

Effects of Flotation Deinking on Environmentally Friendly Offset Paper Printing Ink

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Abstract

Waste paper has become a promising raw material for the pulp and paper industry due to its low cost and because it is conducive to sustainable development. Unfortunately, waste paper contains a high volume of printed paper that is difficult to deink, which restricts its applications. Flotation deinking plays an essential role in the product quality and process cost of wastepaper recycling. This study was performed to evaluate the deinkability of environmentally friendly offset inks by flotation deinking. For this purpose, three series of four-color inks, namely, hybrid light emitting diode ultraviolet (LED–UV), LED–UV, and vegetable oil–based inks, were printed on white lightweight coated papers under laboratory conditions. The deinking methodology involves repulping, deinking agent treatment, flotation, hand sheet making, and evaluation of the produced hand sheets. The obtained results indicated that the hybrid LED–UV prints had the best deinkability. After flotation deinking, the deinking efficiency and the whiteness of the hybrid LED–UV ink increased by 58.1% and 47.6%, respectively. LED–UV ink had a 46.9% increase in the deinking efficiency and a 37.0% increase in the whiteness of the hand sheet. The deinking efficiency of the vegetable oil–based ink was the lowest, at 42.1%, and the whiteness of the hand sheet increased only by 23.8%. The particle size distribution analysis demonstrated that the hybrid LED–UV four-color ink exhibited a larger value of the average particle size than the two other. Scanning electron microscopy revealed that the hybrid LED–UV ink particles on the surface of the fibers were the least abundant after deinking. The physical strength properties of the hand sheets, including tensile index, folding resistance, and cohesion of the hybrid LED–UV, LED–UV inks, and vegetable oil–based inks, increased.

1. Introduction

Recycled paper for the paper industry is of great importance as a basic raw material. Offset printing is a widely used printing technique, and nearly all recycled paper is printed by the means of offset lithography (Barbaric et al. 2013). Lithographic inks, usually called offset oil–based inks, are based on water-resistant vehicles (a carrier medium) and pigments that do not dissolve in water or alcohol. The inks are used to print newspapers, glossy magazines, books, and photographic reproductions, and they are an important portion of waste paper. In lithography, the print process can be divided into two main categories based on the ink–setting mechanism: (a) inks are simply absorbed by the pores of paper at room temperature, leaving the pigment behind on paper surface without drying, which happens in the case of offset–cold oil–based inks (60% vegetable oil) and (b) inks are physically dried using mineral oils evaporated into the atmosphere at a temperature below 60°C, which happens in the case of offset–hot oil–based inks (35–45% mineral oil). However, petroleum-based oils are known to release volatile compounds harmful to both the environment and humans, which poses a challenge in recycling print substrates (Nie et al. 1998; Aydemir et al. 2018).

Increasing environmental and quality demands have resulted in the development of printing inks based on vegetable oils, such as soy beans, rapeseed, castor, and linseed. Vegetable oil–based inks have started receiving widespread attention due to their low volatile organic compound (VOC) content and ecofriendly, sustainable, and renewable nature (Kandile et al. 2017). The use of vegetable oils in non-food

applications has gained considerable interest due to their renewable character, biodegradability, and aptitude to facile chemical modification. From the traditional mineral oil-based inks to the soybean oil-based inks, and then to the 100% pure vegetable oil-based (soybean oil, flaxseed oil, and tung oil) inks, offset printing inks have developed in the direction of a high technical and high vegetable oil content (Chen et al. 2021). However, vegetable oils have shortcomings with respect to dryness and printability behaviors. Currently, with the rapid growth of various of new printing techniques, the ultraviolet (UV)-curing technique, due to its advanced efficiency, energy saving aspect, cost-effectiveness, and being environmentally friendly, has been widely used in industrial applications such as inks (Mendoza et al. 2015; Roberta 2019), coatings (Liang et al. 2021; Paraskar et al. 2020), and adhesives (Bednarczyk et al. 2020; Kim et al. 2021). In the recent past, light emitting diode ultraviolet UV (LED-UV) cured printing inks and varnishes have drawn a great deal of interest because of their outstanding properties such as environmental friendliness, high print speed, quick drying, low VOC emission, and ability to provide an excellent quality in the printed layers, such as high gloss. Different from ordinary offset printing inks, LED-UV cured printing inks are based on formulations containing acrylates, photoinitiator systems, pigments, and other additives (chelating agents, anti-oxidants, surfactants, and biocides) (Marina et al. 2018) that help improve processing and achieve certain properties of the printed layers. Package printing is one of the main application areas of LED-UV cured printing inks that are used especially in high-quality consumer goods or products with expensive designs (Mirschel et al. 2014). However, LED-UV cured inks also have drawbacks such as residual monomers, pungent odor, and allergic potential, especially the monomers and prepolymers derived from acrylic acid. Therefore, combining the advantages of vegetable oil-based inks and LED-UV technology, a hybrid LED-UV product named Montage α was developed. Montage α is a new series of offset inks, which is not just a simple mixture of vegetable oil-based offset and LED-UV inks but a new design based on a resin system with dual curing capability. Vegetable oil-based varnishes served as the biological raw material, and LED-UV was introduced into the system to bring in rapid curing of the hybrid LED-UV ink. The fabrication of hybrid LED-UV presented in this paper not only solves the problems associated with the traditional vegetable oil-based inks but also improves their properties and curing speed. Currently, the main development trend of printing materials is to improve their environmental performance by choosing energy-saving, non-toxic, low consumption, no pollution, and the easy degradation of pollution-free packaging material. Therefore, the volume of these environmentally friendly inks being printed will be increasing, and LED-UV inks have been very popular for their high quality magazine covers. They even have seen considerable growth in use for food packaging applications. Hence, the recycled pulp potentially is of high quality due to the high quality of substrates used with these inks.

