GREEN RECYCLING OF TONER PRINTED PAPERS BY ENZYME DEINKING

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Abstract: *The basic printing material of the printing industry is paper. The paper industry uses trees as a source of raw materials. Due to the increasing need and the environmental effects of tree cutting, recycling of used papers, deinking and making papers reusable are among the popular study subjects. The chemicals used in traditional deinking processes are highly toxic. For this reason, environmental protection, which is one of the main reasons for recycling, cannot be adequately achieved with this method. In studies carried out for this purpose, environmentally friendly enzymatic ink removal methods can be used. The enzymatic deinking process is preferred because it has advantages such as high efficiency, low environmental impact, less harmful chemicals needed to achieve equal gloss, better strength, as well as a lower carbon footprint. One of the printing areas where paper is used most in daily life is the products printed with personal printing machines. In this study, it is aimed to print it with a desktop digital printing machine and deink it with amylase enzyme. In this sense, prints were made on 80g/m2 UPM office papers with black toner. Unprinted papers and printed papers were first chemically deinked according to the Ingede 11 method. Then, treatment with enzyme was added to the system as a secondary cleaning method. The amount of amylase enzyme used is 150 FPU/100 g paper. After the deinking process, filter papers were produced. The surface properties, colour, brightness, amount of contamination and amount of recycled ink of the produced papers were determined. Papers with only chemical deinking and those with additional enzymatic treatment were compared. As a result, it was concluded that cleaner papers were obtained with additional treatment with enzyme.*

Key words: Deinking, Amylase, Green Recycling, Paper

1. INTRODUCTION

With the rapid consumption of natural resources, the problem of eliminating waste has also emerged. In order to solve this problem, new methods have been tried to be found for reducing or evaluating waste. (Lüy, Varınca & Kemirtlek, 2007). In proportion to the increasing population in our world, wood fibre resources are decreasing and paper recycling is gaining great importance. Waste paper constitutes the largest portion of solid waste. Paper, which was previously destroyed by burning, has caused great harm to the world economy. Paper recycling has been widely used since the 1970s with the discovery of deinking. (Faul, 2010). Thanks to paper recycling, wastewater and carbon dioxide emissions are reduced, and energy savings reach up to 70%. (Yılmaz, 2024). It is important to use quality fibres in paper recycling. This is possible by completely separating the ink from the fibres. The ink that is to be removed from the fibres is separated with different processes. (Sežun, Karlovits & Kavčič, 2023). In the washing method, unwanted non-fibre materials are also removed along with ink removal. While the paper pulp is being purified from ink, they are examined under two main headings as disperse or non-disperse according to their status in the solution. In disperse materials, unwanted non-fibre materials and ink are removed from the pulp in the form of small particles by washing. Non-disperse ink can be seen in the recycled and prepared paper as small particles. In order to prevent this, a multi-stage washing process should be carried out. Flotation, washing and bleaching are methods of removing ink from paper. The basic principle of the flotation method is to give air to the prepared paper pulp and thus to obtain clean fibre particles by allowing the ink particles attached to the air bubbles to rise to the surface. The most common method, the flotation method; It is used in the production of papers used in health and personal care, office paper, magazine and newspaper paper. (Sahin, 2016). Chemicals such as NaOH, Na_2SiO_3, NaOH and surfactants are substances used in traditional deinking processes. Chemicals are pollutants in deinking and also reduce the strength of the paper fibre and cause waste. (Malhotra & Chapadgaonkar, 2023). With the increase in office paper usage, these separation processes using toxic chemicals are harming the environment. With the increase in environmental awareness, the need to use environmentally friendly materials instead of chemical toxic substances used to remove ink from paper in recycling technologies has also increased. For this reason, it is necessary to protect the environment by using different surface active substances that do not harm the environment. (Pimenta, 2023). Another method is to remove unwanted substances that could not be removed by washing and flotation by bleaching. Some of these bleaching chemicals are hydrogen peroxide and sodium hypochlorite. In recent years, instead of traditional deinking with chemicals, enzymatic deinking has begun to be used. It has been observed that deinking with enzymes further improves physical and optical properties such as tensile strength, whiteness, brightness, opacity, drainage speed and reduces the amount of ink residues. Among the enzymes that replace harmful chemicals, xylanase, lipase, cellulase and laccase are the most commonly used ones (Cicekler & Tutus, 2020). The aim is to separate all unwanted materials except fibre from the pulp. There are standards developed by the International Association of the Inking Industry (IGNEDE) to determine the deinkability. The IGNEDE 11 laboratory test is used to measure the deink removal efficiency of the flotation cell in the paper-ink combination at defined dimensions. However, the deink removal efficiency can be evaluated with this test using alkaline pulp without the need for bleaching and washing under deink conditions (Cicekler & Tutus, 2020). In this study, office papers were printed with black toner and the ink was chemically removed from the pulp using the IGNEDE 11 method. Then, enzyme purification was performed and filter papers were produced. The physical and optical parameters of the produced filter papers were measured. Papers obtained with different processes were compared.

