Preparation and characterization of EDTAD-modified magnetic-Fe₃O₄ chitosan composite: application of comparative adsorption of dye wastewater with magnetic chitosan

Hongyu Yang, Yunchun Li, Steven Sai Hang Ho, Xiumei Tian, Yunxue Xia, Yaou Shen, Maojun Zhao and Guangtang Pan

ABSTRACT

Ethylenediaminetetraacetic dianhydride (EDTAD)-modified magnetic-Fe₃O₄ chitosan (EMC), prepared using the cross-link agent glutaraldehyde and chemicals Fe₃O₄, chitosan, and EDTAD, was used to compare the adsorption of methylene blue (MB) with magnetic chitosan (MC). The composite structure was confirmed by multiple characterization techniques, including scanning electron microscopy (SEM), X-ray powder diffraction, Fourier transform infrared spectroscopy (FTIR), and potentiometric titration methods. The characterization results suggest that Fe₃O₄ particles successfully bound on the surface of chitosan, and the EDTAD thoroughly modified the MC. Furthermore, EMC had more amino, carboxyl, and hydroxy groups than typical MC. Adsorption conditions, such as pH values, initial concentrations of MB, reaction temperature, and contact time were systematically examined. In comparison, the maximum adsorption capacity of EMC was approximately twice as much as that of MC. The recovery efficiency for EMC was >80% using 0.1 M HCl as an eluent solution. Therefore, the results reported herein indicate that EMC is very attractive and imply a practical application for dye wastewater treatment.

Key words | chitosan, comparative adsorption, dye wastewater, EDTAD, magnetic Fe₃O₄

INTRODUCTION

With the rapid development of economies, many industries including textiles, rubber, paper printing, and tanneries produce large amounts of chemical wastes such as synthetic dyestuffs (Gupta & Suhas 2009). The dye effluent contains a variety of biological toxic organics, which can cause human cancer, genetic mutation, suppression of micro-organisms’ activities, and even destruction of aquatic ecosystems (Hu 2001; Crini 2006). Methylene blue (MB), a typical azo cationic dye, is difficult to degrade in our environment because of its aromatic structure. For animals and humans, direct contact with MB can irritate the respiratory tract and gastrointestinal system. A case of MB toxicity was reported in a neonate with chemolytic anemia, hyperbilirubinemia, and acute renal failure (Albert et al. 2005).

Several analytical methods have thus been developed for removal of synthetic dyes from wastewater, including oxidation, ultrafiltration, electrochemical treatment, and microbiological or enzymatic decomposition (Wu et al. 2007; Avlonitis et al. 2008; Shen et al. 2011). Unfortunately, current technologies are often costly or ineffective, and even lead to the production of secondary pollutants. In recent years, a simpler and more highly efficient technique of adsorption has been applied in wastewater treatment (Wan Ngah et al. 2011; Zhang et al. 2011).

Chitosan is a biopolymer of glucosamine containing a high content of amino and hydroxyl function groups. It has a chelating property to purify dye from wastewater. Working as a promising adsorption material, chitosan is safe for use. However, it is difficult to recycle pure chitosan and its unsatisfactory mechanical properties greatly limit its practical application (Jiang et al. 2012). Recently, magnetic solid-liquid phase separation techniques have been attracting more attention. Many researchers have focused on the removal of pollutants from dye-containing wastewater with
Fe₂O₃ particles (Tian et al. 2010; Zhang et al. 2011). In order to improve the utilization of chitosan, Jiang et al. (2012) fabricated a magnetic γ-Fe₂O₃ chitosan composite which has been used as adsorbent for the removal of methyl orange from wastewater. Nevertheless, such an adsorbent composite only has a maximum adsorption capacity of 29.41 mg/g. Hence, to prepare a faster and more efficient material with a good yield is a daunting task.

