REPULPING HIGH WET-STRENGTH WASTE BANKNOTE PAPER BY A DUAL-PH PRETREATMENT PROCESS

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A repulping approach of waste Chinese banknote paper, *i.e*., Renminbi (RMB) paper with high wet strength, was studied, and a dual-pH pretreatment process was used before refining. Pretreatment temperature, soaking time, and consistency of waste RMB paper were investigated to obtain the optimum repulping parameters. The results showed that when the pretreatment temperature was 80 ^{o}C, soaking time was 60 min, and consistency was 10%, the repulping yield was 88.1%. The arithmetic and weighted mean lengths of fine pulp fibers from the optimum experiment were 0.564 mm and 0.785 mm, respectively, and the mean width was 22.5 μm. Obvious kinks and broken ends, as well as a slight curl of fine pulp fibers were observed by analyses with a Morfi-compact fiber analyzer and a scanning electron microscope. The results from Fourier transform infrared spectroscopy analysis possibly demonstrated that the ester bonds in waste banknote paper were destroyed after the dual-pH pretreatment.

Keywords: Waste banknote paper; Repulping; Wet-strength; Dual-pH pretreatment

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INTRODUCTION

Waste paper has been an important fiber resource for the pulp and paper industry; however, its applicability in the production of paper products is highly dependent upon its water-disintegratability (Michelman and Capella 1991). It is difficult to reuse high wet-strength paper due to its poor repulpability in conventional repulping processes (*e.g*., in a hydropulper). Usually, a large amount of waste high wet-strength paper is either landfilled as solid waste or burned as garbage, which pollutes the environment and wastes fiber resources (Shao *et al.* 2011). In this context, the recycling of wet-strength paper is of great significance (Espy 1992, 1997; Espy and Geist 1993; Darlington and Lanier 1995; Njaa *et al.* 1994; Staib *et al.* 2001).

Wet-strength papers can be divided into either temporary or permanent wet-strength paper. When fully soaked in water, temporary wet-strength paper can significantly lose its wet-strength, which makes it easily repulped by adopting a conventional process (Smith 1997). However, it is almost impossible to completely repulp waste permanent wet-strength paper by merely soaking it in water, as its wet-strength is not easily damaged by water, which limits its recyclability. Waste banknote paper is a kind of waste permanent wet-strength paper and is very difficult to repulp.

The repulping of wet-strength paper has been reported by many researchers. Espy and Geist (1993) found that alkali metal persulfates could effectively defiber paper made with polyamideamine-epichlorohydrin (PAE) resins, though more slowly than hypochlorite. Recycled handsheets from persulfate- and hypochlorite-repulped broke had approximately equal dry strengths. In wet-strength grades made from recycled pulp without washing, residual persulfate interfered much less with wet-strength resin effectiveness than did residual hypochlorite. Fischer (1997) developed a repulping process using an oxidizing agent and a rewetting agent, which is very effective in repulping wet-strength paper. The process involves oxidizing the wet-strength paper at a low pH with inorganic or organic peroxides, and then hydrolyzing the wet-strength paper at a high pH. The process is particularly useful in repulping unbleached paper and old corrugated containers (OCC) containing PAE wet-strength resins.

The recycling of waste Chinese banknote paper, *i.e*. Renminbi (RMB) paper, can be conducted by cooking under high pressure and high temperature conditions; however, the repulping yield is only 60 to 70%, and there is usually a large amount of intractable waste water whose solid content is too low for alkali recovery, and chemical oxygen demand (COD) is too high for biochemical treatment (Gao *et al.* 1999). Wang *et al.* (2004) used potassium persulfate to pretreat the waste RMB paper for subsequent disintegration in a Valley beater, but breaking length of recycled pulp was very low. It was also noted that repulping time, waste paper consistency, soaking time, temperature, and reactant concentration in the repulping stage are major parameters for recycling wet-strength waste paper (Bhardwaj *et al.* 2004).

In this study, a dual-pH pretreatment process (*i.e*., soaking with 5% sulfuric acid solution followed by soaking with 5% caustic soda solution) was adopted to repulp waste RMB paper with high wet strength. The process conditions were optimized, and the fiber morphology of the recycled pulp was analyzed by using a Morfi-compact fiber analyzer and a scanning electron microscope (SEM).

