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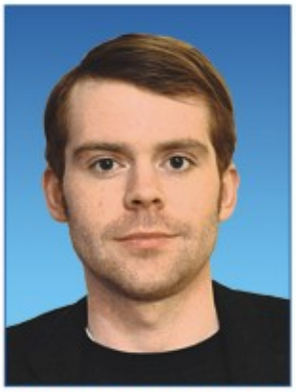

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ADSORPTION DEINKING : OVERVIEW AND AGEING EFFECT

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Summary

In the recent years, ink removal from the recovered paper has gain several importance mainly due to environmental and economic reasons. Deinking industry has made several contributions to improve the existing technologies viz. flotation and washing deinking to remove ink particles from the recovered paper. There is no any further scope of improvement in the existing techniques in form of quality, energy efficiency, eco-friendly and yield to meet the everlasting demands of industry and consumer. So there is an urgent need of new technique to meet these criteria and recently a new methodology was developed to remove ink particles by the use of polymeric beads during pulping and termed as "Adsorption Deinking". These polymeric beads are able to adsorb the ink particles due to their surface chemistry. In my thesis work, I have worked on ensuring the reproducibility of this new deinking method and the effect of ageing of the recovered paper on results of adsorption deinking. The natural ageing of recovered paper decreases the brightness of the pulp after deinking as ageing helps in the strong binding of ink particles with the cellulosic fibres.

During the work, it has been found that Adsorption deinking achieves comparable results as that of existent techniques at much higher consistency, and hence, making the process economic with comparable quality of the product. Adsorption deinking achieves good results for deinking of aged paper stored in climate room which makes this new technique highly suitable for deinking industry.

Introduction

Recycling is not a modern thing; it's an old tradition in paper industry. Recycled fibres serve as an indispensable raw material for global paper industry. Recycling is becoming more efficient, economic and ecofriendly with rapid developments and innovations in

deinking processes for the best utilization of the secondary fibres. Nowadays more than half the paper is produced from recovered papers out of which mostly used to produce brown paper grades and board, but presently there has been a substantial increase in recycling recovered paper to produce white grades such as newsprint, tissue, writing and printing and market pulp to meet the consumer demands **(Carre & Galland, 2007)**.

In the last 2-3 decades, the raw material for pulp and paper industry has seen dramatic shifts and recovered waste paper has emerged as the best substitute. The recovered paper utilization rate was merely 31% during 1980s and currently it has reached above the 50% line, almost beyond imagination a few years back. The figure shows clearly the recycling rate of recovered paper in world regions in 2010. The deinking technique serves the purpose of removing the printing inks and other contaminants that might affect the papermaking process or final properties of paper. Deinking essentially involves the detachment of ink from fibers, removal of detached ink from pulp suspension and then the treatment of waste water for reuse and disposal of removed ink and contaminants. The techniques utilized worldwide to remove ink particles from recovered paper are flotation deinking and washing deinking out of which flotation method is more dominant because of its selectivity **(Gottsching, 2000).** Deinking of recovered paper is also influenced by the ageing of recovered paper as bonding between ink particles and the fibers become stronger with ageing. The information on the mechanism of ageing effect and its role in deinking is not known completely, but definitely the ageing of recovered paper affects adversely the present deinking processes and decreases the brightness levels of the pulp formed. Both of the techniques works satisfactorily at consistencies around 1%, therefore a substantial amount of energy is consumed just to transport water which renders the whole process as energy inefficient. The actual energy demand for any deinking process depends on the energy required to break the bonding between fibers and ink particles. This adhesion energy (bonding forces present between ink and cellulose fibers) can be calculated with the help of Dupre-equation:

