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Performance of different surfactants in deiniking flotation process

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ABSTRACT

Deinking is an important step in recycling of waste paper and flotation is commonly used in this process. Conventional laboratory-scale flotation cell was used to study ink removal from waste printed papers. Different type of surfactants such as, cationic, anionic or non-ionic, were employed in pulping and flotation processes. Two surfactants of each type were used in this comparative study. The effect of concentration and type of surfactant, consistency, pH and temperature on the deinking was investigated. The efficiency of deinking process was determined by measuring of the brightness of hand sheets formed of deinked fibers. The highest brightness was achieved by using 2-octanol alcohol (as a non-ionic surfactant) in pulping and flotation stages. Under optimum conditions for this surfactant, a brightness of 86% is obtained from a feed of 44%.

Introduction

Deinking is a process for detaching and removing printing inks from recycled fibers to improve optical properties of recovered printed papers. In the case of office wastepaper, photocopy and laser-print toner particles are thermally fused and bonded to cellulose fibers, which makes deinking some more difficult than common waste paper. Four-step process involving pulping, washing, froth flotation, and another washing is usually used in deinking process. Chemicals with heat and mechanical energies are used to detach the ink particles and other contaminants from the fibers in a pulper [1]. Dispersed ink particles formed during pulping must be removed to prevent their re-deposition onto the cellulose. Ink particles are then separated from the fibers via a variety of operations like washing and flotation [2]. The first step in deinking waste-paper is pulping. The mechanical force is usually supplied by a pulper where the paper is beaten into its constituent fibers. The ink particles first are detached from the fibers by factors like: hydrodynamic flow of the liquid phase in the pulper, swelling of the fibers, flexing and bending of the fibers, and abrasion of the fibers against each other [3]. The mechanical force in the pulper is not sufficient for effective ink removal therefore surface active chemicals (e.g. NaOH, H_2O_2, chelating agent, etc.) are added in the pulper to decrease adhesion of the printing ink to the fibers and to increase the ink removal efficiency [4].

Flotation, is the most common method used, provides a high yield of fibers. It is a selective separation method using the different surface properties of particles. Air is introduced into a diluted fiber suspension of about 1% consistency. Ink particles attach to the air bubbles and rise to the surface. The hydrophilic fibers remain in the water phase [5,6]. Many researchers described the factors that affect flotation deinking. They recommended optimum values of consistency 0.5–2% [7,8]. High pulping temperature increase ink and other contaminant dispersion. Typical pulping process temperatures for de-inking newsprint are 40-60°C. Mills often process old office papers at 50-90°C [9]. Laboratory flotation runs led to the conclusion that the flotation cell temperature was optimal between 40 and 55°C [5]. The washing process is successful when the ink particles are very small. Flotation requires larger particles [10]. The better results are achieved by a combination system, since wash deinking is less effective in the removal of large ink specks (>20 μm), whilst flotation deinking is less effective in removal of small ink particles (<20 μm) [5]. Sodium hydroxide causes swelling of the fibers resulting in easy removal of printing ink. In flotation, fibers are swollen by NaOH, and this action breaks the bond between fibers and print, because the print does not swell, it also increases final brightness. Another belief is that it hydrolyses ester groups in print particle networks, causing the print to break up into small particles [11]. Calcium soap of stearic acid as a fatty acid collector can be added to the flotation unit which creates foam. Hydrogen peroxide, as another chemical used in deinking, is believed to bleach fibers and increase the brightness. One problem that occurs with the use of peroxide is its decomposition due to micro-biological action. Stressing the bacteria by either rising or lowering the temperature sometime works, and adding large amounts of peroxide can also resolve the problem [11]. Hydrogen peroxide has destructive effect on fibers. Alcohols are one of the most common frothers used in mineral flotation. The effect of different alcohols was studied instead of hydrogen peroxide in different stages like: pulping, flotation, and combination of them. Alcohols as nonionic surfactants are playing the role of frother, collector, and solvent of water-based ink particles simultaneously. Deinking is studied by a combination of an alcohol and soap [12]. Alcohols against hydrogen peroxide have no destructive effect on fibers [13].

