



High-efficient removal of phthalate esters from aqueous solution with an easily regenerative magnetic resin: Hydrolytic degradation and simultaneous adsorption

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ARTICLE INFO

Article history:

Received 10 October 2017

Received in revised form 2 November 2017

Accepted 16 November 2017

Available online xxx

Keywords:

Magnetic anion exchange resin

Dimethyl phthalate

Degradation

Hydrolysis

Regeneration

ABSTRACT

Efficient removal of phthalate esters (PAEs) is of considerable concern since they pose serious ecological and human health risks. In this study, a magnetic strong base anion-exchange resin named MAER-OH was prepared and used as a solid basic catalyst and effective adsorbent. The MAER-OH was systematically characterized by scan electron microscopy, Fourier transform infrared spectroscopy, X-ray diffraction, thermogravimetric analyses and vibrating sample magnetometer. Various factors influencing the removal of dimethyl phthalate (DMP) such as initial DMP concentration, resin dosage and temperature were investigated. The DMP can be completely converted to far less toxic phthalate at the final treatment stage, and more attractively, the potential hydrolysis intermediates were ion-exchanged by the resin simultaneously without obvious change of solution pH. The co-existing chloride was found to obviously enhance the DMP removal efficiency but result in an obvious increase of solution pH and formation of much more hydrolytic intermediates. The exhausted MAER-OH could be regenerated by 8.0% NaOH solution with negligible efficiency loss, and maintain its virgin removal efficiency for 20 successive cycles. Sequencing batch jar tests indicated that more than 5000 bed volumes of DMP solution (10 mg L^{-1}) were efficiently treated by the MAER-OH and the saturated capacity of MAER-OH for DMP removal was 134.9 mg g^{-1} . Taken together, this highly effective and reusable MAER-OH can be easily modularized and separated, promising its huge potential for industrial-scale PAEs wastewater treatment.

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1. Introduction

Water pollution by phthalic acid esters (PAEs) has become a serious environmental concern in recent decades as they can disturb the endocrine system of human and wildlife, even at trace concentration levels (Abdel daiem et al., 2012; Ayranci and Bayram, 2005). Because of the excessive use in manufacturing of plastics, PAEs are capable of migrating into the environment and have been frequently detected in environmental water streams (Bodzek et al., 2004; Gao and Wen, 2016; Zhang et al., 2016). Furthermore, PAEs are highly stable in natural environment (hydrolysis half-lives ranging from 3.2 to 2000 years), and have been listed as top priority pollutants in USA and China (Abdel daiem et al., 2012; Özer et al., 2012a; Gao and Wen, 2016). Therefore, it is highly desirable to get rid of PAEs from wastewater to meet regulatory requirement prior to discharge or for reuse purpose.

Many studies have reported different methods to remove PAEs from global waters, including biodegradation (Boonnorat et al., 2014;

Reyes-Contreras et al., 2011), oxidation (Wen et al., 2011), adsorption (Li et al., 2015; Shi et al., 2014; Wu et al., 2013), and hydrolysis (Xu et al., 2014). Over the last decades, sorption-based water treatment techniques have been increasingly popular to remove and recover organic contaminants compared to other techniques due to their associated techno-economic and environmental advantages. Khan et al. (2015) investigated the adsorption of phthalic acid (PA) and diethyl phthalate (DEP) from aqueous solution with zeolitic imidazolate, which exhibited much higher removal efficiency than activated carbon. Huang et al. (2008) prepared the octadecyl-modified mesoporous SBA-15 silica molecular sieves for adsorption of dimethyl phthalate (DMP) and DEP. The results showed that alkyl SBA-15 particles could efficiently enrich the DMP and DEP from water samples. Zhang et al. (2007) used a hydrolytic hyper-crosslinked polymer resin NDA-702 for removal of DMP and found that the adsorption amount of DMP by using NDA-702 was much higher than that by using commercial XAD-4 resin and granular activated carbon AC-750. Recently, hydrolytic degradation and adsorption of esters by using strongly basic anion exchange resin has been reported. The hydrolytic role in degradation of targeted materials, such as ethyl acetate, ethyl phenylacetate, shikonin ester derivatives, and aziridines, has been well demonstrated (Abdel daiem et al., 2012; Miyazaki et al., 1996; Samelson and Hammett, 1956). Importantly, the resultant intermediates were preferably adsorbed by anion-exchange resin, suggesting

