Improving Adsorption Deinking by Identifying the Optimum Balance between Polymer Beads and Deinking Chemistry

Krithika Ravi,[a,b] Thomas Schrinner,[a,*] Harald Grossmann,[a] Amiyakumar Ray,[b] and Rita Tandon [c]

Ink removal from recovered paper is a very important process in paper and board recycling. The current deinking processes have made obvious contributions to the use of raw materials for the paper and board industries. In contrast to the flotation deinking process, in which small air bubbles are used to remove ink from the pulp, the novel and more energy-efficient method of adsorption deinking technique depends on the attachment and adsorption of ink particles on small polymer beads. The energy savings of adsorption deinking results from the fact that the process is efficient at greater stock consistencies, thus providing water conservation and savings. The present study was carried out to improve the adsorption deinking method by identifying the optimum balance between the deinking chemistry and the polymer beads. Different types of deinking solutions and polymer beads were used for this study with newsprints and mixture of newsprints and magazines. It was found that EGA 3000 solution and polyethylene terephthalate beads worked well with newspaper pulp.

Keywords: Adsorption deinking; Calcium ions; Chemical recipes; Polymer beads

Contact information: a: Institut für Holz-und Papiertechnik, Technische Universität Dresden, 01062 Dresden, Germany; b: Department of Pulp and Paper Technology, Indian Institute of Technology Roorkee (Saharanpur campus), Saharanpur 247001, Uttar Pradesh, India; c: Central Pulp and Paper Research Institute, Saharanpur 247001, Uttar Pradesh, India;
** Corresponding author: thomas.schrinner@tu-dresden.de*

INTRODUCTION

The demand for recovered papers in the Indian paper industry is on the rise because of the environmental conditions and legislation. The National Forest Policy (NFP; India, 1988) has released a statement saying that no forest materials would be available for the paper industry in the near future. Hence, the raw materials needed for the production of paper cannot be provided from forest materials; therefore, the paper industry must arrange their own raw material sources or increase the use of agro-residues or recovered paper. Consequently, the use of recovered paper has been identified as one of the best materials for conserving diminished forest resources. However, this material also requires increasing the environmental awareness in Indian society that paper recycling is an important issue (Avijit and Dipankar 1995).

The technical development of paper quality and printing technology, from the last few years, has revolutionized the process of recycling and deinking, which has resulted in new requirements and challenges. However, technical growth in the recovery of fiber provides economic potential for higher secondary fiber use. Most current efforts in terms of further improvements aim to use more printed recovered paper for the production of new

graphic papers by removing the printing inks from the recycled pulp in the most energy-efficient method (Dash and Patel 1997).

In current industrial practices, two deinking operations are dominant: washing and flotation. Both of these techniques suffer from high stock losses and high specific energy consumption. Flotation deinking produces satisfactory results only at consistencies equal to or less than 1.0%. Furthermore, upstream and downstream processes, such as coarse cleaning, screening, pulping, and dispersing do not require such highly diluted pulp suspensions. This is the main reason for the comparably high energy consumption of this flotation process step (Schrinner *et al.* 2013).

The great difference between the theoretical minimum energy required for deinking and the energy utilized by state-of-the-art-technologies suggests that research should be concentrated on the development of innovative methods for ink removal in the industrial sector. Alternative deinking concepts may provide comparable or better results than flotation, at a significantly lower energy consumption rate. Adsorption deinking is a newly developed alternative method for ink removal from recovered papers, where the ink is adsorbed on polymeric beads. This type of cleaning was attempted for the first time in the textile industry for the removal of dyes and dirt only a few years ago. In the meantime it has become an acknowledged technique which most probably will find its way into the market of household washing machines in the very near future. The first trials to use this, appropriately adapted technique for removing ink residues from newsprints were carried out at Dresden University in Germany some 3 years ago. It turned out that slushing the recovered paper together with polymer beads in a high consistency pulper was basically a suitable process providing both enough time and frequency of collisions to allow the detachment of the particles from the fibres and their adsorption on the surface of the beads (Handke *et al*. 2012).

