Water Down Acid Pretreatment of Wheat Stubble Agro-residues to Eliminate Non-process Components Meant for Papermaking and Its Impact on Mechanical Strength Properties of Paper Products

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Research Article

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Abstract

Wheat stubble agro-residues material contains lingo-cellulose with high level of extractives and metal ions, which may be able to instigate some harmful impacts on the papermaking process. Pretreatment of stubble on the removal of metal ions and extractive and its impact on the content of chemical constituents like holocelluose, lignin, silica, the pulping yield as well as the mechanical properties of paper were examined in the laboratory. Acid pretreatment significantly reduced the content of the metal ions with about more than 50%. The conditions for acid pretreatment of the material were optimized to pH-2 at 5% consistency for 1 hour retention time with more benefits in extractives and metal ions removal and less impact on cellulose degradation. The demand for active alkali charge during pulpmaking was observed to be about 3% lower for the pretreated material as compared to the untreated one. Along with the chemical conservation, a higher pulping yield of about 6 – 7 % was also observed for acid pretreated materials. Improved thickness, more crystalline and a high degree of polymerization of cellulose fibre were noticed due to acid pretreatment and the pulp obtained from acid pretreated material showed improved mechanical strength properties (tensile, tear, burst strength etc.). The study revealed that pretreatment of agro-residue material with dilute acid (optimized conditions) could be used to remove the non-process component and make it suitable for utilization in papermaking process with improved mechanical properties in the paper products.

Statement Of Novelty

The nonprocess components for papermaking mainly are extractives, metal ions and silica content of agro residues like, wheat stubble, these may cause many adverse affects to the papermaking process as well as it can act as a root for producing odorous compounds, like Volatile odorous compounds (VOCs) which causes tainting to the food material when packed in a paper based packaging material. Pretreatment with dilute acid, chemical consumptions during pulp making process were reduced and obtained more crystalline and stronger cellulose fibres, consequently improved all the mechanical properties of paper products, while previous study suggested no significant affects on the mechanical strength properties of paper were observed due to the acid pretreatment of the material.

1. Introduction

Wheat stubble, an agro-waste lingo-cellulosic material burning and its management has become a serious issue in India. Stubble burning in open field causes atmospheric pollution, health issues, and reduction in soil fertility, increasing smog, decreasing visibility, killing useful insects and beneficial microbes etc. Burning of straw also leads to the loss of nutrients such as N, P, K, and S **[1]**. Therefore to avoid the effects of burning, utilization of straw for other various activities are being promoted such as in paper and paper board making, for ethanol and biogas production **[2-5],** regenerated cellulose production etc. By adopting these practices for the utilization of wheta straw, burning can be avoided and consequently reduces harmful emissions. The lingo-cellulosic waste have different chemical constituents like holocellulose (Cellulose and hemicelluloses), lignin, extractive as well as metals ions such as Ca, Fe,

Mg, K, Mn, Cu etc. The extractives and metal ions can have negative impacts on the paper manufacturing processes such as pulping, bleaching, recovery boiler corrosion and plugging etc. as well as the pulp quality. Thus cleaning of raw material before the papermaking process may be used to avoid these problems. Extractives are gummy material and rich in unsaturated fats and mainly includes resin acid, fats, fatty acids, waxes, alkanes, fatty alcohol, terpenes sterols etc. which are present in the raw material get removed and some of them get precipitated on pulp during pulping [6] and may constitute negative impacts on pulping and bleaching process by increasing chemical consumptions. Extractives may also lead to pitch deposition in the mill equipment, requiring high maintenance costs and reduced pulp quality [7]. The unsaturated extractives are susceptible to auto-oxidation in the air and auto-oxidation of these extractives cause formation of volatile organic compounds (VOCs) which lead to odour in the paper and board and cause tainting when absorbed by the food. More than 200 VOCs are produced as a result of oxidation of extractives present in paper and board [8]. If paper and board are to be used for food packaging application, they must be free of all odours.

Transition metals affect the peroxide bleaching by catalytic decomposition of hydrogen peroxide lead to the radical formation that degrades fibres [9-13]. Some transition metals catalysed the decomposition of oxidants derived from oxygen used in the bleaching process. Irrespective of fibre damage transition metals such as Fe and Al effects brightness gain during bleaching and colour reversion in bleached pulps [14-15]. Reduced delignification rate during pulping has been recognized due to the presence of Ca and showed increased pulp yield and viscosity when removed before pulping [16]. Wheat straw contains about 4-10% silica as a small crystal embedded and distributed all over the stem, it is alkali-soluble and come with spent liquor during pulping and inhibits the chemical recovery process. Therefore silica must be removed from the raw material before pulping to prevent their harmful effects in the recovery process. The more effective way to reduce damage caused by these non-process components can be removed from the raw material through acid pretreatment without affecting the quality of pulp produced from these raw materials [17]. Organic and some mineral acids such as H_2SO_4, HCl, HNO_3 etc, are suggested for the pre-treatment of lingo-cellulosic raw materials among these H_2SO_4 is frequently used [18]. Dilute mineral acid pretreatments are preferred for the industrial process mainly due to the minor corrosion problems in the tanks and pipes with more effective removals of constituents [19]. Pretreatment changes the structure of raw materials by removing their structural components and making them more accessible for other treatments such as the alkaline pulping process [20]. The pretreatment process not only removes extractives and metal ions but also remove a significant amount of cellulose and hemicelluloses. It has been studied that pretreatment of feedstock affects the chemical constituent and the pulping behaviour of treated feedstock [21], which enhance the delignification rate as compared to the untreated, results in the reduction of pulping and bleaching chemical cost along with the reduction in time and energy demand [22] and the kappa number will be lower by applying pretreatment process before the pulping [23].

Considering the effects in the manufacturing process and odour generation in food packaging materials by the presence of extractives and metal ions in the raw material, it would be desirable to remove these

contaminants from pulp and the present work was directed to evaluate the optimization of acid-pretreatment conditions with effective removal of extractives and metal ions along with their effects on chemical compositions and mechanical properties of paper. The pulping (Kraft and soda process) yield, as well as the degree of polymerization of the fibrous mass, was considered. Morphological as well as chemical changes in the cellulose fibre were also considered to investigate, which could be happed due to the influences of acid pre-treatment. Because of the high annual yield per hectare, easy availability and the raw material crisis of paper industries, it has been encouraged the industries to utilize wheat straw as a raw material irrespective of high silica content, which is a major limiting factor for the paper industries now a day's. Many research papers have been published focused on the desilication of pulp. Thus this research was also aimed to remove the silica from the raw material before pulping by the acid pretreatment process.

2. Material And Methods

Wheat straw was collected from farmers of Utter Pradesh in India, cleaned by dry and wet dipithing and stored in a bag at room temperature before treatment, considered as an untreated sample.

2.1 Optimization of conditions during acid pretreatments

Conditions for acid pretreatment like pH, time and consistency as tabulated in Table-1, were optimized using a 3-factorial experimental design with 27 runs of experiments were done in duplicate and out of which 9 experiments were considered for the evaluation. As previous work suggested the effects of temperature had the least impact on metal removal, on a view of this temperature was not considered for optimization and the decided temperature 70˚C was used for the optimization of other parameters [24]. To run the optimization 50 gm of raw material were taken in a polythene bag of 2kg capacity, distilled water was added to maintain the consistency, pH was maintained using 4N H_2SO_4 and then the sample was placed in a water bath maintained at 70˚C temperature. After treatment, the filtrate was collected for the analysis of total organic carbon (TOC) using a standard analytical method as per the American Public Health Association (APHA 5310 D) and then the sample was washed with minimum use of distilled water, the washed sample was air-dried and stored for further study. The requisite of sulphuric acid in litre (L) per tonne (t) of raw material during pretreatment and a rough chemical cost analysis in Indian rupees (Rs.) was done to know the feasibility on an economical level from the industry point of view as listed in Table 2. As able to be seen from the table, at high consistency less sulphuric acid is required to maintain the same pH and therefore the cost is also low down.

Table 1: Three factorial designs of the experiments. (Total number of possible experiments = 3 x 3 x 3 = 27)

Factors	Level-1	Level-2	Level-3
pH	1.5	2.0	2.5
Consistency (%)	5	10	15
Time (hr)	0.5	1.0	1.5

Table 2: A rough chemical cost analysis used for acid pretreatment

PH	H_2SO_4 Required (L/t)	Cost (Rs/t)	H_2SO_4 Required (L/t)	Cost (Rs/t)	H_2SO_4 Required (L/t)	Cost (Rs/t)
	Consistency (5%)		Consistency (10%)		Consistency (10%)	
1.5	21.1	739	10.0	350	6.3	220
2.0	12.7	443	6.0	210	3.8	132
2.5	8.4	296	4.0	140	2.5	88

2.2 Chemical composition analysis

The samples (untreated and acid pretreated) were ground in a Wiley mill to make dust and the moisture content of the dust material were evaluated as per Tappi standard and used for the determination of holocellulose, lignin, extractive and silica content using standard methods given in Table 3.

Table 3: Standard followed during the analysis of chemical constituents

Test Parameters	**Standard methods**
Moisture content	Tappi T 550 om-08
Solvent extractive	Tappi T 204 cm-97
Holocellulose	Wise, E., Murphy,M. and D'Addieco,A.A., Paper Trade J., 112(2), 35(1946)
Lignin	Tappi T 222 om-02
Ash	Tappi T 211 om-12
Acid Insoluble	Tappi T 244 cm-11
Silica	Tappi T 245 cm-07
Viscosity of pulp	Tappi T 230 om-08
TOC	APHA 5310 D

2.3 Analysis of metal ions

To explore the efficacy of metal ions removal from the acid pretreated sample, analysis of metal ions content were carried out for all the samples. Samples were first burned in a furnace at about 525 ˚C for the ash analysis as per the Tappi standard. The ash obtained was digested with 6M HCl in a hot plate then filtered with an ash-less Whatman filter paper no.-42 and washed the filter paper with hot water till acids are removed completely. The filtrate was used to make the volume up to 250 ml with distilled water and then it was used for metal ions analysis in a single-phase high dispersion Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES), Prodigy SPEC, Teledyne Leeman Labs. USA. It measures the amount of each wavelength of emitted light to calculate the concentration of each element in the sample, for this a calibration curve was generated for the known concentration of each element to be measure before the sample run.