$$W_{ci} = \gamma_c + \gamma_i - \gamma_{ci}$$

Where W_{ci} is the total adhesion energy and γ_c, γ_i, γ_{ci} are the surface energies of the ink, cellulose and the interface between cellulose and ink particle respectively. Because the theoretical energy required removing ink particles from fiber surfaces and from the pulp suspension is negligible in comparison to the current energy requirements and still the energy gap is very large if we use best available technology for deinking process. The present methodologies flotation and washing deinking have been saturated in terms of further developments by maintaining the same product quality but at reduced cost so this energy gap can be reduced by developing some alternative process that can be the solution instead of modifying the existing processes **(Handke, Schrinner, & Grossmann, 2012)**. Adsorption deinking is a novel deinking method which was quite recently developed at the Professorship of Paper Technology, TU Dresden. By using polymeric beads as ink collector, the deinking process is combined with the sub process of pulping. This should lead to significant water savings and thus to a reduction of operational costs. Especially for newsprint, that means offset cold set, adsorption deinking achieved promising results which could be compared to those of state of the art technology but with water savings of 90%. However, these results are obtained in just small number of trials, which are far too limited to assess the applicability of the new deinking method. By setting the appropriate and uniform boundary conditions through multiple repetitions of a standardized test procedure the existing results should be confirmed and the reproducibility of adsorption deinking to be shown satisfactorily. Furthermore, by individual variation of the influential factors of the standardized test procedure the mode of operation of adsorption deinking should be investigated in more detail. Secondly, the influence of the ageing of recovered paper on adsorption deinking results is also closely examined.

The focus of this paper includes two vital parts:

I) To confirm the reproducibility of Adsorption deinking

II) To check the influence of the ageing of recovered paper on deinking results.

Literature Review:

Recovered paper is the most important raw material for paper industry worldwide and hence, the utilization rate of recovered paper has been dramatically increased in the past few years.

Deinking:

Deinking technique is a series of unit operations that consists of detachment of ink particles from cellulosic fibers and then separation of the detached ink from pulp suspension **(Borchardt, Mechanistic insights into de-inking, 1994)**.Basically 3 types of forces are used to detach ink from fibers viz. Mechanical, chemical and thermal forces. Deinking chemicals are generally added during the pulping where it can take the advantage of all the 3 forces.

Table 1: Chemicals used in Deinking process

Chemical	Addition point	Function
Sodium hydroxide	pulper	It increases pH to 8-10 and enhance fiber swelling and hence, • helps in ink removal. • disintegration of paper into fibers.
Sodium silicate	Pulper	• Act as dispersant for the detached ink particles. • Increases pH as well as act as buffer. • Form colloidal structure with heavy metal ions.
Hydrogen peroxide	Bleach tower &/or Pulper	• Prevents the lignin-yellowing of pulp. • Increases pulp brightness.
Surfactants	Pulper	• Promotes ink detachment from fibers. • Helps in removal of ink particles by dispersion. • Helps in ink removal by boosting ink attachment to air bubbles during flotation and in foam stabilization.
Chelating agent	Bleach tower &/or Pulper	Prevents decomposition of H_2O_2 by forming soluble complexes with heavy metal ions.
Fatty acid	Flotation cell	Helps ink particles to become hydrophobic and stabilizes foam.

Table 2: Properties used for the removal of contaminants(Amand, 2005)

Properties	Separation process used
size	Washing: if contaminants are smaller than fibers and Screening: if contaminants are larger than fibers.
Density	Centrifugal cleaning: if sufficiently large contaminants having density other than 1(maybe >1 or <1).
Surface properties	Flotation: removal of contaminants on the basis of their surface properties (hydrophobicity).

This figure shows the different techniques removal efficiency based on the separation process used:

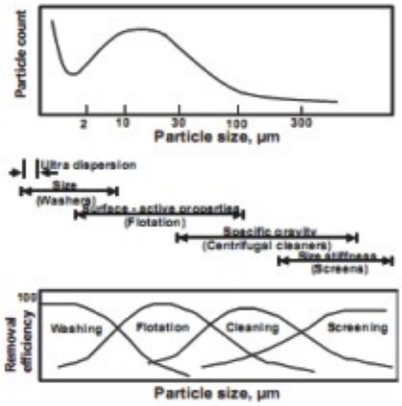

Fig 1: Particle size distribution and unit operation removal efficieny (Carre & Galland, 2007)

Adsorption deinking

It is recently developed at Dresden University of technology based on the functional principle of polymeric beads as ink collectors. Attachment of ink particles on the surface of polymeric beads take the advantage of fact that certain polymers, due to their surface properties, are able to extract the ink particles like in the textile industry. The deinking process was combined with the pulping process in special laboratory pulper (Hobart Pupler). Main advantages of the Adsorption deinking method developed:

- Performed at high consistency (best results at 15%) and therefore, significantly reduce the energy consumption.
- Causes disperging effect which can allow in the renunication of the most enrgy intensive process in paper recycling.
- Very low undesirable stock losses.
- Provide alternative of combining some basic processes of paper recycling like pulping and deinking in just one single process, and hence, helps in making the overall process more simpler.

