

# APPLICATION OF MAGNETICALLY RECYCLABLE ZSM-5 ZEOLITE FOR ENHANCEMENT OF PEROXIDE BLEACHING OF THERMAL-MECHANICAL PULP

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A new efficient magnetically recyclable ZSM-5 zeolite (MZZ) has been successfully applied for alkaline peroxide bleaching of TMP pulp of *Acacia mangium* to enhance the bleaching process. The zeolite particles exhibited high efficiency in adsorbing transition metal ions (manganese, copper etc.) that could lead to decomposition of hydrogen peroxide during the bleaching process. These particles also increased the brightness of pulp after bleaching. Furthermore, the optimum conditions for peroxide bleaching of TMP pulp, such as hydrogen peroxide dosage, MZZ particle charge and temperature, were determined through a series of experiments. By applying an appropriate external magnetic field, the MZZ particles were separated easily without agglomeration and then reused efficiently with no significant loss of metal adsorption capacity. The performance of the developed MZZ particles would make their application in peroxide bleaching efficient, economical and feasible. Moreover, the use of zeolite would not cause any operational issues and would not influence the quality of pulp and paper products, due to this convenient separation.

**Keywords:** adsorption, ISO brightness, magnetic separation, peroxide bleaching, ZSM-5 zeolite

## INTRODUCTION

Pulp and paper production is a field of industry that has long been recognized as a pollution source. Since the development of modern pulp mills, the reduction of effluents has been one of the main targets in improving this technology.<sup>1</sup> Environmental regulations coupled to market demands have forced the pulp and paper industry to develop technical processes, including the exploration of alternatives to chlorine based bleaching practices for the production of bleached pulp.<sup>2</sup> New methods are currently being sought to delignify and bleach pulps selectively, while having a minimum impact on the environment. Research has intensively focused on new bleaching technologies to replace elemental chlorine and possibly chlorine dioxide. Various technologies and bleaching chemicals have been investigated, such as oxygen, hydrogen peroxide and ozone, sometimes aided by enzymes, which are the leading candidates for chlorine replacement.<sup>2-7</sup>

The bleaching stage in the pulping process is a major step with the objective of delignifying and increasing the brightness of pulp. Recently, hydrogen peroxide has become the preferred bleaching chemical widely used for mechanical pulps as it is an environment friendly and cheap reagent. However, one of the main problems in peroxide bleaching of mechanical pulps is the catalysed decomposition of hydrogen peroxide by transition metal ions, such as copper, manganese, etc.<sup>8-11</sup> The peroxide decomposition limits the bleaching potential of the peroxide charged. Therefore, metal chelation (or metal adsorption) is an inevitable stage for peroxide bleaching of mechanical pulp.<sup>12</sup> Chelating agents are used to form stable and water-soluble complexes with transition metal ions. The transition metal complexes can then be removed from the pulp in the pressing and washing stages.<sup>12-14</sup> Moreover, stabilizing chemicals, such as magnesium sulfate and sodium silicate, form complexes with transition metal ions, such as  $Mn^{2+}$  ion. It is believed that  $Mn^{2+}$  can be incorporated into the magnesium precipitate, and hence be protected from oxidation.<sup>15</sup> Among the many successful chelating agents, ethylene diaminetetraacetic acid (EDTA) and diethylenetriaminepentaacetic acid (DTPA) are the agents mostly used on an industrial scale. Unfortunately, these chemicals have their own drawbacks, such as their poor biodegradability. Therefore, there is some concern over the possible environmental impact of existing chelating agents, which are often criticized from an

ecological point of view.<sup>12</sup> Furthermore, stabilizing chemicals that are dissolved in the bleaching solution are then eliminated as bleaching effluents at the end of the process and could cause environmental pollution. Sodium silicate is known to precipitate, which may lead to clogging of wires and felts downstream of the bleach plant.<sup>16</sup> To solve these problems, alternative and ecologically sound chemicals have been investigated to replace EDTA and DTPA chelating agents, as well as stabilizing chemicals. Replacement compounds with better biodegradability and environmental friendliness have been tested on virgin mechanical pulp on a laboratory scale.