The results of many trials suggested that calcium plays an important role in the deinking process (Costa and Rubio 2005). Therefore, an investigation was carried out with different amountS of calcium to evaluate its effect on paper brightness. Apart from this, 3 different chemical solutions (see experimental part for details) and 8 different types of polymer beads were tried for adsorption deinking on different print products and the results were compared with un-deinked and flotation deinked pulps.

EXPERIMENTAL

The attachment of ink particles from the recovered paper to the polymeric beads took place in a Kenwood KM 416 kitchen machine (Tokyo), which is similar to a Hobart pulper. The moisture content of the recovered paper was measured and recorded. Then, the oven-dried pulp was torn into 2 cm^2 pieces and weighed for 200 g. Deionized water (45 °C) was used for the dilution process and calcium water. Calcium chloride was added to deionized water with different concentrations used for the calcium trials. The torn recovered paper, the chemical solution, and the deionized water were transferred into a Kenwood KM 416 kitchen machine and a 15% consistency was maintained. The polymer to paper ratio was 1:1, and the pulping duration lasted for 20 min. Polypropylene beads were used for all of the trials (except for those which served to study the behavior of alternative polymers). Handsheets were produced (INGEDE method 1, 2007) for optical (Elrepho spectrophotometer) and residual ink concentration (Digital Optical Measurement and Analysis System) assessments by diluting the stock to a consistency of approximately

1.0%, which made the manual separation of loaded polymeric beads easier (In laboratory scale). It was observed in preliminary work that if the beads are lighter than water, then they float and can be easily removed from the top of the suspension with the help of a spoon. In all other cases, the separation was accomplished by decanting the suspension from one jar to another, which retained the beads at the bottom of the first jar. In large scale, the beads can be separated by a screening process, as the beads are large enough (3 mm) to be separated by hole/slot screens. In order to make these results comparable, trials were also performed with the standard laboratory flotation process (INGEDE method 11, 2012).

Calcium Trials

The calcium level for the dilution water suggested by INGEDE (International Association of the Deinking Industry) was 128 mg Ca^{2+}/L. For the experiments, 5 different concentrations of calcium chloride were added to deionized water, making the final concentration of dilution water to 0, 64, 128, 192, and 256 mg Ca^{2+}/L. Adsorption deinking trials were carried out from these different values of dilution water of hardness varying from 0 to 640 mg/L of $CaCO_3$. The chemical solutions used for these trials were made according to the INGEDE method 11. The recovered paper used for this study was 100% newspaper.

EGA 3000 and EGA 1100 Chemical Solutions

The adsorption deinking process was tested using the INGEDE solution (INGEDE method 11) and two different chemical solutions: EGA 3000 contained 1.25% NaOH, 2.0% sodium silicate, 0.7% H_2O_2, and 0.6% EGA 3000; and EGA 1100 contained 1% NaOH, 0.03% RST/Na, 1% sodium silicate, 0.7% H_2O_2, and 0.01% EGA 1100. The chemicals for EGA 3000 and EGA 1100 were commercially obtained from Nopco, Germany. These trials were carried out with either 100% newspaper, 100% magazines (50% coated magazines and 50% uncoated magazines), or a mixture of 40% newspaper, 35% uncoated magazines, and 25% coated magazines. The flotation deinking trials were carried out using the same solutions as a comparison.

Trials with Different Polymer Beads

Different types of polymer beads were used for the adsorption deinking process with the INGEDE chemical solution. Trials were performed with both newspapers and magazines separately. The beads were obtained commercially (BASF, Germany), and the types used were: Polyvinyl alcohol with 25% chitosan, Polyvinyl alcohol with 25% Polyvinylpyrrolidone (PVP), Polyvinyl alcohol with 20% sodium bentonite, Polyamide 6,6 (Teknor Apex, USA), Polyethylene terephthalate (Teknor Apex), Nylon 6,6 (Polyamide 6,6) (DuPont, USA), Polyamide 6,6 (Solvay, Brussels), and Polypropylene (Borealis, Germany).