Results and Discussion

Ensuring the Reproducibility of Adsorption Deinking:

The brightness level was found to be around 59% measured by Elrepho spectrophotometer.

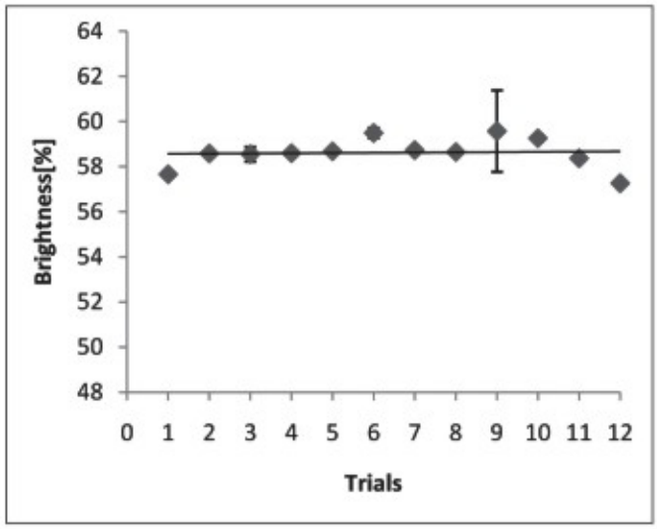

Fig 2 : Brightness of Handsheets samples of Adsorption deinked pulp

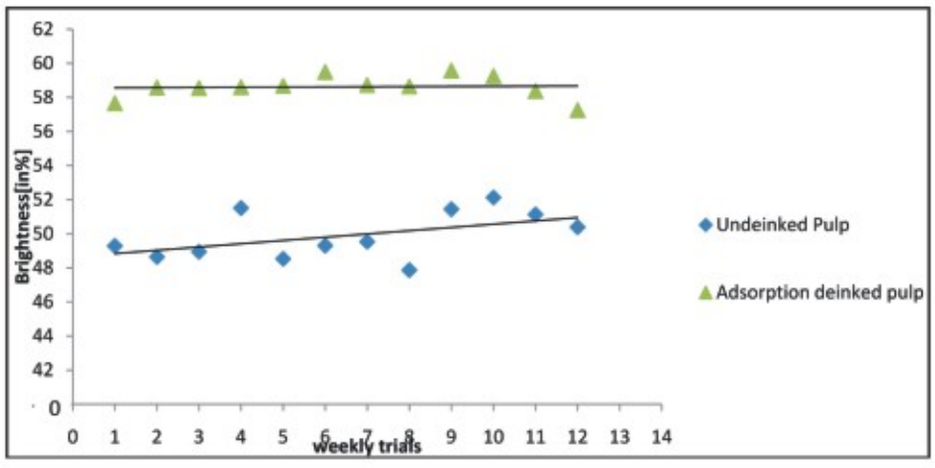

Fig 3: Comparison of brightness of filter pads of undeinked and Adsorption deinked samples