EXPERIMENTAL

Materials

Waste RMB paper was kindly provided by Shandong Sun Paper Group Co., Ltd., China. Before pretreatment, the impurities and dust were removed using an 80-mesh screen. The chemicals used in the current study were all of chemically pure grade.

Repulping of RMB Paper

A dual-pH pretreatment (soaking) process was adopted. Low-cost sulfuric acid and caustic soda were used. The waste RMB paper was soaked with a 5% sulfuric acid solution for 30 min, and was then washed to a neutral pH with deionized water. Subsequently, it was soaked again with 5% caustic soda solution at the same concentration and temperature for another 30 min, and was then washed to a neutral pH with deionized water. Finally, it was centrifuged to about 25% consistency for use. The pretreated waste RMB paper was refined in a PFI mill at 5% consistency and 0.2 mm clearance for 4,900 revolutions. A slit screen (ZQS5, Shanxi University of Science and Technology) was employed to estimate the repulping yield. A 0.30 mm slit width sieve plate was used, and the pulp consistency was adjusted to 0.5%. The repulping yield (*Y*) of waste RMB paper can be calculated by the following formula:

$$Y = (1-m/M)\times 100\% \quad (1)$$

where m and M are the dry weights of repulping rejects and waste RMB paper, respectively.

The handsheets were made from the pulp through the sieve under the above conditions and are called fine pulp.

Test and Analysis of Fine Pulp from Waste RMB Paper

The handsheets of the fine pulp from waste RMB paper were prepared using a handsheet former with a target grammage of 60 g/m^2. The quality indices of the handsheets were then tested using the lab instruments made in China.

A Morfi-compact fiber analyzer (MÜTEK ANALYTIC, Germany) and a scanning electron microscope (Philips FEI Quanta 200, SEM-300) were employed to analyze the morphology of the fine pulp. The samples were coated with gold before SEM observation.

The waste RMB paper and the handsheets of fine pulp were analyzed by Fourier transform infrared spectroscopy (Magna-IR 560 E.S.P, Nicolet Corp.) to investigate the changes of the chemical bonds between wet-strength polymer molecules and cellulose fibers.

RESULTS AND DISCUSSION

Results of Repulping of Waste RMB Paper

It is well known that RMB paper is a high wet-strength paper. The repulping yield and pulp quality are of critical importance when industrial practice of the recycling of RMB is taken into account. With high yield and low quality, it can be used for the production of some low-grade paper or paperboard. However, if the yield is too low, it's not economical from the cost point of view. A key point of this study was to get a high repulping yield. For pretreatment of waste RMB paper, temperature, soaking time, and consistency were studied, and the results are shown in Figs. 1 to 3. Temperature and soaking time showed similar trends; when they increased, repulping yield and tensile index increased as well. The acid and alkali hydrolysis of ester bonds between wet-strength polymer molecules and pulp fibers might be accelerated with increasing the pretreatment (soaking) temperature, which is beneficial for the increase of repulping yield. Similarly, the increase of pretreatment time can also enhance the destruction of these ester bonds. When the temperature increased from 25 ^{o}C to 80 ^{o}C, the repulping yield and tensile index increased by 18.9% and 10.7 N m g^{-1}, respectively. Compared with pretreatment temperature, when pretreatment time was increased from 20 to 60 min, the repulping yield and tensile index increased 14.9% and 6.3 N m g^{-1}, respectively. From the results in Fig. 3, when the consistency of pretreatment was 10%, the repulping yield and tensile index reached optimum values. Obviously, the higher the consistency of waste paper, the slightly higher the intensity of the acid and alkali pretreatment (see Fig. 4). However, high consistency can result in a non-uniformity in terms of the pulp pretreatment, thereby adversely affecting the repulping yield and tensile index. Based on the above analysis, the optimum conditions of pretreatment are the temperature 80 ^{o}C, waste paper consistency 10%, and time 60 min. The recycled pulp had 88.1% repulping yield, 51.4 N m g^{-1} tensile index, and 41 °SR beating degree under these conditions. Other major quality indices of fine pulp are shown in Table 1.