2.4 Pulp generations (Pulping)

Pulp generation or pulping is the process of removing lignin and extracting cellulosic fibres from the lingo-cellulosic material using mechanical and chemical methods (Kraft and soda process). Kraft pulping process involves the digestion of lingo-cellulosic material at high temperature and pressure with liquor solution containing sodium hydroxide and sodium sulphite, while the soda pulping process occurred at high temperature and pressure in sodium hydroxide solution. It has been studied that kraft pulping produces stronger pulp in comparison to other processes. Chemical pulping by Kraft and Soda process of the untreated and acid pretreated (at optimized conditions) samples was carried out to explore the effects of acid pretreatment on cooking performance with a targeted kappa number of 15±1 in a rotary digester having four SS bombs of 100 gm capacity. Measured straw was taken in this bomb and active alkali was charged and to maintain 1:4 bath ratios, extra water was added into the bomb and kept in the digester which was full of water as a heating medium. Cooking was done at 165˚C for about 30 minutes, excluding time to achieve this temperature from ambient which was about 60 minutes (time to temperature). Targeted kappa numbers were achieved by keeping all the conditions the same except active alkali charges. After cooking, black liquor was collected to analyse residual active alkali and the pulp was thoroughly washed with hot and cold water to remove black liquor from the pulps and the pulp generated were coded as KC, KA (Kraft controlled/untreated and acid pretreated) and SC, SA (Soda controlled/untreated and acid pretreated). The washed unbleached pulp was further used to measure the pulping yield, pulp characterization and hand-sheet preparation for the measurement of mechanical strength properties.

2.5 Pulp Characterizations

2.5.1 Degree of polymerization (DP)

The effects of acid pretreatment on the DP of pulp were evaluated which is direct counts for the physical properties especially tensile strength of fibres. Viscosity was deliberate by measuring the reflux time of pulp solution dissolved in 0.5 M CED solution (cupirethylenediamine) in a capillary viscometer tube kept at temperature 25±1 ˚C, as Tappi Test method T-230 om-08 (Capillary viscometer method). The viscosity

of pulp was calculated by using equation-1 and the intrinsic viscosity was obtained from the viscosity conversion table (Tappi 206 m-55) for the determination of DP by using equation-2 [25].

$$V = C \times t \times d \quad (1)$$

$$DP^{0.85} = 1.1 \times \eta \quad (2)$$

Where, V = Viscosity of cupirethylenediamine solution at 25˚C, mpa.s (cP)

C = Viscosity constant of capillary tube found by calibration

t = Average reflux time, s

d = Density of pulp solution, g/cm^3 (1.052)

η = intrinsic viscosity

2.5.2 X-ray diffraction pattern (XRD)

The Crystallinity index of the samples was confirmed by X-ray diffraction analysis. This technique is used for the determination of the atomic and molecular structure of a material by measuring the intensity of incident and scattered X-ray at an angle through the material. Kraft and soda pulp was oven-dried at 70˚C overnight and ground to powder before use. Diffraction patterns were obtained by X-ray diffractometer (Rigaku Ultima) operating at 40kV/40mA, at an angle of diffraction ranging from θ = 5˚ - 80˚, at a scan rate of Å/minute. The crystallinity index was calculated [26] using the following equation-3.

$$CI = [(I_c - I_{am})/I_c] \times 100 \quad (3)$$

Where, I_c = Maximum intensity peak (002), which stand for the crystalline part of the peak

I_{am} = Minimum intensity peak of the amorphous band (101)

2.5.3 Attenuated total reflectance – Fourier transform infrared spectroscopy (ATR-FTIR)

ATR-FTIR spectroscopy provides information regarding the presence or absence of a specific functional group as well as the chemical structure of the materials, any change or shift in the frequency of the absorption band indicates the change in the chemical structure of these materials. ATR-FTIR of kraft and soda pulp sample was performed at room temperature and the spectra were collected in the range of 450 – 4000 cm^{-1} with 16 running scans at a resolution of 4 cm^{-1}.

2.5.4 FE-SEM (Field Emission Electron Microscope)

FE-SEM is a microscope that works with electrons instead of light. Electrons are generated by heating a tungsten filament through a current to a temperature of about 2800˚C. The object is scanned by these

electrons. Morphological characteristics of pulp samples were performed by a TESCAN MIRA3 (TESCAN; Brno, Czech Republic) FE-SEM. The image of dried powdered samples was taken at different magnifications.

2.6 Papermaking and the measurement of its mechanical strength properties

The unbleached pulps of untreated and pretreated material were used to prepare hand-sheets of about 70 GSM. The pulp was refined in a valley beater according to the Tappi test method T-200 sp-01 to reach 500±10 CSF. Four different pulp samples coded as KC, KA, SC and SA were disintegrated separately in a disintegrator for about 10-15 minutes at a revolution of 3000rpm. The stock of about 0.3 % pulp consistency was prepared by diluting the pulp samples with tap water. The stock was then used further for hand-sheets preparation in a British sheet former. During hand-sheet making all the procedure was followed as per the standard Tappi test method T 205 sp-02. The prepared hand sheet was then air- dried overnight. Afterwards, for the measurement of mechanical strength properties such as tensile index (Tappi T 494 om-01), tear index (Tappi T 414 om-98), burst index (Tappi T-403 om-97), double fold (Tappi T 511 om-02) etc., the air-dried hand-sheets were kept for conditioning as per the standard method ISO 187 which followed temperature 27±2 ˚C and relative humidity 65±2% for about 24 hours.

3. Results And Discussion

3.1 Chemical composition analysis

The proximate chemical analysis of untreated material was carried out and the comparisons with the other raw materials are depicted in Table 4. The extractive content of wheat straw was found to be 2.6% which is lower than that of rice straw (3.4%) and higher than hardwood reported (1.8%) and our finding of solvent extractive for wheat straw was approximately near to the previous finding. The 1% NaOH solubility of the wheat straw was noted to be 43.1% compared to the previous result of the same material, even though it was slightly lower than rice straw and higher than hardwood. Holocellulose is the total fraction of hemicelluloses and cellulose; it is the main component of paper and its products, thus its quality and quantity both play a very important role in the papermaking process. The holocellulose content of wheat straw was evaluated to be 67.5%, which was as good as the previous results and almost alike to the holocellulose content of hardwood and rice straw. Ash and silica content of wheat straw were found to be very high in comparison to the ash content of hardwood and the Klason lignin content of the wheat straw was found to be 15.3% lower than that of hardwood and similar to the rice straw. High ash content, which indicates the high in-organic content of the agro-waste raw material like, wheat and rice straw, is the main trouble for the papermaking process nowadays. The ash content in the wheat straw was recorded to be 10.2 %, which is very high for the hardwood (1.4%) and parallel to rice straw ash content reported earlier (12.7%).

Table 4: Comparison of chemical composition of untreated wheat straw with other raw materials

Parameters	Wheat Straw			Rice straw	Hardwood,
	(Present study)	[27]	[28]	[26]	[29]
Solvent extractives (%)	2.6±0.21	5.0	1.30	3.4	1.8±0.1
1% NaOH solubility (%)	43.1	–	38.99	46.2	17.8±0.5
Hemi cellulose (%)	38.3±0.95	50	–	39.2	20.8±0.6
Cellulose (%)	34.4±0.98	30	–	36.5	52.8±0.4
Holocellulose (%)	67.5	–	70.1	66.6	–
Lignin (%)	15.3±0.57	15.0	22.38	13.2	25.7±0.5
Ash (%)	10.2±0.57	–	9.58	12.7	1.4±0.0
Silica (%)	9.1	–	–	7.6	–

3.2 Effects on the chemical compositions

The acid pretreatment process only benefits with the removal of extractives and metal ions unless the cellulose fibres are not adversely affected. The impact of pH, retention time and consistency during acid pretreatment on the chemical compositions are studied. As be able to see from Fig.1, increased pH (1.5 to 2.5) and the consistency (5 to 15%) of the sample during pretreatment, the losses of total organic carbon (TOC) in the filtrate were found to be declined from 1473 to 1250 mg/L and 1473 to 1179 mg/L respectively. Although the TOC contents in the filtrate were found to be increased with rising the retention time (0.5 to 1.5 hr) from 1219 to 1844 mg/L. TOC content in the filtrate is directly related to the reduction in the holocellulose content of raw material, as can be seen from Fig.2, the reduction in the holocellulose content was found to be decreased (from 7.8 to 4.3%) with the increase in pH (1.5 to 2.5) in a similar way, the reduction in the holocellulose content was also found to be decreased (7.8 to 5.3%) with increased consistency (5 to 15%). Although with increased retention time (0.5 to 1.5 hrs) the reduction in holocelulose content was observed to be increased from 3.9 to 15.6%. Thus pretreatment at increased pH and consistency will benefit the process with minimal cellulose degradation and confirms the fitness of material for papermaking, the slight degradation of carbohydrate (Holocellulose) was also reported earlier throughout acid pretreatment at pH-2 [30]. A prior study also recognized that acid pretreatment of Kenaf biomass with dilute acid enhanced the cellulose content by 26.6%, this is due to cross-linking of glucan chain, forms during treatment forming hydrogen bond with cellulose molecules [31]. The effects on the total lignin content during acid pretreatment was not observed significant changes at different pH, consistency and retention time as can be seen from Fig.3. Even though the earlier report confirmed the enhanced lignin content of wheat straw up to 25.67% due to pretreated with 0.1N H_2SO_4 at 125^{o}C for 120 minutes [28]. While in the case of extractive removal, acid pretreatment caused its removal to a greater extent at higher pH and high retention time, it means increased pH (1.5 – 2.5) and increased retention time (0.5 – 1.5 hr) resulted in higher removal of extractive from 24.8 to 50% and from 26.9 to 65.4 % respectively, while increased consistency resulted in decreased extractives removal as shown in Fig.4, the

previous study also reported the removal of extractive from wood chips material after the acid pretreatment [32]. About 20 to 25 % silica removal was observed due to acid pretreatment of the material, as observed throughout pretreatment increased pH and consistency resulted in decreased silica removal, even though increased retention time resulted in increased silica removal as shown in Fig. 5. An effort was also done in the previous study to remove silica from rice straw by acetic acid pulping and about 25% silica was removed [33]. Thus acid pretreatment of raw material with increased pH was observed benefits in enhanced extractive removal and decreased cellulose degradation of the material.

3.3 Effects on the removal of metal ions

The effectiveness of metal ions removal due to acid pretreatment was investigated and the data for the metal ions analysis at different pH, consistency and retention times are reported in Fig.6. Initially, the metal ions content of untreated material was found to be higher as presented in Table-5. It was observed during acid pretreatment that the removal rate of metal ions content in terms of percentage reduction was found to be decreased with increase in the pH as shown in Fig.6. The effective removal of metal ions was observed to be decreased with an increase in the consistency during pretreatment, this was might be because, at low consistency more acid was required to maintain the pH as compared to a high consistency, although the increased retention time metal ions removal was found to be increased as the previous study confirmed that pH and retention time has very effective in the removal of metal ions [24]. Although in most of the cases more than 50% of metal ions removal was achieved due to acid pretreatment with highest removal rate (greater than about 80%) of Ni and Mg metals were found followed by K, Ca, Fe, Mn, Cu and Zn.