Increasing energy demands and environmental pollution have become the most serious problems of the 21st century. The environmental impact of paper and its production on the environment is significant. In 2020, the production of paper and paperboard is estimated to reach approximately 500 million tons (Rita et al. 2019). The paper and pulp industry accounts for 34% of municipal waste and is considered as the third largest polluter of air, water, and land (Rourke 2019). Hence, the recycling of waste paper has attracted extensive attention as it is a means of reducing global environmental problems such as carbon

dioxide emissions, deforestation, and destruction of natural resources (Jiang et al. 2020; Adediran et al. 2021; Tao et al. 2021; Stevulova et al. 2021). Recycling one ton of waste paper can produce approximately 0.8 tons of recycled pulp, can replace approximately 30 eucalyptus trees, and save 7000 gallons of water, 400 kWh of electricity, 380 gallons of oil, and reduce toxic waste emissions (Kumar et al. 2021). Paper is a felted sheet of cellulose fibers formed during the papermaking process. Inks of various compositions are absorbed by or fused with the cellulose fibers to form prints and images (Nie et al. 2021). Therefore, the conversion of this relatively abundant and inexpensive raw material into high-quality products requires the development of effective methods to remove contaminants. Deinking is necessary step in recycling some kinds of waste paper. It can be achieved by various means, which include chemical (Tsatsis et al. 2019; Allix et al. 2011), enzymatic (Sango et al. 2021; Nathan et al. 2020), and physical methods (Tatsumi et al. 2000; Fricker et al. 2006). These methods can be used to deink different types of inks. Among these methods, flotation deinking is the most commonly adopted by the paper industry due to its simple, easy operation, short preparation period, and relatively high yield of fibers. It also is a critical step in the process of waste paper recycling and a widely adopted standard practice for ink removal in Europe, North America, as well as many other countries (Vashisth et al. 2011). This method is the oldest technology for deinking wastepaper and has been used commercially for several decades. In the last few years, many studies regarding waste paper deinking placed much more importance on the enzymatic technology (Chee et al. 2013; Feng et al. 2018; Mustafa et al. 2020). Although there have been considerable advances in the application of biotechnology to paper recycling, enzymatic deinking processes still face problems that have limited their commercialization.

In the deinking flotation process, the bubble size, pH, temperature, printing process used, ink thickness, size of ink particles, and the age of printed products were the main areas of concern. Heindel (1999) described that flotation mainly removes the hydrophobic contaminants and ink particles in the size range 20–300 μm . However, the optimum sizes for flotation deinking can be dependent upon the type of ink and added chemicals. Dorris and Page (1997) found that the optimal size for a high flotation efficiency for photocopier and laser print ink was between 60 and 100 μm . Additionally, it has also been reported that the thermal ageing of ink occurs during the summer season, and this affects ink detachment and fragmentation (Castro et al. 2002). Hence, the age of printed products has been well known to cause tremendous effects that offset ink deinkability (Marina et al. 2016). The magnitude of this problem depends on the type of ink used in the printing process. Nevertheless, effective deinking of printed paper based on some new offset inks, e.g., vegetable oil-based inks and LED-UV inks, especially hybrid LED-UV inks, could not be achieved, even in recent years.

The overall objective of this study is to investigate the deinkability of hybrid LED-UV ink, LED-UV inks, and vegetable oil-based inks using the flotation deinking method. The particle size distribution (PSD) was used to analyze the size of the ink particles. Fourier-transform infrared spectra (FT-IR) was employed to realize the structure of vehicles. Furthermore, the deinking efficiencies of hybrid LED-UV, LED-UV, and vegetable oil-based inks on the same paper using the flotation method are proven, and the changes in the physical properties of the paper before and after deinking are studied.

2. Materials And Methods

2.1 Materials

Hybrid LED–UV four-color inks, LED–UV four-color inks, and vegetable oil–based four-color inks were obtained from Hangzhou Toka Ink Co., Ltd, China. Lightweight coated papers, with a basic weight of 100 g/m² used as the substrate for offset printing were supplied by Shandong Sun Paper Co., Ltd, China. Sodium hydroxide (30 wt% NaOH) and the deinking agent (industrial soap) were obtained from Ningbo Asia Pulp and Paper Co., Ltd, China. All other experimental equipment, such as high–concentration pulper (N–185VT, China), flotation deinking cell (L–100, USA), paper standard press (1600, USA), Whiteness meter (SE071, SE,) and tensile strength instrument (L&W SE062, SE) were obtained from Ningbo Asia Pulp and Paper Co., Ltd, China. An effective residual ink particle concentration tester (ERIC, T567 om–04, USA) was provided by Laboratory of South China University of Technology.

2.2 Experimental

The methodology applied in this study for investigating the deinking ability of the three ecofriendly offset printing inks, namely, hybrid LED–UV, LED–UV, and vegetable oil–based inks, using the flotation method, is schematically illustrated in Fig. 1. A detailed description is as follows: The print samples were placed in a room (23±1°C and 50±2% humidity) for at least six months before deinking. In order to study the efficiency of the hybrid LED–UV, LED–UV, and vegetable oil–based inks, the samples were printed using the same image and paper under the same printing conditions.

The print samples were weighed, and the moisture contents were determined by oven drying at 105°C. The samples were then manually shredded into small pieces of approximately 5 cm×5 cm, and about 500 g of the prepared dry print samples was placed in a high–concentration pulper, where the paper is beaten into its constituent fibers. Then, 5 L of 50°C water was gradually poured into the pulper at 145 rpm for 5 min for repulping to form the pulp slurry, after which 0.8% (based on a dry paper weight) sodium hydroxide solution (30 wt%) was added to the pulper to achieve a pH of around 10.0. Subsequently, the pulp slurry was continuously repulped at 400 rpm for another 15 min. The whole repulping process was conducted at 50°C for 20 min. After the repulping process was run for the desired duration, 20 g (based on dry weight) pulp was taken out, poured into a filtrate mold to form a filter pad, and was dried in an oven at 135°C for 15 min to gain the pulp consistency. The pulp consistency (keep two decimals, wt%) was calculated as the ratio of the filter pad quality (oven–dried) to 20 g pulp. Based on the pulp slurry consistency, 400 g (oven–dried stock) of pulp slurry was retained in the high–concentration pulper, and 8 g (5 wt%) deinking agent was injected into the pulper. Afterwards, ink from the fiber of the emulsification reaction was performed at 50°C for 15 min under repulping at 400 rpm.

Flotation was achieved after repulping: 280 g pulp mixture (oven–dried stock) was immediately transferred into the flotation deinking cell and its concentration was adjusted to 1.0 wt% with 28 L hot water. Another 2.8 g (5 wt%) deinking agent was injected as a surfactant. The pulp was then floated for

20 min in a flotation cell at 50°C, with an air flow of 7–8 dm³/min. The foam generated was collected and used to determine the flotation yield.

Eventually, to evaluate the physical properties of the pulp samples including the undeinked and deinked pulp, hand sheets (60 g/m²) were made in accordance with the standard method of SCAN–C26:76; The hand sheets were placed into a constant temperature (23±1°C) and humidity (50±2%) laboratory for 12 h to balance the moisture.