2. MATERİAL AND METHODS

2.1 Materials

Office paper (80 g/m^2) was purcased from Sodium dodecyle sulphate,amylase (≥500 units/mg protein) and other chemicals obtained from sigma aldrich.

2.2 Methods

Firstly In the this study test prints were made on uncoated 80 g/m^2 office paper with Canon F166400 black toner-based laser digital printer (Figure 1).

Figure 1: Black toner printed papers

After printing, the papers were kept for 2 years. Then, the printed papers were torn into small pieces of 20 mm x 20 mm and kept in airtight plastic bags for 1 day. Then, the papers were pulped using sodium hydroxide 0.6%; hydrogen peroxide 0.7%; sodium silicate 1.8% and oleic acid 0.8% according to the standard İNDEGE method 11 p (Figure 2). method. Sodium hydroxide was used to swell the ink on office papers and separate them from the fibres, hydrogen peroxide was used to whiten the papers without yellowing, sodium silicate was used to loosen the ink particles on the fibres and prevent them from accumulating on the fibres again, and oleic acid was used to capture the ink particles removed from the fibres and carry them to the surface.

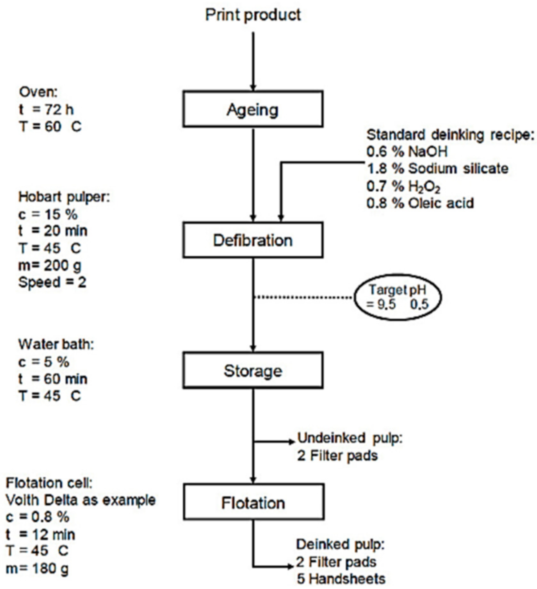

Figure 2: Flow chart of INGEDE method 11p

The pulping process was carried out in two stages. 103.11 g (completely dry) pulp was used in each stage. The pulping process was carried out at 250 rpm speed, for 20 minutes and at 15% concentration at 45 °C. Half of the pulp was separated and 0.2% amylase enzyme was added to the pulp and it was shaken at 45-500°C for 2 hours at pH 7. Then, 0.15% sodium dodecyl sulphate was added to make the ink released into the medium easier to separate (Figure 3). After the shaking continued for another 15 minutes, the flotation process was started.