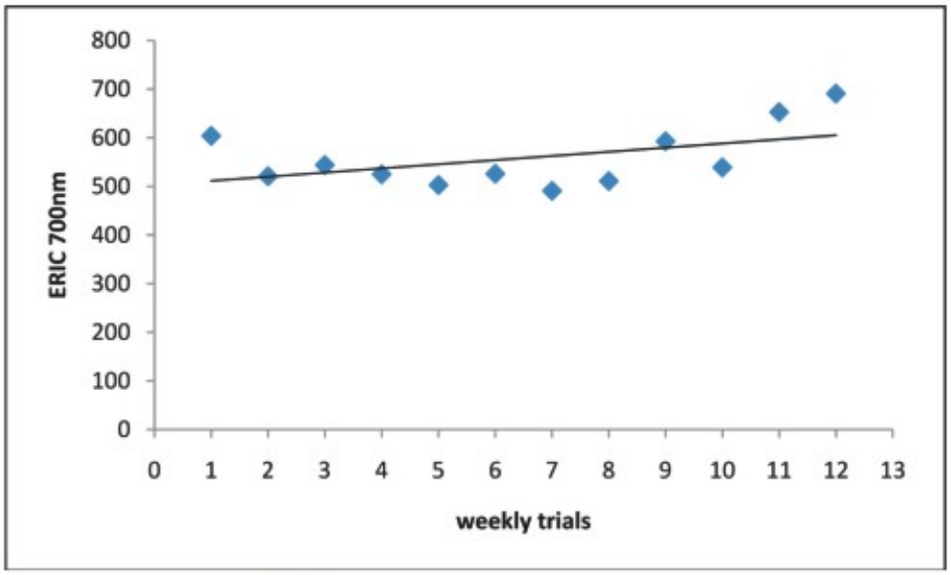

Fig 4 : ERIC for reproducibility trials

Long term trials

To measure the effect of ageing of recovered paper (stored enough at the starting) on adsorption deinked (AD) pulp samples and adsorption-flotation deinked (AD-FD) pulp samples trials were performed on weekly basis.

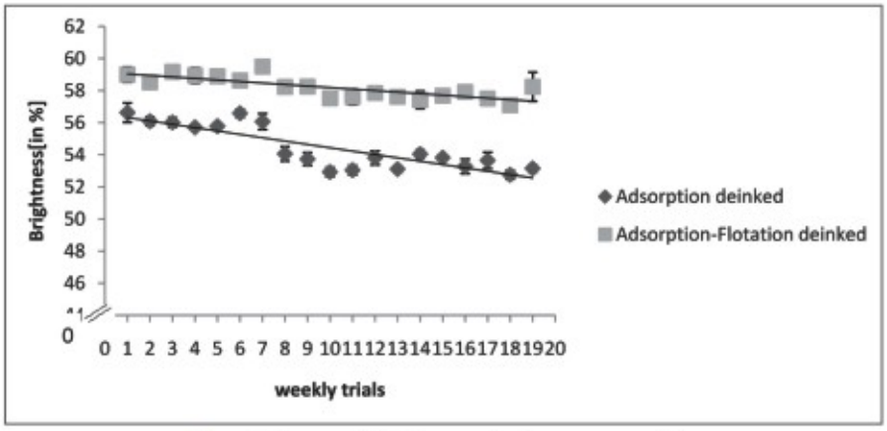

Fig 5: Filter pad brightness for long term trials

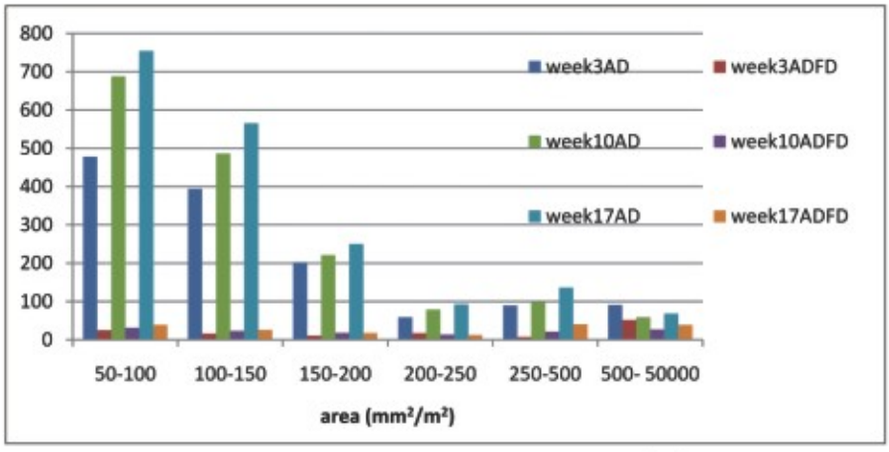

Fig 6: Number of dirt specks vs area (mm^2/m^2)