In this paper, we report an unprecedented method for generating a novel magnetic compositied adsorbent of magnetic chitosan (MC) using a glutaraldehyde cross-linking method. Ethylenediaminetetraacetic dianhydride (EDTAD), a powerful complexing agent which contains two anhydride groups in its molecule, is used to produce EDTAD-modified magnetic-Fe₂O₃ chitosan (EMC) through esterification. Both MC and EMC were characterized by scanning electron microscopy (SEM), X-ray powder diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), and potentiometric titration methods. Parameters such as acidity, initial concentration, temperature, and contact time affecting the dye removal by MC and EMC have been systematically investigated. Desorption and regeneration tests of the adsorbents have also been conducted.

**EXPERIMENTAL**

**Preparation of MC**

Chitosan (85% acetylation degree and molecular weight = 2.1 × 10⁵) was purchased from KeLong Crop (Chengdu, China). Magnetic-Fe₃O₄ fluid was synthesized according to the method described in Shan et al. (2007). To prepare a colloidal solution, 2.0 g of chitosan was dispersed into 150 mL of 0.2% dilute acetic acid (w/w) solution with continuous magnetic stirring at 20 ± 1 °C for 3 h. Two grams of magnetic fluid and colloidal solution were mixed in a ratio of 1:1 (w/w) into 150 mL of 0.5% glutaraldehyde (w/w) solution. The mixture was adjusted to a pH value of 9–10 with 0.1 M sodium hydroxide (NaOH) and stirred over a rotary shaker (DHZ-DA, Shanghai, China) at a rate of 200 rpm at 63 °C for 2 h. MC was separated from the mixture by an external magnet and rinsed three times with distilled water to remove any glutaraldehyde molecules that were attached. The purified MC was freeze-dried in a high vacuum for 24 h to completely remove water and then stored in a desiccator before use.

**Preparation of EMC**

EDTAD was synthesized following the procedures described in Junior et al. (2009). Two grams of EDTAD was added to a 100 mL N-N-dimethylacetamide (DMAC) solution containing 2.0 g of MC. The mixture was placed in a three-necked round-bottomed flask, which connected with a condenser, and stirred at 60 °C for 4 h. After reaction, EMC was magnetically separated from the mixture and rinsed with the following three solutions in order of DMAC (200 mL), distilled water (500 mL), and 10% sodium bicarbonate (NaHCO₃) solution (100 mL). The purified EMC was freeze-dried in a high vacuum for 24 h to completely remove water and then stored in a desiccator before use. The calculated costs of 1 g synthesized MC and EMC are only USD0.06 and 0.08, respectively.

**Adsorption and desorption tests**

The main synthesis scheme for EMC and the adsorption/desorption mechanism of MB are shown in Figure 1(a). The adsorption tests were carried out with a jar test (Tian et al. 2010; Zhang et al. 2011; Jiang et al. 2012) due to its convenient, efficient, and cost-saving advantages compared to a column test. All the dye adsorption tests were performed in 250 mL conical flasks maintained at temperatures varying from 15 to 40 °C. One hundred micrograms of adsorbents was added to 100 mL of diluted MB (Xiangshi Chemical Reagent Company Hunan, China) solution and then stirred over a rotary shaker at 150 rpm. Acidity effect on the adsorption was also examined by adjusting pH values of the solutions, which ranged from 3.0 to 10.0, using 0.1 M HCl or 0.1 M NaOH. The mixtures were also agitated at different adsorption times. The adsorbents were then collected using an external magnet and the residual MB concentrations in the supernatant were monitored by the colorimetric method with a spectrophotometer (V-1100D, Shanghai, China) at λmax of 640 nm. The amount of adsorbed MB per unit mass of adsorbents qe (mg/g) was calculated using the mass balance equation:

\[ q_e = (C_0 - C_t) \times \frac{V}{m} \]

where \( C_0 \) is the initial concentration of MB (mg/L), \( C_t \) is the MB concentration at time \( t \) (mg/L), \( V \) is the volume of solution (L), and \( m \) is the mass of adsorbents (g).