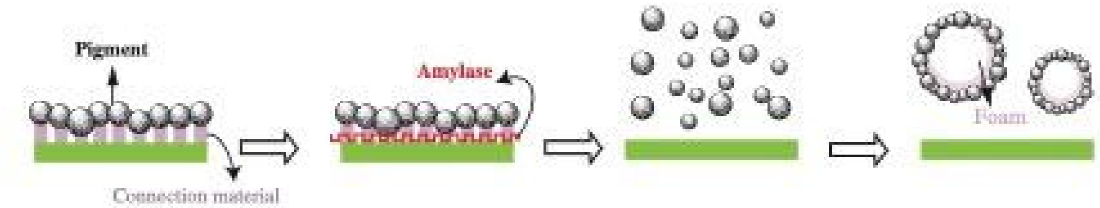

Figure 3: Deinking mechanism diagram of amylase and SDS

In the flotation process, the system with 1% concentration was operated at 45°C., 1450 rpm and 10 minutes. The air pressure was set as 0.566 m^3/min. While the flotation cell was operating, the dirty foamy part formed on the surface was scraped off at certain intervals with the apparatus on the system. After the flotation process, the deinked pulp with 1% concentration was filled into the inner chamber of the device at certain intervals and the waste water was left to flow out of the sieve on its own (Figure 4).

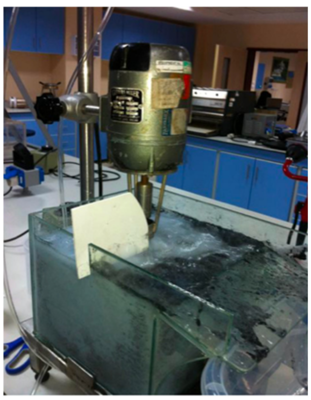

Figure 4: Flotation cell image

Then, the pulp remaining in the inner chamber was squeezed to ensure that the concentration reached around 30-32%. The high concentration pulps were placed in polyethylene bags and stored in a refrigerator at ¬16°C for further processing. The standard raw material preparation method was applied to obtain the pulps as an aqueous suspension. Then, standard laboratory test papers were made from pulp suspensions of known concentration. In the production of hand papers, the Tappi T 205 sp-06 standard was used in the Standard British Handsheet Former device. In the production of handsheets on the Standard British Handsheet Former, at least 6 test papers were made for each trial of each pulp, and the water was removed between the drying discs and absorbent blotter papers in the laboratory press at 80 PSI pressure for 40 seconds and then completely dried in the drying cylinder. The papers obtained were conditioned in a controlled room at 23±1°C and 50±2% relative humidity in accordance with the Tappi T 402 om-88 standard for at least one day. The optical properties of the obtained base paper (BP), base paper subjected to deinking (DBP), defibrillated non-flotation printed paper (UPP), enzyme-treated deinking printed paper (EDPP) and only deinking printed paper (DPP) samples were determined. Colour, whiteness values were measured using the X-Rite eXact spectrophotometer according to the colour ISO 12647-2:2013. The measurement conditions were carried out according to the relevant appropriate standards. The difference between the colours of the different prints were calculated according to the CIE ΔE 2000 colour difference Equation (1) ISO 11664-6:2014. Calculations were made by taking the average of five measurements. ΔL*, Δa*, Δb*: Difference in L*, a*, and b* values between specimen colour and target colour. Lightness is represented by the L* axis which ranges from white to black. The red area is connected to the green by the a* axis, while the b* axis runs from yellow to blue.

$$\Delta E_{00} = \sqrt{\left(\frac{\Delta L\prime}{k_L S_L}\right)^2 + \left(\frac{\Delta C\prime}{k_C S_C}\right)^2 + \left(\frac{\Delta H\prime}{k_H S_H}\right)^2 + R_T \frac{\Delta C\prime\ \Delta H\prime}{k_C S_C k_H S_H}} \quad (1)$$