This work aims to study the performance of different type of surfactants such as, cationic, anionic or non-ionic, in deinking process with flotation. Nonionic Surfactants do not ionize in aqueous solution, because their hydrophilic group is of a non-dissociable type, such as alcohol, phenol, ether, ester, or amide. Anionic Surfactants are organic compounds dissociated in water into an anionic alkyl and a cation, which is in general an alkaline metal. They include alkylbenzene sulfonates, fatty acids, lauryl

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sulfate, etc… Cationic Surfactants are dissociated in water into a cationic alkyl and an anion. They include fatty amine salts and quaternary ammoniums, with one or several long chain of the alkyl type. These surfactants are in general more expensive than anionics. They are only used in cases in which there is no cheaper substitute [14].

Materials and methods

Materials

The anionic surfactants, Sodium Dodecyl Sulphate CH_3-$(CH_2)_{11}$-SO_4Na, (SDS) and Calcium Oleate CH_3-$(CH_2)_7$-CH=CH-$(CH_2)_7$-COOCa (99%) were supplied by Sigma Chemical Co. The cationic surfactants, cetyl trimethyl ammonium bromide $(C_{16}H_{33})$-N-$(CH_3)_3Br$ (CTAB), 98% and Dodecyl amine CH_3-$(CH_2)_{11}$-NH_2 (DA), 99% were supplied by Fluka Co., Switzerland. The 4-heptanol and 2-octanol (97%) as non-ionic surfactants were supplied by Sigma Aldrich Chemical Co. Inorganic chemical used sodium hydroxide was of Pro Analysis grade and supplied by Merck.

Experimental Methods

The pulping of old printed paper (7–15% weight) mixed with tap water was produced in a disintegrator operating for approximately 5 min at temperature (35–55°C). All the chemical reagents used were proportional to the weight of the dry newspaper. The pulp was homogenized for 1 h. To produce the right consistency for flotation, the pulp was diluted to 1 wt% [1]. All flotation tests were carried out using a "Denver D12" flotation machine. Collectors were added during stirring at speed (2000 rpm) for 5 min at desired temperature. The purpose was to release the fibers and facilitate the detachment of the ink from the paper. The flotation was carried out for 10 min by activating an air inlet located below the stirring shaft at speed (1000 rpm). The froth was then scraped off the top of the flotation cell by hand using a small paddle [15]. Then, the deinked pulp from the flotation cell was carefully washed by 1 liter of distilled water. The deinked pulp was then set to dry overnight after screening and pressing the final pulp by hand. To determine the efficiency of deinking, the pulp has to be fitted into a form suitable for testing; this is achieved by reforming paper sheets (known as hand sheets or brightness pads) from the pulp [16]. The brightness of the hand sheets thus formed was measured with a Minolta Inc. Spectra Match, model CM 508d spectrophotometer [17].

Results and discussions

Non-ionic surfactants

Fig.1 shows the effect of temperature and consistency of paper pulp with alcohols in stage of pulping. The pulp was washed with 1 liter distilled water and then the brightness was measured. The brightness of feed pulp was 44%. A brightness of 58% and 62% were obtained as result of using 3% of 4-Heptanol and 2-Octanol surfactants, respectively. Increased temperature has a significant effect on brightness. High pulping temperature increase ink and other contaminant dispersion [5]. The higher brightness was achievable at temperature range 45–55°C. Pulping is important for the chemical dosages since these are calculated on the amount of air-dry paper. A higher stock consistency in a pulper means less water and a higher concentration of chemicals [1].

The decrease in pulp consistency may be irrelevant to the pulp's brightness since the ink removal efficiency increases only slightly. In this case, low consistency is unimportant because larger unit sizes would be required to treat the same amount of pulp, and the yield would decrease. Since, brightness is almost constant with pulping consistency up to 12%.

Fig.2. shows the effect of alcohol concentration and pH on brightness of paper pulp. The brightness increased with increasing alcohol concentration which may be due to increasing its solvation power of ink. Also, the brightness increased with increasing pH. Higher pH means higher concentration of sodium hydroxide (NaOH) used. Sodium hydroxide causes swelling of the fibers resulting in easy removal of printing ink by the action of breaking the bond between fibers and print, because the print does not swell, it also increases final brightness. Another belief is that it hydrolyses ester groups in print particle networks, causing the print to break up into small particles [11].