Desorption experiments were carried out in 250 mL conical flasks as well. Approximately 0.1 g of the used materials were added to 50 mL of eluents of 0.1 M HCl and absolute...
ethanol (HPLC (high-performance liquid chromatography) grade), respectively. The suspensions were shaken at 150 rpm for 30 min to release MB from MC and EMC. The recovery and regeneration efficiency were calculated as follows:

\[
\text{Recovery efficiency} = \frac{\text{Amount of dye recovery}}{\text{Amount of dye adsorbed}} \times 100\%
\]

\[
\text{Regeneration efficiency} = \frac{\text{Regeneration adsorption capacity}}{\text{Original adsorption capacity}} \times 100\%
\]

**Characterization of EMC**

A SEM (JSM-7500F, JEOL, Japan), an XRD spectrometer (Philip-X’Pert Pro, Holland), an FTIR spectrophotometer (Shimadzu FTIR-8400S, Japan), and an autotitrator (ZD-2, Shanghai, China) were employed to confirm the structure of the adsorbents.

**RESULTS AND DISCUSSION**

**SEM analysis**

The microstructure and surface morphology for chitosan, MC, and EMC were examined by SEM (Figure 1(b)–(d)). Figure 1(b) shows an image of pristine chitosan, indicating that it is a tightly layered structure with smooth and even surfaces. When the magnetic Fe₃O₄ was quickly loaded onto the surface of chitosan, it became rough and aggregated (Figure 1(c)). This leads to the formation of irregular spherical particles. Different to chitosan and MC, EMC was uniformly covered with a layer of powder and the particles were more compact (Figure 1(d)), revealing that EDTAD molecules were successfully attached on the surface of MC. Due to its characteristic structure, EMC has benefits for the adsorption of MB.

**XRD analysis**

The XRD patterns of pure Fe₃O₄, MC, and EMC composite materials are shown in Figure 2(A) (a–c), respectively. For the Fe₃O₄ crystals, diffraction peaks at 30.34°, 35.56°, 43.18°, 53.51°, 57.22°, and 62.84° correspond to the (220), (311), (400), (422), (511), and (440) crystal planes, respectively. They are matched well with the inverse cubic spinel structure (JCPDS 19-0629). Though the XRD patterns of MC and EMC showed similar characteristic peaks to that of magnetic Fe₃O₄, their peak intensities were comparatively lower together with a broader peak width. This indicates that MC and EMC have a lower crystallinity and smaller crystallite size, which could be attributed to chitosan and EDTAD bound with Fe₃O₄.
In order to confirm the adsorption mechanism, the FTIR spectra of MC and EMC before and after adsorption were examined respectively. Figure 2(B) (a) shows that MC displays absorption peaks varying in type and intensity. The weak absorption band at 3,379 cm\(^{-1}\) suggests the stretching vibration of \(-\text{NH}/-\text{OH}\) groups in chitosan. The characteristic peaks at 1,651 and 1,551 cm\(^{-1}\) correspond to the stretching bands of C\(-\text{O}\) from amide I and N\(-\text{H}\) from amide II, respectively, which belong to the cross-linking agent of glutaraldehyde (Zhu et al. 2010; Wang et al. 2011). Furthermore, the stretching band at 1,027 cm\(^{-1}\) corresponds to a glycitol group (C\(-\text{OH}\)). An evident peak at 567 cm\(^{-1}\) represents the characteristic group of magnetic Fe\(_3\)O\(_4\). All the above evidence confirms that both amino and hydroxyl groups are present on the surface of MC.

Figure 2(B) (b) and (c) show the FTIR spectra of EMC before and after adsorption of MB, respectively. When MC was modified with EDTAD, the absorption peaks significantly changed. First, not only the intensity of the most characteristic peak increased, it also rose from 3,379 to 3,439 cm\(^{-1}\). In addition, the two absorption peaks at 1,651 and 1,551 cm\(^{-1}\) merged into a new peak at 1,605 cm\(^{-1}\). The stretching band of \(-\text{CH}\) increased from 1,408 to 1,418 cm\(^{-1}\) as well. These alterations represent the appearance of a carboxylate (\(-\text{COO}^-\)) group. Moreover, the peak at 1,027 cm\(^{-1}\) with respect to the C\(-\text{OH}\) group shifted to 1,080 cm\(^{-1}\) and its peak intensity obviously increased. All of these changes prove that when EDTAD was introduced to the surface of MC, the carboxyl, hydroxyl, and amino groups were released to allow efficient adsorption of MB. After adsorption of MB, the characteristic peaks of EMC also changed. For instance, the intensity of 3,439 cm\(^{-1}\) (\(-\text{NH}/-\text{OH}\) stretching vibration) decreased; peaks of 1,605 cm\(^{-1}\) (C\(-\text{O}\)) and 1,080 cm\(^{-1}\) (C\(-\text{OH}\)) shifted to 1,645 and 1,114 cm\(^{-1}\), respectively, together with decreases in intensity. More importantly, a new peak at 1,525 cm\(^{-1}\) belongs to the ring stretching vibration of MB that appeared. These suggest that hydroxyl, carboxyl, and amino groups are involved in the adsorption of MB in an aqueous environment.