Zeolites are a class of porous, crystalline, aluminosilicate minerals with a three-dimensional framework that consists of an assemblage of  $\text{AlO}_4$  and  $\text{SiO}_4$  tetrahedra. These tetrahedra are joined in various regular arrangements through shared oxygen atoms to form an open crystal lattice, consisting of defined channels and cages.<sup>12,17-20</sup> Zeolites with unique properties, such as pores of uniform size, low toxicity, high surface area, functional groups for grafting or attachment, high dispersability and strong acidity, have been widely used in ion exchange, adsorption, separation, catalysis for organic synthesis and others.<sup>17,21-23</sup> The aluminium atoms in the zeolite give its ion exchange capacity towards cations and the defined pores of the zeolite endow it with the ability to act selectively towards different ions when they are ion exchanged into the zeolite. Moreover, zeolites are water-insoluble inorganic materials. They are environmentally friendly and non-toxic via the oral, dermal, ocular or respiratory routes.<sup>12,23</sup> ZSM-5, a type of aluminium-containing zeolites, is one of the most important catalysts in organic synthesis, as well as an efficient ion exchanger and adsorbent, owing to its high surface area, shape selectivity, and strong acidity.<sup>17,23,24</sup> Thus, zeolites, including the ZSM-5 type, could be considered as a promising alternative to both environmentally unfriendly chelating agents and homogeneous stabilising chemicals in peroxide bleaching of mechanical pulp. They could act as inhibitors, impeding the transition metal catalysed decomposition of peroxide, due to the fact that zeolites have surface and internal anionic sites, which can bind the transition metal ions, such as manganese, thus decreasing their activities in catalysing peroxide decomposition. However, using zeolite for peroxide bleaching of pulp also involves some difficulties in recycling and reusing the zeolite, because of its incorporation into the pulp. This leads to loss of zeolite, which would greatly affect the costs of the bleaching process. Besides, the incorporation of zeolites into the pulp and paper during the manufacturing process could cause some operational issues and influence the quality of the end products.

Magnetic separation has emerged as a robust, highly efficient and rapid particle separation tool with many advantages, compared to other isolation techniques using liquid–liquid extraction, chromatography, filtration or centrifugation.<sup>19,24</sup> It provides a convenient method for removing and recycling magnetized species by applying an appropriate magnetic field. This approach may prevent the agglomeration of the catalyst particles during recovery and can increase the durability of the catalysts.<sup>25</sup>

In previous studies,<sup>19,20</sup> we reported on the fabrication of a new material, core-shell magnetic ZSM-5 zeolite particles, which exhibited the assets of magnetic separation. The achieved zeolite catalyst particles were found to high catalytic activity for organic synthesis, along with other advantages, such as easy manipulation, separation and recycling.

In continuation of our efforts to develop a new type of sorbent and catalyst material, as well as to investigate their potential applications, the current work presents the application of the core/shell-structured magnetic ZSM-5 zeolite (MZZ) with uniform particle sizes in peroxide bleaching of mechanical pulp. The aim of this study is to investigate the benefit of adding the magnetic ZSM-5 zeolite (MZZ) during peroxide bleaching of thermal-mechanical pulp, as well as its recycling ability.

## EXPERIMENTAL

### Materials

All chemicals were of analytical grade quality, except when stated otherwise, and were used without any further purification. The thermal-mechanical pulp (TMP) used for this study was a hardwood pulp (*Acacia mangium* pulp). The pulp sample was supplied by Van Diem Paper Joint Stock Company (Hanoi, Vietnam).