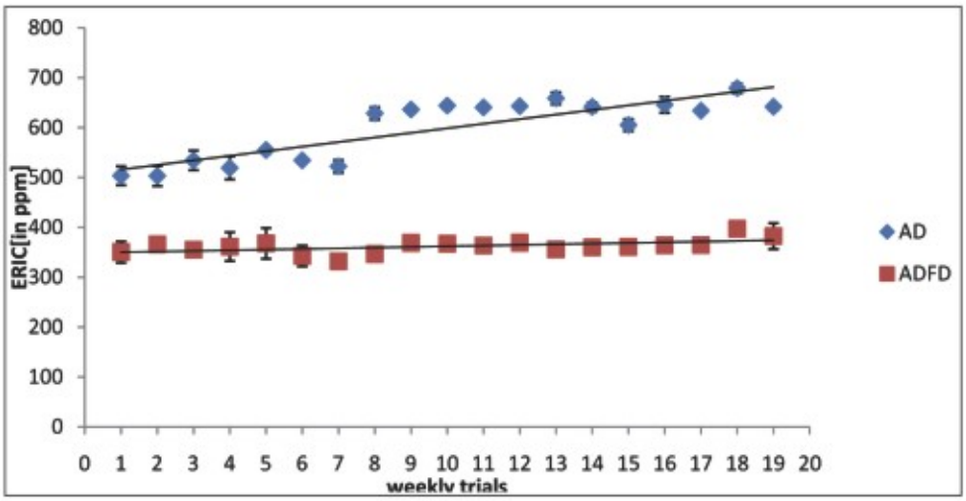

Fig 7 : ERIC for AD & ADFD samples

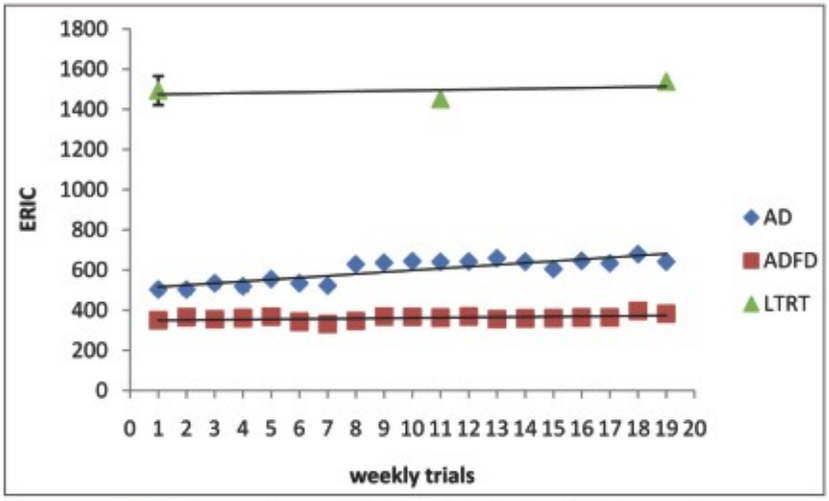

Fig 8 : Comparison of ERIC for AD, ADFD& LTRT samples

It clearly shows that Adsorption deinked pulp samples ERIC value increases with the age of the recovered paper, but the Adsorption-Flotation deinked samples have almost same level of ERIC measurements which conveys that if subsequent flotation deinking is also performed after adsorption deinking then the effect of ageing of recovered paper on ERIC value is negligible if the paper is aged according to storage conditions helpful for deinking.

The next graph shows the comparison of ERIC values of undeinked samples (UD), conventional deinked without flotation (CD) and Adsorption deinked (AD) samples, Normal conventional deinking with flotation (CDFD), Adsorption deinked-flotation deinked (ADFD) according to the age of the recovered paper used.

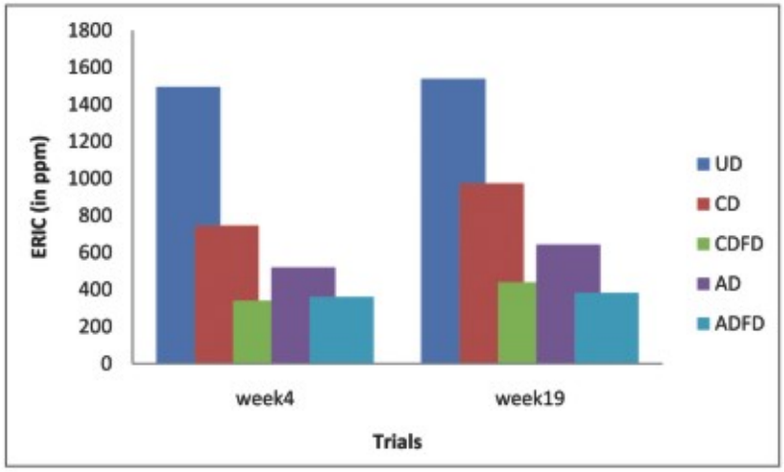

Fig 9: Comparison of ERIC values

Effect of Accelerated Ageing

To compare the effect of natural ageing with accelerated ageing, trials were done for the deinking of accelerated aged samples also.