**Potentiometric titration**

The potentiometric titration is of great importance in analyzing the amount of functional groups and proton-binding
active zone of adsorbents. Figure 2(C) illustrates the titration curves with MC, EMC, and 0.1 M NaCl electrolyte. Due to the consumption and donation of protons, the composite materials provided a significant buffering capacity to the solution over a wide range of pH. In comparison, the titration curve of EMC had a larger degree of changes.

In order to understand the functional group changes on the surface of chitosan after the EDTAD and magnetic modification, the pK_a values of organic functional groups and the corresponding site densities C_Ai were calculated using Pro-fit Version 2.0 software (Zhang et al. 2010). According to the titration data, the four-site model provided a good fit for MC and EMC. As shown in Table 1, the concentrations of carboxyl, hydroxyl, and amine groups on EMC are higher than those on MC. The higher concentration of hydroxyl groups may be attributed to repeating vacuum freeze-drying and dissolution of N,N-dimethylformamide (DMF), which result in destruction of the outer layer of chitosan and lead to explosion of inner hydroxyl groups.

**Adsorption behaviors of MB**

**Effect of acidity on adsorption**

The acidity effect on adsorption was examined at an initial concentration of MB of 300 mg/L at 35 °C. During adsorption, the acidity of the solution alters the adsorbent surface charge. This process is thus directly related to the functional groups present on its surface. If the pH value of the solution is lower than the pK_a, the adsorbent would release H^+. When the pH value of the solution is higher than the pK_a, a reverse reaction will occur. Three functional groups including carboxyl, hydroxyl, and amine are on the adsorbent surface. Any change of acidity would affect the amount of the deprotonated and protonated forms of these functional groups.

As shown in Figure 2(D), the uptake of MB on MC and EMC increased with the increasing pH value from 3.0 to 6.0 of the solution. In a weak acid solution, more functional groups (i.e., –NH_2, –OH, and –COOH) appeared on the surface of the composite materials. Under a strong acidic environment more H^+ are available, which leads to the formation of more positively charged adsorption sites in chitosan chains, and both the electrostatic repulsion and competition with positively charged MB ions consequently occur. However, when the solution becomes alkali, the functional groups would be deprotonated and the binding sites for the adsorption of MB ions increased (Huang & Morehart 1999). In comparison, EMC showed a much higher adsorption capacity than MC. As well as this, our results revealed that the adsorption capacities of MC and EMC remained at a constant value when pH was >6.0. Accordingly, taking account of this in the real application, the pH value of 7.0 was chosen for the further experimental demonstrations.

### Adsorption isotherm

The maximum adsorption capacities of MC and EMC were determined at different initial concentrations of MB. The adsorption equilibrium data were fitted by the Langmuir adsorption isotherm model as follows:

\[
\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{bq_m}
\]