A core/shell-structured magnetic ZSM-5 zeolite (MZZ) was prepared by following a method reported earlier.<sup>19</sup> Uniform magnetite ( $\text{Fe}_3\text{O}_4$ ) nanoparticles were synthesized by a co-precipitation method and used as core for the fabrication of silica coated magnetite beads ( $\text{Fe}_3\text{O}_4/\text{SiO}_2$ ), followed by the synthesis of the core/shell magnetic ZSM-5 zeolite (MZZ) catalyst.

### **Pulp bleaching**

Before the bleaching with peroxide, the pulp was pretreated with an appropriate amount of magnetic zeolite particles. The pretreatment of the pulp was carried out at a pulp consistency of 12% under mixing for 30 minutes.

Peroxide bleaching of TMP pulp was conducted in polyethylene bags at 10% pulp consistency. Sodium hydroxide and hydrogen peroxide were added to the above pulp slurry and the samples sealed in polyethylene bags. Then, the pulp slurry was kept at the desired temperature for a specific retention time. All chemical charges were expressed as % (w/w) on pulp. After the bleaching step, the MZZ zeolite particles were separated, using an external magnetic field, in order to recycle them for another run. The pulp slurry was diluted, neutralized with 5% sulphuric acid solution and washed until the pH of the washing water was neutral. A volume of the bleaching liquor was kept to measure the residual peroxide by iodometric dosage. A sufficient amount of pulp was taken to make TAPPI handsheets (Test Method T205 om-88) for testing ISO brightness.

### **Zeolite desorption**

Desorption experiments were conducted by placing metal adsorbed zeolite into the desorbing solution (1M KCl) in a beaker. The solution remained without agitation at room temperature until equilibrium was reached.<sup>26</sup> The samples were then filtered through Whatman membranes with a pore size of 0.2  $\mu\text{m}$  and were further used for other runs to examine the separation and recycle potential. The filtrate was measured in AAS of VARIAN AA24OFS for metal ion content when needed.

### **Characterization**

The handsheets were allowed to dry overnight before brightness testing with a Datalog Elrepho 2000 and physical testing. Lignin content analyses were done in accordance with TAPPI Standard T-222 om-85 with minor modification.<sup>27</sup> The amount of metal ions, such as manganese, was determined based on the Atomic Absorbance method (Tappi Testing Method, T241 cm-83), which was used extensively in a previous report.<sup>28</sup> Residual peroxide measurements were made on the remaining bleaching liquor taken from the pulp slurry by the method described below.<sup>8</sup>

The bleached pulp slurry was filtered to get bleaching liquor for residual peroxide determination. A 10 mL sample was pipetted into a 250 mL conical flask containing 10 mL of 10% m/m sulfuric acid, 1 drop of 10% m/m ammonium molybdate and 50 mL of distilled water. Potassium iodide (2.0 g) was added to the flask, swirled and the contents were titrated against standardized 0.01 M sodium thiosulfate. The residual peroxide was then calculated based on the volume of standardized 0.01 M sodium thiosulfate used.

## **RESULTS AND DISCUSSION**

The core/shell-structured magnetically recyclable ZSM-5 zeolite (MZZ) was obtained by a previously reported method developed by our own group.<sup>19,20</sup> It is well known that zeolites have been widely used in ion exchange, adsorption, separation and catalysis for organic synthesis. Magnetic separation is considered a highly efficient separation tool allowing to remove particles by applying an appropriate magnetic field and then to recycle them.<sup>19,20,23</sup> With these considerations in mind, synthesized MZZ particles were applied in hydrogen peroxide bleaching of TMP pulp to assess their adsorption capacity towards metal ions and their effects on handsheets, as well as their recycle efficiency. First, the potential of magnetic ZSM-5 zeolite (MZZ) in the chelating process (adsorption) of several metal ions that could decompose hydrogen peroxide during the peroxide bleaching of pulp was investigated. Metal ions, such as manganese (Mn) and copper (Cu), are the main factors that cause the degradation of peroxide, which results in lower brightness and residual peroxide.<sup>12</sup> The composition of these metal ions was determined (Table 1). Several metal ions have been detected, such as manganese, iron, copper, silicon and calcium. Among these metals, manganese is the main metal ion in this kind of pulp, with the greatest amount, as well as the main factor that decomposes hydrogen peroxide. Figure 1 illustrates the effects of using the core-shell magnetic ZSM-5 zeolite (MZZ) on the decomposition of peroxide induced by transition metal ions. It can be seen that without the addition of MZZ particles, the metal ions induced extensive peroxide decomposition under typical bleaching conditions. When MZZ was added, the amount of residual peroxide increased. It indicated that the addition of MZZ had a beneficial effect on residual peroxide concentration in peroxide bleaching of *Acacia mangium* TMP pulp in the presence of manganese ions.