where ΔL*, ΔC*, and ΔH* are the CIEL*a*b* metric light- ness, chroma, and hue differences, respectively, calculat- ed between the standard and sample in a pair, ΔR is an interactive term between chroma and hue differences. The SL, SC, and SH are the weighting functions for the lightness, chroma, and hue components, respectively. The values calculated for these functions vary according to the positions of the sample pair being considered in CIEL*a*b* colour space. The kL, kC, and kH values are the parametric factors to be adjusted according to different viewing parameters such as textures, backgrounds, sep- arations, etc., for the lightness, chroma, and hue compo- nents, respectively. All paper's glosses were measured with BYK Gardner GmbH BYK Gardner GmbH micro Tri-gloss 60° geometry in accor- dance with ISO 2813:2014. The surface properties of the produced papers were determined by scanning electron microscope (SEM) (Phillips XL 30 ESEM-FEG). Bio based papers were cryo-fractured with liquid nitrogen. Fractured films surfaces coated with gold before SEM imaging. In addition, the surface structure and cleanliness of the papers were examined by LEİCa optical microscope at 2.5 magnification. The obtained papers were printed using Micheal Huber München magenta oil based ink with the help of IGT C1 under a printing pressure of 300 newtons and the obtained prints were subjected to the above examinations.

3. RESULTS AND DISCUSSION

Generally, traditional chemical deinking uses alkaline pulping. Although composite surfactant can effectively disperse ink particles in the fibre, deinking uses NaOH, Na_2SiO_3, EDTA, H_2O_2 and other chemicals, which not only increases the cost of deinking, but also leads to serious chemical pollution in wastewater and increases the cost of wastewater treatment. In addition, the presence of these chemicals can damage the fibres, reduce the quality of the fibres, and reduce the number of fibres recycled. In addition, the use of surfactant can help remove ink. the surfactant itself can adsorb on the surface of the ink to reduce the surface tension of the ink and promote the emulsification and dispersion, which is favourable for the removal of ink and prevents the redeposition of ink via dispersion. In this study, SDS, one of the most widely used surfactants, was used and it was determined that it provided effective separation. As seen in Figure 3, the deinking process performed with amylase leaves fewer toner particles than other processes, which is an indication of this. In this study, laser printed papers were evaluated on account of deinkability by using enzyme and chemical process. In order to evaluate the enzyme influence, chemically deinked samples were used as control samples. Papers were produced again from the obtained fibres. The image of the produced papers is given in Figure 5.

Figure 5: Papers produced using chemical process and enzymatic process (Enzyme treated deinking printed paper (EDPP), chemical deinking printed paper (DPP), Defibrillated undeinking printed paper (UPP), deinking base paper (DBP) respectively)

When Figure 5 is examined, it is seen that the paper that was subjected to only deinking processes without any printing on the base paper is visually and tactilely more stable than all other papers, as expected. When the other papers are examined, it is determined that the paper subjected to enzymatic deinking gives the closest visual effect to the paper produced in the recycled form of the base paper, but has a smoother surface in terms of touch. It is concluded that the printed paper that was not subjected to deinking looks the dirtiest and the ink particles are not separated. When they are ranked among themselves, it is determined by eye that there is ink separation as paper produced with enzymatic deinking, paper produced only with chemical deinking and paper that has not been deinked at all. In addition, the deinking rates of the produced papers are calculated according to Equation (2).

$$Deinking\ ability = \frac{Brightness\ of\ the\ treated\ sample - Brightness\ of\ the\ untreated\ sample}{Brightness\ of\ the\ untreated\ sample}\ x\ 100 \quad (2)$$

When calculating deinking abilities, the brightness of newly produced papers was used as treated sample and base paper without any treatment was used as untreated sample. Accordingly, for enzyme applied deinking applied printed paper (EDPP), chemically deinking applied printed paper (DPP), defibrillated undeinking printed paper (UPP), deinking applied base paper (DBP) it was found as 6.8; 4.6; 2.14; 0.34 respectively (Figure 6). This result also gives us the conclusion that enzyme treated paper has a better deinking ability than papers with only chemical deinking and without deinking, parallel to the result with visual effect.