2.2.1 The deinking efficiency

The deinking efficiency was calculated as follows (Bennington et al. 2001):

$$\text{Deinking efficiency (\%)} = (D_{\text{blank pulp}} - D_{\text{deinked pulp}}) / D_{\text{blank pulp}} \times 100\%, \quad (1)$$

Where D is the effective residual ink concentration (ERIC)

2.2.2 Particle size distribution (PSD) analysis

The PSDs of the hybrid LED–UV four-color inks, the LED–UV four-color inks, and the vegetable oil–based four-color inks were determined using the Malvern Zetasizer Nano ZS90 sampler (Malvern Instruments Ltd, UK).

2.2.3 Fourier transform infrared (FTIR)

Fourier transform infrared (FTIR) spectroscopy was recorded in the spectral range of 4000–500 cm⁻¹ with a 4 cm resolution and 16 scans on a NICOLETTE 10 FTIR spectrometer, and the samples were smeared on a KBr wafer to form a thin film.

2.3 Measurement of the paper properties after deinking

2.3.1 Measurement of brightness

Brightness was determined according to the TAPPI T 452 –92 standard method.

2.3.2 Effective residual ink concentration (ERIC)

The effective residual ink concentration (ERIC), whiteness, and dirt particle area are commonly used to evaluate the quality of the deinked pulp and deinking efficiencies during the paper recycling process. Measured on whole pulp after pulping, ERIC values provide information on the initial amount of ink and/or the ink fragmentation on the paper, the higher the ERIC value, the greater the amount of ink

present and/or the higher the ink fragmentation. The dirt count is simply the number of dirt/ink specks detected in the total area scanned, which can also be expressed as count per m².

This method measures the light absorption, light reflectance, and light transmission in an infrared wavelength range of 700–950 nm (this literature specifies the wavelength of 950 nm, yielding ERIC 950 as the standard ERIC index) and then converts the measurements to calculate the residual ink content. ERIC measurements are based on the reflectance measurement at 950 nm. Six points each on the positive and negative sides of the handsheet were measured, from which the average value was calculated.

2.3.3 Scanning electron microscopy (SEM)

A scanning electron microscope (Phenom PRO, China) with an accelerating voltage of 10 KV and a magnification of 2500× was employed to observe the morphology of the hand sheets.

2.3.4 Determination of the mechanical properties of undeinked and deinked hand sheets

The hand sheet samples were treated for 12 h at 23±1°C and 50±2% relative humidity prior to mechanical measurements. The measurements including the tensile index and folding endurance of the undeinked and deinked hand sheets made according to the relevant TAPPI standards.

3. Results And Discussion

3.1 The deinking efficiency of hybrid LED–UV, LED–UV, and vegetable oil–based inks

To prove the deinking efficiency of environmentally friendly offset inks, the hybrid LED–UV, LED–UV, and vegetable oil–based inks were deinked using flotation. The deinking efficiencies and the optical properties (brightness and whiteness) of the undeinked and deinked hand sheets are listed in Table 1. It can be seen that the ERIC of the hybrid LED–UV, LED–UV, and vegetable oil–based undeinked hand sheets were 131.8 ppm, 148.0 ppm, and 185.3 ppm, respectively, and the ERIC of the hybrid LED–UV, LED–UV, and vegetable oil–based deinked hand sheets were 55.2 ppm, 78.6 ppm, and 107.3 ppm, respectively. The significant difference in the ERIC between the undeinked and deinked hand sheets demonstrated that the flotation treatment had a positive effect on the hybrid LED–UV, LED–UV, and vegetable oil–based ink removals. Furthermore, according to Equation (1), the deinking efficiency of the hybrid LED–UV, LED–UV, and vegetable oil–based inks are shown in Table 1. This table shows that the deinking efficiency of the hybrid LED–UV, the LED–UV, and the vegetable oil–based inks were 58.1%, 46.9%, and 42.1%, respectively. The highest deinking efficiency of 58.1% was acquired with the hybrid LED–UV ink, which were much higher than those reported in recent work (Singh et al. 2020). Based on Table 1, the whiteness and brightness of the hybrid LED–UV deinked pulp reached the maximum values of 77.2% and 85.5%, respectively. The whiteness and brightness of the hybrid LED–UV deinked hand

sheets improved by 47.6% and were 16.0% higher than those of LED–UV (whiteness, 37.0%; brightness, 13.1%) and vegetable oil–based (whiteness, 23.8%; brightness, 9.3%) deinked hand sheets. The change in the opacity indicated that the chemical treatment caused changes to the reflectivity of the hand sheets.

The reasons for the above results can be explained by the following two points. First, the conventional deinking process employs sodium hydroxide to keep the pH value of the pulp slurry near 10.0. Hence, high pH values favor fiber swelling, increase their flexibility, and consequently facilitate the detachment of the adhered ink. Subsequently, sodium hydroxide may also act directly on the printed ink film and weaken its structure, leading to fragmentation. Following this process, the liberation of ink particles by the repulping treatment is broken down into small particles that can be efficiently removed by flotation. Katarina et al. (2004) suggested that small particles cannot be removed, not even by prolonged flotation. The size of particles is important because small ink particles affect the whiteness of the pulp the most. This has been found to be the main reason for the poor flotation ability of small particles. Therefore, the PSDs and the average sizes of the hybrid LED –UV four-color inks, LED–UV four-color inks, and vegetable oil–based four-color inks were determined in the subsequent procedures of this study. The second reason for the experimental results may be that the poor deinkability of vegetable oil–based inks has been ascribed to an oxido–polymerization of the vegetable oils in inks. The vegetable oil–based inks, they were dried mainly by penetration of the vehicle in the paper structure. The oil and resin component left on the paper surface with the pigment can react slowly with oxygen to form a three dimensional polymer network. This conversion of a liquid into a solid film not only increases the cohesiveness of the print, but also its degree of bonding to the paper surface. Castro and colleagues^[33] reported the oxidation reactions of vegetable oils by a free radical mechanism involves several steps: (1) oxygen reacts slowly with oil to form hydroperoxides, and this is known as the induction period; (2) the decomposition of hydroperoxides followed by the propagation of free radicals; and (3) the formation of cross links, meaning the termination of the free radical. The hybrid LED–UV ink deinking efficiency was the highest, indicating that this type of ink film basically completed the curing in under the LED–UV curing conditions, effectively reducing the time it took for the oil substances to penetrate into the paper fiber, inhibiting the oxidation reaction of the vegetable in three steps. Hence, the vegetable oil surplus, vegetable oil, and other high biomass, renewable resource ingredients in the alkali washing decolorization process to make the ink film were more easily decomposed. The printed products with the hybrid LED–UV ink were exposed to UV–radiation, and this may also have affected the kinetics of aging. In summary, the differences in the ink removal rates of these inks quite likely reflected the differences in their compositions.