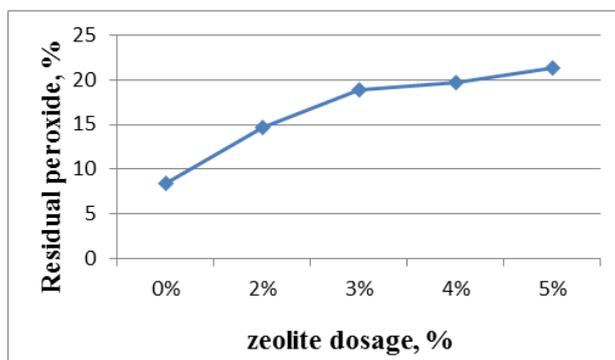


Figure 1: Effect of MZZ particles on metal ion-induced peroxide decomposition (bleaching conditions: 3% NaOH, 3% H<sub>2</sub>O<sub>2</sub>, 70 °C, 90 min reaction time)

Table 1  
Metal ion characterization of TMP pulp of *Acacia mangium* from Vietnam

Metal ions	Quantity (mg/kg)
Mn (Manganese)	114.7
Fe (Iron)	15.6
Cu (Copper)	1.8
Ca (Calcium)	102.4
Si (Silicon)	95.9

Moreover, the amount of residual peroxide increased with the increase of zeolite dosage. These results are in agreement with those reported in the literature.<sup>8,12,13</sup> When zeolite was added to the pulp slurry, the peroxide decomposition decreased. This suggests that the core-shell magnetic ZSM-5 zeolite (MZZ) could act as chelation agent for metal ions, as well as stabilizer for the alkaline medium in alkaline peroxide bleaching. The zeolite has a cage structure and Na<sup>+</sup> ions to neutralise the negative charges on the cage. The ZSM-5 zeolite shell of MZZ particles has a high Si/Al ratio (86:1) and thus has many anionic groups. The polyelectrolyte titration shows that this zeolite has  $4.1 \times 10^{-5}$  eq/g anionic groups. It could be assumed that the anionic groups of the zeolite can provide binding sites for Mn<sup>2+</sup> ions, protecting them against the redox process under alkaline conditions. This Mn<sup>2+</sup>/Mn<sup>3+</sup> redox cycle has been proposed as mechanism for the manganese-induced peroxide decomposition in an industrial peroxide bleaching process.<sup>13,29</sup> The zeolites have both the surface sites and internal sites available for the interaction with Mn and adsorb this metal ion. It is likely that the internal sites would be more efficient in reducing the Mn-induced peroxide decomposition, due to the steric hindrance compared to the surface sites.<sup>8,13</sup>