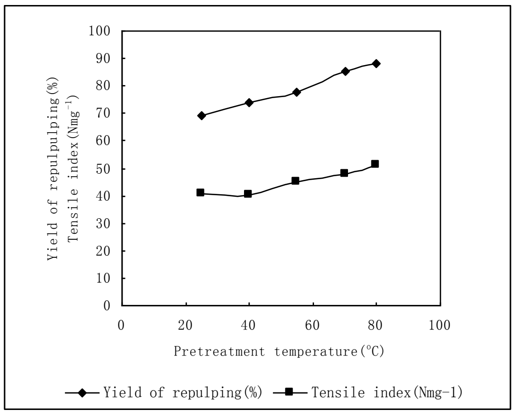


Fig. 1. Effect of pretreatment temperature on repulping yield and tensile index (Pretreatment time 60 min and waste paper consistency 10%)

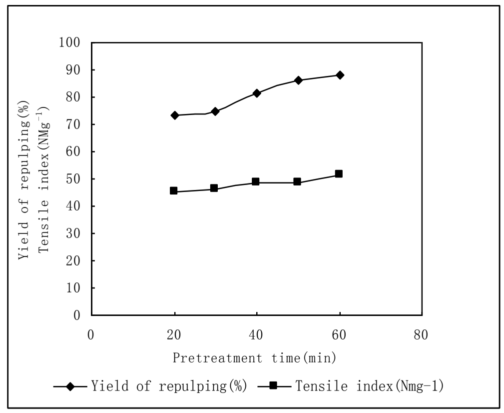


Fig. 2. Effect of pretreatment time on yield of repulping and tensile index (Pretreatment temperature 80 ^{o}C, waste paper consistency 10%, pretreatment time comprises of acid and alkali pretreatment)

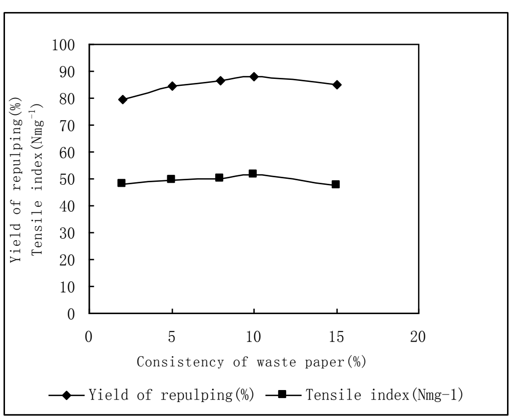


Fig. 3. Effect of pretreatment concentration on yield of repulping and tensile index (Pretreatment time 60 min and pretreatment temperature 80 ^{o}C)

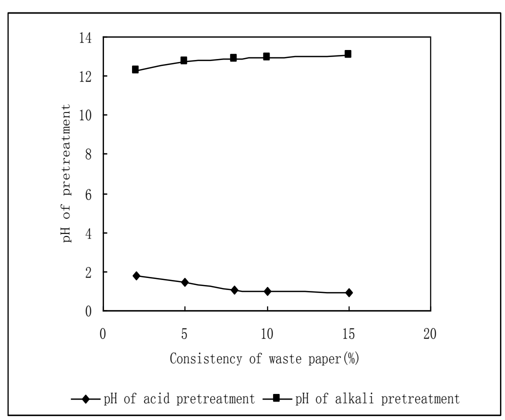


Fig. 4. pH of pretreatment *vs.* varied concentration of pretreatment (Pretreatment time 60 min, waste paper consistency 10% and pretreatment temperature 80 ^{o}C)

Table. 1. Quality Indices of Fine Pulp

Beating Degree (°SR)	Wet Weight (g)	Brightness (%ISO)	Tensile Index (N m g^{-1})	Tear Index (mN m^2 g^{-1})	Burst Index (kPa m^2 g^{-1})	Folding Endurance (Number of times)
41	1.3	49.6	51.4	7.3	2.6	11