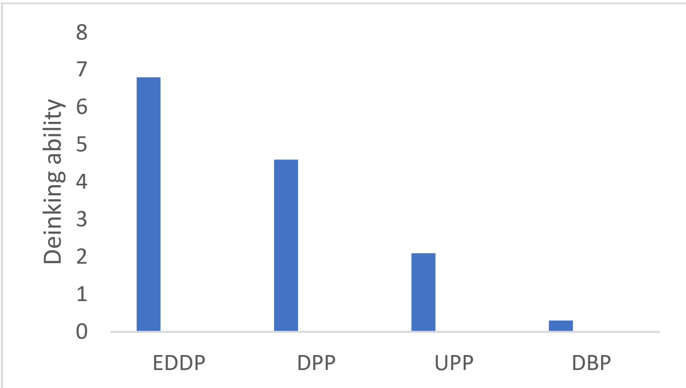

Figure 6: Deinking ability of produced papers

The colour, gloss and printability properties of the produced papers were examined and are given in Table 1. When the gloss values were examined, the gloss was the lowest in the enzyme added recycling. This was due to the principle of amylase deinking, where the enzyme hydrolyzes the resin binder in the ink and separates the ink from the fibres. In the chemical method, some decrease in gloss is due to the protonation of the resin particles. The gloss changed less in the other two recycled papers. When the colour values are examined, the base paper that has not been recycled in unprinted papers is used as a reference. When the unprinted papers are examined among themselves, it is seen that the difference is due to the L and b values. The decrease in the L value is due to the toner particles found as residue in the processed paper. When the enzyme and unprinted recycled papers are examined, it is determined that the L value is closest to the reference. This shows that the best deinking is performed with enzymes. There is a blue shift in the b values of all papers subjected to the deinking process. The reason for this is that the resin used as a binder in the paper is removed with the processes performed, and accordingly, the colour changes occur. The most change is seen in the enzyme-treated papers as expected from gloss, while the least change occurs in unprinted papers. When the colour differences are examined, it is clearly seen that the lowest difference is in the unprinted processed paper. It has been determined that the main reasons for the colour differences are the blue shifts originating from the resin removal and the filler material removed from the environment. The CIE whiteness is a measurement of the light reflected by the paper across the visible (daylight) spectrum. The CIE have set a standard of D65 illumination which is a standard representation of outdoor daylight under which the amount of light reflected is measured. For a perfect reflecting, non-fluorescent white material, the CIE whiteness would be 100, however most 'white' paper will increase CIE whiteness measures up to 100-140 due to the addition of Optical Brightening Agents (OBAs) which are designed to reflect light from the non-visible range (mainly ultra-violet) back in the visible spectrum. When the whiteness values are examined, it can be concluded that the whiteness value of the untreated paper is over 100 and therefore contains optical brighteners. It has been observed that the whiteness value increases the most in papers that have been subjected to enzyme and chemical deinking processes. This can be concluded that the filler in the paper is removed from the paper environment by the processes, but the optical brightener cannot be removed, thus increasing the CIE whiteness of the paper. It has been determined that the least change in whiteness is in unprinted paper.

Table 1: Colour, gloss and printability properties of the produced papers

	L	a	b	Gloss	Whiteness (CIE)	Opacity	Delta E (ΔE)
Base paper	94,00	1,38	-5,88	95,76	109,89	0,92	REF
Unprinted EDPP	93,07	2,67	-11,67	89,53	129,77	0,91	6,00
Unprinted DPP	90,87	2,26	-10,31	91,26	114,14	0,91	5,50
Unprinted UPP	90,90	2,37	-10,10	94,38	110,11	0,91	5,33
Unprinted DBP	93,89	1,64	-9,40	94,34	109,92	0.92	3,53
Printed EDPP	54,66	57,55	0,72		Not measured	Not measured	0,95
Printed DPP	54,10	56,18	1,21		Not measured	Not measured	1,75
Printed UPP	52,91	56,72	2,37		Not measured	Not measured	2,11
Printed DBP	53,76	57,84	0,79		Not measured	Not measured	REF

All papers produced were successfully printed and the results obtained were parallel to unprinted papers. However, colour differences were significantly reduced. This shows us that the ink tolerates colour differences.