Thus at overall pre-treatment at higher pH improved removal rate of extractive with reduced metal ions removal and holocellulose degradation was observed. Although at high consistency of pretreatment reduced rate of extractive removal with the reduced rate of metal ions removals and holocellulose degradation was observed and for high retention time, increased degradation of holocellulose with improving the rate of metal ions and extractives removal were observed. Thus based on the above observation during the acid pretreatment process, it was resolute that the treatment of the raw material must be done using the midway conditions like pH-2, consistency-5% and retention time-1 hr, to an obtained pulp with less impact on degraded cellulose and more benefits with extractive and metal ions removal. The optimized condition (Midway conditions) for acid pretreatment was used to produce pulp for the investigation of its impact on active alkali demand, pulping yield, degree of polymerization as well as mechanical properties of paper.

Table 5: The concentration of metal ions present in the original raw material (Untreated)

The concentration of metal ions (ppm)							
Ca	Fe	Zn	Cu	K	Mg	Ni	Mn
13203	493.6	42.2	3.4	155.1	4086.2	83.8	57.7

3.4 Effects on pulping Yield and Degree of polymerization

The chemical demand during the kraft and soda pulping process for the untreated and acid pretreated raw material were investigated and found that lower active alkali (AA) were needed for the raw material which was treated with acid as compared to the untreated material for producing a targeted 15 kappa pulp as shown in Fig. 7 & 8. This happened might be because of the good penetration of liquor to the pretreated material, which was caused by the removal of impurities and some low molecular weight carbohydrates resulted in the exposure of the internal structure of the material. During kraft pulping process about 16.5 % of AA charge was required for the pretreated material even if the untreated material were required about 17% of AA charge for the same targeted kappa pulp. Similarly, with the soda pulping process, this was required about 18% and 17.5% of AA charge for untreated and acid pretreated materials respectively; consequently, about 3% of AA can be preserved with the use of acid pretreated raw materials in both cases of pulping. Along with the chemical saving higher pulping yield of about 6.6 % and 7.3% for the acid pretreated raw materials were observed in the case of soda and kraft process respectively. Our finding of the improved pulping yield of acid pre-treated material is of great importance, as the previous study suggested that, acid leaching did not affect the pulping yield rather it improved delignification rate [24]. Improved pulping yield for the acid pretreated wheat straw was also reported earlier near to 10.6% at 16% of alkali charge, which is close conformity with our finding [28]. Related to our finding of lower AA demand of acid pretreated material during pulping was suggested and it could be due to a decline in the extractive content [13]. A high delignification rate for acid pretreated raw material have been reported, which was resulted in low chemical demand for a given kappa pulp [24]. The earlier study proved that the metal ions present in the raw material may consume some considerable amount of AA which may lead to high alkali demand during pulping, thus the possible explanation for the decreased alkali demand was due to the removal of metal ions during pretreatment. Calcium was suggested to cause hindering the delignification rate as well as the selectivity of cooking during the pulping process [16] and due to the acid pretreatment lignin-carbohydrate complex can be removed, which may also explain the lower alkali demand during pulping of the raw materials (34). As a result, the increased pulping yield indicated that acid pretreatment (at the optimized or midway condition) did not show the impacts on cellulose degradation and it was as well reported that mild conditions of acid pretreatment were not enough to cause to degrade the cellulose component, which could result in yield loss [32]. The degree of polymerization is the number of glucose molecules per unit chain of fibre was found to be 1663 and 1726 for the kraft pulp of untreated and acid pretreated material respectively and for soda pulp it was 1663 and 1726 respectively for untreated and acid pretreated material; the results are depicted in Fig.9. Thus the results showed that acid pre-treatment even improved or protect the cellulose fibre from degrading, which might happen during the pulping process through the peeling reaction of cellulose [35]. An earlier study suggested that high DP of acid pre-treated samples was achieved due to the removal of metal ions from the raw material [36] which also confirms our finding of improved DP for pulp extracted from acid pretreated material.

3.5 Fibre Characterizations

From the XRD analysis, it was confirmed that acid pretreatment renewed the cellulose and hemicelluloses fibre into more crystalline form, it might be happened due to the destruction of some amorphous regions of the fibres. As can be seen from the X-ray diffraction pattern of the pulp (Kraft and Soda) of untreated and treated samples in Fig.10 that one major and minor peaks at 22.6° (crystalline region) and 16.3° (amorphous region) were observed which stands for cellulose and hemicelluloses respectively that has been deliberated previously [37]. The CI at minor peak 16.3° for KC, KA, SC and SA were calculated to be 29.9%, 31.8%, 19.3% and 38.6% respectively, which is below the CI of cellulose, varies from 39% to 69% [38] and confirmed the presence of amorphous hemicelluloses in the samples, thus hemicelluloses content were not very much affected by acid pretreatment at optimum conditions, although the CI of amorphous hemicelluloses were found to be increased due to the pretreatment. The CI at 22.6° was also calculated to be 54.2%, 56.6%, 43.4% and 65.7% respectively for KC, KA, SC and SA samples and found that CI is getting increased for the sample which has been treated with acid. Increased CI of wood samples was also premeditated earlier due to acid pretreatment [39] and hypothesized that acid pretreatment of fibrous mass might destroy some defective crystalline and amorphous regions in the material [40-42].

FTIR-ATR characteristics of kraft and soda pulps extracted from untreated and acid pretreated raw material at different absorption bands ranging from 4000 – 500 cm^{-1} are carried out as shown in Fig.11. The peak located near the 3300 cm^{-1} indicated the presence of –OH stretching of alcohol and carboxylic group [43].The low-intensity peak at this region for acid pretreated pulp in comparison to the untreated pulp indicated the low concentration of –OH groups in the cellulose chain, due to the disruption of hydrogen bond during pretreatment [44]. The low-intensity peak at this region was also suggested earlier for the acid pretreated Napier grass fibre [45]. The high degree of polymerization of the acid pretreated pulp can also be explained by this reduced hydroxyl concentration in the cellulose matrix. Since, during pulping in the presence of alkali and high temperature, the glycoside linkages containing the reducing end of cellulose got de-protonated and form an ionic intermediate, which gets converted into degradation products [46], which lead to decreased DP. Thus by acid pretreatment –OH concentration can be reduced from the matrix of cellulose and degradation of cellulose can be avoided by stopping the peeling reaction during pulping. The absorption band near 2900 cm^{-1} confirmed the C-H stretching of methyl and methylene portion of cellulose [47], the low intensity at this region for acid pretreated sample indicated the dissolution of oligomers [41,48]. The low-intensity absorption band near 1645cm^{-1} for acid pretreated pulp, represent the –OH bending of absorbed water [49-50], thus hygroscopic nature of fibre got reduced by acid pretreatment. The carbonyl, C=O stretching were indicated by the absorption peak near 1732 cm-1, which is associated with the lignin content [51] and no considerable changes in the absorption band were detected in this region for untreated and pretreated samples, thus acid pretreatment has no effects on the lignin content of the material. The earlier study demonstrated that due to the pretreatment of raw material with NaOH, the absorption peak near 1734cm^{-1} were disappeared, indicating the strong effects of alkali on lignin, although the peak was still existed after acid pretreatment and suggested slight effects of acid on lignin removal [51]. Some low-intensity absorption peaks near 1023 cm^{-1} – 1030 cm^{-1} were identified for acid pretreated material, indicating the presence of C-O, C-C, C-OH stretching vibration of

hemicelluloses, cellulose and lignin [41, 52, 53]. The absorption peak near the frequency ranges at 894cm^{-1}, which stands for the β-1, 4-glycosidic linkage of xylan (hemicelluloses) were not observed any changes for both the sample, consequently pretreatment of raw material with dilute acid has a little impact on hemicelluloses content, this can also be proved from the presence of amorphous peak during XRD analysis which is depicted in Fig.10.

The effects of acid pretreatment on the morphological characteristics of fibre were detected through FE-SEM micrograph image analysis and the morphological changes that occurred in the fibres due to acid pretreatments at different magnifications are illustrated in Fig.12. The impurities like fine elements may be extractives, hemicelluloses etc. which are attached to the surface of fibre can be seen from the figures. In addition to the good penetration of liquor, impurities removal may be caused by more inter-fibre bonding resulting in the improved mechanical properties of paper. It was observed that due to acid pretreatment these impurities got removed and the surface of acid pretreated fibre got exposed, resulting in the increased fibre width from about 12.7μm to 30.9 μm in case of kraft pulp (Fig.12a &b) and from 8.3 μm to 15.4 μm for soda pulp (Fig. 12c &d) and it is well known that the fibre width also plays a great importance for the development of mechanical strength of paper and its products. It was supposed that, because of refining of pulp, all mechanical properties except tear strength get improved, because of the increased width of fibre [54], which causes more surface area available for hydrogen bond formation between the pulp fibres.