Fiber Morphology Analysis of Fine Pulp from Waste RMB Paper

The fine pulp obtained from the optimum conditions was tested using the Morfi-compact fiber analyzer. The data are shown in Table 2. The arithmetic and weighted mean lengths of pulp fibers were 0.564 mm and 0.785 mm, respectively, and the mean width was 22.5 μm. Such pulp would be expected to have a better papermaking performance than fir CTMP (chemi-thermomechanical pulp) and other chemi-mechanical pulps when considering its fiber morphology alone. However, the fibers are shorter than softwood kraft pulp fibers (Liu *et al*. 2009). The intense shear and friction of waste banknote paper in PFI mill resulted in 33.4% kinking and 44.14% end breaking of fine pulp fibers. More kinked fibers could reduce tensile and tear strength but improve burst strength to a certain extent. More broken ends of pulp fibers could improve the tensile strength. The more broken ends of pulp fibers, the more exposed hydroxyls, which can improve the hydrogen bonding between pulp fibers.

Table. 2. Data from Morfi-Compact Fiber Analyzer

Average Characteristics		No. Objects
Fibers (million/g)	15.170	Total = 67216
Length average (arithm. & length-weighted)	0.546 & 0.785	5010
Width (μm)	22.5	
Coarseness (mg/m)	0.1120	
Kink angle(°)	133	
Kinked fibers (%)	33.4	
Curl (%)	9.1	
Rate in length of Macrofibrils (%)	1.223	
Broken ends (%)	44.14	
Fine elements (% in length)	48.6	
Percentage of fine elements (% in area)	12.68	62206

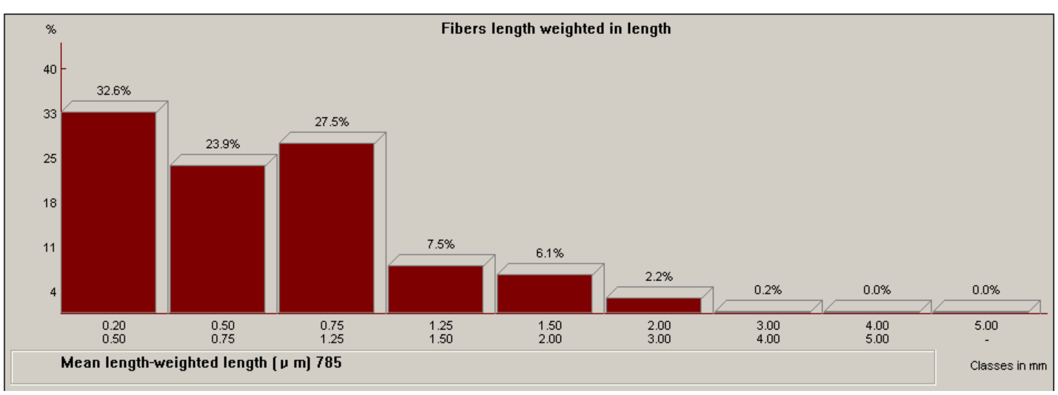


Fig. 5. Distribution of fibers in length-weighted length

As shown in Fig. 5, 97.6% of pulp fibers from waste banknote paper ranged from 0.2 to 2 mm in length. 56.5% of pulp fibers were less than 0.75 mm in length, similar to non-wood pulp fibers. A large proportion of long fiber pulps, *e.g.*, softwood pulp, flax pulp, and cotton pulp, may be contained in waste RMB banknote paper; they can be shortened due to intense shear and friction action in PFI mill.

The pulp fiber was 22.5 μm in width, similar to softwood kraft pulp fibers. The width of 97.6% fibers was distributed from 5 to 47 μm. 5 to 17, 17 to 27, and 27 to 47 μm of fibers in width each accounted for about one third of the whole fibers. The distribution of fibers in width was more uniform compared with that of fibers in length (Fig. 6).