The above-mentioned results are also consistent with the contents of transition metal ions determined in the thermo-mechanical pulp after the treatment with the zeolites (Table 2). The content of manganese has been found to be reduced to 21.8 mg/kg, which corresponds to an efficiency of 81%. At a dosage of 1%, MZZ is not very efficient in chelating manganese. To improve the chelation process, the amount of zeolite was increased above 1%. Zeolite dosages of 2, 3, 4 and 5% led to 88.6, 53.6, 40.1 and 21.8 mg/kg of manganese, respectively, after the chelation operation, equating to efficiencies of 22.7, 53.3, 65 and 81%. However, as can be noted from Table 2, the chelation of iron was not improved with the use of zeolites. Moreover, increasing zeolite dosages was not efficient in chelating this ion either. It seems that this ion is well fixed to the fibre, resulting in lower efficiency in the chelation process.<sup>12</sup> Furthermore, the results showed that the zeolite was unable to protect peroxide against decomposition if the solutions were alkaline prior to zeolite addition. This suggests that the zeolite is unable to deactivate the active manganese species once it is formed. It is possible that the zeolite does not interact as effectively with the larger uncharged manganese dioxide or manganese-oxygen species as with the manganese cation.<sup>13,16</sup> MZZ zeolite particles were only able to prevent the decomposition of manganese in its Mn<sup>2+</sup> state. Thus, to exploit the ability of MZZ zeolite to prevent decomposition, the zeolite should be added prior to the alkali and peroxide.

In order to investigate the efficiency of MZZ zeolite particles in peroxide bleaching of TMP pulp, the brightness of the obtained handsheets was tested. Thus, ISO brightness measurements were carried

out to reveal any changes of the chromophoric system in the pulp. It has been reported that the total of alkali (TA) is an important factor in alkaline peroxide bleaching, which directly affects the efficiency of the bleaching process, consequently, the brightness of the pulp. Hydrogen peroxide is an excellent bleaching reagent, which is active toward chromophoric structures of pulp in alkaline media, bleaching both the (most important) lignin chromophores and the chromophoric groups bonded to the carbohydrates.<sup>30,31</sup> It was found that the ratio of TA/H<sub>2</sub>O<sub>2</sub> = 1 resulted in the highest efficiency in peroxide bleaching (data not shown). Therefore, to find out the most suitable conditions for alkaline peroxide bleaching of TMP pulp, different preparation modes of the bleach liquor were used, while maintaining the ratio of TA/H<sub>2</sub>O<sub>2</sub> = 1. The data in Table 3 illustrate the effect of H<sub>2</sub>O<sub>2</sub> charge on peroxide bleaching of TMP pulp in the presence of MZZ particles.

It could be observed that the pulp brightness increased with the increase in the hydrogen peroxide content (the ratio of TA/H<sub>2</sub>O<sub>2</sub> was kept constant throughout all experiments). A peroxide dosage of 3% gave the highest brightness of the pulp – of 72.8% ISO. It is known that, in alkaline peroxide bleaching, the hydroperoxide anion (HOO<sup>-</sup>) that is formed in an alkaline medium would attack and react with the chromophoric units and functional groups in the pulp that come mainly from lignin. Thus, a higher chemical charge, a higher concentration of the HOO<sup>-</sup> anion was generated and hence greater lignin amounts, as well as chromophoric structures, in the pulp were degraded. Moreover, the difference between the brightness degrees achieved under bleaching conditions of 2 and 3% peroxide dosage was the highest. Besides, as the hydrogen peroxide dosage was further increased, the brightness of the pulp continued to show a rising trend, but very slowly and even insignificantly, while a peroxide dosage exceeding 4% is not economically feasible at an industrial level. Thus, the hydrogen peroxide dosage of 3% was chosen as the most suitable. To further evidence the effects of zeolite addition in peroxide bleaching, tests were carried out on the control sample at the same peroxide dosage without zeolite pretreatment. The results (Table 3) indicated that regardless of the peroxide dosage, the residual peroxide in the sample not subjected to zeolite pretreatment was lower than that in the zeolite pretreated sample. This demonstrated that the addition of MZZ particles can lower the peroxide decomposition due to the adsorption of metal ions into the zeolite matrix.

