

2. The Role of Oxygen Nitrogen Bubbles in Flotation Deinking using A Commercial Surfactant and The Fatty Acid of Morinda Citrifolia L

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THE ROLE OF OXYGEN/NITROGEN BUBBLES IN FLOTATION DEINKING USING A COMMERCIAL SURFACTANT AND THE FATTY ACID OF MORINDA CITRIFOLIA L.

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ABSTRACT

Despite surfactant-based ink removal being extensively investigated, the best quality deinked pulp obtained by flotation deinking exhibits effective residual ink concentration (ERIC) and brightness values that are consistently lower than expected. To understand this, the effect of oxygen and nitrogen bubbling on the behavior of a commercial surfactant and the fatty acid of *Morindacitrifolia L.* (FAMC) was investigated in this study. Oxidation was found to enable binding between the surfactant / FAMC and the ink components and enhance flotation deinking. The hydrophilic properties of the surfactant also enable the surfactant and FAMC molecules to physically contact or interact with ink components.

KEYWORDS: Ink Removal, Commercial Surfactant, *Morindacitrifolia L.* Fatty Acid & Flotation Deinking

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1. INTRODUCTION

Flotation deinking using a biodegradable surfactant is among the most favorable processes for removing detached ink from fiber surfaces. Ink becomes detached during re-pulping, in which shear force dominates along with chemical, enzymatic, and surfactant actions. The detached ink is separated during flotation, which is established by injecting pressurized air into a dilute ink-contaminated fiber suspension, and the surface tension of water (as the suspension medium) is modified by the addition of a surface active agent (surfactant). The surfactant covers the bubbles that form the interface; as a consequence, the bubbles lift the detached ink from the fiber. Although the bubbles have uniform properties, the interactions between air, oxygen, or nitrogen bubbles, and the surfactant responsible for detaching the ink are unknown. Accordingly, these interactions were evaluated in this study by investigating their effects on flotation. In this study, the fatty acid of *Morindacitrifolia L.* (FAMC) and a commercial surfactant (CS) were used as the biodegradable surfactants.

Studies on flotation deinking [1, 2, 3] and microbubble dispersion [4] have been reported. Enzymes are commonly added during the re-pulping step, and enzymatic deinking has been studied for its overall deinking efficiency [5, 6, 7]. Surfactants are commonly added to the flotation tank, and the effect of surfactant adsorption on the hydrophilic solid-water interface has been studied [8]. Relevant to flotation deinking, surfactant behavior has also been investigated and modeled [9]; the separation process in a flotation system has also been simulated [10] and a mathematical model for the flotation deinking process has been developed [11]. Studies comparing the performance of the flotation deinking of old newspaper (ONP) using FAMC and CS have been reported [12, 13, 14, 15], with the commercial surfactant outperforming FAMC, with 2.36% and 11.70% differences

in brightness and effective residual ink concentration (ERIC) values, respectively, reported [12].

Pigments (mostly organic compounds) in ink are formulated with other organic compounds, such as binders, varnishes, and vehicles that mostly contain hydrocarbon chains and are stabilized by the surfactant [16]. On the other hand, hydrophobic ink dyes or pigments in the surfactant solution (above the critical micelle concentration) are solubilizing [17]. Upon dissolution, the surfactant influences specific physical properties of water by decreasing its surface tension, decreasing the mean bubble diameter, and increasing gas hold up and gas movement [18, 19]. Bubbles coalesce differently in pure solvent and aqueous mixtures, with the surface tension less important in the pure liquid than in an aqueous solution, which is the result of the specific behavior of the surfactant [18].

Surfactants exhibit different kinetics and equilibrium adsorption behavior at solid–liquid interfaces when mixed with silica, cotton, or cellulose, and show synergism, such as enhanced surface activity, spreading, foaming, and detergency [8]. The hydrophilic–lipophilic balance (HLB) values of surfactants significantly affect flotation deinking [20, 13, 14]. Surfactants with different hydrocarbon chain lengths perform differently during flotation [21]. Most compounds containing long hydrocarbon chains (such as surfactants and fatty acids) undergo oxidative cross-linking when exposed to oxygen. Cross-linking determines the yield of the flotation process, as interpreted using a model equation that describes particle removal [22, 13]. When alkyd and linseed oil form emulsions, such as in wood-coating formulations [23], they dry when applied to wood surfaces due to oxidative cross-linking promoted by air [24].