3.6 Effects on mechanical strength properties of paper.

Mechanical strength properties of unbleached pulp hand-sheet of untreated and acid pretreated wheat straw were investigated to know the effects of acid pretreatment. From the analysis, it was observed that the paper made of kraft pulp was of better strength properties than soda pulp as shown in Table-6. The paper made of cellulosic fibre may contain small intra-fibre pores as well as large-sized inter-fibre voids, which allow air to pass through them [55]. The Gurley porosity is the measure of the time (second) required to pass 100 ml of air through the voids present in the paper, indicating the lower porosity for the pulp hand-sheets of acid pretreated raw material compared to the untreated. The voids in the paper might get reduced due to the improved inter fibre bonding caused by the removal of impurities like extractive, metal ions etc. from the surface of cellulose fibre due to acid pretreatment. The impact of the removal of impurities could also be seen from the increased bulk density from 0.794 to 0.806 g/cm^3 and 0.862 to 0.900 g/cm^3 respectively for kraft and soda pulp. Folding endurance determines how many times a paper can be folded under constant load until it breaks; it measures the number of double folds and indicates the durability of a paper. The folding endurance was increased from 169 to 199 in the case of kraft pulp while it increased from 101 to 130 in the case of soda pulp due to the pretreatment. Burst strength is the measure of pressure needed to rupture a paper when applied uniformly through a diaphragm. The burst index of wheat straw was found to be increased appreciably from 3.2 to 3.7 k.pa m^2/g and 2.9 to 3.3 k.pa m^2/g for kraft and soda pulp respectively because of pretreatment. Tensile strength is the maximum tensile force required to break the strip of a paper, which is derived from many factors like individual fibre

strength, fibre length and the bonding between the fibres of the network, this was measured for the hand-sheets and found to be increased from 50.9 to 52.3 and 47.1 to 49.0 N.m/g respectively for kraft and soda pulp for the reason of pretreatment. The tensile energy absorption (TEA) measures the toughness of a paper, which measures the energy absorbed or work has to be done when a paper strip of 15mm width stressed to break, it was observed that more work has to be done for the paper of acid pretreated material than untreated. Because of the elastic nature of cellulose fibre, the paper gets stretched or elongate before its break, which is the measure of the ratio of increased length due to the external mechanical force to its original length and the elongation properties have been of significant importance for some packaging grades of papers. It has been formerly deliberated that chemical treatment to the fibre induces its deformation, which improves their elongation and TEA properties of paper [56-58), this approach is being used by the industries for manufacturing sack and bag grade of papers. The measurement of stretch or elongation of paper before its break was found to be about 3.03% and 3.12% for kraft pulp of untreated and treated samples respectively, whereas in the case of soda pulp it was 2.81 and 2.88% respectively for untreated and treated samples, thus acid pretreatment of fibrous raw material developed the fibre with more modulus of elasticity. Paper with increased tear index from 5.0 to 5.3 $mN.m^2/g$ and 4.5 to 4.9 $mN.m^2/g$ was identified for kraft and soda respectively when the raw material was pretreated with acid, an increased tear index of wheat straw pulp from 6.94 $mN.m^2/g$ to 7.1 $mN.m^2/g$ was investigated earlier due to acid pretreatment of wheat straw which was pulped at 16% active alkali [28]. Bending stiffness is the ability of a paper to resist the force that causes its bending, these properties have much important for the packaging material or paper products that have to maintain their shape during filling operations. Hand-sheets of high stiffness were observed due to acid pretreatment of wheat straw than the untreated sample. Thus acid pretreatment of wheat straw benefits the properties with regards to the mechanical strength of paper and its products, these improvements in the mechanical properties of paper might be because of removal of impurities after acid pretreatment like, extractives metal ions etc, which was resulted in the more inter fibre hydrogen bonding. With regards to the mechanical strength development in the acid-pre-treated sample, our finding is of great importance, as the earlier study recommended that, no significant difference in the strength properties were developed for bleached pulp extracted from acid pretreated and untreated materials [24].

Table 6: Mechanical strength properties of hand-sheets unbleached kraft and soda pulp of untreated and pretreated raw materials.

Parameters	KC	KA	SC	SA
Bulk density (g/cm^3)	0.794±0.02	0.806±0.02	0.862±0.03	0.900±0.01
Gurley porosity (second)	141±6	229±12	145±10	199±31
Folding Endurances (Number)	169±8	199±4	101±8	130±5
Burst Index (k.pa.m^2/g)	3.2±0.4	3.7±0.3	2.9±0.3	3.3±0.4
Tensile Index(N.m/g)	50.9±1.5	52.3±1.1	47.1±1.5	49.0±1.2
TEA (J/m^2)	76.0±4.1	80.6±6.0	64.4±5.8	70.6±4.9
Elongation (%)	3.03±0.30	3.12±0.37	2.81±0.23	2.88±0.22
Tear Index (mN.m^2/g	5.0±0.22	5.3±0.22	4.5±0.03	4.9±0.09
Bending Stiffness (N.mm)	0.306±0.0	0.315±0.01	0.332±0.04	0.357±0.02

Mean of four reading are reported along with the standard deviation

4. Conclusions

Dilute acid pretreatment of wheat straw resulted in improved pulp quality in terms of mechanical strength properties by removing more than 50% metal ions and the extractives. The conditions followed during the acid pretreatment like pH, retention time and consistency greatly influenced the removal rate of these components. Ni and Mg were found to be the highest removal rate of about 80% followed by K, Ca, Fe, Mn, Cu and Zn metal ions. Acid pretreatment influenced the holocellulose content of the material; however, the degradation rate was found to be decreased with an increase in the reaction pH and consistency. Optimum process parameters for acid pretreatment, like pH (2.0), consistency (5%) and retention time (1 hr) were generated with minimum holocellulose degradation and more benefits in the removal rate of these non-process papermaking components. Irrespective of finding in the reduction of metal ions and extractive content from the materials, acid pretreatment caused about 3% alkali saving during pulping and about 6 – 7% higher pulping yield of cellulosic fibrous mass of high degree of polymerization as compared to the untreated materials. Due to acid pretreatment, the porosity of hand-sheets of kraft and soda pulp was found to be reduced by about 62 and 37% respectively, which caused more compactness fibre and reduced the gaps between the fibres and accordingly improved strength properties of paper. Unlike porosity all other physical properties like tensile, tear and burst index along with the double folds are found to be increased by 2.7, 6, 15.6 and 17.75% correspondingly for the kraft and 4.0, 8.9, 13.8 and 28.7 % for the soda pulp. Due to the removal of these impurities or non-process components from the fibrous material, acid pretreatments caused to improve better quality of paper products by increasing more fibre-fibre H-bonding which get exposed after treatment, also by protecting the fibre from degradation during the pulping process, acid pretreatment also improved the fibre quality by removing the amorphous structure from the cellular mass, therefore authors are suggested to extract

stronger fibre by dilute acid pretreatment of the raw material at optimized conditions. Our next step will be to investigate the effects of acid pretreatments on the bleaching performance like chemical consumptions; brightness development etc during elemental chlorine-free (ECF) and total chlorine-free (TCF) bleaching stages and their effects on mechanical strength properties as well.

Declarations

Statement and Declarations:

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Competing Interest: Agro-residues lingo-cellulosic bio-waste contains a huge amount of extractives and metal ions, which can impose some negative impacts on the papermaking process. Thus the authors are wanted to develop suitable methods for removing these unwanted elements from the raw material before the papermaking process, by chemical pre-treatment of the raw material with minimum effects in the chemical constituent's.

Data availability: The dataset generated during this study can be available from the author's on request.

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Figures

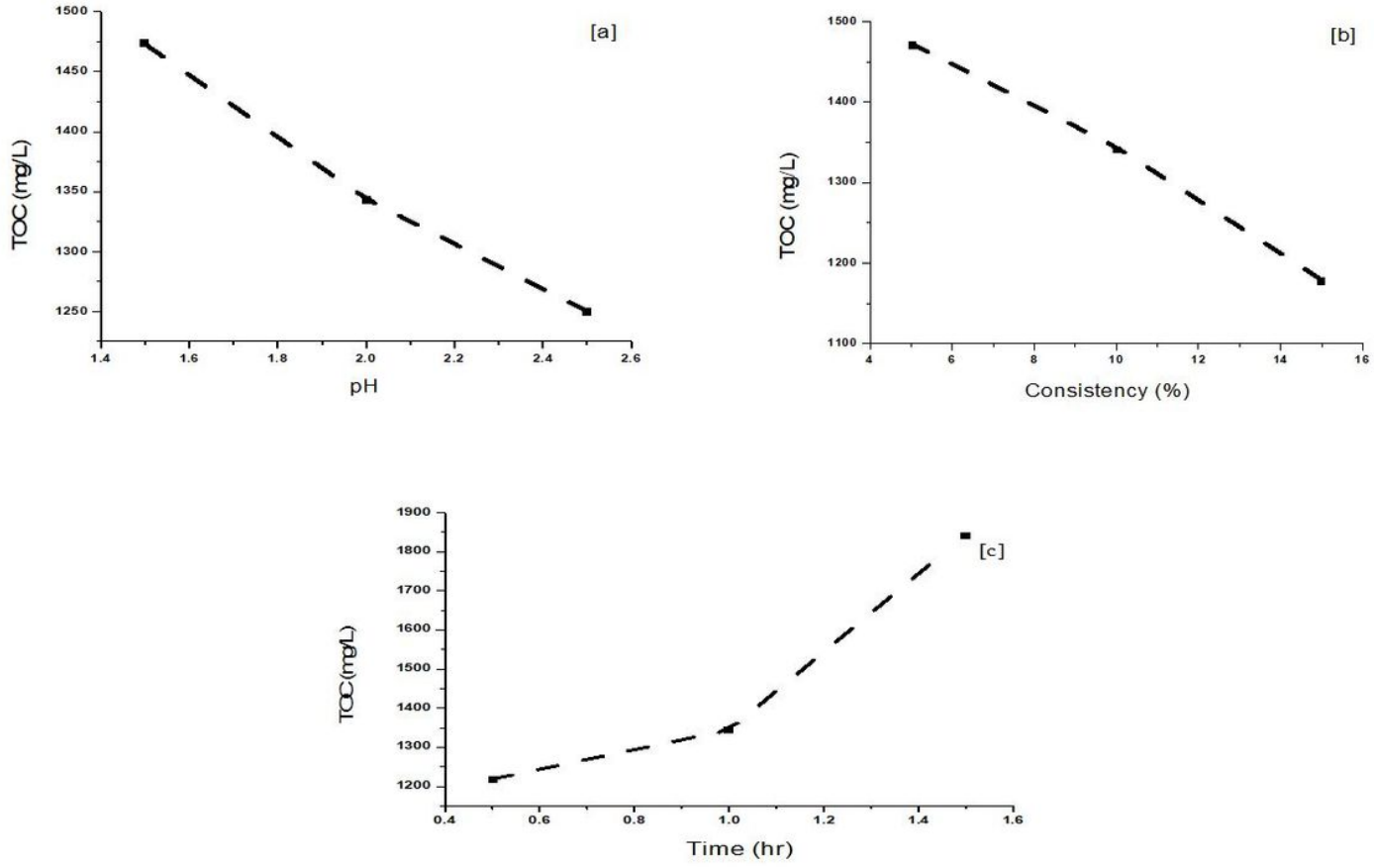

Figure 1

Effects of [a] pH [b] consistency (%) and [c] time (hr) on total organic carbon (TOC) removal due to acid pre-treatment