Accelerated Ageing: Recovered paper samples were placed in an oven for accelerated ageing at 60±3°C for 36 hours and for 72 hours respectively.The accelerated ageing conditions correspond to 3-6 months of natural ageing.

Accelerated ageing of the samples were done in order to find that how the storage conditions of the recovered paper can influence their deinking ability.

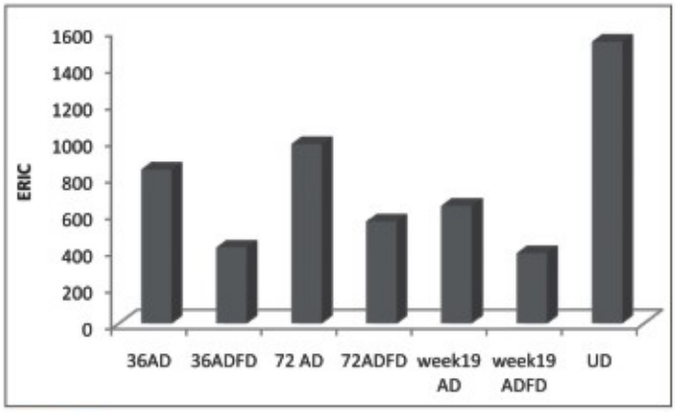

Fig 10 : Comparison of ERIC values with accelerated ageing

Conclusion

Reproducibility of Adsorption deinking : This work confirmed the Reproducibility of Adsorption Deinking method, and further it can also be concluded that it achieves comparable results with existent technologies in terms of end product quality. There was a clear increase of brightness level of nearly 10 points and number of dirt specks was also reduced. Further, ERIC results also confirmed the reproducibility of method as the results obtained have shown the common trend.

Effect of Ageing on Adsorption deinking results : There was only a drop of nearly 4% brightness level at the end of long term trial and ERIC value has increased nearly by 200ppm for adsorption deinking results. Further, number of dirt specks have also been increased, which has clearly shown that with ageing the end product quality decreases.Adsorption deinking followed by subsequent flotation has led to only a slight improvement in all the properties like brightness level, number of dirt specks and ERIC value. Adsorption deinking method achieves good results despite the ageing of recovered paper. These good results can be attributed to the fact that either the storage conditions of the recovered paper in the climate room has been good for deinking or adsorption deinking removes ink particles efficiently even after ageing of the recovered paper. These results were obtained with less overall energy consumption and high water savings with negligible fiber loss.

Experimental Methodology

Preparation of recovered paper sample for pulping:

First moisture content of the recovered was calculated and was found to be 6.9%.The Adrem recovered paper (local newspaper) was crushed into 2*2cm small pieces manually and then weighed to get 200g OD paper or ~214g air dried.Temperature of Dilution water used for experiment was 45°C.

Instruments used: For wet lab work- Weighing balance, water bath, Magnetic stirrer and heater, pH meter, Hobart Pulper, Distribution device, Rapid Kothen sheet former and dryer, Flotation cell, Buchner funnel

For dry lab analysis: DOMAS, Elrepho spectrophotometer.

Preparation of deinking solution: (According to INGEDE method 11p) Dissolve 6g NaOH in 500ml dilution water and heat it up to 60°C, add 8g of oleic acid, stir until solution was clear and add 18g of sodium silicate and fill up to a volume of 2l . Now, 400ml of this solution for 200g oven-dry recovered paper represents, 0.6% NaOH, 0.8% oleic acid and 1.8% sodium silicate.

1.4g peroxide was dissolved in 100ml deionized cold water to get 0.7% hydrogen peroxide (100%), but the hydrogen peroxide used was 30% pure therefore, 4.66g peroxide was added in 100ml deionized cold water.