When the opacity results in Table 1 were examined, it was determined that there was no noticeable difference between the opacity values. The results are consistent with the literature. (Lasheva et al, 2016)

Tensile strength depends on the amount and strength of the binding forces between the fibres in the finished paper sheet. When Figure 7 is examined, it is determined that the chemicals and enzymes used in the produced paper reduce the binding and therefore the tensile strength decreases, but this decrease is quite small.

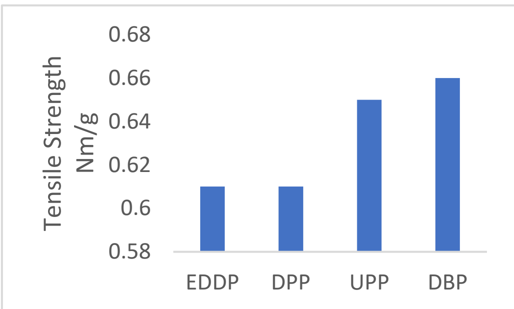

Figure 7: Tensile strength of produced paper

The bursting resistance of the produced papers is shown in Figure 8. The bursting resistance depends primarily on the structure of the paper samples obtained. In the examinations, it was concluded that the processes performed did not change the bursting resistance of the paper noticeably.

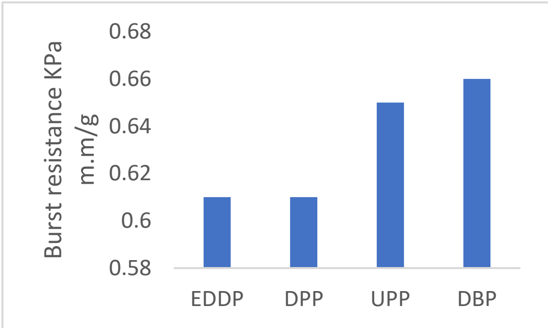

Figure 8: Burst resistance of produced paper

Tear resistance depends primarily on the strength of the nature of the fibres that make up the paper obtained. As shown in Figure 9, it was determined that flotation did not cause much change in the fibre length and nature of the fibres and had the highest tear resistance. Since the fibres were slightly shortened by chemical or enzymatic treatments, a small decrease in tear resistance occurred. The produced papers were examined with SEM and optical microscope. SEM images are given in Figure 10.