RESULTS AND DISCUSSION

In contrast to flotation deinking, where detached ink particles are collected by air bubbles, the adsorptive approach uses plastic granules as adsorbents that are able to adsorb ink molecules on their surface. Compared to an air bubble, which requires more space, *i.e.*, a highly diluted suspension in order to allow flotation with a probability of bubble

coalescence, adsorption on solid beads can be performed at significantly higher stock consistencies (Handke *et al.* 2012). The chemistry of the adsorbents and their surfaces allowed for free ink particles to adhere strongly enough for separation in a subsequent step. The brightening of the pulp was accompanied by a corresponding blackening of the plastic granules, which provided evidence for the detaching of ink particles from the fibers. In addition to the expected deinking effect, an astonishing pronounced defibration effect was observed.

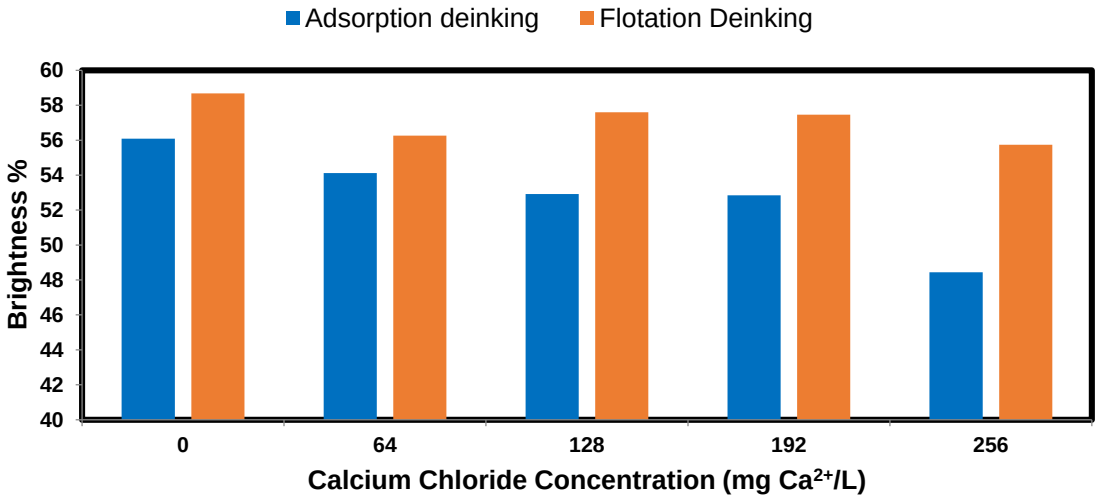

Fig. 1. Influence of calcium chloride concentration (in the dilution water) on the brightness (%) of the paper after adsorption deinking and flotation deinking processes

The calcium tests for the adsorption deinking and flotation deinking processes yielded the highest percent brightness with 0 mg Ca^{2+}/L, as shown in Fig. 1.