3.2 The dirt specks of the undeinked and deinked handsheets

In addition to the increase in whiteness, it is also necessary to determine the amount of visible ink specks on the deinked hand sheets. For waste paper deinking, the latter measure is considered even more important than the whiteness gain. Table 2 illustrates the values of the dirt speck surfaces of the undeinked and deinked hand sheets. In Table 2, the total dirt specks were very high after the pulping stage (a step prior to flotation). Thanks to flotation, 90% of the dirt specks were removed. Interestingly, the

dirt area results showed that the vegetable oil-based ink undeinked and deinked hand sheets had the least number of ink particles, but had the worst whiteness. This may have been due to an increased number of smaller particles that were produced during the vegetable oil-based ink printed paper pulping. Smaller particles were not floated from the pulp, and they had a great a tendency to redeposit on the fibers rather than the larger ones and affect the pulp whiteness adversely (Amit et al. 2021). Furthermore, it can be seen from Table 2 that the successful flotation separation strongly depended on particle sizes. Ink particles of sizes 40 μm –150 μm were found to be the ones that were the most likely to be adsorbed onto the surface of the foam and removed via the flotation deinking method (Vyas et al. 2003; Fricker et al. 2007). Qian (2005) found that flotation operations are more efficient when particle sizes are < 225 μm (0.04 mm^2). If the ink particles are fine enough (< 0.01 mm), they will easily dissolve in water and will be adsorbed onto the fiber, resulting in poor whiteness. Furthermore, the distribution of the ink particles were also measured in order to provide greater detail on the particle sizes of the three kinds of inks.

3.3 The PSDs of hybrid LED–UV, LED–UV, and vegetable oil–based inks

In the literature, there have been limited studies regarding the particles sizes of ink itself. In this study, the PSDs and the average sizes of the hybrid LED–UV four-color inks, LED–UV four-color inks, and vegetable oil–based four-color inks were determined, and the results are shown in Fig. 2. The size of a majority of the hybrid LED–UV four-color ink particles was in the range of 5–7 μm . The LED–UV and vegetable oil–based four-color inks exhibited a similar trend in PSD, whereas the latter showed a narrower distribution for part of the particles with a size that approached 100 nm. The narrower particle size of the vegetable oil–based four-color inks may explain the dirt area results compared to that the vegetable oil–based ink undeinked and deinked hand sheets that had the least number of ink particles. The results also presented that the type of ink played an important role in the surface chemical and physical properties of the printed ink, which in turn can have a critical effect on the efficiency of flotation deinking. To improve the efficiency of the deinking flotation of both print paper and waste paper, factors must be taken into consideration. Improvements may be made both by the design of new pigment particles and modification of the surface properties of the printed pigment particles.

3.4 The FT–IR analyses of the vehicle samples

Although the ink sizes dispersion classification of the hybrid LED–UV four-color inks, the LED–UV four-color inks, and the vegetable oil–based four-color inks were studied by the Malvern Zetasizer Nano ZS90 sampler, and this provided more information, the FT–IR analyses of the vehicle samples helped further our understanding. Fig. 3 shows the FT–IR spectra of the vehicles used for the hybrid LED–UV, the LED–UV, and the vegetable oil–based inks. As a whole, for the three kinds of vehicles, a strong band appeared at approximately 2926 cm^{-1} that was related to the C–H stretch (Rengasamy et al. 2013). The characteristic peak near 1743 cm^{-1} was due to the absorption of the ester group (Zhang et al. 2020). In the hybrid LED–UV and vegetable oil–based ink vehicles infrared spectrum, the new peak at 1620 cm^{-1} corresponded to the stretching vibration peak of the acrylic acid double bond in the hybrid LED–UV

vehicles, and 744 cm^{-1} was the characteristic absorption peak of the epoxy soybean oil epoxy group, which indicated the introduction of acrylic acid double bonds. This further proved that the hybrid LED–UV vehicle was successfully prepared by esterification. The 3466 cm^{-1} peak was assigned to be the –OH intense absorption peak in the hybrid LED–UV spectrum, and this indicated the successful ring opening of the epoxy groups (Mandal et al. 2018; Wuzella et al. 2012). This also explained that the hybrid LED–UV four-color inks had the best deinking efficiency. Furthermore, according to the analysis of the FT–IR fingerprint characteristics absorption ($-1500\text{ cm}^{-1}-500\text{ cm}^{-1}$), the LED–UV ink vehicle showed a structural difference from the two other vehicles. The LED–UV ink vehicle spectrum displayed characteristic peaks at 1406, 1385, 1119, and 810 representing the scissoring of the $\text{CH}_2=\text{CH}$ groups and stretching of the asymmetric $\text{O}=\text{O}-\text{C}$, $\text{C}=\text{O}$, and $-\text{C}=\text{C}$ bend groups (Liu et al. 2017; Salih et al. 2015). These groups may have been the reason that the paper printed UV offset ink was the most difficult raw materials to be deinked by the conventional deinking process. In the present study, the LED–UV ink demonstrated a higher efficiency than the vegetable oil–based ink. This may have been due to the differences in the properties of the varnish layers cured by the classical UV lamp and the LED lamp. Dawidowicz et al. (2020) studied some physicochemical properties of polyacrylate varnish layers cured using classical and LED–UV sources. In their work, they noted that the classical UV lamps strongly cross–linked the varnish layers than the LED lamps did.

3.5 Scanning electron micrographs of the fibers of LED – UV ink, the LED – UV ink, and the vegetable oil – based ink undeinked and deinked hand sheets

Scanning electron microscopy (SEM) is widely used to more intuitively observe changes in the surface morphology of fibers after physical and chemical treatments (Meng et al. 2013). In the present study, the SEM images of the printed product and the undeinked and deinked hand sheets were used to analyze the surface morphology changes during the deinking process. As shown in Fig. 4, in the printed product samples images, overall the paper fiber irregular particles or granules appeared on the fiber surface (H, L, and V). From a comparison of the SEM, it may be seen that a large number of ink particles were enriched in the surface of the fibers (A_1 , B_1 , C_1) in the pulping process, and the adhesion between the fibers was strong. After flotation deinking, the ink particles on the surface of the fibers (H_2 , L_2 , V_2) were significantly reduced. More fibrils appeared on the surface of the fiber, and the fibers became rougher. The fibers were more closely connected, and this indicated that flotation activated the surface of the fiber to a certain extent and increased the degree of fiber fibrillation. Hybrid LED–UV ink particles on the surface of the fibers were the least abundant (H_2), and the fiber surface became smoother with the best deinking efficiency.