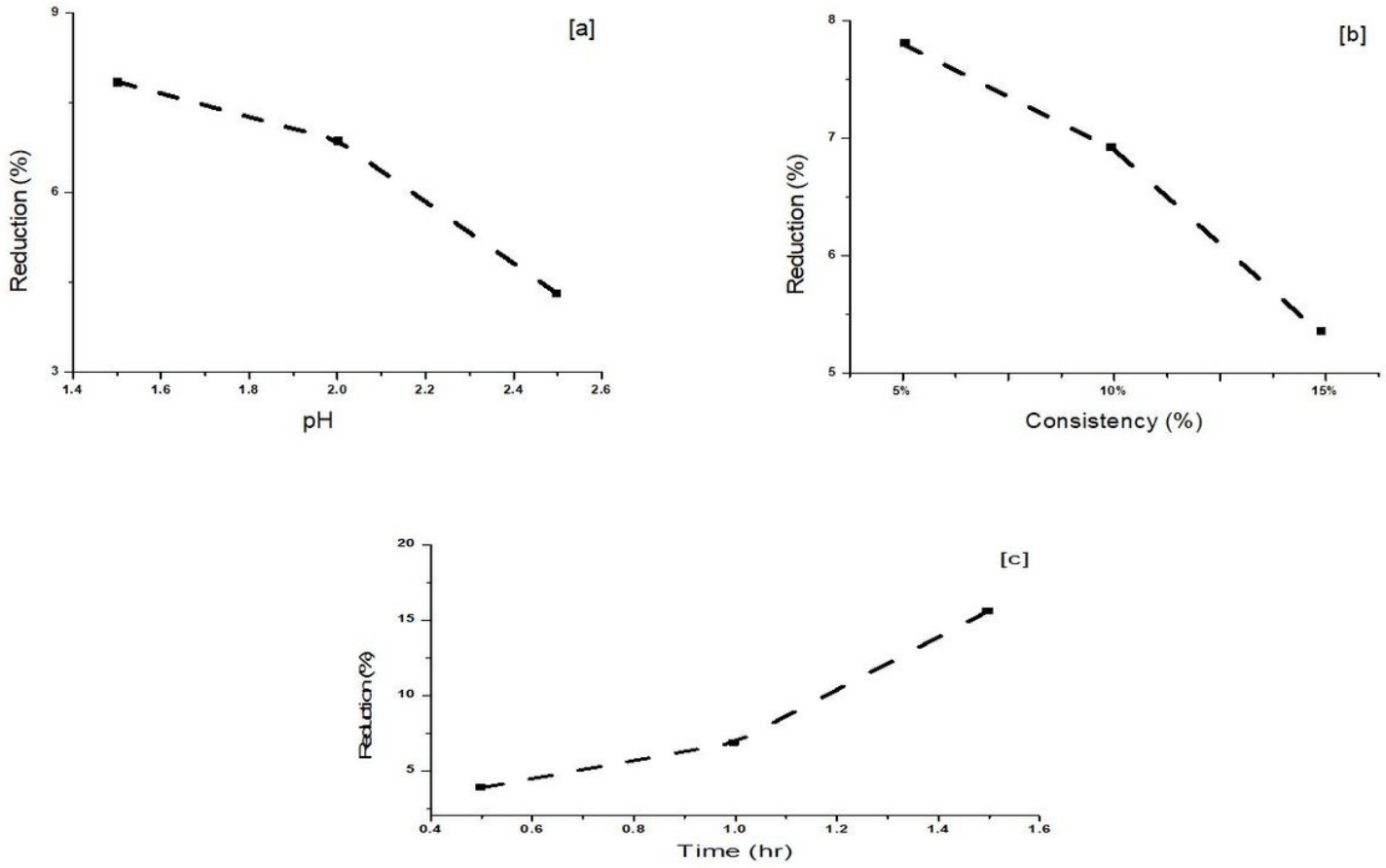

Figure 2

Effects of [a] pH [b] consistency (%) and [c] time (hr) on the reduction in Holocellulose content due to acid pre-treatment.

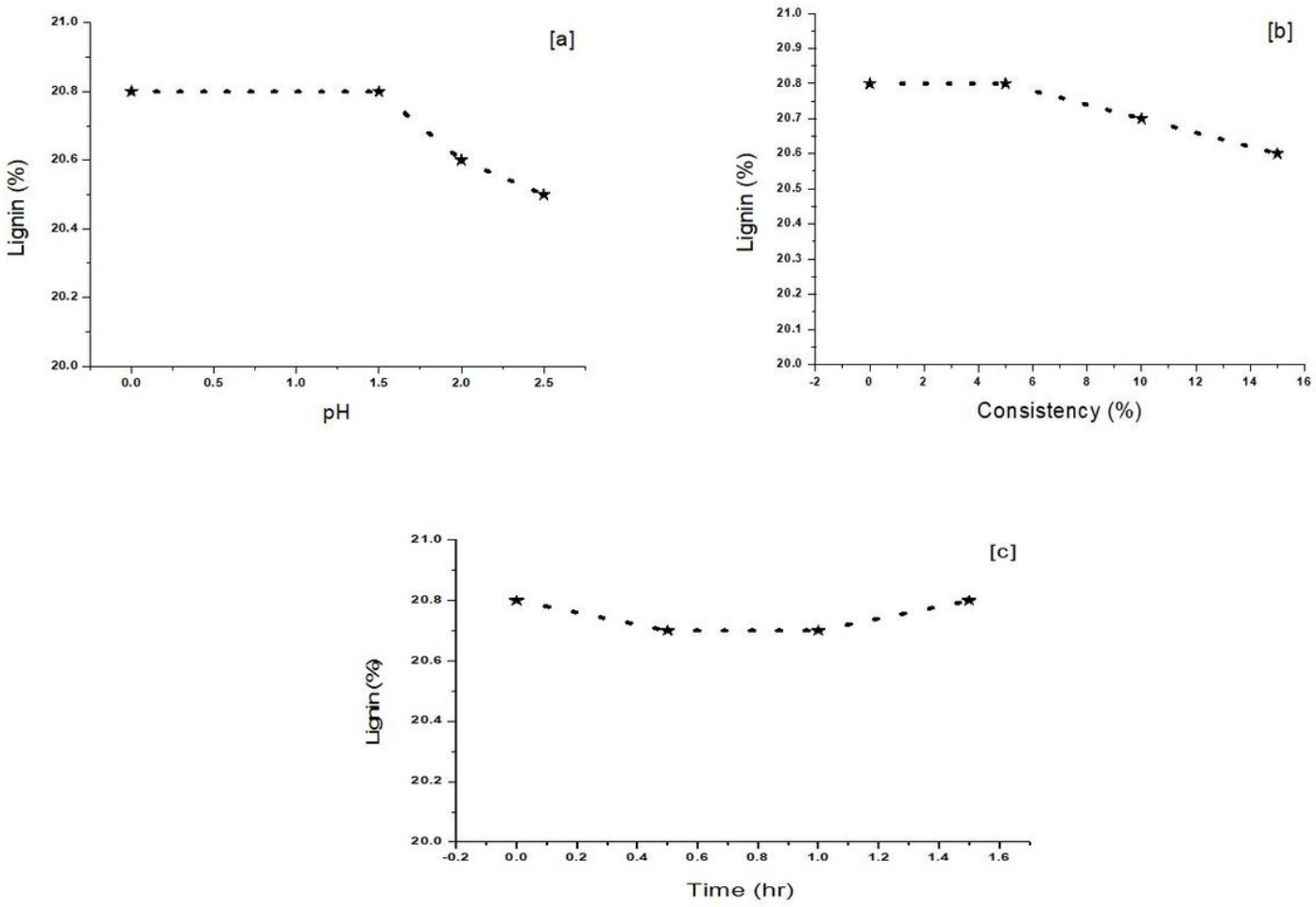

Figure 3

Effects of [a] pH [b] consistency, % [c] time on the lignin content due to acid pre-treatment

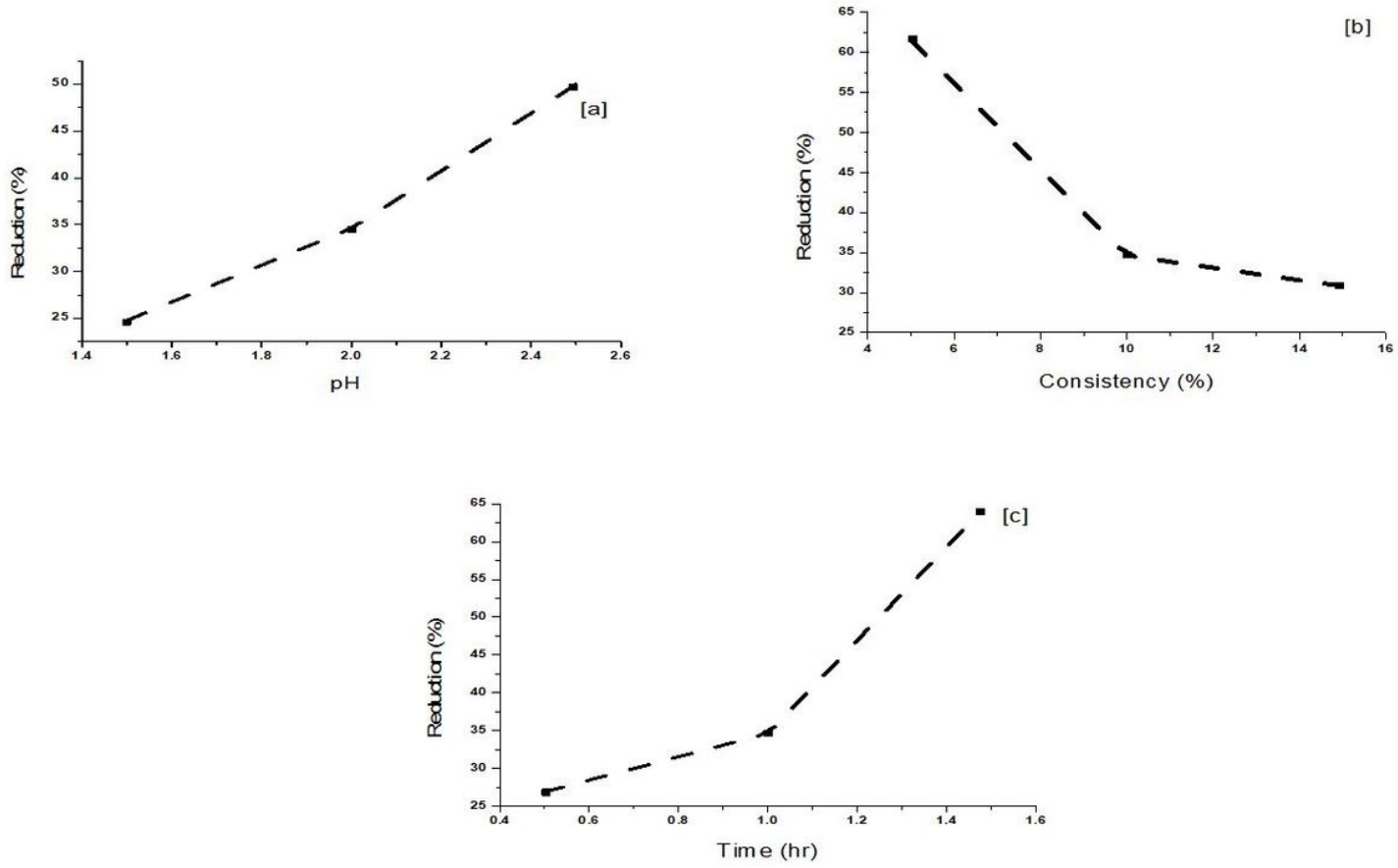

Figure 4

Effects of [a] pH [b] consistency (%) and [c] time (hr) on the reduction in Extractives content due acid pre-treatment.

