% Pulp consistency, pH 5.0, flotation under room temperature for 10 min.



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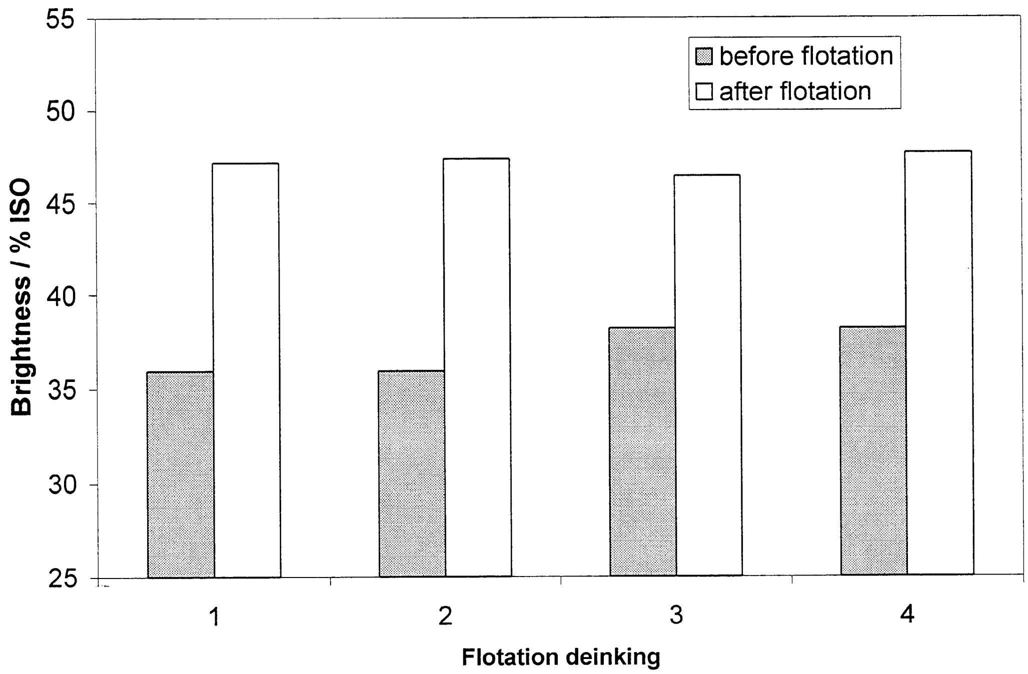

Fig. 4. The comparison of brightness of handsheets prepared from polyDADMAC system and fatty acid calcium system. Sample 1: pH 10, 150 ppm fatty acid calcium; Sample 2: pH 10, 15 ppm polyDADMAC; Sample 3: pH 5, 150 ppm fatty acid calcium; Sample 4: pH 5, 15 ppm polyDADMAC. For all samples, the flotation was carried out with 1% pulp consistency, under room temperature for 10 min.