In industry, aeration is mostly performed by bubbling air (21% oxygen and 79% nitrogen), and innovations that improve flotation performance are always sought after. Oxygen is a reactive molecule that can interact with the double bonds present in unsaturated hydrocarbon molecules through hydrogen bonding, but the same cannot be said for nitrogen. An innovative deinking process using a mixture of ozone (O₃) and oxygen has been studied [25]. To reduce the risk of explosion in producing clarified water in oil industry, nitrogen is used instead of air [26]. Oxygen spontaneously reacts with unsaturated fatty acids to produce allylic hydroperoxides, dihydroperoxides, and cyclic peroxides [27].

2. MATERIALS AND METHODS

A commercial surfactant and FAMC were used in these experiments. To determine which gas has a positive effect on flotation deinking, three gases were used, namely air, oxygen, and nitrogen. Flotation was conducted in a laboratory glass flotation tank and the flotation-deinking results using oxygen, nitrogen, and air were compared. The brightness and ERIC values of the deinked pulp were measured. The results were interpreted theoretically by considering possible interactions between the gas (air, oxygen, and nitrogen) and the surfactant or FAMC that are related to their effects on deinking flotation.

2.1 Materials

The following materials were used: a commercial surfactant (CS; a fatty acid derivative composed mostly of long-chain unsaturated C18:2 hydrocarbons) [manufactured by KAO], FAMC extracted from the seeds of *Morinda citrifolia* L. (composed mostly of long-chain unsaturated C19:2 octadecanoic acid) [14], sodium lauryl sulfate (SLS) [manufactured by KAO], papyrase enzyme [manufactured by KAO], ONP [local ONP waste], air, oxygen, and nitrogen [SAMATOR Industrial Gases], and water.

2.2 Methods

The following two steps were used:

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The Pulping Step. ONP was torn into small pieces, and 50 g of the shredded ONP was disintegrated in 0.9 L of water for 10 min using a 2000-rpm mixer at 30 °C and pH 7. The ONP pulp was poured into a collecting flask. The vessel was rinsed with 0.1 L of washing water, with the pulp maintained at 5% consistency [12]. The amount of prepared pulp was sufficient for several flotation experiments.

The Flotation Step. The setup used for flotation in this study is shown in Fig. 1. The pulp sample (500 mL) was mixed with 1% papyrase enzyme for 10 min before pouring into a flotation tank filled with 5 L of water to a consistency of 0.5% after which 0.15% CS and 0.6% SLS was added [12]. ³ Flotation was carried out for 10 min at pH 7 and 30 °C, at oxygen, nitrogen, or air pressures of 1–5 kg/cm² through several sizes of orifice (20, 40, and 60 μm). The ink-contaminated froth was removed from the upper part of the flotation tank, and the deinked pulp was drained from the bottom part of the flotation tank and washed over a 48-mesh screen and transformed into a sheet using a handsheet maker according to the Tappi method (Tappi T 218-om 91). Deinking performance was evaluated in terms of brightness and ERIC using a Technidyne Color Touch 2 ISO instrument [12]. The same experiment was also performed for FAMC instead of the commercial surfactant.

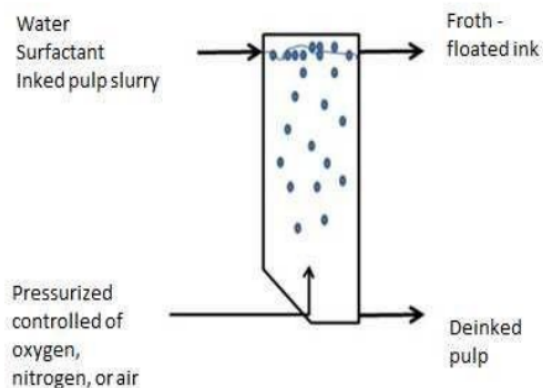


Figure 1: Setup for Flotation-Deinking Experiments.