3.6 Effect of ink type on the mechanical properties of paper during flotation

Parameters such as the ash content, tensile strength, folding endurance, and interlayer bonding strength were introduced to evaluate the mechanical properties of the handsheets during the pulping and flotation processes. Fig. 5 presents the physical properties of the handsheets before and after flotation deinking. In

Fig. 5, the tensile index, folding, and interlayer bonding strength of the hybrid LED–UV ink hand sheets were 45.4 N m/g, 19 times, and 334 J/m² after deinking, respectively. The tensile index, folding, and interlayer bonding strength of the LED–UV ink hand sheets were 45.5 N m/g, 22 times, and 367 J/m², respectively. The tensile index, folding, and interlayer bonding strength of the vegetable oil–based ink hand sheets were 43.6 N m/g, 15 times, and 259 J/m². The paper strength increase was attributed to the fact that more ink detached from the fibers and exposed the fresh surface, which not only enhanced the softness of fibers, but also exposed more hydroxyl groups on the fiber surface promoting interfibrillar binding (Feng et al. 2011). However, the mechanical properties improving conferred by different inks to the handsheets were different, the results are shown in Table 3. The handsheets with the hybrid LED–UV ink exhibited an increase of 21.4%, 37%, and 39.7% in the tensile strength, folding endurance, and interlayer bonding strength, respectively. All of the corresponding mechanical strength parameters reached the maximum for handsheets with the hybrid LED–UV ink. Actually, this may possibly be explained by the deinking agent dispersing particle sizes of the hybrid LED–UV ink into suitable particles that very easily floated with foam. Furthermore, the least of the residual ink particles and the most fibrils appeared on the fiber surfaces after flotation, thus resulting in the strength of the hand sheets with hybrid the LED–UV ink reaching the highest valued compare with the other two kinds of ink. These results were proven by the SEM micrographs. The ash content of the treated paper sheets decreased to 3.3% for the hybrid LED–UV ink. This decrease is the ability of flotation in eliminating the ink. The ink has some inorganic constituents connected to a polymer matrix (Behin et al. 2007).

4. Conclusions

The hybrid LED–UV, LED–UV, and vegetable oil–based inks with low volatile organic compound (VOC) contents are originally hydrophobic; hence, the separation of ink can be achieved by flotation from the cellulose fiber. During the printing process, their chemical properties undergo no significant change, specifically their hydrophobic characteristics. However, during the printing process, vegetable oil–based inks primarily utilize penetration as the vehicle into the paper structure. Oil and resin components left on the paper surface with the pigment can react slowly with oxygen to form a three dimensional polymer network. An increased number of smaller particles are produced in vegetable oil–based ink printed paper pulping. Both factors accounted for the poor efficiency in the flotation deinking. For the hybrid LED–UV inks, the LED–UV lamp effectively reduced the length of time needed for the oil substances to penetrate into the paper fiber, inhibiting the oxidation reaction of the vegetable oil. This made the whiteness and deinking efficiency of the hybrid LED–UV ink increase by 47.6% and 58.1%, respectively. After deinking, the deinking paper tensile index, folding resistance, and cohesion of the hybrid LED–UV, LED–UV, and vegetable oil–based inks increased.

Declarations

Authors' Contributions: All authors contributed to the study conception and design. Material preparation, data collection and analysis were performed by Shujie Yang, Jianbin Shen, Tiefei He, Chao Chen,

Junming Wang and Yanjun Tang. The first draft of the manuscript was written by Shujie Yang and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

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Tables

Table 1 Comparison of handsheets optical properties and pulp deinking efficiency of hybrid LED–UV ink, LED–UV ink and vegetable oil-based ink

Pulp	ERIC /ppm	Brightness /%	Whiteness /%	Deinking efficiency/%
Hybrid LED–UV ink undeink pulp	131.8	73.7	52.3	58.1
Hybrid LED–UV ink deink pulp	55.2	85.5	77.2	
LED–UV ink undeink pulp	148.0	74.2	52.7	46.9
LED–UV ink deink pulp	78.6	83.9	72.2	
Vegetableoil–based ink undeink pulp	185.3	71.7	48.8	42.1
Vegetableoil–based ink deink pulp	107.3	78.4	60.4	

Table 2 Comparison of handsheets dirt particle area of hybrid LED–UV ink, LED–UV ink and vegetable oil-based ink

		• Ink particle size range/mm						Decrease Percentage (%)
		0.01	0.04	0.15	0.4	1.0	5.0-	
		-	-	-	-	-		
Dirt particle Area (mm ² ·m ⁻²)	Hybrid LED–UV ink-undeinked handsheets	460	267,078	1043	388	135	/	98.8
	Hybrid LED–UV ink deinked handsheets	4	3319	12	/	/	/	
Dirt particle Area (mm ² ·m ⁻²)	LED–UV ink undeinked handsheets	320	250,436	285	79	/	/	96.4
	LED–UV ink deinked handsheets	307	8690	103	/	/	/	
Dirt particle Area (mm ² ·m ⁻²)	Vegetableoil–based ink undeinked handsheets	24	54522	587	515	367	/	89.6
	Vegetableoil–based ink deinked handsheets	10	5749	40	/	/	/	

Table 3 Effect of ink type on the mechanical properties of paper in flotation process

Parameter	Hybrid LED–UV ink	LED–UV ink	Vegetable oil–based ink
Ash content decrease /%	3.3	13.6	14.7
Tensile index increase/%	21.4	9.04	25.9
Folding increase/%	37	22	25
Interlayer bonding strength/%	39.7	20.3	18.3