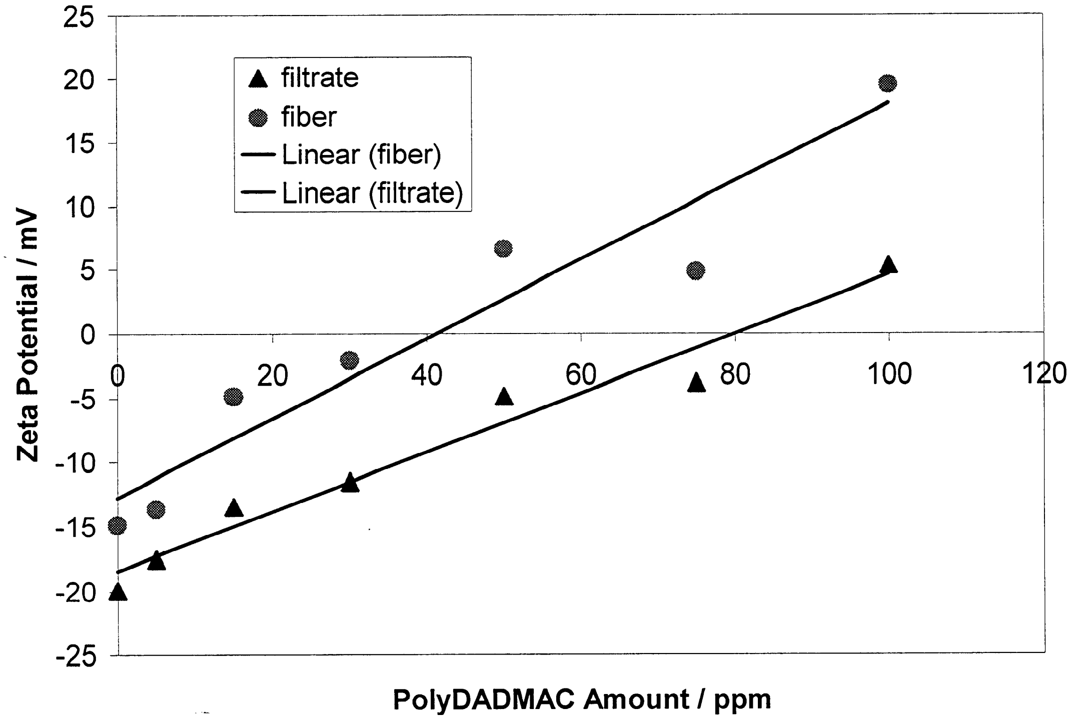

Fig. 5. Effect of polyDADMAC amount on zeta potentials of both fibers and filtrated fines. 1% pulp consistency, pH 5.1.

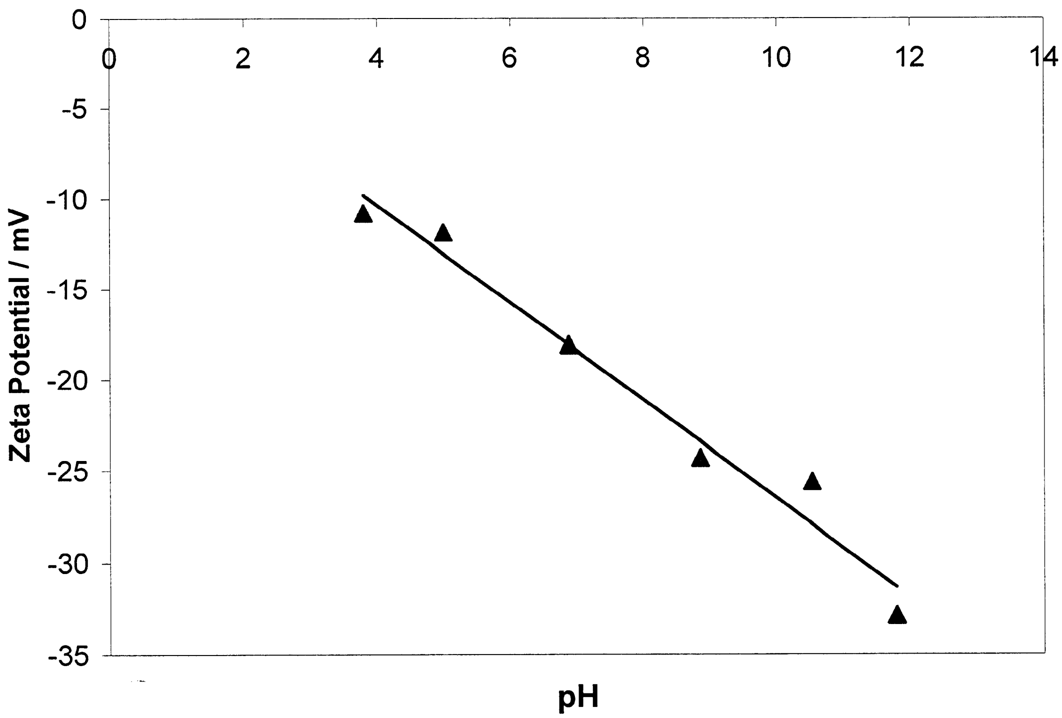

Fig. 6. Effect of pH on zeta potentials of filtrated fines. 15 ppm polyDADMAC.