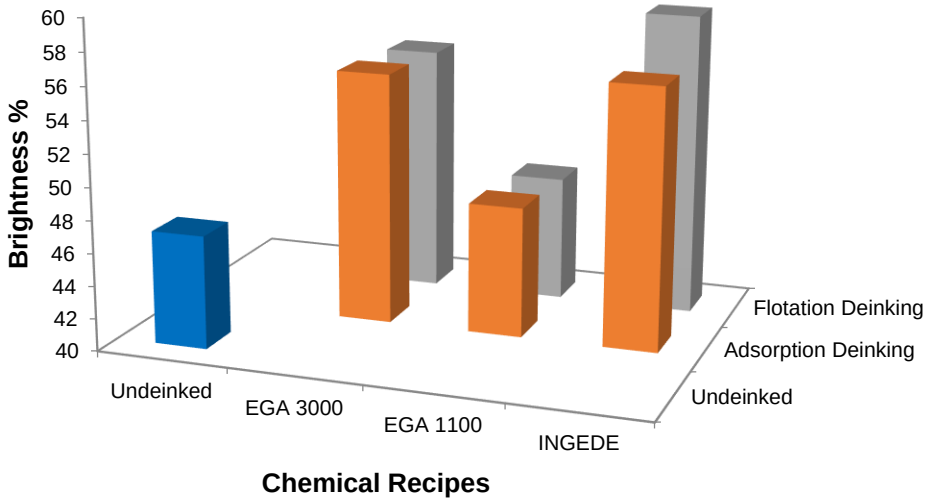

Fig. 2. The effect of different types of chemical solutions on paper brightness (%) after adsorption deinking and flotation deinking processes. Un-deinked samples was used as a reference for comparison

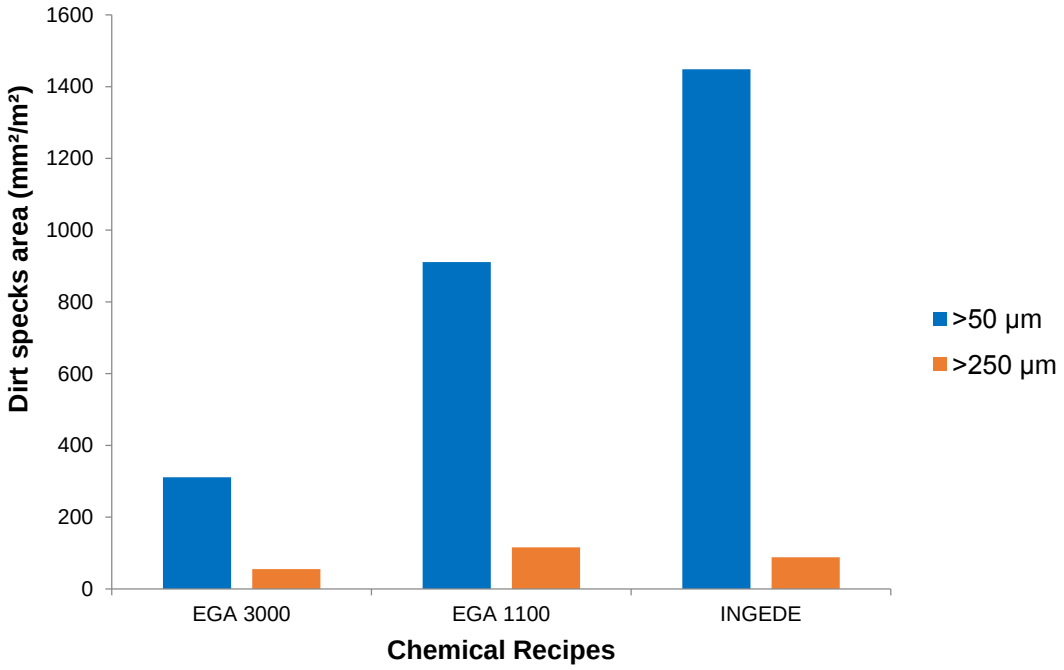

Fig. 3. The dirt specks area analysis of papers produced after adsorption deinking with different types of chemical solutions

Results showed that the adsorption deinking processes exhibited a decrease in brightness (%) as the calcium concentration in the dilution water increased. Thus, for adsorption deinking, the availability of calcium ions does not promote the adsorption of ink particles on the beads. When calcium ions (positively charged molecules) are present in the dilution water during the adsorption deinking process, there is a possibility that these ions will be adsorbed on the polymer's surface, thereby reducing the surface availability for ink adsorption. Therefore, this consequence may be the reason for the decrease in brightness when there was an increase of calcium ions present in the solution. However, the flotation deinking process exhibited the second highest brightness (%) with 128 mg Ca^{2+}/L, which was suggested by INGEDE. For flotation deinking, the availability of calcium should actually promote the removal of ink, because the calcium ions attach with the air bubble.