Figures

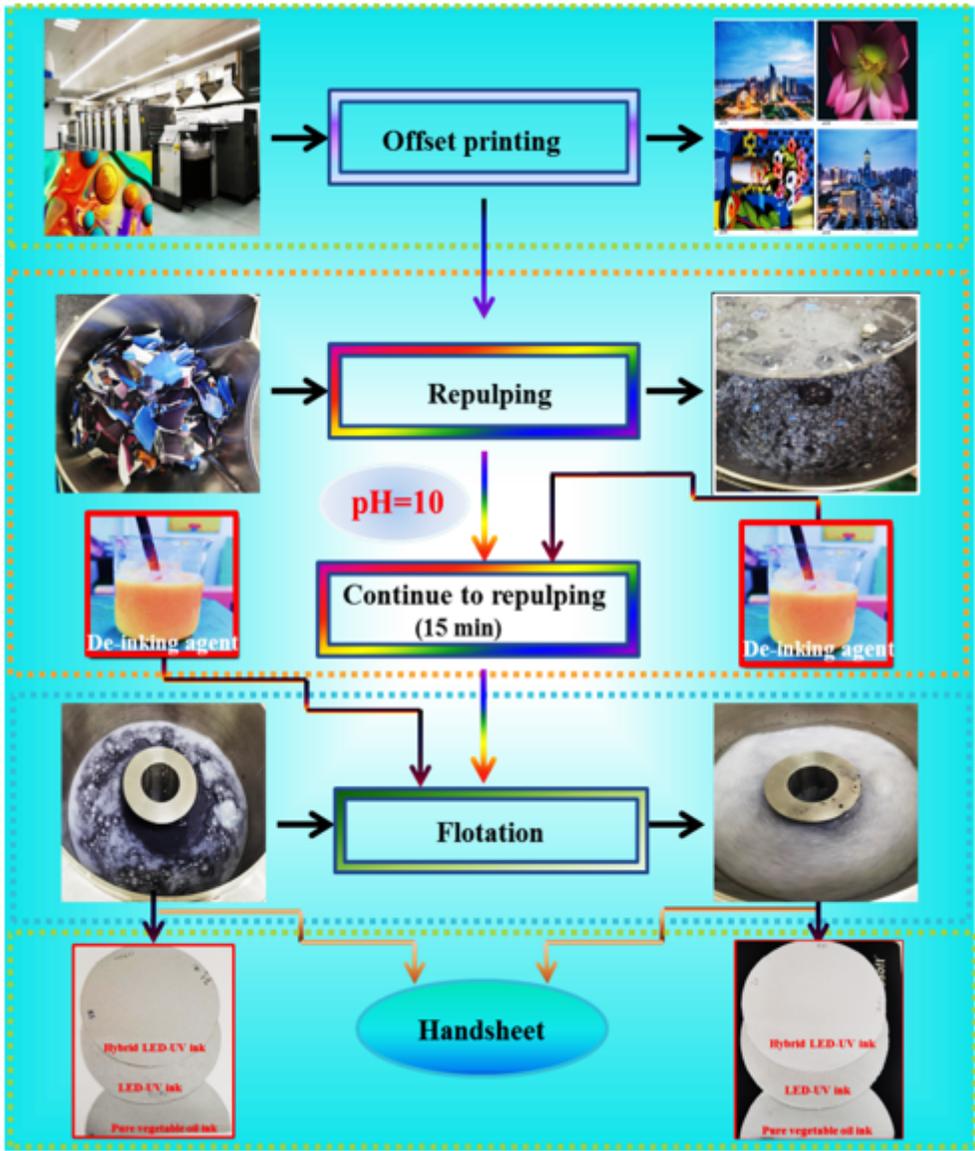


Figure 1

Deinking experiment process via flotation

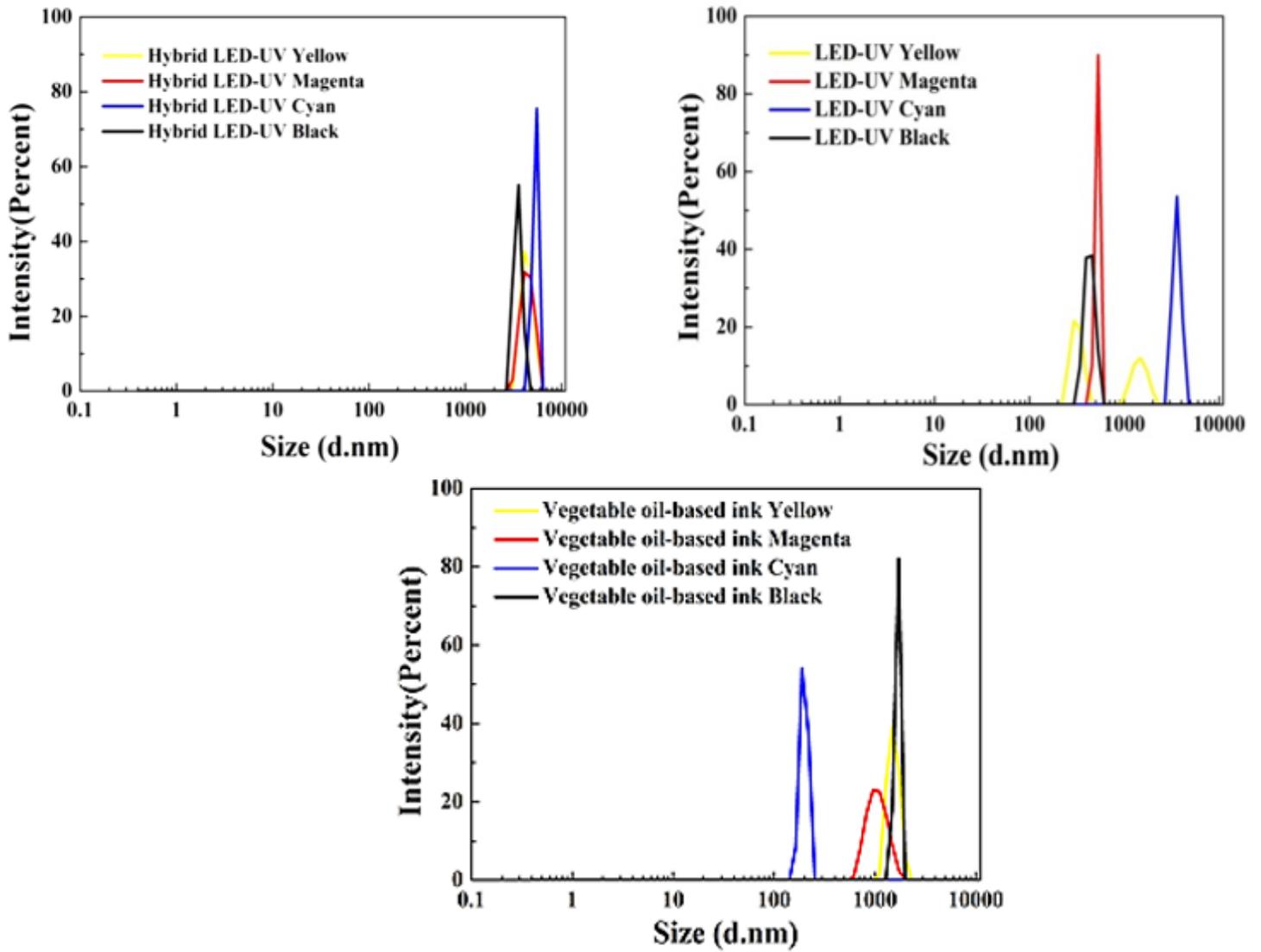


Figure 2

The PSDs sizes of the hybrid LED-UV four-color inks, LED-UV four-color inks, and vegetable oil-based four-color inks