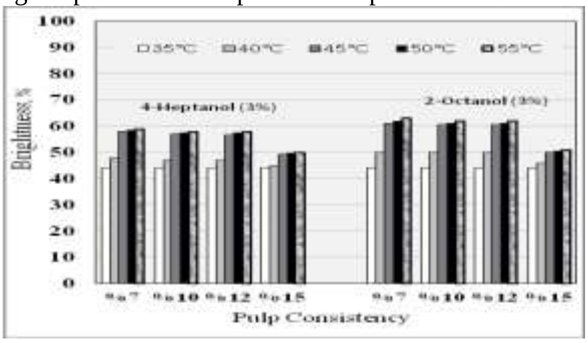

Fig.1. Effect of Pulp Consistency and Temperature on Brightness of Product Pulp at pH 10

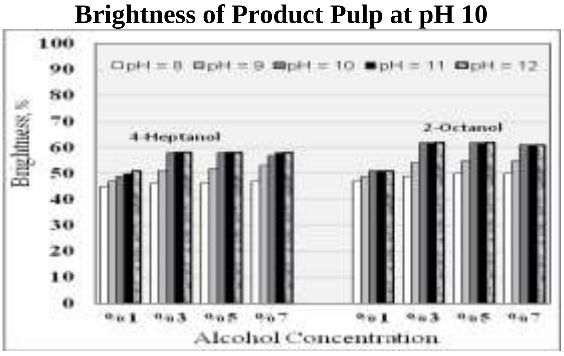

Fig.2. Effect of pH and Alcohol Concentration on Brightness of 12% Pulp at 45 – 55°C.

Fig.3. shows the effect of pH and alcohol concentration on the flotation process. Deinking efficiency increases with increasing concentration and molecular weight of alcohol. A brightness of 80% and 86% were obtained by of using 3% of 4-Heptanol and 2-Octanol, respectively. The brightness increased with increasing alcohol concentration up to 3% then slightly decreased at 5% then sharply decreased. At low concentrations of alcohol in water the hydrocarbon chains will actually lie flat on the surface (air–water interface). It is only when there are a sufficient number of alcohol molecules at the interface that hydrocarbon chain of alcohol molecule is oriented normally to air–water interface [12]. Also, alcohols of C7 atoms at dosage of more than 5% have limited solubility, so their froth stability decreases.

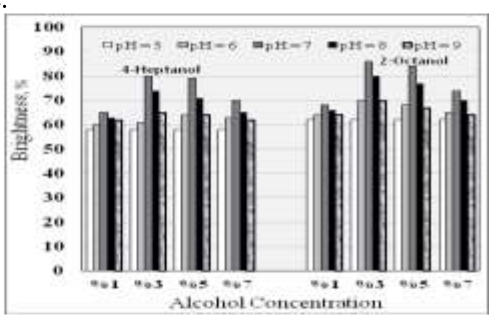

Fig.3. Effect of pH and Alcohol concentration on Brightness of the Flotation Product at 45–55°C.

The insoluble alcohol has a very low surface tension and inclusion of small droplets of it in the air–liquid interface of a liquid film causes the droplet to spread rapidly over the surface, owing the large differential interfacial tension between the droplet and the surrounding medium. This rapid spreading in turn causes a rapid thinning of the liquid film to the point of rupture and an unstable froth results. Alcohols reduce average bubble size due to a reduction in surface tension [18]. Alcohol with long chain tends to accumulate at the gas–liquid interface and lower interfacial tension. This leads to an increase in the bubble interfacial area and a decrease in its rise velocity [19]. The deinking efficiency of 2-Octanol is better than that of 4-Heptanol. This is may be due to alcohols having frother power increases with the number of carbon atoms [20]. On the other hand, the brightness increases with increasing pH up to 7 then decreased in strong alkaline medium. This may be due to the decreasing of frothing power of alcohols at alkaline medium. In general, alcohols have no destructive effect on fibers and are preferred agent to gives higher brightness. Frother remaining in the water may be undesirable from environmental and water recycling perspectives, but those and economic point of view are other matters. The alcohol dosage more than 3% was not recommended because of environment and economic problems, therefore, the low dosage of alcohol is proposed [12].