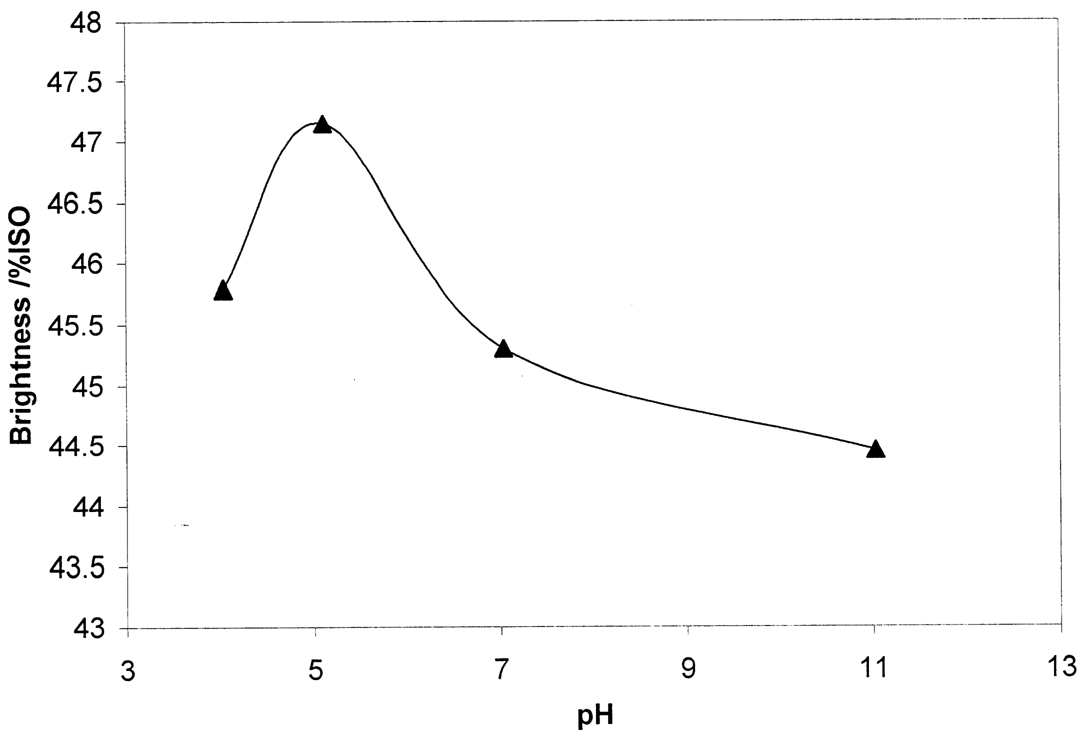

Fig. 7. Effect of flotation pH on the brightness of handsheets. For all samples, the flotation was carried out with 1% pulp consistency, 20 ppm polyDADMAC, under room temperature for 10 min.

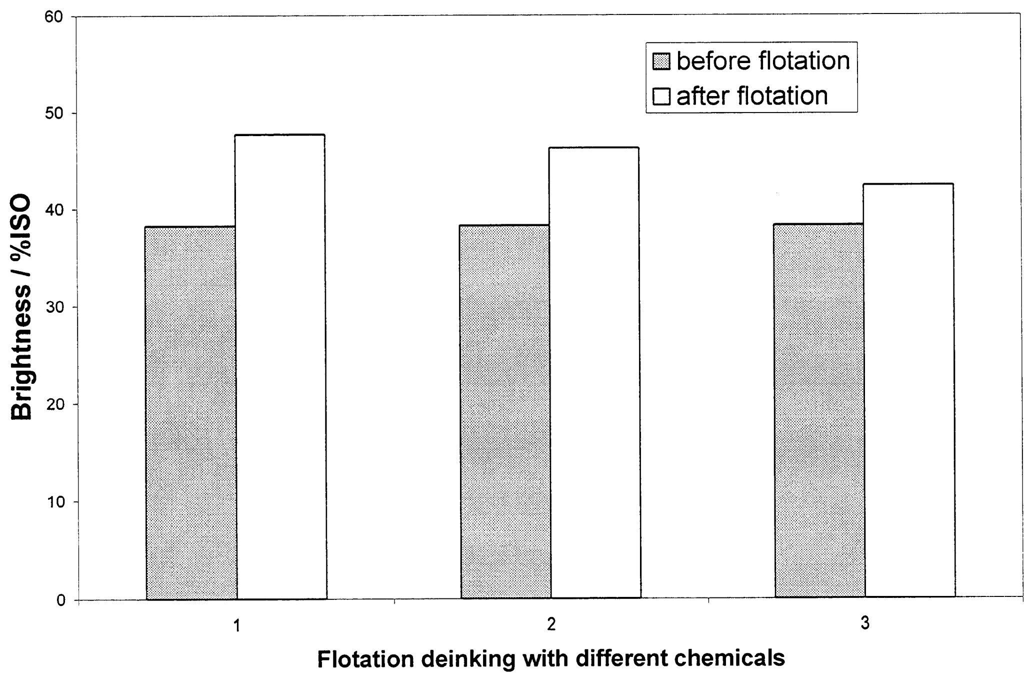

Fig. 8. The comparison of brightness of handsheets prepared using a polyDADMAC system, fatty acid calcium system, and alum system. Sample 1, 15 ppm polyDADMAC, pH 5.0; Sample 2, 150 ppm oleate and 300 ppm calcium, pH 10; Sample 3, 1.0 g/L alum, pH 5.0. For all samples, the flotation was carried out with 1% pulp consistency, at room temperature for 10 min.