When trials were performed with different chemical solutions, such as EGA 3000, EGA 1100, and INGEDE, it was found that the EGA 3000 solution was the most effective and achieved a brightness value that was equal to the standard, *i.e.*, flotation deinking. From Fig. 2, it is evident that for adsorption deinking the brightness results were similar for the EGA 3000 and INGEDE solutions. There was approximately a 10% increase in brightness for the EGA 3000 solution with adsorption deinking compared to un-deinked pulp.

Figure 3 also shows that the dirt specks area was lowest for the EGA 3000 solution. This is because of the excellent surfactant action of EGA 3000, which attracts and eliminates the maximum amount of dirt particles. This appreciable foaming behavior of the EGA 3000 solution was observed while performing the flotation deinking experiments. However, the results of the EGA 1100 solution were unremarkable.

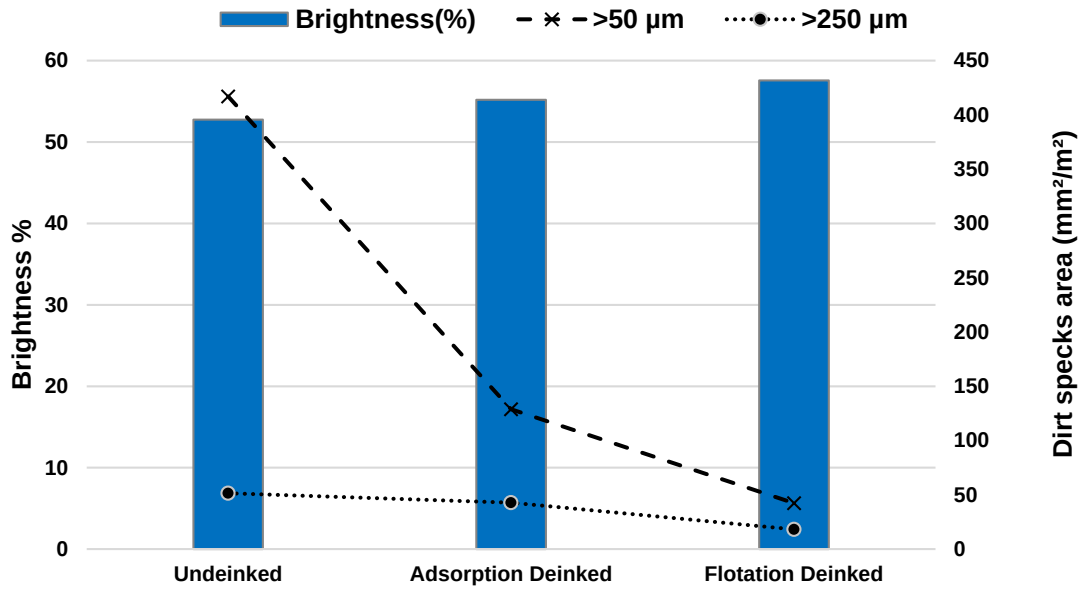

Fig. 4. Paper brightness (%) and dirt specks analysis of un-deinked, adsorption deinked, and flotation deinked pulps for mixed printed products using the EGA 3000 solution

Since the EGA 3000 solution worked well for the newspapers, the same experiment was repeated with a mixture of materials (newspaper and uncoated or coated magazines). There was approximately a 3 percentage point increase in brightness compared with the un-deinked pulp. In addition, there was a substantial reduction in the dirt specks area, especially for dirt specks larger than 50 µm, as depicted in Fig. 4. The number of dirt specks for adsorption deinking was reduced to an extent almost similar to flotation deinking, which is well appreciable. Later trials were carried out with only magazines, however these results were unsatisfactory.