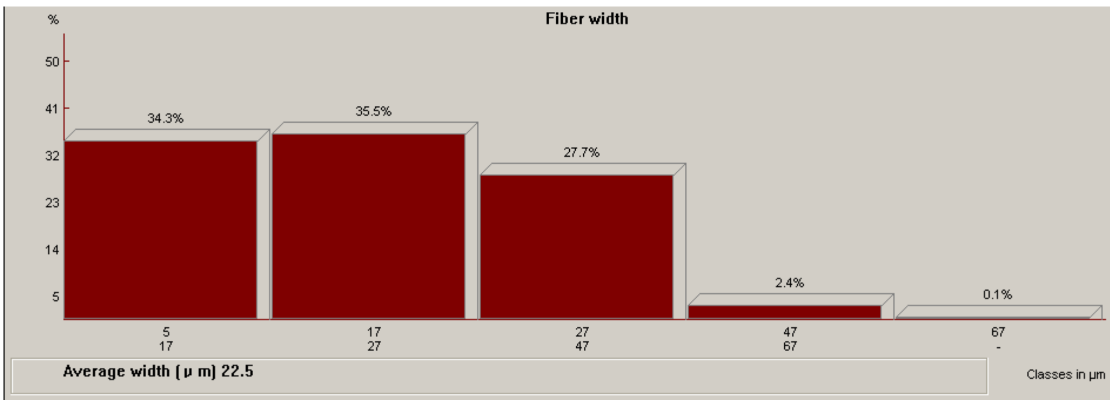


Fig. 6. Distribution of fibers in width

As seen in Fig. 7, the kink angles of 82.3% fibers ranged from 120^{o} to 150^{o}. Fiber kinking refers to an abrupt turn due to the damage of the cell wall. Waste banknote paper is difficult to be repulped due to its high wet-strength. Thus, intense mechanical shear and fiber-to-fiber friction is needed, which can result in kinks in more fibers and some loss of tensile and tear strength.

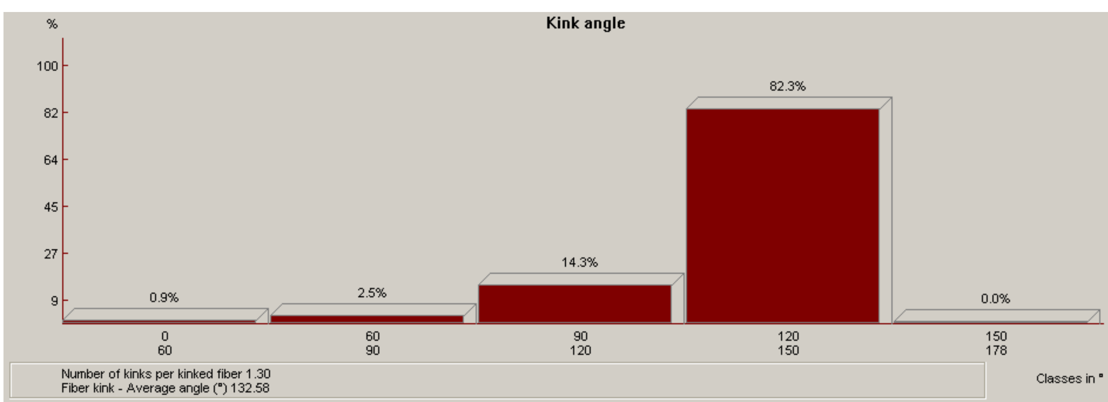
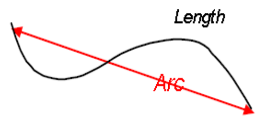


Fig. 7. Distribution of fibers in kink angle

Curl index of the fibers can be calculated by Formula 2, in which the 'Arc' is the straight-line distance between the fiber ends, and 'length' is the true length of the fiber. The value of curl index is from 0 to 100%, and a larger value indicates more severe curling. Curl indexes of 94.5% fibers were in the range from 0 to 25%, which indicated that less curling occurred during refining. As a high wet-strength paper, more mechanical shear in PFI mill is needed to separate fibers from the waste paper, although waste banknote paper was pretreated by the dual-pH approach. As seen in Fig. 8, fiber-to-fiber friction was not dominant and fiber curling occurred less when waste banknote paper was refined in PFI mill.