Pulping and Adsorption deinking:

Prepared sample paper, chemical solution (deinking recipe) and dilution water was transferred to Hobart Pulper in amounts equal to 200g recovered paper, 400ml chemical solution and 633ml dilution water respectively, to get 15% final consistency. Duration of pulping was for 20 minutes and initially pulping was started for some seconds and any scrap of paper was brushed down from the vessel wall. Now, 200g of polymeric beads (polypropylene) were added to the pulper and simultaneously the 100ml peroxide solution was added. Pulping cum Deinking process was started at 1.5 energy level of Pulper and from time to time any scrap was brushed down. The process was terminated after 20 minutes. During the process and after the completion you can clearly see the loading of PP particles with ink by change in their color.

Fig 11: Systematic processes during Adsorption Deinking

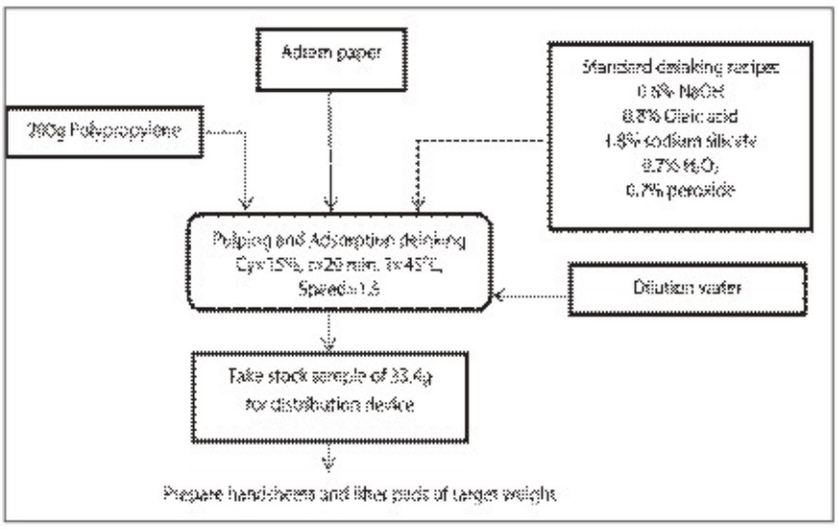

Fig 12: Flow chart for Adsorption deinking to carry out reproducibility trial

Fig 13: Distribution device

At the end of pulping measure the pH and the target pH is 9.5.

pH tolerances:

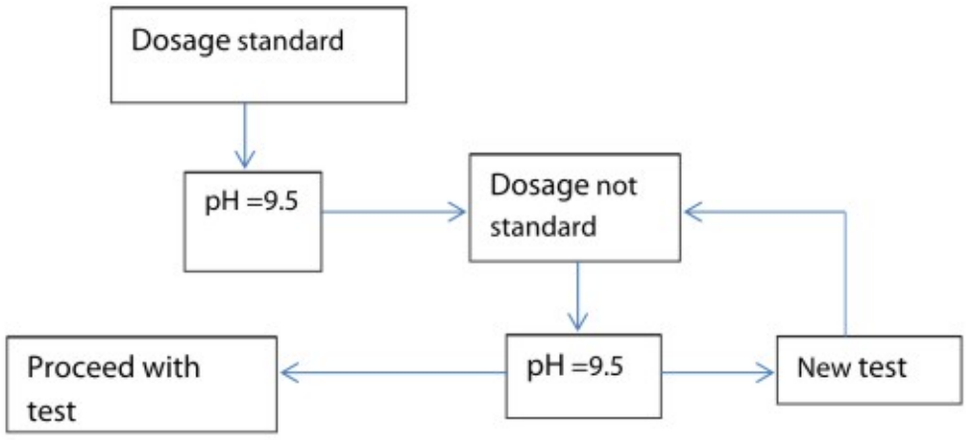

Fig 14 : pH tolerance chart.

Reference trial : For each reproducibility trial, reference trial without any deinking solution and polypropylene beads was also performed in order to compare the results and to check the effect of Adsorption deinking.