3. RESULTS AND DISCUSSIONS

The commercial surfactant and FAMC were used as surface-active agents to modify the surface tension of the solution during flotation. The fibers and suspended ink-particle solids should be separated by flotation, and flotation was performed by bubbling oxygen or nitrogen gas. The results obtained using these two gases were compared with those obtained when flotation was performed by bubbling air, as used in the standard operating procedure. The performance of the commercial surfactant and FAMC in flotation deinking was analyzed in terms of the ³ brightness and ERIC values of the deinked pulp.

Figure 2 shows that oxygen gas facilitated the best flotation-deinking performance (in terms of brightness) with both CS and FAMC. These results confirm that oxygen, as a reactive gas, improves the surface properties (surface activities) of bubbles covered by either the commercial surfactant or FAMC. On the contrary, nitrogen, as an inert gas, performed most poorly; nitrogen was unable to facilitate good flotation deinking performance.

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Figure 3 shows the ERIC values of deinked pulp produced under various conditions. There was less effective residual ink left on the deinked pulp when bubbled with oxygen gas; it seems that more ink particles were removed using oxygen as the bubbling gas. Hence, we conclude that the activities of CS and FAMC are enhanced by oxygen to afford better adsorption properties for ink particles.

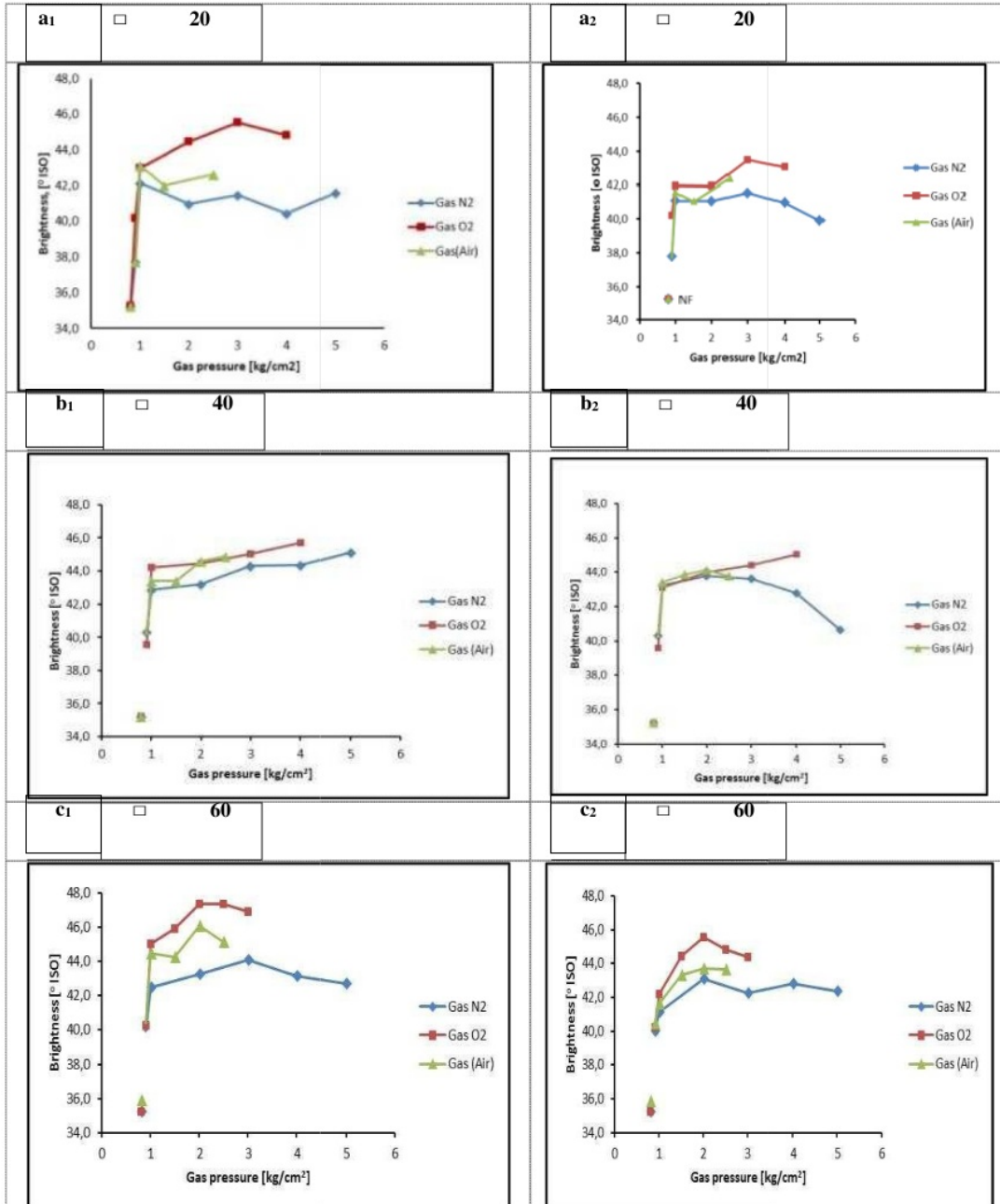


Figure 2: Brightness values obtained using: (a₁, b₁, c₁) the Commercial Surfactant and (a₂, b₂, c₂) FAMC as functions of Gas Pressure at various Orifice Diameters.