where q_e is the equilibrium adsorption capacity (mg/g), C_e is the equilibrium MB concentration in solution (mg/L), q_m is the maximum adsorption capacity of the adsorbent (mg/g), and b is the Langmuir adsorption equilibrium constant (L/mg) which is related to the free energy and affinity of adsorption. Table 2 shows the maximum adsorption quantities of MB by MC and EMC and their determination coefficients (R^2). The maximum adsorption quantity of MB on EMC is significantly higher than that of MC. This could be explained by an increased b value of EMC as a result of the attracting forces.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Functional group</th>
<th>pK_a values reported</th>
<th>pK_a values obtained</th>
<th>Concentration (mmol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MC</td>
<td>Carboxyl</td>
<td>2.00–6.00</td>
<td>5.00–5.55</td>
<td>0.65 ± 0.04</td>
</tr>
<tr>
<td></td>
<td>Amine</td>
<td>9.00–11.00</td>
<td>9.69–10.20</td>
<td>0.25 ± 0.10</td>
</tr>
<tr>
<td></td>
<td>Hydroxyl</td>
<td>8.00–12.00</td>
<td>10.90–11.90</td>
<td>0.09 ± 0.03</td>
</tr>
<tr>
<td>EMC</td>
<td>Carboxyl</td>
<td>2.00–6.00</td>
<td>4.56–4.70</td>
<td>0.88 ± 0.02</td>
</tr>
<tr>
<td></td>
<td>Amine</td>
<td>9.00–11.00</td>
<td>9.00–9.50</td>
<td>0.50 ± 0.04</td>
</tr>
<tr>
<td></td>
<td>Hydroxyl</td>
<td>8.00–12.00</td>
<td>9.35–10.45</td>
<td>0.49 ± 0.04</td>
</tr>
</tbody>
</table>

Table 1 Concentrations and acidity constants of surface functional groups of MC and EMC (MC and EMC: 3 g/L; titrant: 0.1 M NaOH; reaction temperature: 25 ± 0.5 °C; background electrolyte: 0.1 M NaCl)
between dye molecules and adsorbents, such as van der Waals forces, and electrostatic attraction increase during the adsorption process. Furthermore, the density of functional groups, especially carboxyl groups, plays a key role in the removal of MB. The number of carboxyl groups on EMC is higher than that on MC. As well, the EDTAD modification can increase the number of adsorption sites on the MC surface, enhancing the adsorption capacity of EMC.

**Temperature and adsorption thermodynamics**

Figure 2(E) illustrates the influence of temperature on MB adsorption by MC and EMC. More MB can be removed when the solution temperature increases from 15 to 35 °C. The amount of the non-protonated functional groups on the MC and EMC surfaces increased at higher temperatures (Abramian & El-Rassy 2009). Moreover, the internal structures of chitosan swelled and the mobility of MB ions increased, enabling the dye ions to penetrate further (Padmavathy 2008). However, for EMC, higher temperatures can cause hydrolysis of the ester bond between EDTAD and chitosan, in addition to the possibility of EDTAD molecules being separated from the surface. The adsorption efficiency of EMC thus decreased significantly when the temperature was >35 °C.

In order to describe the thermodynamic of the adsorption of MB by MC and EMC, parameters such as enthalpy change (ΔH), Gibbs free energy change (ΔG), and entropy change (ΔS) were estimated by the following equations:

\[ K = \frac{C_{AE}}{C_e} \]

\[ \Delta G = -RT \ln K \]

\[ \Delta G = \Delta H - T \Delta S \]

where K is the equilibrium constant, \( C_{AE} \) is the amount adsorbed on solid at equilibrium (mg/L), \( C_e \) is the equilibrium MB concentration in solution (mg/L), \( R \) is the universal gas constant, 8.314 (J/(mol·K)), and \( T \) is the absolute temperature (K). As shown in Table 3, the negative value of \( \Delta G \) indicates that all the adsorption processes are spontaneous in nature, and the more negative the value of \( \Delta G \), the higher the degree of spontaneity. Therefore, the spontaneity degree of EMC is higher than that of MC. The values of \( \Delta H \) and \( \Delta S \) were determined from the slope and intercept of the Van’t Hoff plot. The plots of lnK versus 1/T show good linearity (\( R^2 >0.999 \)). The positive \( \Delta H \) value suggests that the adsorption process is endothermic. The positive value of \( \Delta S \) also shows the increased randomness at the solid–liquid interface during the adsorption process. However, chelation is an entropy increasing process and therefore the chelation between MB and functional groups on the surface of MC and EMC evidently occurred during the adsorption process. Therefore, the confusion degree of the system increases.