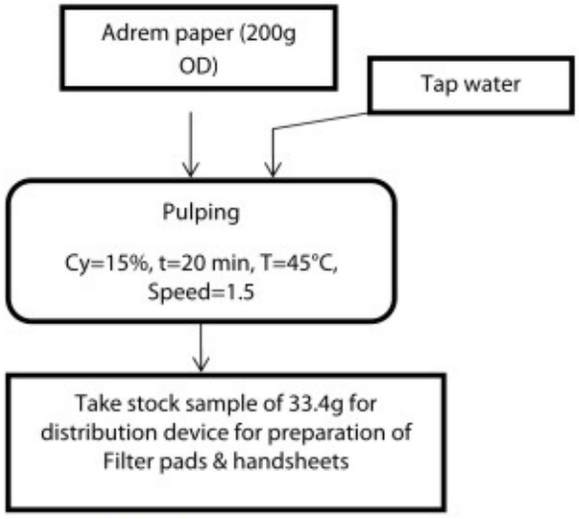

Fig 15 : Flow chart for Reference trial

For effect of ageing, after adsorption deinking:

Storage in water bath: Three pulp samples were prepared for storage for subsequent treatment: 12g for flotation, it means that approximately 92g Adsorption deinked (AD) pulp sample was taken which is equivalent to 12g fibers, 12g for flotation (for security to ensure enough amount of stock) and 33.4g stock for distribution device to form handsheets and filter pads, means nearly 256g of AD pulp sample was taken and stock consistency maintained during storage was 5% for 1hr at 60°C. Stock was stored together with polymeric beads

Preparation of sample hand sheets and filter pads of adsorption deinked pulp before storage:

A pulp sample of 33.4g was put in the distribution device and fills it upto a volume of 6.67l to maintain a stock consistency around 0.5%. After 3 minutes of homogenization in distribution device, samples were taken for the preparation of: Handsheets (target wt.-1.36g), Filter pads (target weight: 2.15g).

Flotation cell :

First 12g stored sample in water bath was transferred to flotation cell. Then it was filled up to maximum volume with dilution water (45°C) to have final consistency 0.8 %. Flotation was started for 10 min. at rotation speed of 1200U/min and

airflow of 60l/h. Stock was flotated together with polypropylene beads. Within few minutes after the start of flotation, maximum number of ink particles come to the surface and forth was removed without losing fibres with scrapper from time to time. After 5 minutes, there was the visible difference in the pulp after floatation as now there were very less ink particles on the surface making the pulp suspension less dark **(Ortner, 1993)**.

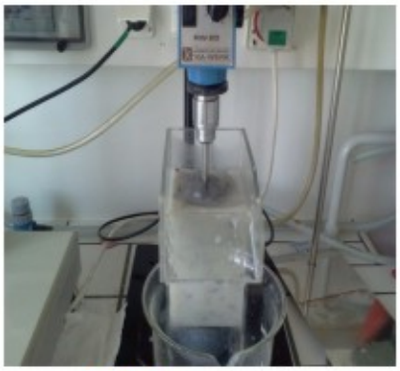

Fig 16 : Flotation cell

ERIC (700nm)=(k_sheet)/(k_ink)*1000000

Conventional deinking (CD)

It means deinking of the recovered paper which is performed generally in the industrial practice and only flotation deinking method according to INGEDE was performed without adding any polymeric beads to it.

Two experiments were performed:

1. Conventional deinking of paper recovered on 6th march 2013 was performed on 25th march i.e almost 3 weeks aged paper was used.
2. Conventional deinking of paper recovered at the beginning of long term trial means on 24th Oct, 2012 was performed. It was done in order to compare the effect of ageing of recovered paper on conventional deinking and on Adsorption deinking.

Standards used for carrying out the experiments:

Characteristics	Norm/Standard used
Assessment of Print Product Recyclability - Deinkability Test -	INGEDE-Method 11p
Test Sheet Preparation of Pulps and Filtrates from Deinking Processes	INGEDE-Method 1
Measurement of Optical Characteristics of Pulps and Filtrates from Deinking Processes	INGEDE-Method 2
pH-value	DIN 53124
Stock consistency	DIN EN ISO 4119, 05/96
Handsheets preparation	ISO 5269-2, 03/05
moisture content	DIN EN 20287, 09/94
Sample pretreatment	DIN EN ISO 20187, 11/93
Standard atmosphere	DIN 50014
Grammage	DIN EN ISO 536, 08/96
Dirt specks analysis	TAPPI-Norm T 213 OM-89, INGEDE-Method 2
Brightness	DIN 53145-1, 03/00
$ERIC_{700}$	ISO 22754, TAPPI T567 and PATAC E.8

Table 3 : Standards used for various measurements

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