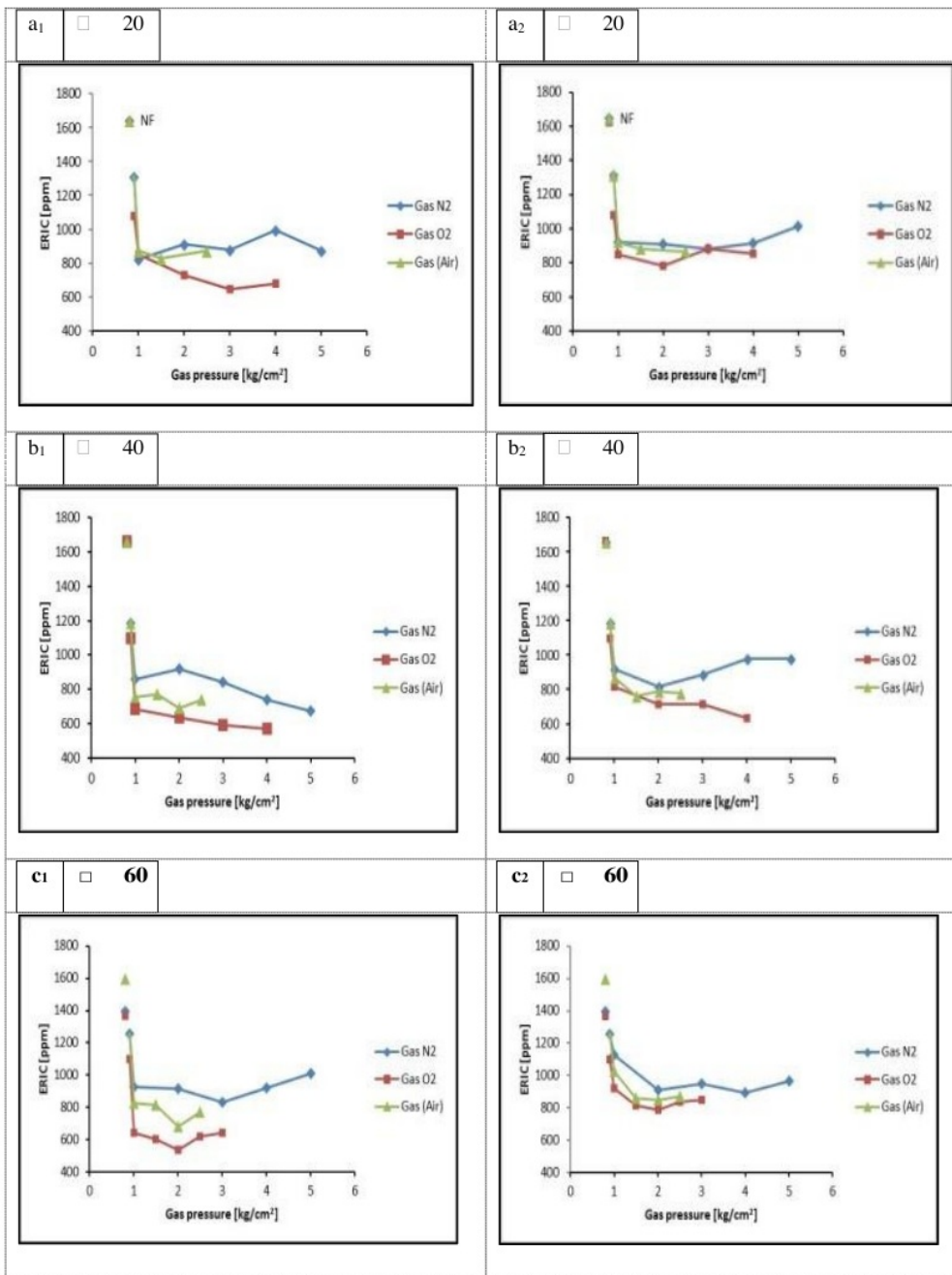


Figure 3:ERIC values obtained using: (a₁, b₁, c₁) the Commercial Surfactant and (a₂, b₂, c₂) FAMC as Functions of Gas Pressure at various Orifice Diameters.

As a fatty acid derivative, the CS contains an unsaturated bond in its structure, and FAMC also has an unsaturated bond in its structure. These double bonds, as well as those in ink, appear to be favorable for oxygen attachment as

illustrated by the interactions shown in Figs. 4 (a, b, and c). These interactions may promote the cross-linking of both fatty acids with themselves, or with specific components present in the ink particles, in agreement with previous reports [28, 13, 14]. Reactions between oxygen and unsaturated fatty acids lead to the production of compounds such as allylic hydroperoxides, dihydroperoxides, or cyclic peroxides [27]. These interaction products and reaction products may impact the ink-separation process during flotation deinking. As a result, the deinked pulp has higher brightness and lower ERIC values; hence, the effects of these compounds on flotation deinking need to be studied further.

During flotation deinking, phase contact occurs immediately between water (the surfactant solution, in which the surfactant is hydrophilic) and oxygen through liquid and gas contact (two-phase contact) by bubbling (in this case the surfactant concentration should be above its critical micelle concentration (CMC), and between water (the hydrophilic surfactant solution) and the ink (the detached ink particles) through liquid, gas, and solid contact (three-phase contact) during flotation. The interaction probability is less for solid and gas phase contact (ink particles and oxygen) because the ink particles are distributed as detached particles in the water phase and are not in the gas phase. In addition, the ink particles are hydrophobic while the oxygen gas bubbles are covered by the hydrophilic surfactant solution.