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that organic acids may form during the hydrolysis reaction and be simultaneously removed via electrostatic attraction (Elwakeel and Atia, 2014; Kanazawa et al., 2004; Xu et al., 2010). Due to the advantages of no chemical sludge, clean operation and high removal efficiency, the treatment of PAEs wastewater by anion-exchange resin may be a promising approach. According to the report by Xu et al. (2014, 2010), a macroporous strongly basic anion-exchange resin (OH-type) named D201-OH was used for efficiently catalytic degradation of DMP. The hydrolysis products were completely removed by the resin and the removal process exerted negligible adverse effects to the environment. However, this resin has a hydrophobic matrix and may cause serious resin fouling during hundreds to thousands of adsorption-regeneration cycles in real applications (Deng et al., 2010; Li et al., 2014; Mergen et al., 2008; Zaki et al., 2000; Zhu et al., 2013). The polyacrylic resin has been reported to have much better anti-fouling performance for organic matters removal (Fu et al., 2015; Li et al., 2014; Ysla, 2012), but its reusability for degradation and adsorption of PAEs has rarely been reported.

On the other hand, the treated volume is considerably limited in the form of traditional fixed-bed resin column, along with the high capital cost (Cheng et al., 2014; Li et al., 2017a). The applications of magnetic adsorbents have received considerable attention in recent years for their advantage of easy separation (Boyer, 2015; Ma et al., 2014). MIEX resin, developed by Orica Co. Ltd., is currently the most widely applied magnetic adsorbent for multiple water treatment projects, which are mainly owing to its recognized advantages: good stability, high exchange capacity, improved kinetics and feasible regeneration (Arias-Paic et al., 2016; Boyer and Singer, 2008). Furthermore, due to its high density and excellent settling property, MIEX resin could be applied in the form of fluidized bed reactor in a continuous process, which could greatly improve the treatment flux and get a high recovery rate (>99.9%) (Indarawis and Boyer, 2012). As a result, the resin amount is reduced to only 2–12% of conventional fixed-bed column resin dosage (Boyer, 2015; Boyer and Singer, 2008). In this scenario, catalytic degradation of PAEs by using OH-type magnetic anion exchange resin seems more attractive. However, very limited studies are performed in this regard.

The main objective of this study was to effectively remove PAEs in aqueous phase by using the prepared magnetic strongly basic anion exchange resin (MAER-OH) act as a solid basic catalyst and adsorbent. The MAER-OH was systematically characterized before use. DMP was chosen as the representative PAE for it is one of the top-priority pollutants and has been widely detected in aqueous environment (Xu et al., 2010). The removal mechanism and effects of various factors for DMP removal, such as initial DMP concentration, resin dosage, and reaction temperature were systematically investigated. In addition, desorption and reusability performances of MAER-OH were evaluated.

2. Material and methods

2.1. Materials

Glycidyl methacrylate (GMA, > 99%), divinylbenzene (DVB, 63.3%), benzoyl peroxide (BPO), trimethylamine hydrochloride, toluene and polyvinyl alcohol (PVA, GH20) were all industrial products and supplied by J&K Chemical Co. Ltd., China. Commercial γ -Fe₂O₃ was obtained from Tangyin Zhongke magnetoelectric Co., Ltd. Tetraethoxysilane (TEOS) and dimethyldiethoxysilane (DMDES) were purchased from Nanjing Capture Chemical Co., Ltd. The mono-methyl phthalate (MMP) and PA were obtained from Nanjing Chemical Reagent Company. DMP ($\geq 98.7\%$) was purchased from Sigma-

Aldrich Chemical Company. All these chemicals were used as supplied.

The magnetic resin MAER was prepared by suspension polymerization and subsequent amination reaction. The detailed preparation steps were shown in Supplementary Text S1. The resultant strongly basic anion resin MAER-Cl (in chloride form) was then converted to OH-form (denoted MAER-OH). About 50 mL MAER-Cl was rinsed with 500 mL of NaOH solution (2.0 M, 1 BV min⁻¹), and then washed by DI water to near neutral. Prior to use, the resins were purified with methanol and acetone for 12 h by Soxhlet extraction, and vacuum-dried at 323 K to constant weight.