$$\text{Curl index} = (1 - \text{Arc/Length}) \times 100\% \qquad (2)$$

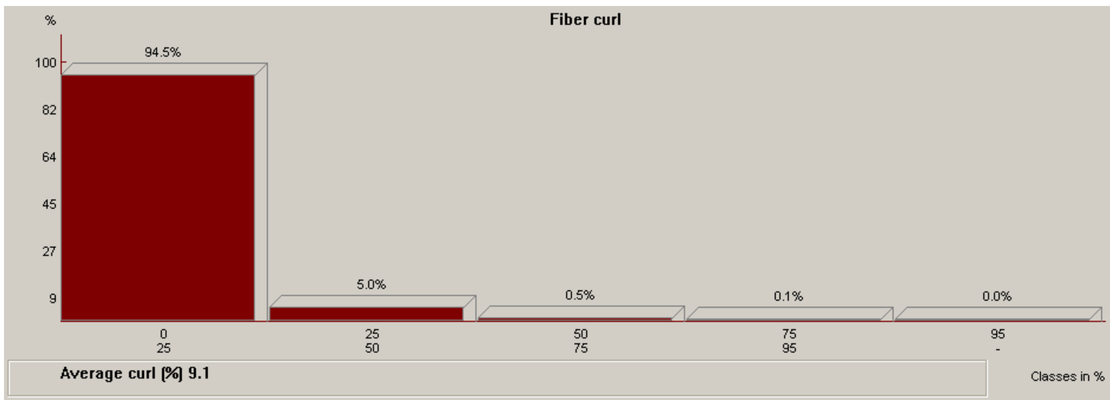


Fig. 8. Distribution of fibers in curl index

The SEM images of waste RMB paper and handsheets of fine pulp from waste RMB paper are shown in Fig. 9. The broken ends of fibers could be clearly observed. The results from SEM observation are consistent with those from the Morfi-compact fiber analyzer. Also, due to high sizing and high wet-strength additive content of the RMB paper, fiber morphology of paper is somewhat blurry in the SEM image.

FTIR Analysis of Fine Pulp from Waste RMB Paper

The control sample (waste banknote paper) and the handsheet samples from the recycled pulp (obtained under optimum conditions) were analyzed using Fourier transform infrared spectroscopy to investigate chemical bond changes in waste banknote paper before and after dual-pH pretreatment. Spectra **a** and **b** in Fig. 10 represent the spectra of control sample and handsheet samples from optimum conditions, respectively. As seen in spectrum **a** in Fig. 10, the absorption band at 1720 cm^{-1} due to carbonyl group stretching vibration of ester bonds formed between wet-strength polymer molecules and pulp fibers (Fischer 1996; Obokata and Isogai 2007) was detected in the control sample. However, this absorption band could not be observed in the handsheet samples (see spectra **b**). It might be clear that the dual-pH pretreatment destroyed the ester bonds, which gave strong wet-strength to banknote paper. Once waste banknote paper loses its wet-strength, its repulping would become easier.