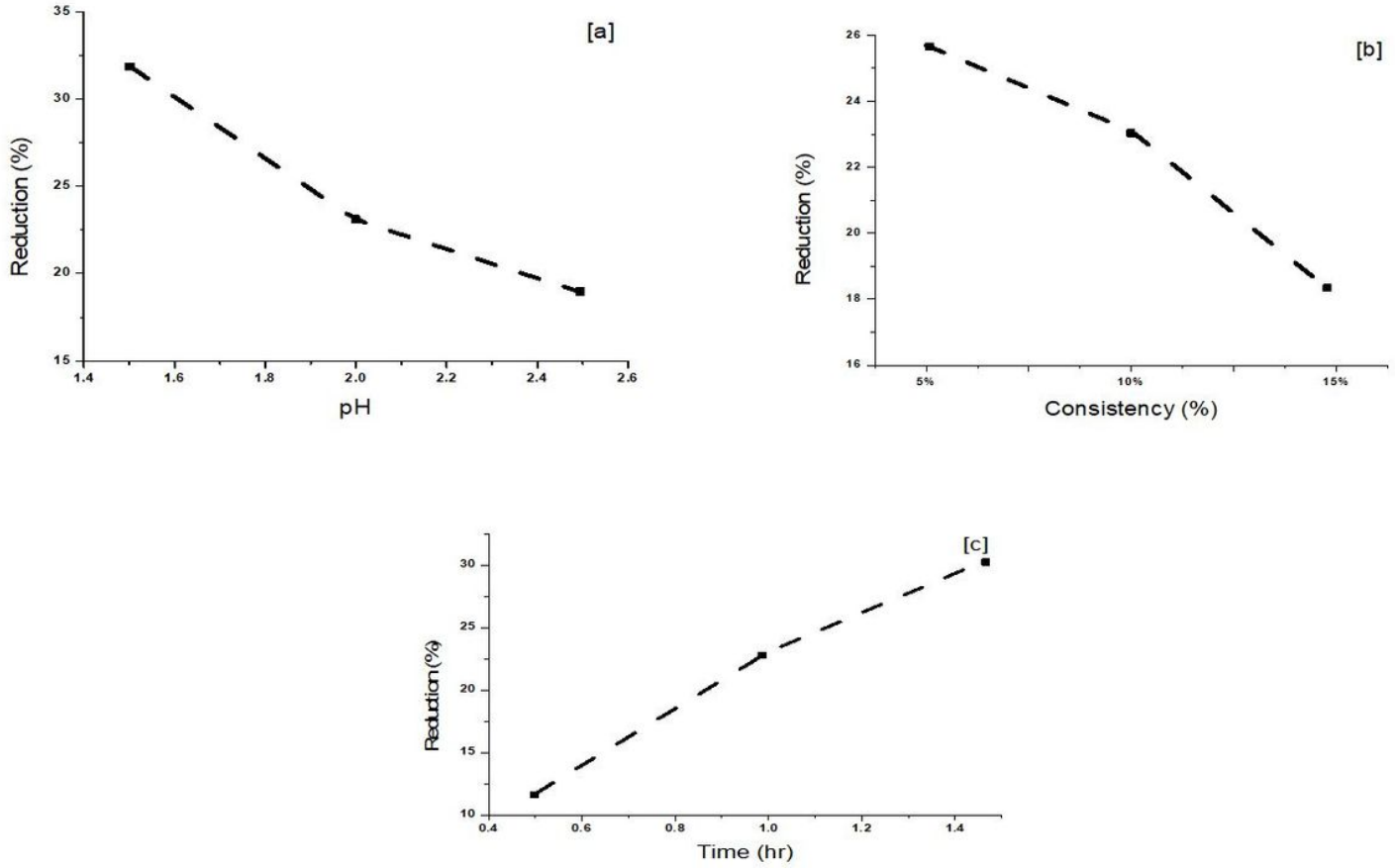

Figure 5

Effects of [a] pH [b] consistency, % [c] time (hr) on reduction in Silica content due to acid pre-treatment.

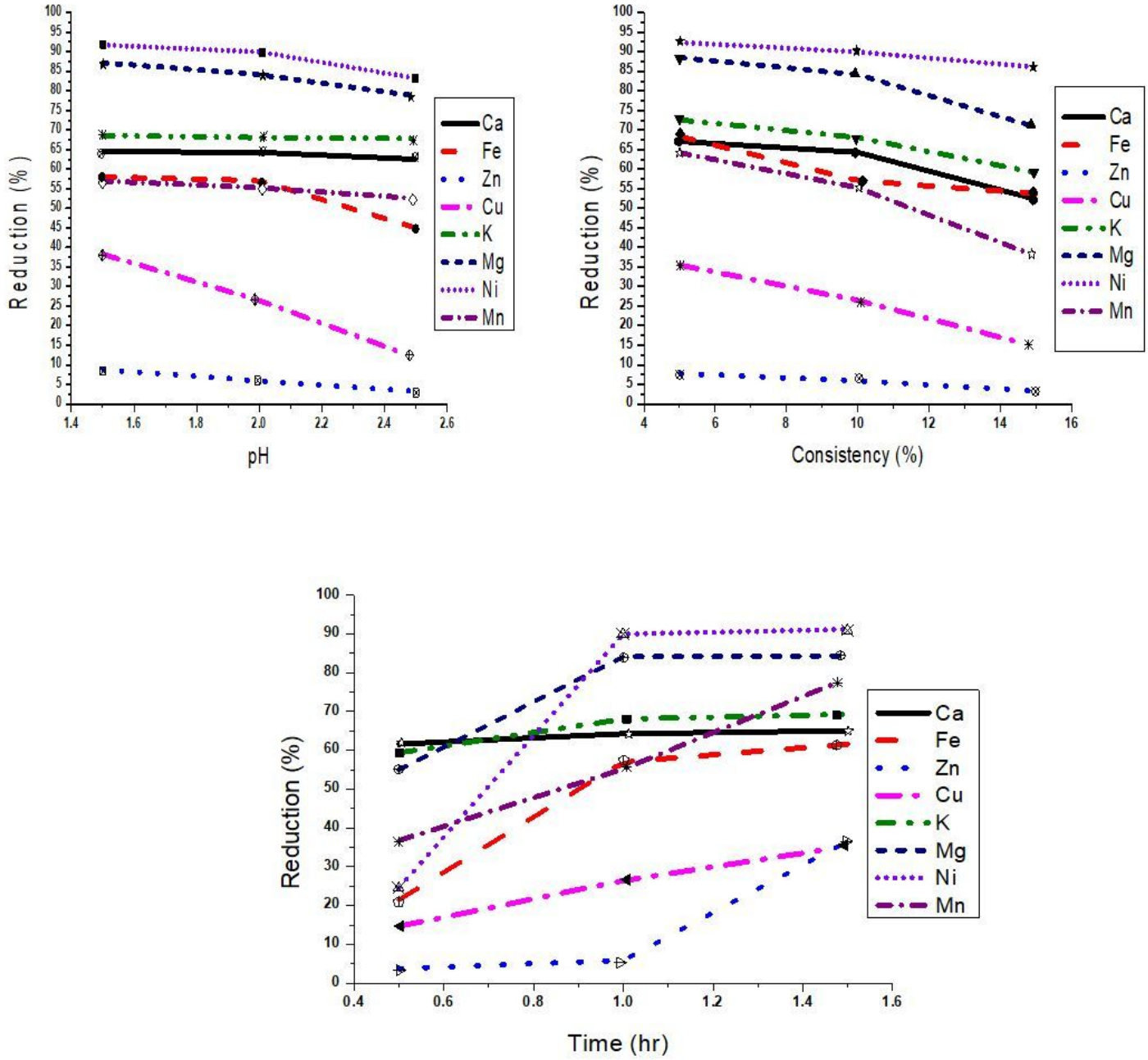

Figure 6

Effects of pH, consistency (%) and retention time (hr) on the removal of metal ions content due to pretreatment