2.2. Characterization

The morphologies of microbeads were characterized via scanning electron microscopy (SEM, S-3400, Hitachi). FTIR analysis was carried out by a FTIR spectrophotometer (Nexus 870, USA). The crystal structure of MAER-OH was assessed by X-ray diffraction (XRD) analysis with 2θ ranging from 10° to 70° (Shimadzu XRD-6000, Japan). Thermo-gravimetric analyses (TGA) were carried out on Pyris 1 DSC with the heating rate of 20 °C/min (PerkinElmer, USA). The magnetic characteristics of MAER were estimated by a vibrating sample magnetometer (VSM, LS 7307-9309). The specific surface area and pore distribution of the resins were measured by N₂ adsorption-desorption experiments at 77 K (ASAP, Micromeritics, USA) based on the standard Brunauer–Emmett–Teller (BET) method.

2.3. Batch removal experiments

Batch DMP removal experiments were performed with a given amount of MAER-OH (0.10–0.90 g) and 500 mL DMP solution of known concentrations (10, 20, 40 and 50 mg L⁻¹) in 1000 mL conical flasks, and shaken in an incubator shaker at different temperatures (283, 293 and 318 K) and 150 rpm. At pre-settled time intervals, 1 mL of the solution was extracted and detected by HPLC (Agilent 1200, DAD detector, USA) with the mobile phase consisting of 55% methanol and 45% 0.2 M KH₂PO₄. The detective wavelength was 228 nm and column temperature was fixed at 303 K.

2.4. Desorption and reusability

The desorption and regeneration performance of MAER-OH could directly reflect its reusability. Batch parallel DMP removal experiments (0.10 g MAER-OH, 100 mL of 50 mg L⁻¹ DMP solution) were conducted at 318 K for 12 h. The saturated resins were then regenerated by 20 mL of 8.0% NaOH solution at 150 rpm and 318 K for 1 h. Afterwards, the microbeads were rinsed by an excess amount of deionized water to neutral pH, and then used for next operation run. Successive cycles were undertaken for 20 times to verify the loss of virgin removal efficiency, and alternatively to know the extent of resin regeneration. The desorption efficiency (*DE*) was calculated as follows:

$$DE = 100\% \cdot V_d C_d / W q_e \quad (1)$$

where V_d (L) is desorption agent volume, and C_d (mmol L⁻¹) is the adsorbate concentration in desorption solution. W (g) and q_e are the weight of dried resin and removal adsorbate amount, respectively.

Continuous DMP removal jar tests were carried out with 1 mL resin and 100 mL DMP solution of 10 mg L⁻¹ at 318 K and 150 rpm. At pre-determined time intervals, 1 mL solution was withdrawn and analyzed. After 3 h, the MAER-OH beads were separated by a mag-

net and transferred into another 100 mL untreated solution, which was similar as the former operation run.

3. Results and discussion

3.1. Characterization

The essential physicochemical characteristics of MAER-OH were shown in Table 1. The BET surface area and total pore volume of MAER-OH were $1.30 \text{ m}^2 \text{ g}^{-1}$ and $4.86 \text{ mm}^3 \text{ g}^{-1}$ respectively, both were lower than that of traditional polystyrene anion-exchange resin (Wang et al., 2010; Xu et al., 2010). With the addition of $\gamma\text{-Fe}_2\text{O}_3$ in resin matrix, the MAER-OH exhibited high density and mechanical strength. Furthermore, the modification of $\gamma\text{-Fe}_2\text{O}_3$ on the surface was of great benefits for protection of magnetic cores under acid conditions. Besides, the MAER-OH possessed a polyacrylic matrix and high moisture content, suggesting a better anti-fouling performance during continuous adsorption-desorption operation cycles (Li et al., 2014).