Anionic Surfactants

Fig.4 shows the effect of temperature and consistency of paper pulp with anionic surfactants in stage of pulping. A brightness of 50% and 56% were obtained with 1g/l of SDS and Ca-oleate surfactants, respectively. Increased temperature has a significant effect on brightness due to increasing ink dispersion and solubility of surfactant and no precipitation of it [5]. The higher brightness was achievable at temperature range 40–45°C. The brightness is almost constant with pulping consistency up to 10% and then decreased.

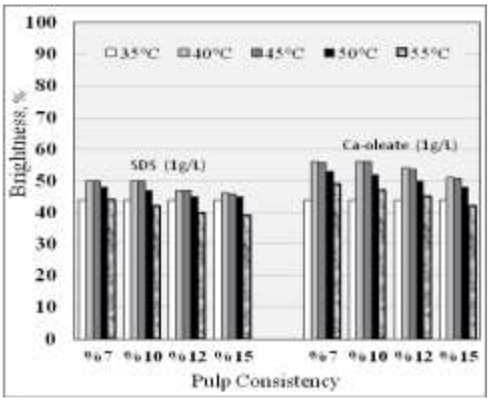

Fig.4. Effect of Pulp Consistency and Temperature on Brightness of Product Pulp at pH = 10.

Fig.5. shows the effect of SDS and Ca-oleate concentration and pH on brightness of paper pulp. The brightness increased with increasing both surfactant concentrations. The maximum brightness was obtained at 0.8 and 0.9 g/l for SDS and Ca-oleate, respectively. Higher concentrations did not significantly improve the pulp's brightness or yield. This is may be due to maximum coagulation speed of these surfactants at concentrations [21]. Detergency is generally more effective at high pH, as more negative charges are imposed on the contaminant and on the substrate, making them more repulsive from each other [22, 23]. The brightness increases with increasing pH up to 12, which means higher concentration of sodium hydroxide used. In addition to that sodium hydroxide causes swelling of the fibers resulting in easy removal of printing ink by the action of breaking the bond between fibers and print, because the print does not swell, it also increases final brightness and hydrolyses ester groups in print particle networks [11].

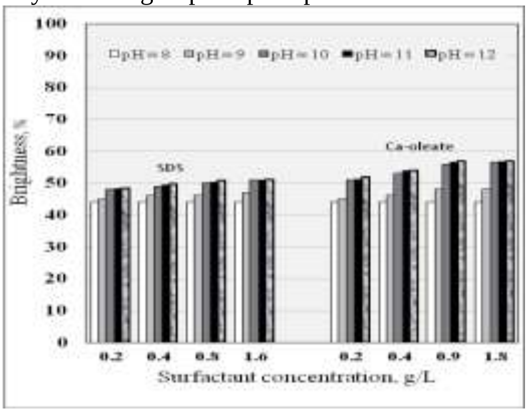

Fig.5. Effect of Anionic Surfactant Concentration and pH on Brightness of 10% Pulp at 40 – 45°C.

Fig.6. shows the effect of SDS and Ca-oleate concentration and pH on the flotation process. Deinking efficiency increases with increasing concentration up to 0.8 and 0.9 g/l for SDS and Ca-oleate, respectively and then slightly decreased. The brightness was 68 and 77 with using 0.8 and 0.9 g/l of SDS and Ca-oleate, respectively. The point of zero charge (PZC) of the ink particles in water was observed at a pH of about 3.3, which means that the ink particles exhibit a positive charge at pH < 3.3, while they are negatively charged when pH > 3.3 [24]. Since the anionic species of surfactants as Ca-oleate and the ink particles are fairly strongly negatively charged over the alkaline pH range where flotation usually occurs, there have been implications that the calcium induces a bridging mechanism between the two surfaces. This would result in the strongly bonding of the surface functional groups on the ink particles to the carboxyl groups on the collector [25]. The floatability was reduced with increasing surfactant concentration which may increase the collision frequency. This effect also occurred above CMC for the surfactant [26]. Ink removal efficiency of SDS is not good as Ca-oleate due to a non-specific interaction between the SDS and the ink particles. The SDS adsorbs on carbon black as a tail-down monolayer (hemimicelle) while on paper fiber as a head-down, head-out bilayer (admicelle). On the other hand, oleate forms admicelles on both carbon black and paper fiber indicating the stronger interaction of the carboxylate group with the carbon surface than the surfactant sulfate group, causing the oleate to adsorb at higher levels than SDS on carbon black. This helps explain why soaps are used widely as the surfactant in flotation deinking operations [8].