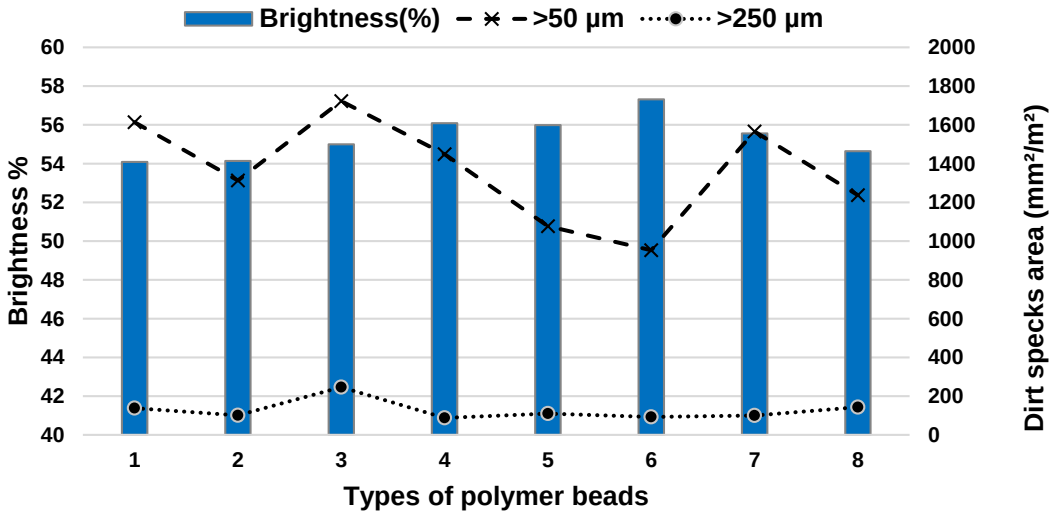

Fig. 5. Paper brightness (%) and dirt specks analysis of the adsorption deinked pulps with the 8 types of polymer beads: 1) Polyvinyl alcohol with 25% chitosan; 2) Polyvinyl alcohol with 25% Polyvinylpyrrolidone (PVP); 3) Polyvinyl alcohol with 20% sodium bentonite; 4) Polypropylene; 5) Polyamide 6,6 (A); 6) Polyethylene terephthalate; 7) Nylon 6,6; and 8) Polyamide 6,6 (B)

As mentioned previously, the mechanism for adsorption deinking is the intensive mechanical interactions between the plastic granules and the pulp, accompanied by a strong dispersing effect. The decisive factor is the adsorption capacity of the used plastic granules. This is a direct function of the granules' specific surface, *i.e.*, a function of their shape, size, and surface geometry, as well as the surface chemistry of the granules. Also, the dispersing properties of the adsorbents, meaning their ability to detach ink particles from the fiber and to comminute and homogenize them, are mainly determined by their shape and size, as well as the mechanical properties (density and hardness). In addition, the amount of plastic granules used is important.

Regarding the present investigation, 8 types of polymer beads were used for adsorption deinking. When these beads were mixed in equal quantities and used together for a single trial, almost none of them turned black, which was a surprising observation. Then, individual trials were carried out with all the beads separately. The results obtained are shown in Fig. 5. Bead 6 worked well with old, recovered newspapers, and not only yielded a maximum brightness but also produced very minimal dirt specks, comparatively. Bead 5 is also comparably good. When these trials were carried out with magazines only, none of the beads worked successfully. There was no ink adsorption on the beads and the color of the pulp and the beads were the same before and after adsorption deinking. This may be attributed to the coated magazines having printing inks that had adhered on the coating pigments even after pulping. Because the polymeric beads were not able to remove such mineral coating pigments, they remained in the pulp. Also, colloids, dispersants, and surfactants, which are present in the magazines, are released during pulping and remain in the solution. These particles are probably adsorbed on the polymer beads, resulting in the low surface availability for ink adsorption.

CONCLUSIONS

1. There was a strong influence of calcium on the adsorption of ink particles by the polymer beads.
2. The EGA 3000 solution worked well for the newspaper pulp and produced the lowest dirt specks area, comparatively.
3. The polyethylene terephthalate beads yielded the highest percent brightness and the lowest dirt specks area, when used with newspaper pulp and the INGEDE solution.
4. Adsorption deinking was not successful for removing ink from the recovered magazines.

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