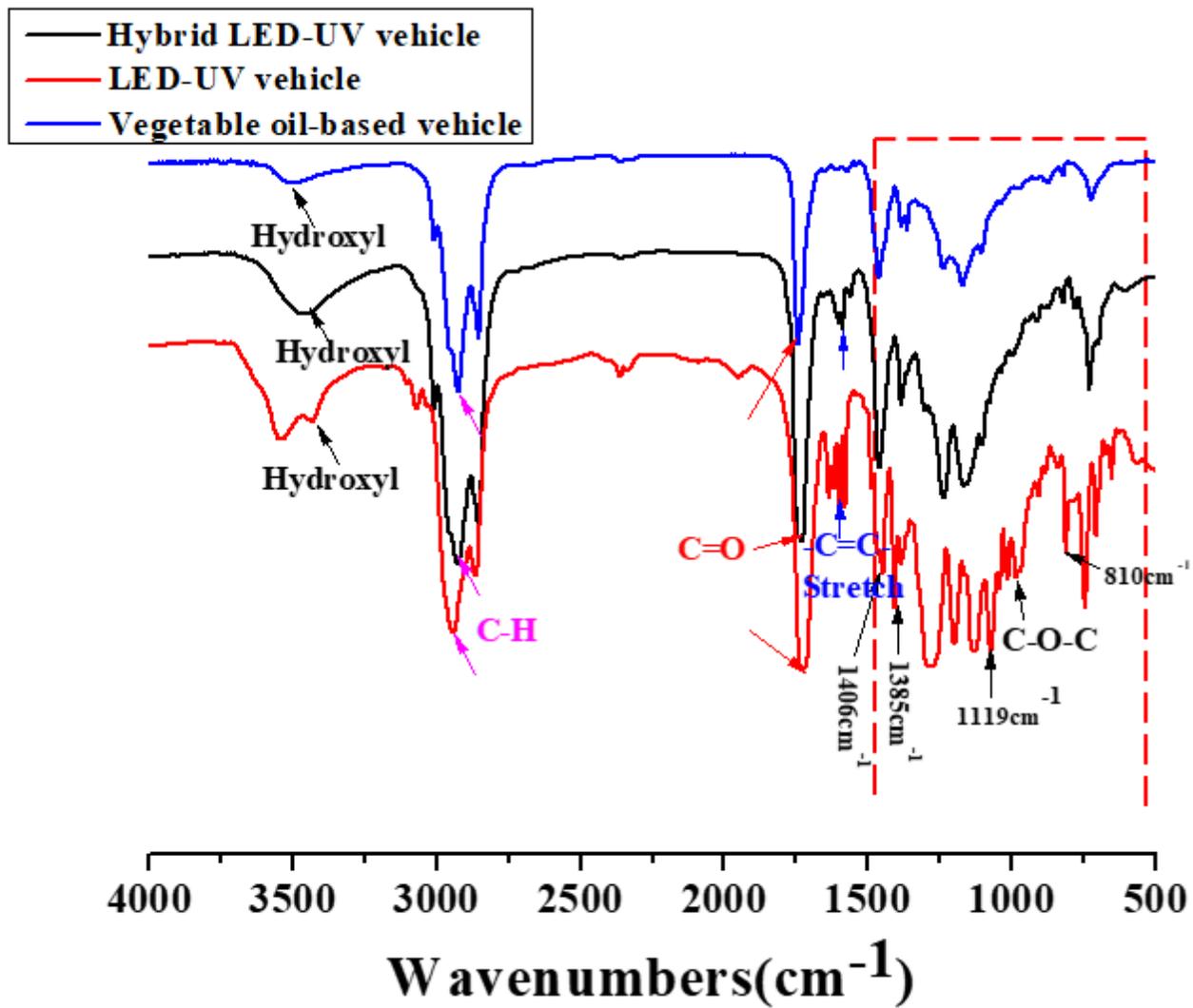


Figure 3

FT-IR spectra of the vehicle samples

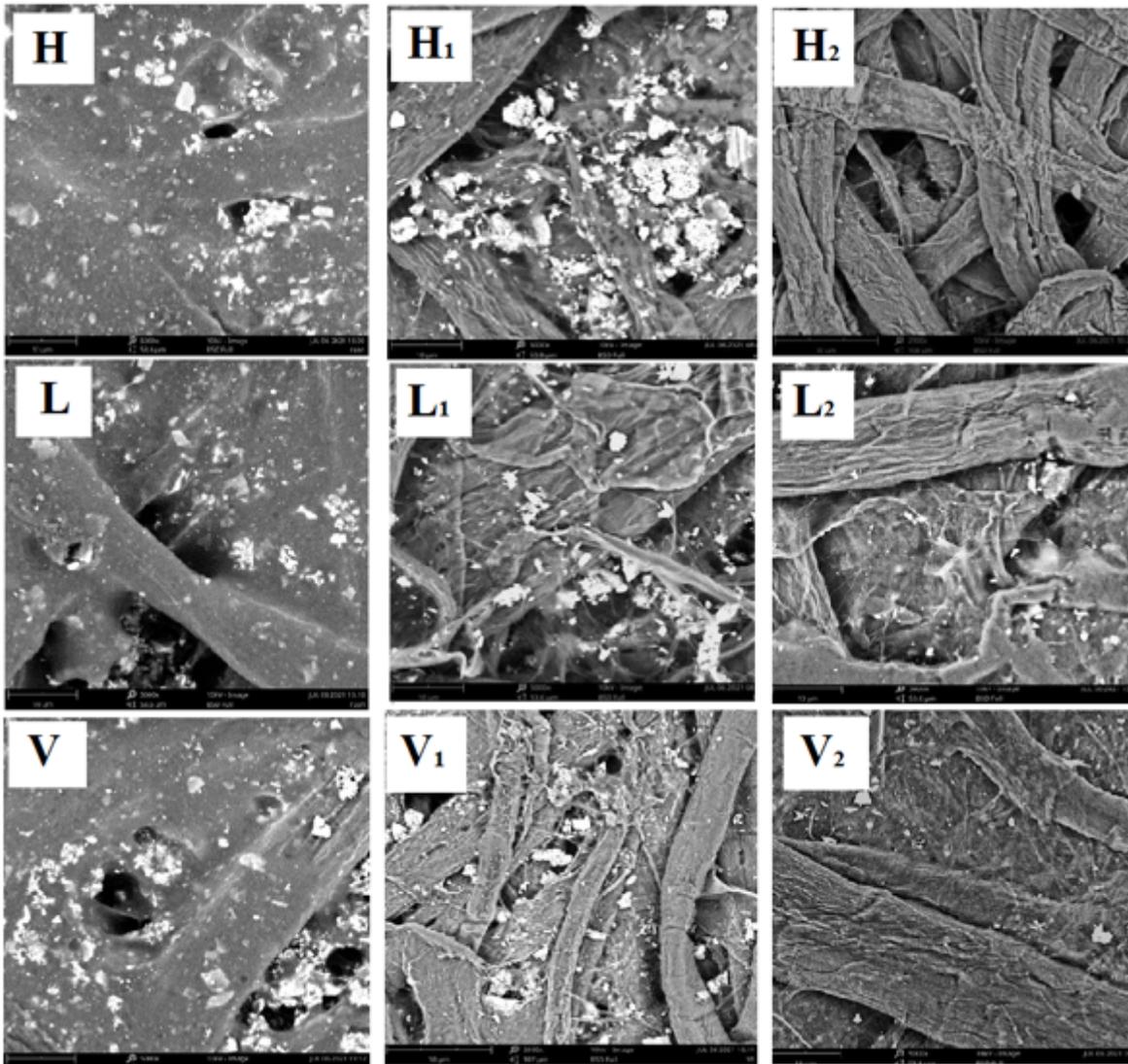


Figure 4

Scanning electron micrographs of the fibers of (H) Hybrid LED-UV ink print product,(H₁) Hybrid LED-UV ink undeinked pulp and (H₂) Hybrid LED-UV ink deinked pulp. (L) LED-UV ink print