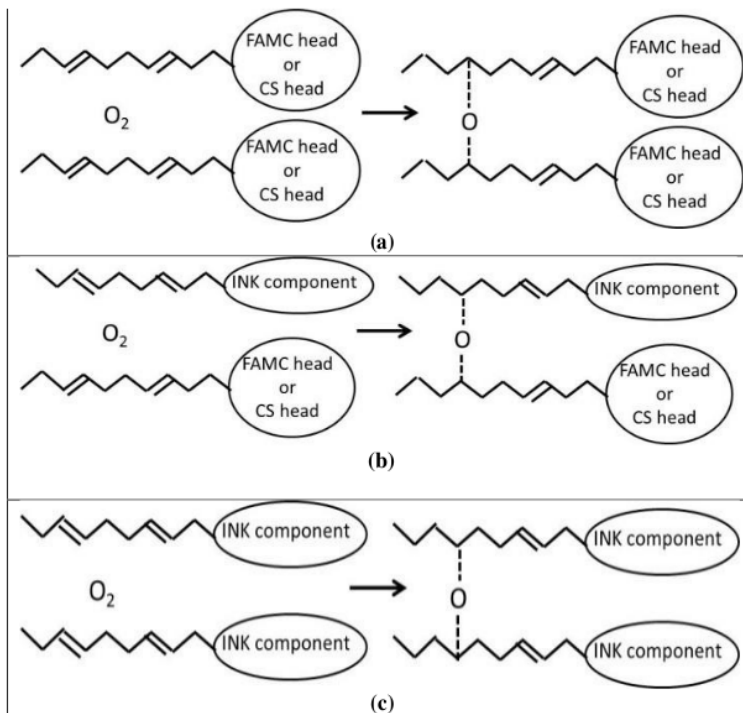


Figure 4: Illustrating possible Interactions between Surfactants (a), between Surfactants and ink, and between ink Components it Selves (c).

FAMC is less effective than the CS when used as an alternative surfactant during flotation deinking. In this case, FAMC is less hydrophilic (HLB value of 5) than the commercial surfactant (HLB value of 13); hence, when it is injected into the water and bubbling is performed, FAMC is distributed as a micro suspension, rather than the solution formed by the commercial surfactant. In the presence of oxygen, the possibility of FAMC molecules interacting with themselves, and FAMC molecules interacting with the molecules in the ink particles through hydrogen bonding, as shown in Fig 4 (a and b),

is lower than that of the commercial surfactant. This is the reason that FAMC performs more poorly than the commercial surfactant.

Bubbles produced from the larger orifice gave better results than those produced from the smaller ones. At the same operating pressure, larger bubble diameters resulted in increased turbulence in the flotation medium, which results in hydrodynamic properties more suitable for fiber and ink-particle separation. In this case, oxygen exerts a significantly improved effect than that of nitrogen or air, which is likely related to interactions between oxygen, the surfactant, and some specific ingredients in the printing ink, as discussed above and supported by other research results [27].

The brightness and ERIC values of the deinked pulp treated using the commercial surfactant are superior to those of FAMC (Figs. 2 and 3). It has been noted that a commercial surfactant has special properties that depend on its chemical structure and modifications. Indeed, commercial surfactants with longer hydrocarbon chains provide better flotation results [21]. In the case of the hydrophobic lipophilic balance (HLB) value, an ethoxylated fatty alcohol with an HLB value of 12 afforded deinked ONP pulp with the best properties [28]. The commercial surfactant has a suitable HLB value for flotation deinking, and physically, it is not as oily as FAMC.

4. CONCLUSIONS

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The effectiveness of oxygen/nitrogen bubbles in flotation deinking using a commercial surfactant and FAMC was investigated. The following observations are made:

- Oxygen oxidizes CS and FAMC, thereby binding the structure of CS or FAMC to itself, or specific ink ingredients composed of fatty acids, alkyd resins, or other compounds. This binding is suggested to result in cross-linking with ink particles, which leads to enhanced flotation deinking.
- The best bubbling gas for flotation deinking is oxygen, followed by air and nitrogen.
- The diameters of the bubbles exuded from the D₆₀ orifices exhibit better flotation-deinking performance than those from orifices of other diameters.
- Inert nitrogen gas is inferior in flotation deinking.
- The commercial surfactant promotes better flotation deinking than FAMC, which correlates with its hydrophilic properties.

NOMENCLATURE

CS	commercial surfactant
CMC	critical micelle concentration
ERIC	effective residual ink concentration
FAMC	fatty acid of Morinda citrifolia L.
HLB	hydrophobic lipophilic balance
ONP	old newspaper
SLS	sodium lauryl sulfate
□ ₂₀	code for the smallest orifice, 20 μm
□ ₄₀	code for the medium orifice, 40 μm
□ ₆₀	code for the largest orifice, 60 μm

Highlights

- Biodegradable surfactant is one of the best mediums for flotation deinking to remove detached ink from fiber surfaces.