The surface morphologies of obtained resin beads are observed in Fig. 1a. It is clearly seen that the microbeads are satisfactorily monodisperse in spherical form of 100–250 μm , much smaller than conventional resins. Besides, the magnetic resins appear regular but not smooth, with 1–2 μm rod-like bulging on their surface, which confirms the combination of needle-shape $\gamma\text{-Fe}_2\text{O}_3$ within the resin skeleton. The FTIR spectra presented in Fig. 1b display the characteristic peaks of $\gamma\text{-Fe}_2\text{O}_3$, precursor resin and MAER-OH. The typical adsorption band belonging to Fe—O stretching vibration is observed at 553 cm^{-1} . The absorption bands at 904 and 844 cm^{-1} of precursor resin are corresponding to the epoxy groups, which disappeared after the amination reaction. The peak at 1481 cm^{-1} is attrib-

uted to the C—N stretching of quaternary ammonium group of the final MAER-OH. With this functional group in resin, the MAER-OH is positively charged and maintains relatively stable over a wide pH range, which is demonstrated by the zeta potentials of MAER-OH (+25–30 mV) and shown in Supplementary Fig. S1. In Fig. 1c, the characteristic diffraction peaks of XRD patterns for $\gamma\text{-Fe}_2\text{O}_3$ and MAER-OH are shown. These peaks are in agreement with the planes of (220), (311), (400), (422), (440) and (551) respectively, which are in accordance with the inverse spinel structure of the maghemite (Li et al., 2017a). The thermal stability of MAER-OH can be seen in Fig. 1d. The main weight loss is ranging from 250 to 450°C , which is ascribed to the decarboxylation and carbonization reaction of the polymer chain. At temperatures higher than 650°C , the resin is further decomposed to inorganic ash. The magnetic characteristics of MAER-OH are displayed in Fig. 1e. The saturation magnetization of the resin is 9.71 emu/g . Notably, the MAER-OH microbeads show a hard magnetic behavior and could easily agglomerate with others without an external magnetic field, which results in the rapid settling of resin in aqueous solution.

3.2. Removal kinetics

Fig. 2 shows the DMP removal and variation of solution pH as a function of time by using MAER-OH and MAER-Cl. The control test without any resin was also performed in our preliminary experiment, and no DMP loss was found at 318 K during 24 h. It is evident that little variation of DMP concentration was observed in the presence of MAER-Cl, suggesting the resin matrix was useless for DMP removal. However, by using MAER-OH, an efficient removal of DMP was observed, which confirmed the essential roles of hydroxyl counter-anion for the hydrolytic degradation of DMP. During the first 4 h, the DMP content declined quickly and more than 80% of DMP was removed, while it was undetected in the final solution. According to previous literature, the DMP could be hydrolyzed to MMP and PA under basic condition (Xu et al., 2014). Surprisingly, these potential hydrolysis intermediates were not detected during the experiment, which was attributed to the fact that the resultant intermediates MMP and PA had high adsorption affinity to anion exchange resin and thus could be simultaneously removed from the solution. This finding was extremely important since no aromatic pollu-

Table 1
The primary physicochemical characteristics of MAER-OH.

Matrix	Polyacrylic-divinylbenzene
Functional group	$-\text{CH}_2\text{N}^+(\text{CH}_3)_3\text{OH}^-$
Anion exchange capacity (mmol g^{-1})	3.20
Moisture (%)	50–60
BET surface area ($\text{m}^2 \text{ g}^{-1}$)	1.30
Pore volume ($\text{mm}^3 \text{ g}^{-1}$)	4.86
Average pore diameter (nm)	14.91