product,(L₁) LED-UV ink undeinked pulp and (L₂) LED-UV ink deinked pulp. (V) Vegetableoil-based ink print product,(V₁) Vegetableoil-based ink undeinked pulp and (V₂) Vegetableoil-based ink deinked pulp

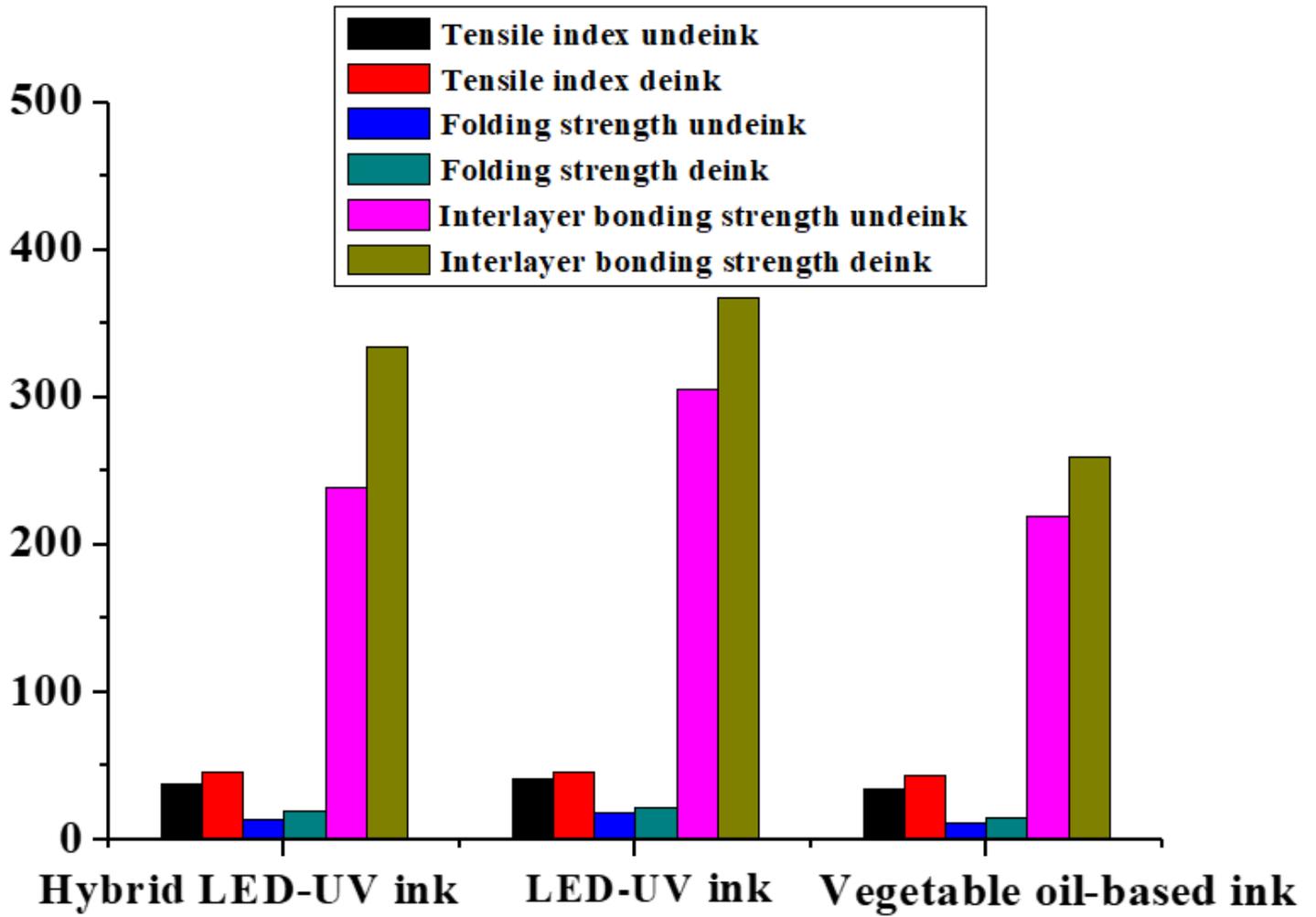


Figure 5

These physical properties of the handsheets before and after flotation deinking