Table 2  
Transition metal ions characterization of TMP pulp after pretreatment with MZZ particles <sup>a</sup>

Transition metal ions	Quantity (mg/kg)				
	1% zeolite	2% zeolite	3% zeolite	4% zeolite	5% zeolite
Mn (Manganese)	105.9	88.6	53.6	40.1	21.8
Fe (Iron)	15.2	14.8	14.1	14.5	14.2
Cu (Copper)	0.6	0.3	-	-	-

<sup>a</sup>TMP pulp was pretreated at different zeolite dosage prior to bleaching step

Table 3  
Effect of chemical charge (H<sub>2</sub>O<sub>2</sub> and NaOH in equal amounts) on peroxide bleaching of thermo-mechanical pulp in the presence of MZZ particles <sup>a</sup>

No.	H <sub>2</sub> O <sub>2</sub> charge (% on pulp)	Residual H <sub>2</sub> O <sub>2</sub> (% on pulp)	% ISO brightness
1	0.5	0.06 (n.a)	67.6
2	1	0.14 (0.07)	69.1
3	2	0.29 (0.15)	70.5
4	3	0.43 (0.23)	72.8

<sup>a</sup> bleaching at a temperature of 70 °C, 2% MZZ particles for 90 min reaction time  
(...) the results obtained without addition of MZZ particles

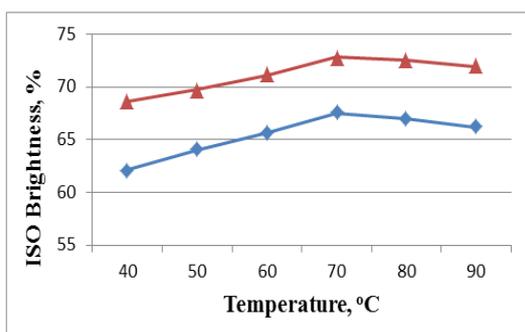


Figure 2: Effect of bleaching temperature on ISO brightness value of pulp (▲ MZZ pretreated pulp, ■ untreated pulp; bleaching conditions: 3% NaOH, 3% H<sub>2</sub>O<sub>2</sub>, 2% MZZ, 70 °C, 90 min reaction time)

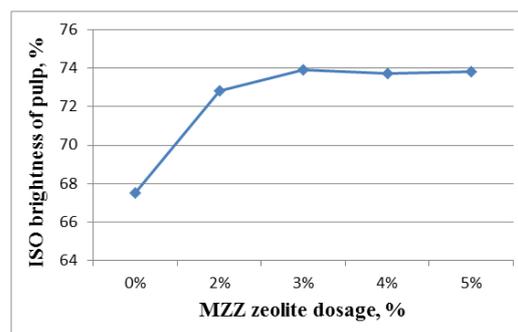


Figure 3: Effect of MZZ particle dosage on ISO brightness value of TMP pulp (bleaching conditions: 3% NaOH, 3% H<sub>2</sub>O<sub>2</sub>, 70 °C, 90 min reaction time)

It is known that the efficiency of peroxide bleaching is strongly influenced by temperature.<sup>31</sup> It may be noted in Figure 2 that the ISO brightness values increased with the increase of temperature from 40 to 70 °C. There are many chromophoric units in the pulp originating predominantly from lignin. The hydroperoxide anion is a strong nucleophile that, during bleaching, preferentially attacks the ethylenic and carbonyl groups of the lignin complex. As a consequence, such chromophores as quinones, cinnamaldehyde, and ring-conjugated ketones are converted to non-chromophoric species during alkaline peroxide bleaching.<sup>30</sup> This kind of reaction was favoured at high temperature. Thus, higher ISO brightness was obtained at higher temperature. Furthermore, due to the fact that in alkaline peroxide bleaching the modification of chromophores to non-chromophoric species is preferred to delignifying, relatively high ISO brightness values were obtained even at a medium delignification level, as may be seen in Figure 2. However, as the temperature was further increased over 70 °C, the ISO brightness of the pulp slightly decreased, even at a temperature of 80 °C, showing the highest degradation of lignin. It is assumed that in pulp, in addition to lignin, there are many other chromophores that would not be degraded during peroxide bleaching. Besides, at high temperature, the hydrogen peroxide becomes more reactive and might create not only new chromophoric structures, including carbonyl groups,<sup>3</sup> but also stable lignin structures through radical coupling reactions in phenolic lignin moieties, which also make lignin harder to oxidize in the bleaching process.<sup>31</sup> Hence, this would determine a decrease in ISO brightness of pulp. Moreover, at high temperature, the rate of hydrogen peroxide decomposition increased. Therefore, the most suitable temperature for hydrogen peroxide bleaching of TMP pulp was chosen as 70 °C. For the sake of comparison, the study was also carried out on a control sample (without zeolite pretreatment) at the same temperature. The results revealed that without the addition of MZZ particles, the ISO brightness of the pulp was lower than that obtained for the zeolite pretreated pulp. This can be explained by the more extensive peroxide decomposition that was induced by metal ions when the experiments were carried out without addition of zeolite.