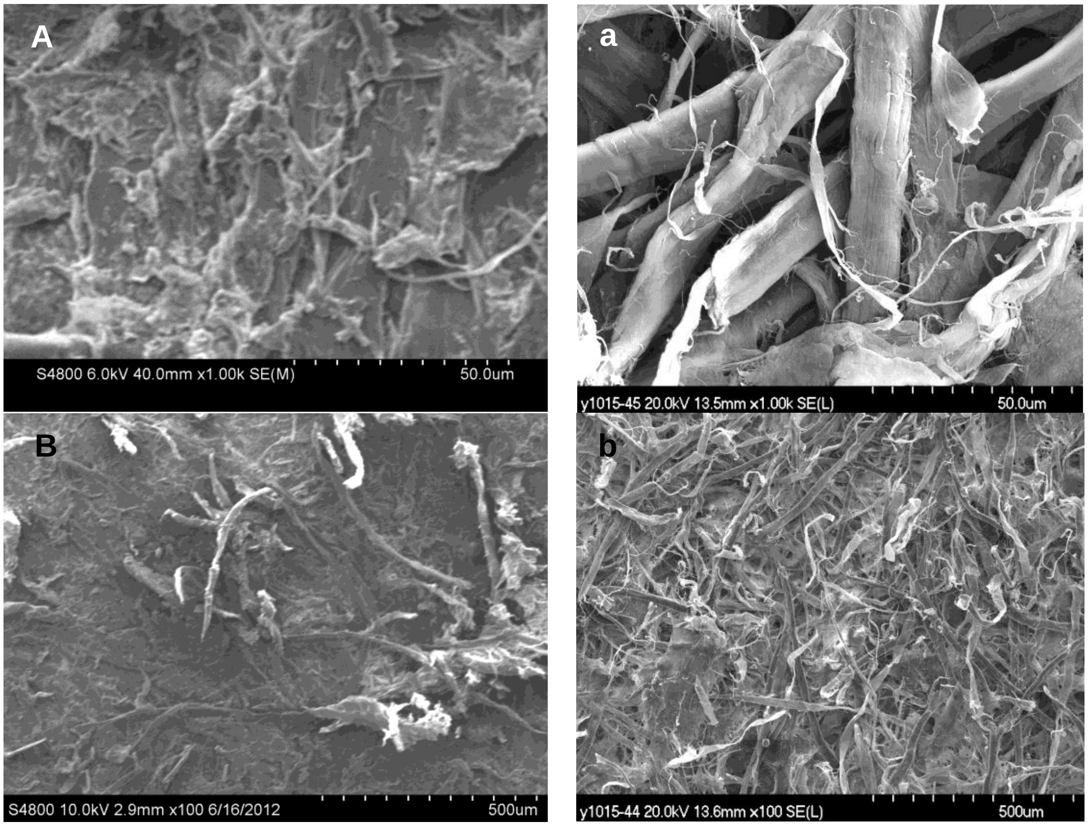


Fig. 9. SEM images of waste RMB paper at 1000× (A) and 100× (B) magnifications, and handsheets of fine pulp from waste RMB paper at 1000× (a) and 100× (b) magnifications

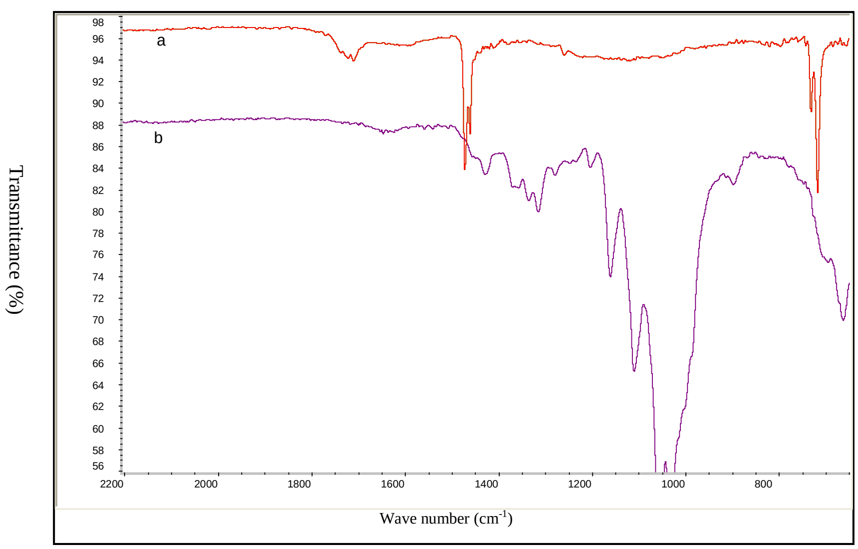


Fig. 10. FTIR spectra of control sample (a) and handsheet samples (b) from experiment carried out under optimum conditions

CONCLUSIONS

1. A dual-pH pretreatment before refining could be used to repulp waste banknote paper (Chinese Renminbi paper). The optimum pretreatment conditions were as follows: pretreatment temperature of 80 ^oC, pretreatment time of 60 min (including sulfuric acid and caustic soda pretreatment), and waste paper consistency of 10%; PFI mill clearance and refining revolutions are 5%, 0.2 mm, and 4,900 rev., respectively. A repulping yield of 88.1% was achieved under the optimum conditions.
2. Arithmetic and weighted mean lengths of pulp fibers from the optimum experiment were 0.564 mm and 0.785 mm, respectively, and mean width was 22.5 μm. The obvious kinks, broken ends of fibers, and less curl of the fibers were observed through fiber morphology analysis.
3. FTIR analysis demonstrated that the dual-pH pretreatment of waste banknote paper was able to destroy the ester bonds formed between wet-strength polymer molecules and pulp fibers. Waste banknote paper became easier to be repulped after the pretreatment.

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