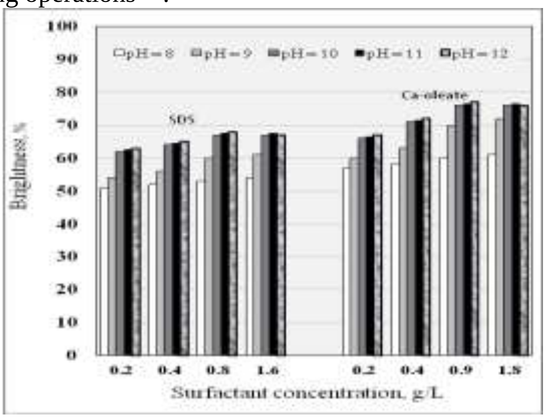

Fig.6. Effect of Anionic surfactant concentration and pH on Brightness of the Flotation Product at 40–45°C

Cationic Surfactants

Fig.7. shows the effect of temperature and consistency of paper pulp with cationic surfactants in stage of pulping. A brightness of 49% and 50% were obtained with 1g/l of Dodecyl amine (DA) and CTAB, respectively. Increased temperature has a significant effect on brightness. Increasing the temperature causes the aggregation number to decrease. The decreased aggregation number translates into less micellar volume that can accommodate solubilized ink binder [27]. The higher brightness was achievable at temperature range 45–50°C. The brightness is almost constant with pulping consistency range from 6 and 8% and then decreased with increasing pulp consistency.

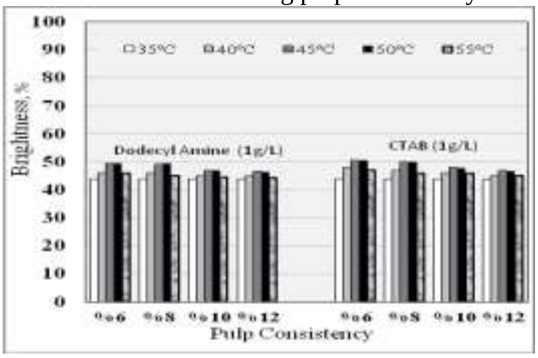

Fig.7. Effect of Pulp Consistency and Temperature on Brightness of Product Pulp at pH = 10.

Fig.8. shows the effect of DA and CTAB, concentration and pH on brightness of paper pulp. The brightness increased with increasing both surfactant concentrations. The maximum brightness was obtained at 1.5 g/l for both cationic surfactants. All epoxy molecules can be solubilize essentially in high cationic surfactant concentration [28]. The surfactant can also improve wetting of paper and prevent the ink from re-adsorbing by dispersing solid ink particles by adsorbing in the ink surface, emulsifying liquid ink droplets and dissolving ink molecules in micelles. Another possibility is that the micelles are dissolving the ink binder [24]. A pronounced pH dependence was observed, surface activity of the amine increasing with pH up to pH 12 then declining sharply. Hydrolysis of the amine ion to amine molecule is shown to be an incomplete explanation; ion-molecule complexes are proposed [29]. High pH (at least 11.5) is crucial for effective ink removal. Of course, under these extremely basic conditions, materials constraints increase process equipment costs substantially.