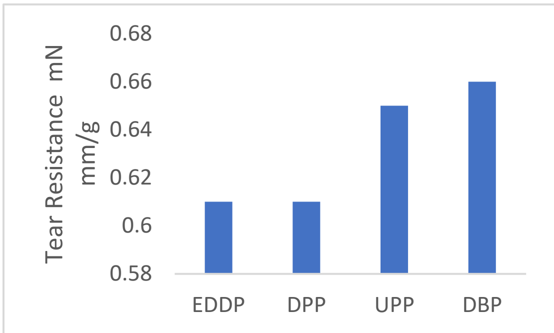

Figure 9: Tear resistance of the obtained paper

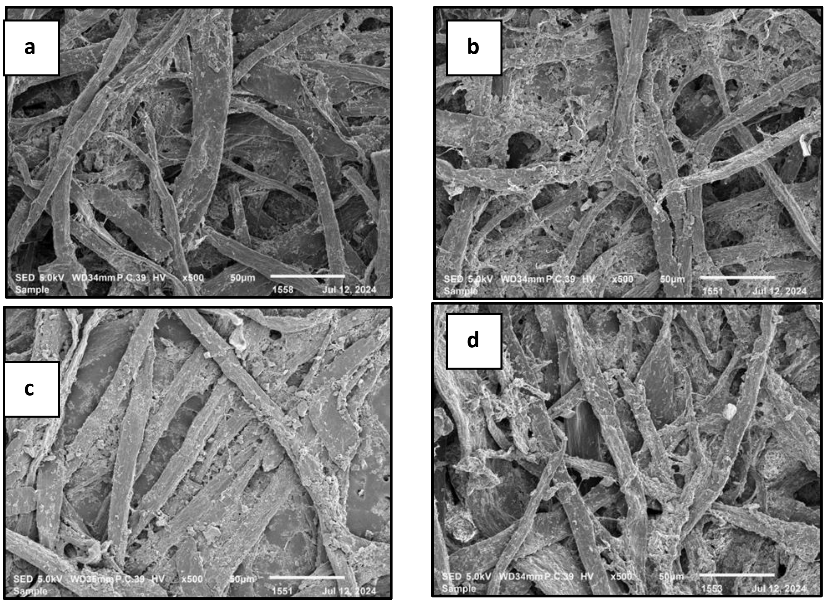

Figure 10: SEM images of produced papers.(a:EDDP, b:DPP, c:UPP, d:DBP)

When the SEM results were examined, it was determined that the papers deinked with enzymes had less toner residue and filler, similar to the visual examination, but there were deformations in the fibres. In the recycled form of the unprinted base paper, the fibres were subjected to the least deformation, but there were filler residues. It was seen that the paper that was not subjected to the deinking process could not be cleaned of both toner and filler. There were toner residues and filler in the papers subjected to chemical deinking. However, the amount of toner is less than the paper that was not deinked, the results are consistent with the visual data.

At the same time, the produced papers were also examined with an optical microscope. When the optical microscope results (Figure 11) were examined, toner residues could be seen in the undeinked paper and the chemically deinked paper. It could be clearly seen that the fibres of the enzyme deinked paper had undergone some deformation. The results are consistent with the SEM results and visual results.

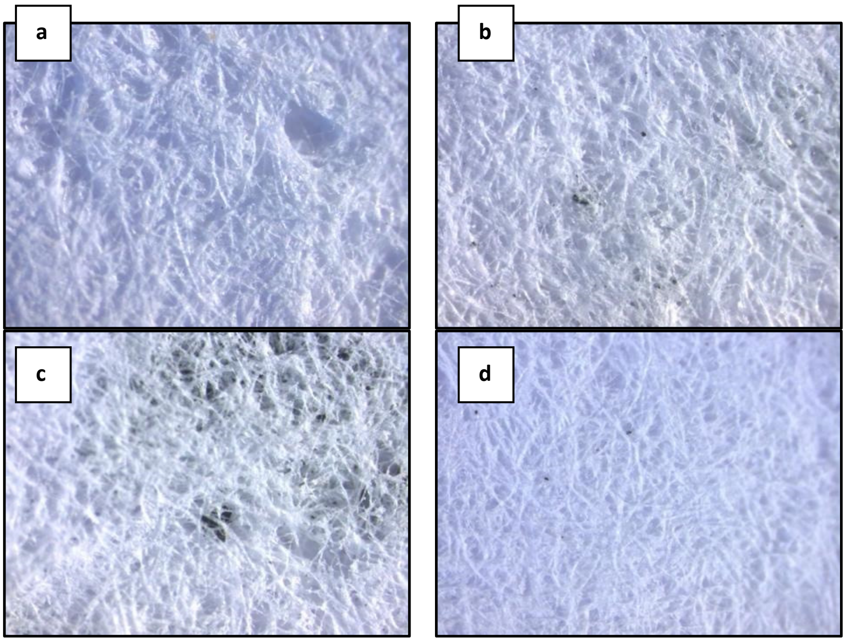

Figure 11: Optic microscope images of produced paper (a:EDDP, b:DPP, c:UPP, d:DBP)

4. CONCLUSIONS

As a result, using enzymes improves the properties of paper such as colour and ink separation processes. However, using only enzymes was not examined in this study. It was concluded that it exhibited a synergetic effect with chemical deinking. While deinking, amylase enzyme also removes the resin and filler of the ink, therefore, it creates changes in colour, gloss and whiteness. The best cleaning is done with enzymes. It was determined that not all toner could be removed in chemical deinking. It was concluded that chemical and enzyme+chemical processes caused deformation in paper fibres. It was concluded that enzyme use can be used as an effective, environmentally friendly method in office paper deinking.

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