Figure 3 shows the effect of MZZ particle dosage on the bleaching process. It could be found that increasing the zeolite dosages from 0% to 3% led to an increase in ISO brightness, as well as in delignification. There is a significant difference between the ISO brightness values of the samples bleached with and without adding MZZ zeolite particles. Adding MZZ zeolite at 3% dosage resulted in an increased brightness value of pulp (73.9% ISO), when comparing the control trial (bleaching without addition of zeolite, 67.5% ISO) and unbleached pulp (58.6% ISO). The ISO brightness of TMP obtained under these conditions is quite typical for an industrial peroxide system for TMP pulp and is comparable with the brightness obtained in conventional systems using EDTA as chelating agent and silicate as stabilizing agent. An addition of stabilizers in alkaline medium, which improves the technologic efficiency of the peroxide treatment, resulted in some decrease of the chromophoric groups, mainly originating from lignin accompanied by a reduction in peroxide decomposition, thus resulting higher ISO brightness of pulp. A further increase in the zeolite dosage from 3% did not yield additional benefits. Hence the zeolite dosage of 3% was considered as most suitable condition for stabilizing the system in alkaline peroxide bleaching.

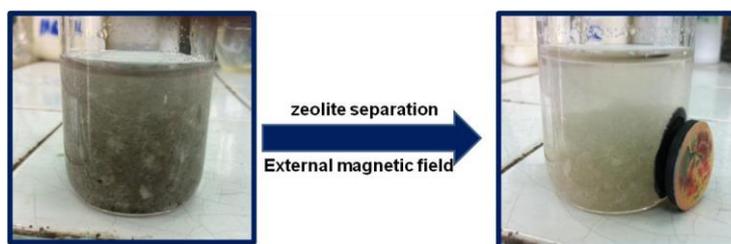


Figure 4: Magnetic separation and recycling of MZZ zeolite particles in hydrogen peroxide bleaching

Table 4  
Separation and reuse of core-shell magnetic ZSM-5 zeolite (MZZ) particles in alkaline hydrogen peroxide bleaching of TMP pulp<sup>a</sup>

Nr of recycling runs	Mn content in treated pulp, mg/kg	ISO brightness of pulp, %
1	53.6	73.9
2	53.8	73.6
3	53.9	73.3
4	54.2	72.8
5	54.5	72.4

<sup>a</sup> Bleaching conditions: 3% NaOH, 3% H<sub>2</sub>O<sub>2</sub>, 3% MZZ charge, 70 °C, 90 min reaction time