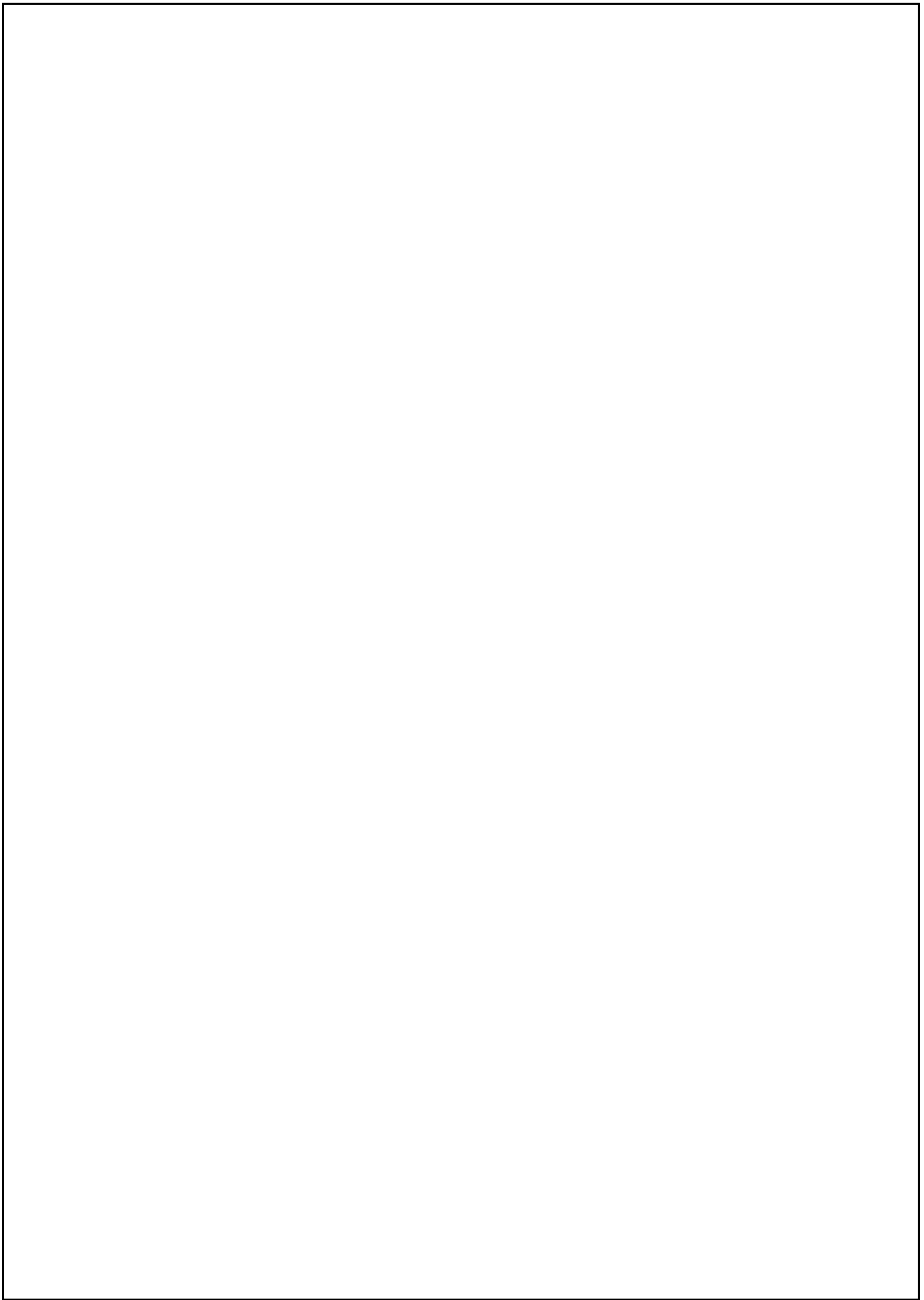
- Unknown results is still found on the interactions between air, oxygen or nitrogen bubbles, and the surfactant.
- The interactions were evaluated by considering the fatty acid of *Morindacitrifolia* L. and a commercial surfactant as the biodegradable surfactants.
- Bubbles exuded from the D₆₀ orifices indicate better performance than other experimental configurations.
- It is explicitly noted that inert nitrogen gas is not effective for flotation deinking process.

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