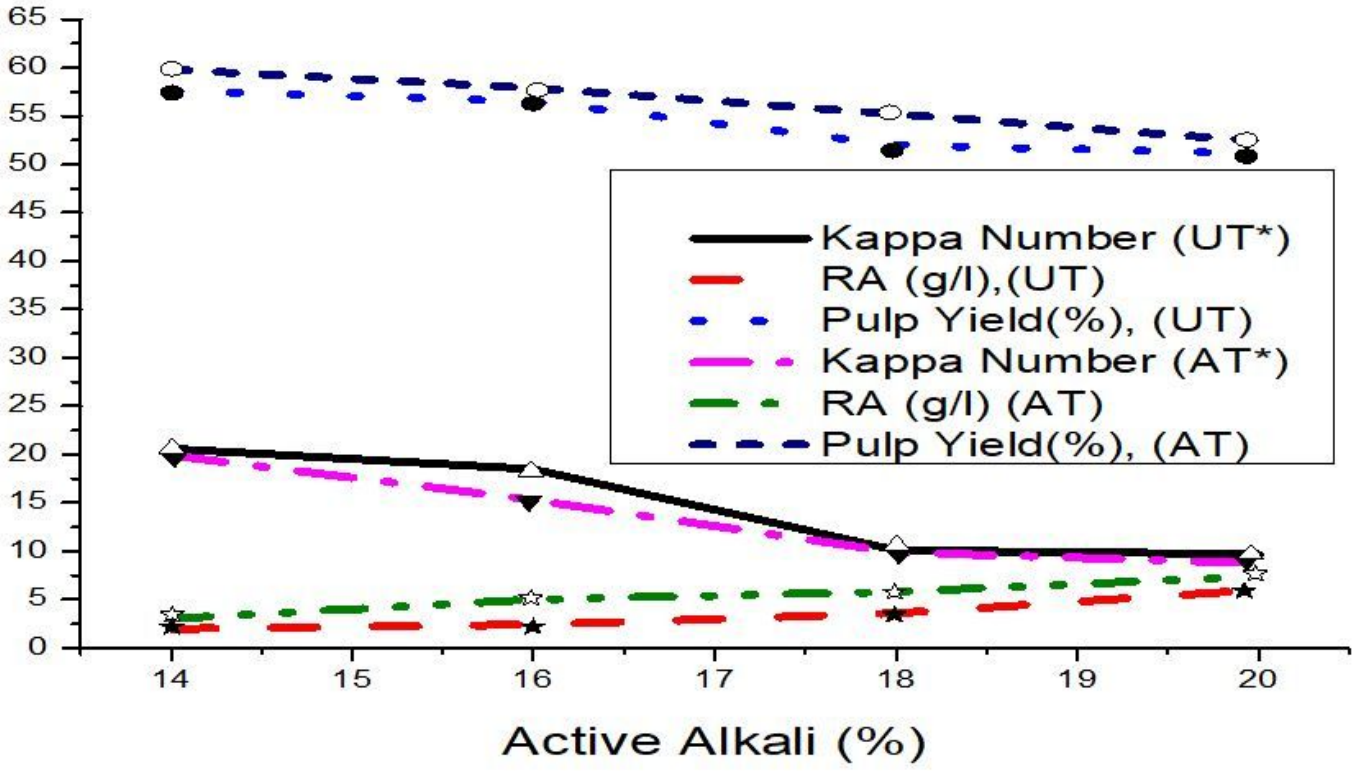

Figure 7

Effects of acid pre-treatment on kraft pulping of wheat straw (*UT- Untreated, *AT- Acid treated)

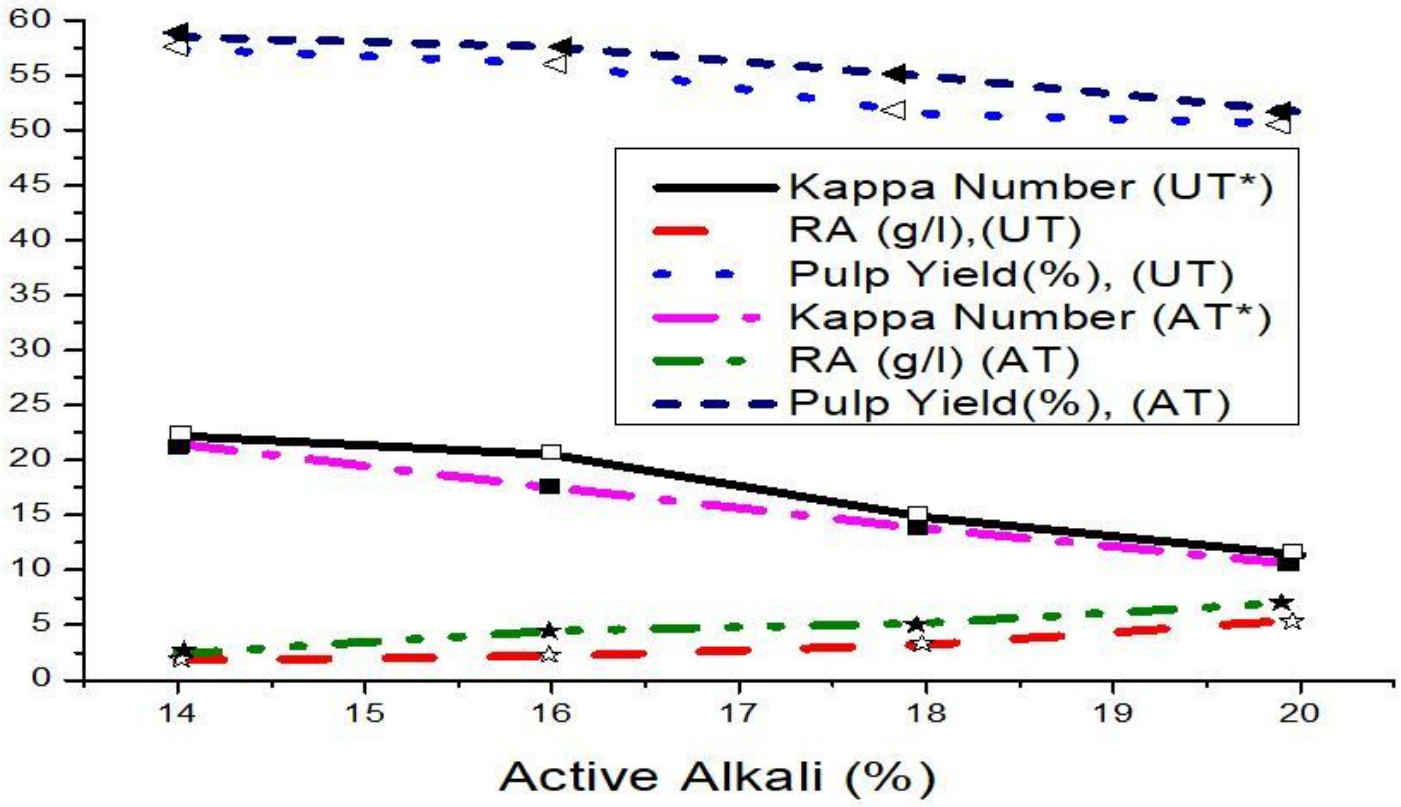

Figure 8

Effects of acid pre-treatment on soda pulping of wheat straw (*UT- Untreated, *AT- Acid treated)