The separation and recycle efficiency of the core-shell magnetic ZSM-5 zeolite particles were also demonstrated, as the same particles could be used several times after metal ion desorption (Fig. 4). Typically, the samples of MZZ particles that were recovered from the bleaching system by using an external magnetic field were regenerated by transition metal desorption and then reused in alkaline peroxide bleaching of TMP pulp. Table 4 shows the results of the investigation on the recycle efficiency of MZZ particles. It can be seen that the magnetic ZSM-5 zeolite particles could be recycled and reused efficiently for several times with only a modest reduction in the removal of transition metals, especially Mn<sup>2+</sup> ions, and in ISO brightness of the pulp. This indicates that the magnetic zeolite remained stable after several adsorption/desorption cycles, exhibiting no significant loss of the adsorption capacity. It can be probably attributed to the easy removal and recycling of the core-shell magnetic ZSM-5 zeolite by applying an appropriate external magnetic field, which prevents the agglomeration of the MZZ particles and thus causes no significant changes in the zeolite surface or structure.<sup>26</sup> Moreover, the homogeneity of the core-shell magnetic zeolite particles was maintained even after recycling them several times. Furthermore, by applying an external magnetic field, the magnetic ZSM-5 zeolite was facile and convenient to remove and recover from the bleaching slurry. This makes the application of MZZ particles for peroxide bleaching feasible and economical. The use of zeolite would not cause any operational issues and would not influence the quality of pulp and paper products, due to this easy separation.

The peroxide bleaching process using other kinds of zeolites, such as pristine zeolite ZSM-5, which was obtained with a similar molar ratio composition of the zeolite synthetic gel as that of MZZ particles, and analcime zeolite, was investigated. Under similar bleaching conditions, using pristine ZSM-5 zeolite and analcime zeolite resulted in ISO brightness values of 72.0% and 70.9%, respectively. These brightness values were lower than that obtained when using MZZ particles (ISO brightness of 73.9%). This behaviour could be attributed to the higher adsorption capacity of MZZ compared to those of pristine ZSM-5 and analcime zeolites, due to the slightly higher surface area, as well as higher external surface area of MZZ particles compared to that of pristine ZSM-5,<sup>19</sup> and the higher pore volume and higher surface area of MZZ particles than those of analcime zeolite. Furthermore, in order to assess the advantage of peroxide bleaching using MZZ particles in comparison with conventional peroxide bleaching using DTPA, Na<sub>2</sub>SiO<sub>3</sub> and MgSO<sub>4</sub>, the peroxide bleaching was also conducted conventionally under identical conditions. The results showed that peroxide bleaching using MZZ gave a slightly higher ISO brightness value than conventional bleaching (73.9% compared to 73.0%). Moreover, by applying an external magnetic field, MZZ particles were easy to recover from the bleaching slurry and could be recycled several times. However, conventional stabilizing chemicals were dissolved in the bleaching solution and then eliminated as

bleaching effluents at the end of the process, which could cause environmental pollution. Sodium silicate is known to precipitate, leading to clogging of wires and felts downstream of the bleach plant. EDTA and DTPA are well-known carcinogens, and thus handling needs to be strictly controlled.<sup>16</sup> Therefore, it can be concluded that magnetic ZSM-5 zeolite (MZZ) could be considered as an alternative ecologically sound candidate to replace EDTA and DTPA chelating agents, as well as stabilizing chemicals.

## CONCLUSION

In this research work, we applied core-shell magnetic ZSM-5 zeolite (MZZ) particles for alkaline hydrogen peroxide bleaching of *Acacia mangium* TMP pulp to evaluate the potential of the zeolite as a chelating agent for adsorbing transition metal ions (manganese, copper), which are responsible for the decomposition of hydrogen peroxide during the bleaching stage. These zeolite particles showed a beneficial effect on residual peroxide concentration in peroxide bleaching of TMP due to adsorption of transition metals in the starting pulp. Using MZZ particles therefore enhanced the delignification and ISO brightness value of the pulp in alkaline peroxide bleaching. Moreover, the optimal conditions for bleaching of TMP pulp were found to be as follows: total alkali dosage of 3%, hydrogen peroxide dosage of 3%, MZZ zeolite particle dosage of 3%, temperature of 70 °C and bleaching time of 90 min. Under these conditions, a pulp brightness of 73.9% ISO was achieved. Furthermore, the study also demonstrated the good superparamagnetic behavior of these MZZ particles, thus allowing their easy separation and reusability, with no significant loss of metal adsorption capacity.

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