**Contact time**

Figure 2(F) presents the adsorption capacity of MB by MC and EMC for different contact times. The adsorption efficiency by EMC was about 77.4% for the contact time of 10 min due to surface adsorption with functional sites. Further on in the reaction, MB molecules gradually diffused into the pores of the adsorbents for further physical adsorption. Thereafter, MB ions combined with adsorbents through electrostatic attraction and the adsorption behavior increased with the reaction time of 30 min (Li et al. 2010). With the decrease of active groups, the dynamic equilibrium was then reached. For MC, the adsorption equilibrium was reached at 100 min. Although various functional groups such as carboxyl, hydroxyl, and amine were present on the MC surface, their amount of adsorption was still limited. The adsorption capacity was thus lower than that of EMC.

**Desorption and regeneration tests**

In order to make the adsorbent reusable, desorption experiments were repeated three times with different eluents.

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**Table 2 | Langmuir isotherm constants for adsorption of MB by MC and EMC**

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>( q_{max} ) (mg/g)</th>
<th>( b ) (L/mg)</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>MC</td>
<td>52.314</td>
<td>0.0226</td>
<td>0.9862</td>
</tr>
<tr>
<td>EMC</td>
<td>112.058</td>
<td>0.0298</td>
<td>0.9657</td>
</tr>
</tbody>
</table>

**Table 3 | Thermodynamic parameters for the adsorption of MB by MC and EMC**

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>( T ) (K)</th>
<th>( \Delta G ) (kJ/mol)</th>
<th>( \Delta H ) (kJ/mol)</th>
<th>( \Delta S ) (J/(mol·K))</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>MC</td>
<td>298.15</td>
<td>-0.852</td>
<td>35.016</td>
<td>120.30</td>
<td>0.9999</td>
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<td></td>
<td>303.15</td>
<td>-1.453</td>
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<td></td>
<td>308.15</td>
<td>-2.055</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>EMC</td>
<td>298.15</td>
<td>-2.291</td>
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<td>80.00</td>
<td>0.9996</td>
</tr>
<tr>
<td></td>
<td>303.15</td>
<td>-2.701</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>308.15</td>
<td>-3.091</td>
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<td></td>
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</table>
The results are shown in Table 4. It was found that HCl was more powerful than the absolute ethanol used for regeneration of the adsorbents. Meanwhile, the recovery of EMC was faster than that of MC. With regard to HCl, ionized $H^+$ competitively occupied the adsorption sites on the MC and EMC surfaces, thereby releasing dye ions. According to the theory of *similarity* and *immiscibility*, MB was eluted with absolute ethanol through dissolution. In comparison, HCl solution was confirmed as an optimal eluent for the regeneration. The experiments also show that EMC had a stronger removal performance than MC after reuse cycles.

CONCLUSION

In this study, a novel, efficient and low-cost magnetic adsorbent material, EMC, was synthesized by $\text{Fe}_3\text{O}_4$, EDTAD, and environmentally friendly chitosan according to the scheme shown in Figure 1(a). Compared with MC, the synthetic EMC not only was easily recoverable, but also had more amino, carboxyl, and hydroxy groups on the surface, which resulted in better electrostatic adsorption with MB dye wastewater. The maximum adsorption capacities of MB were 52.3 and 112.1 mg/g for MC and EMC, respectively. In summary, this study opens an avenue for the preparation of high-quality composite adsorbent. It has the profound potential for real applications for treating dye-containing wastewater.

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REFERENCES


### Table 4. Desorption and regeneration of MB-loaded EMC and MC

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>A/D cycle</th>
<th>HCl Regeneration efficiency (%)</th>
<th>MB recovery efficiency (%)</th>
<th>C$_2$H$_5$OH Regeneration efficiency (%)</th>
<th>MB recovery efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MC</td>
<td>1</td>
<td>85.31</td>
<td>88.42</td>
<td>80.53</td>
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</tr>
<tr>
<td></td>
<td>2</td>
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<td>84.73</td>
<td>73.52</td>
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<td>3</td>
<td>72.16</td>
<td>81.31</td>
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<tr>
<td>EMC</td>
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