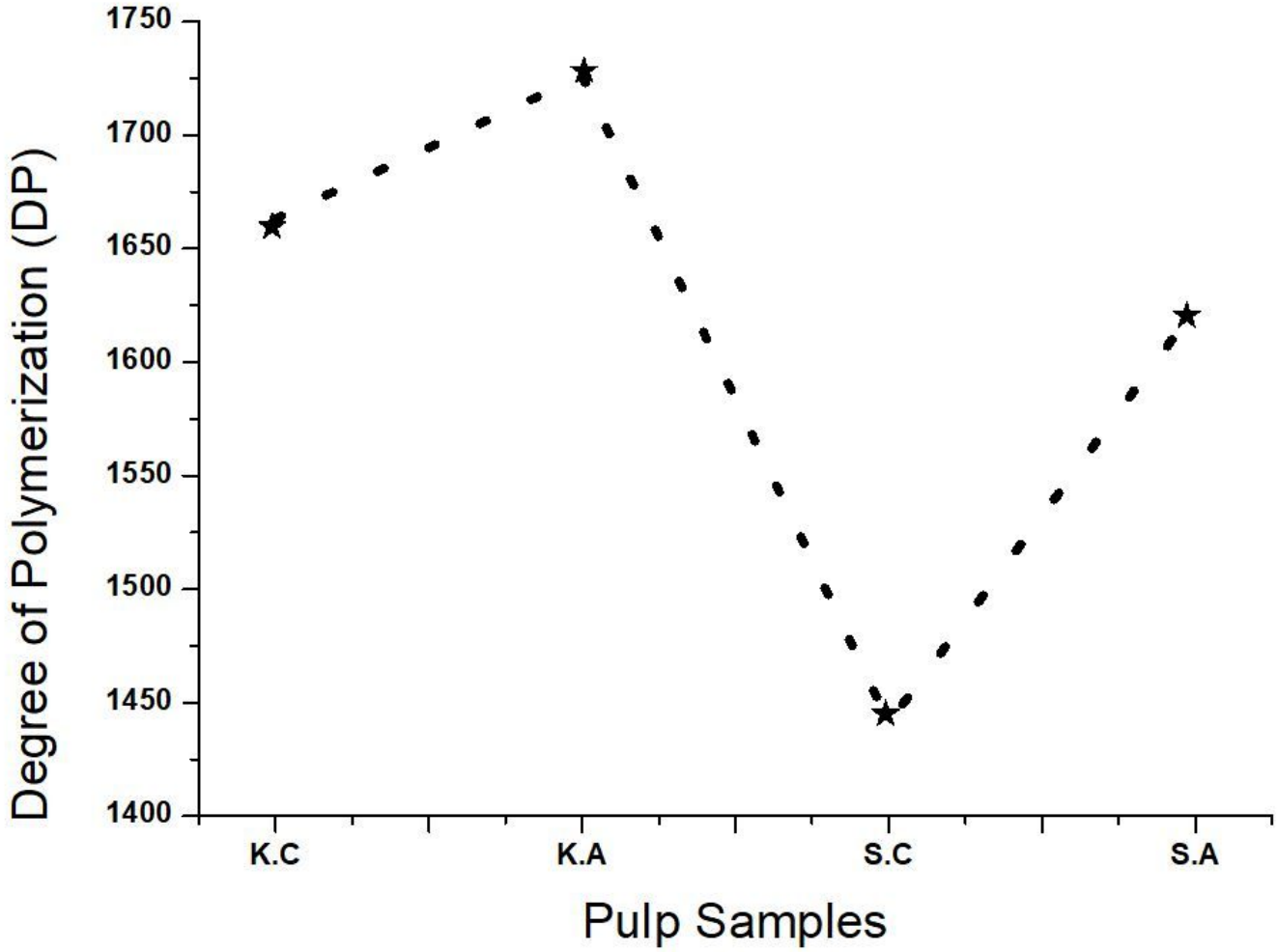

Figure 9

Effects of acid pre-treatment on DP of unbleached pulp samples

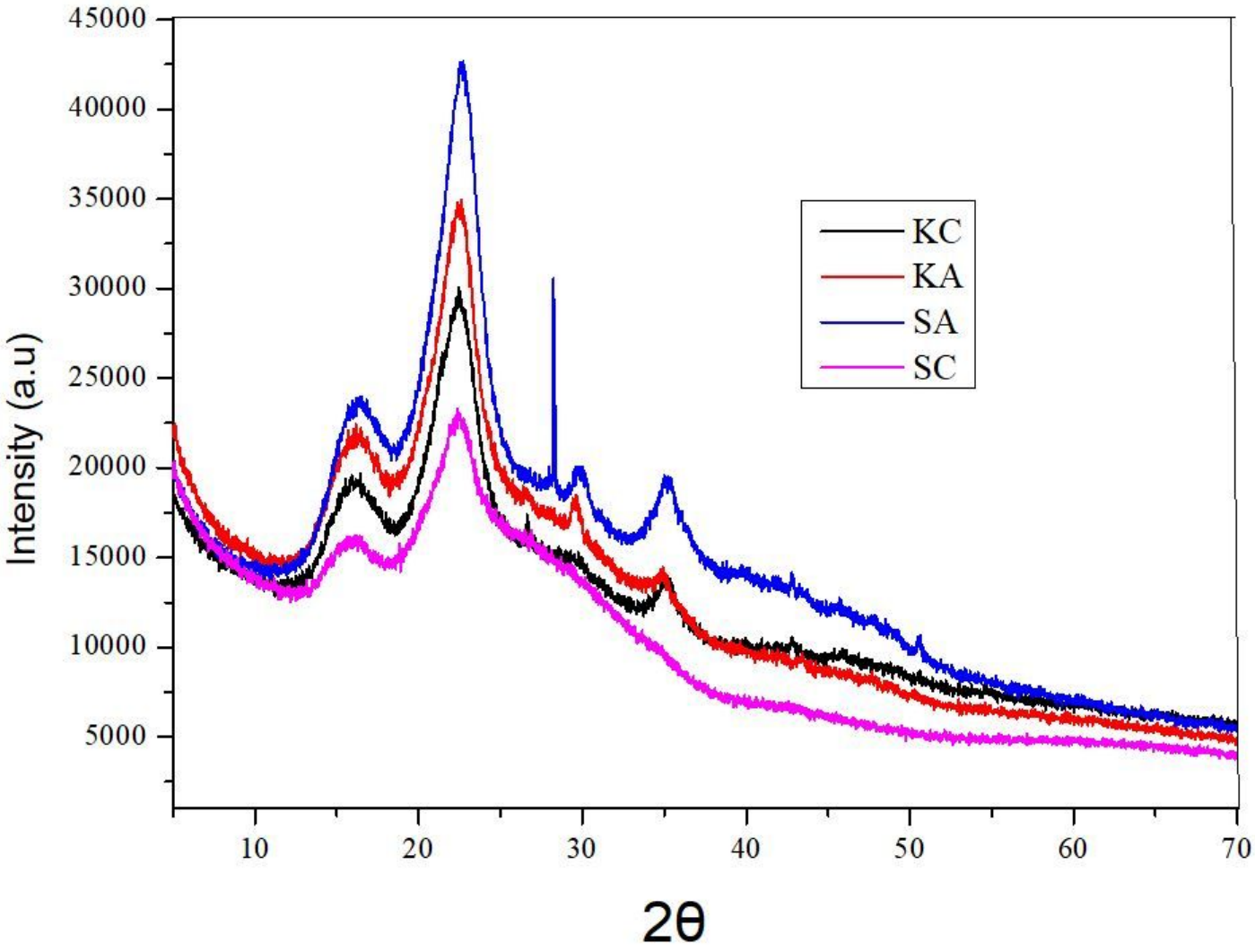

Figure 10

X-ray diffraction pattern of kraft and soda pulp (Untreated and acid treated)

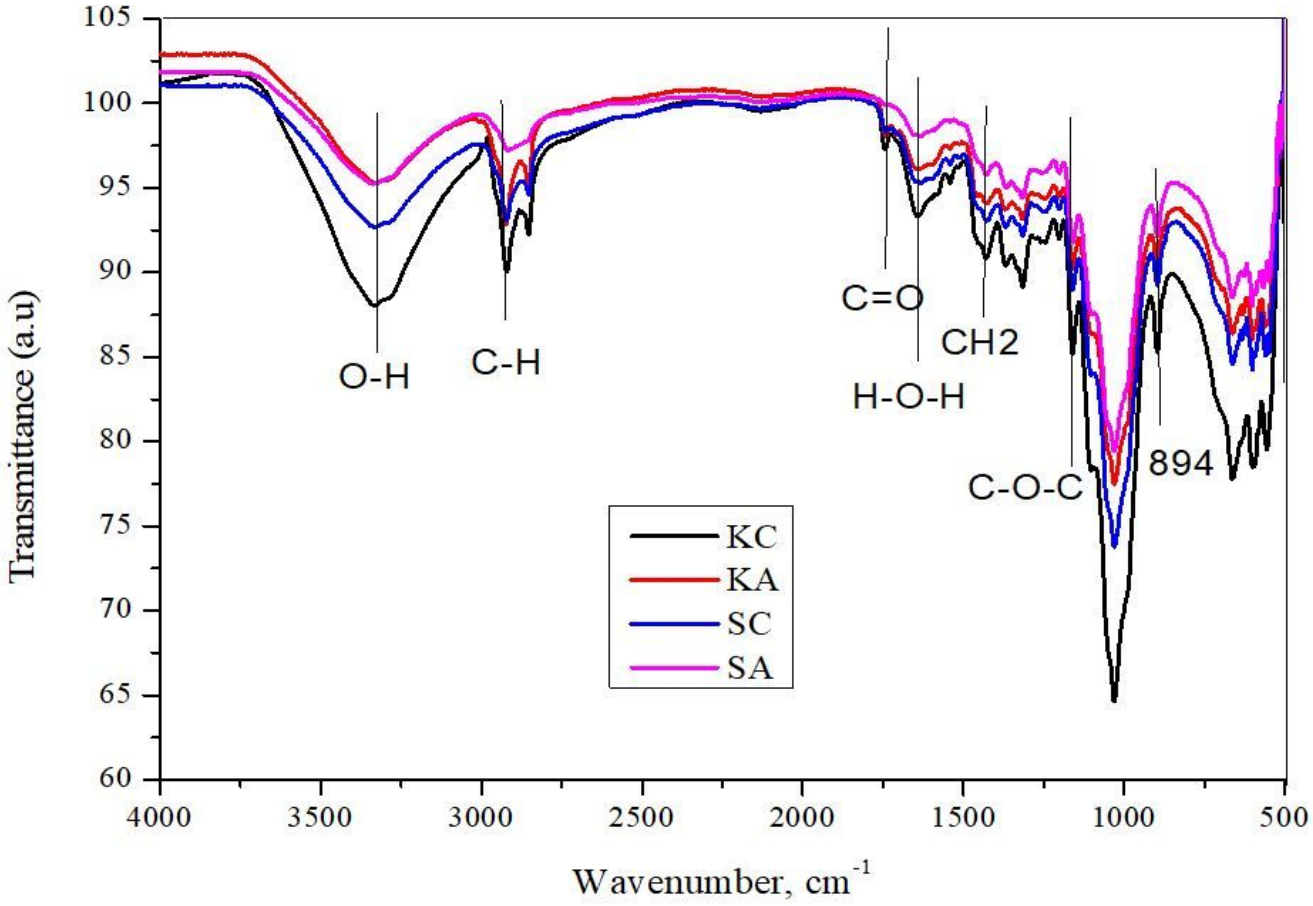

Figure 11

FTIR spectra of kraft and soda pulp (untreated and acid treated)

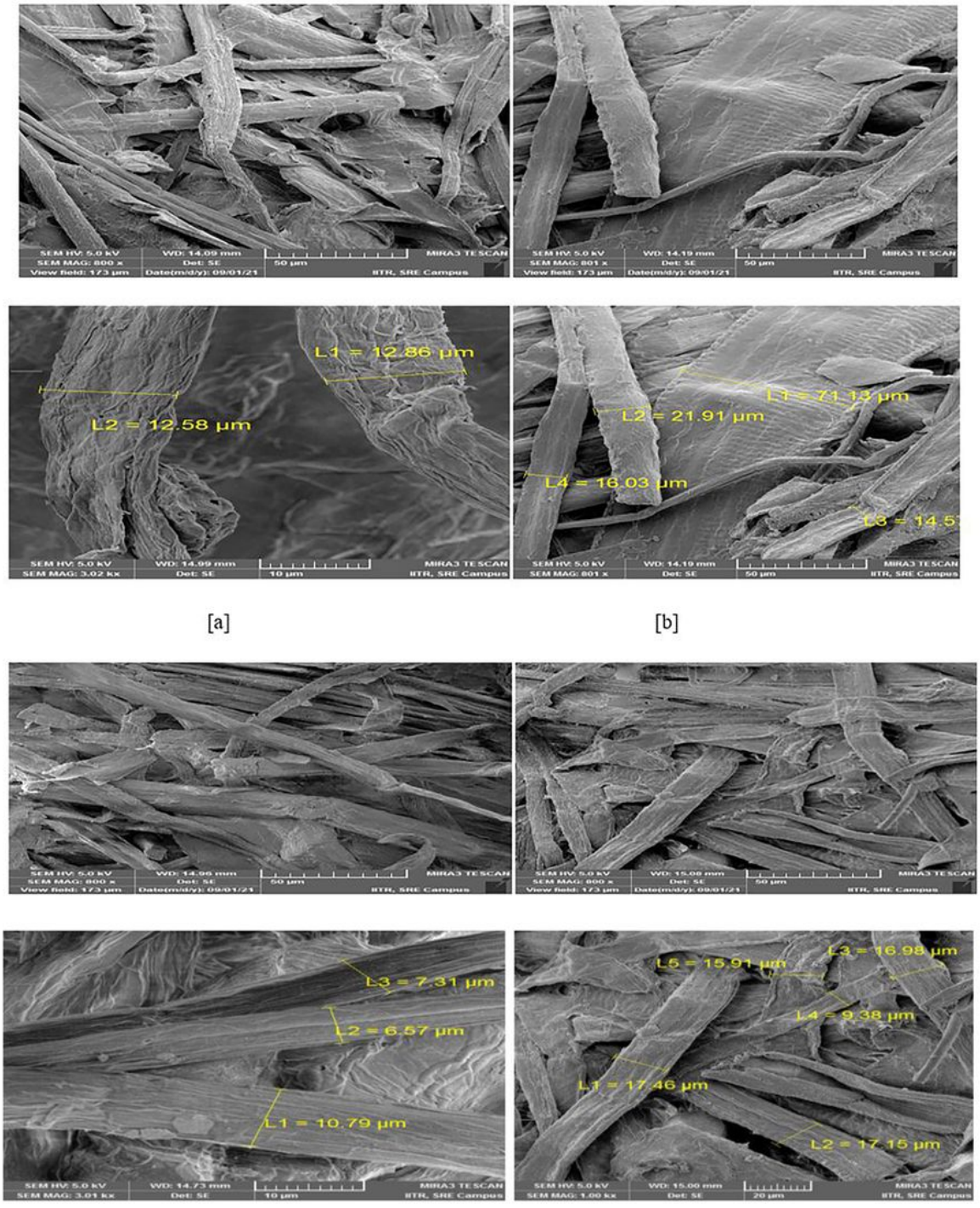

Figure 12

FE-SEM micrographs of [a] KC, [b] KA, [c] SC, [d] SA

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- graphicsabstract.jpg