Fig.9. shows the effect of DA and CTAB, concentration and pH on the flotation process. Deinking efficiency increases with increasing concentration up to 0.6 and 1 g/l for DA and CTAB, respectively and then decreased. The floatability was reduced with increasing surfactant concentration which may increase the collision frequency. This effect also occurred above CMC for the surfactant. The thin-film and contact angle measurements show that the increase in surfactant tends to increase the thin film stability and reduce the flotation [26]. The brightness obtained at latter concentration is 64 and 71 for DA and CTAB, respectively. As mentioned before the ink particles exhibit a negative charge at pH > 3.3. The cationic species of cationic surfactants as Dodecyl amine (DA) and CTAB are strongly positively charged over the alkaline pH range where flotation usually occurs. The adsorption of cationic species on the ink pigment surfaces is driven by both electrostatic and van der Waal forces. Since the possibility for the formation of negatively-charged moieties of the epoxy binder and on the pigment is greater at a higher pH, increasing the pH value also renders greater adsorption of cationic monomers onto the ink pigment surfaces. On the other hand, pH does not affect the van der Waal interactions between the tail groups of the adsorbed cationic monomers and the hydrophobic part of the pigment surfaces greatly. In addition, the van der Waal interactions should increase with the length of the hydrophobic part of the surfactant molecules. Thus, the better result of CTAB which has longer carbon chain is expected.

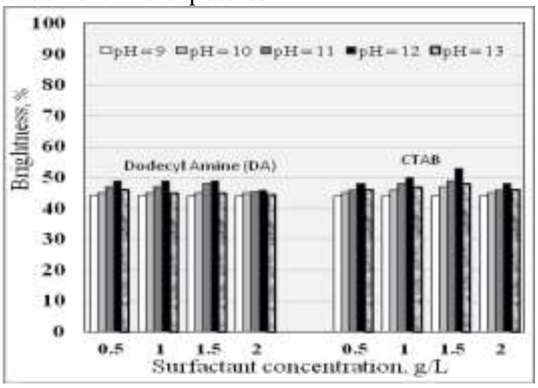

Fig.8. Effect of Cationic Surfactant Concentration and pH on Brightness of 8% Pulp at 45 – 50°C.

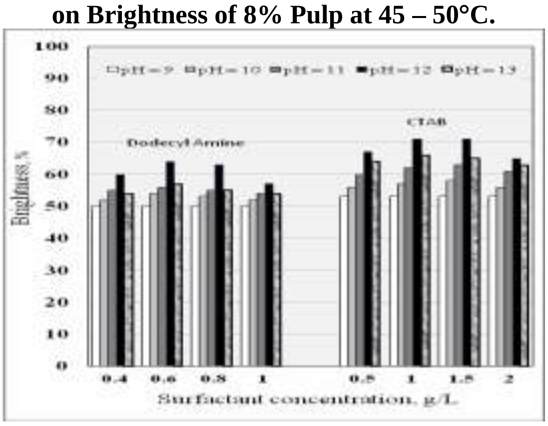

Fig.9. Effect of Cationic Surfactant Concentration and pH on Brightness of the Flotation Product at 45–50°C

Conclusions

A two-step deinking process involving pulping and flotation steps and utilizing different types of surfactants was studied for laser printed papers. Deinking performance of each surfactant was used without further use of a chemical additive except pH regulator. The brightness of feed pulp was 44%. The higher brightness of pulping step of 62% was achievable with 3% alcohols as nonionic surfactants compared to anionic and cationic surfactants. The 2-Octanol alcohol (C=8) is better than 4-Heptanol alcohol (C=7). Increased temperature has a significant effect on brightness for all surfactant types. The higher brightness was achievable at temperature range 45–55°C, 40–45°C and 45–50°C for nonionic, anionic and cationic surfactants, respectively. The higher brightness was achievable at pulp consistency of 12, 10 and 8% for nonionic, anionic and cationic surfactants, respectively. The higher brightness was achievable at pulp pH 10, 11 and 12 for nonionic, anionic and cationic surfactants, respectively.

In flotation step the higher brightness of 86% was achievable with 3% alcohols as nonionic surfactants compared to anionic and cationic surfactants. The 2-Octanol alcohol (C=8) is better than 4-Heptanol alcohol (C=7). On the other hand, anionic is better than cationic surfactant. The surfactant with longer carbon chain obtains better result compared to shorter one. The higher brightness of flotation product was achievable at pulp pH 7, 11 and 12 for nonionic, anionic and cationic surfactants, respectively.

Alcohols have no destructive effect on fibers and are preferred agent to gives higher brightness. Frother remaining in the water may be undesirable from environmental and water recycling perspectives, but those and economic point of view are other matters.

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