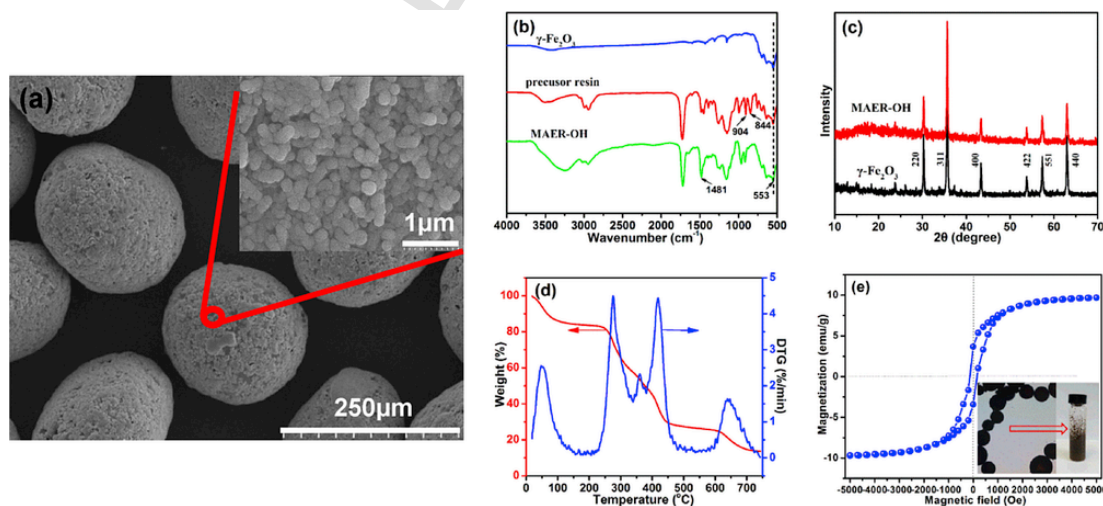


Fig. 1. Characterization of MAER-OH microbeads: (a) SEM micrographs, (b) FTIR spectra, (c) XRD patterns, (d) TGA curves and (e) hysteresis loop.

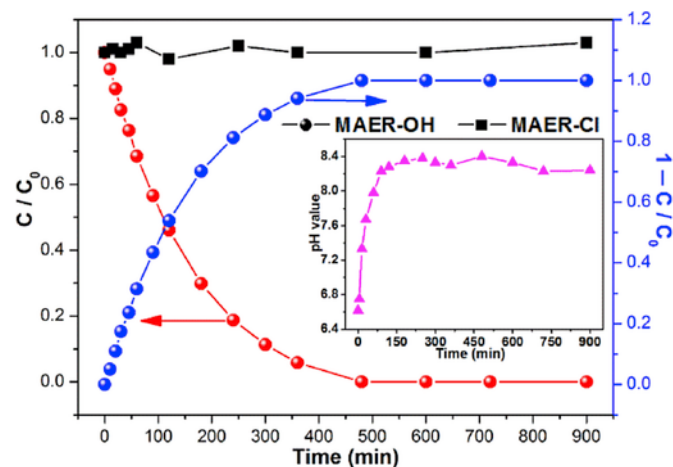


Fig. 2. The DMP removal and variation of solution pH as a function of reaction time (1.0 g resin L⁻¹, 318 K, 20 mg L⁻¹ DMP).

tants were released during the DMP hydrolysis. Besides, with the use of MAER-OH, the solution pH increased from 6.6 to about 8.2 within 60 min and maintained stable thereafter, indicating that the DMP removal process did not need additional neutralization treatment. Taken together, this process can achieve both the goals of degrading DMP and simultaneous removal of resultant pollutants from aqueous solution.

For further investigating the DMP removal processes, the effects of initial DMP concentration, resin dosage and temperature were evaluated and presented in Fig. 3. For all set of experiments, the removal amount of DMP increased quickly with time at initial stage and gradually attained a plateau. The final pH values of the treated solution were all near neutral.

As can be seen in Fig. 3a, the DMP removal efficiency decreased with an increase of initial DMP concentration. This was most likely due to the limited number of available active sites. However, the hydroxyl anion was concentrated within the resin phase and declined slightly during the DMP catalytic degradation, resulting in a negligible impact of initial DMP concentration on the removal performance.

The resin dosage is one of the most effective factors for DMP removal. It was shown in Fig. 3b that the DMP removal efficiency increased gradually with the increasing resin dosage, which was mainly because of the more abundant reactive sites. In addition, increasing resin dosage beyond 1.4 g L⁻¹ did not result in an obvious enhancement of the DMP removal efficiency. Therefore, resin dosage of 1.4 g L⁻¹ was recommended to save operation expenditure.

From Fig. 3c, it can be seen that the removal processes were strongly dependent on the reaction temperature. The final DMP removal efficiency increased from 81.6% to 100% within 24 h as the temperatures increased from 283 to 318 K, demonstrating that higher temperature was more favorable for DMP removal. This phenomenon could be explained by the fact that the increasing temperature greatly improved the driving force, and on the other hand, diminished the resistance of the mass transfer of adsorbate (Cheng et al., 2014; Jia et al., 2016). Similar results were also found in the literature by Thompson et al. (2008) for basic hydrolysis of esters such as poly (2-aminoethyl methacrylate).

To elucidate the removal behaviors at different conditions, the pseudo-first-order and pseudo-second-order models are applied (Supplementary Text S2). The theoretical values of *RE* and constants *k*₁, *k*₂, and *R*² are summarized in Tables S1–S3. Based on the correlation coefficients, the experimental data fitted better by the pseudo-

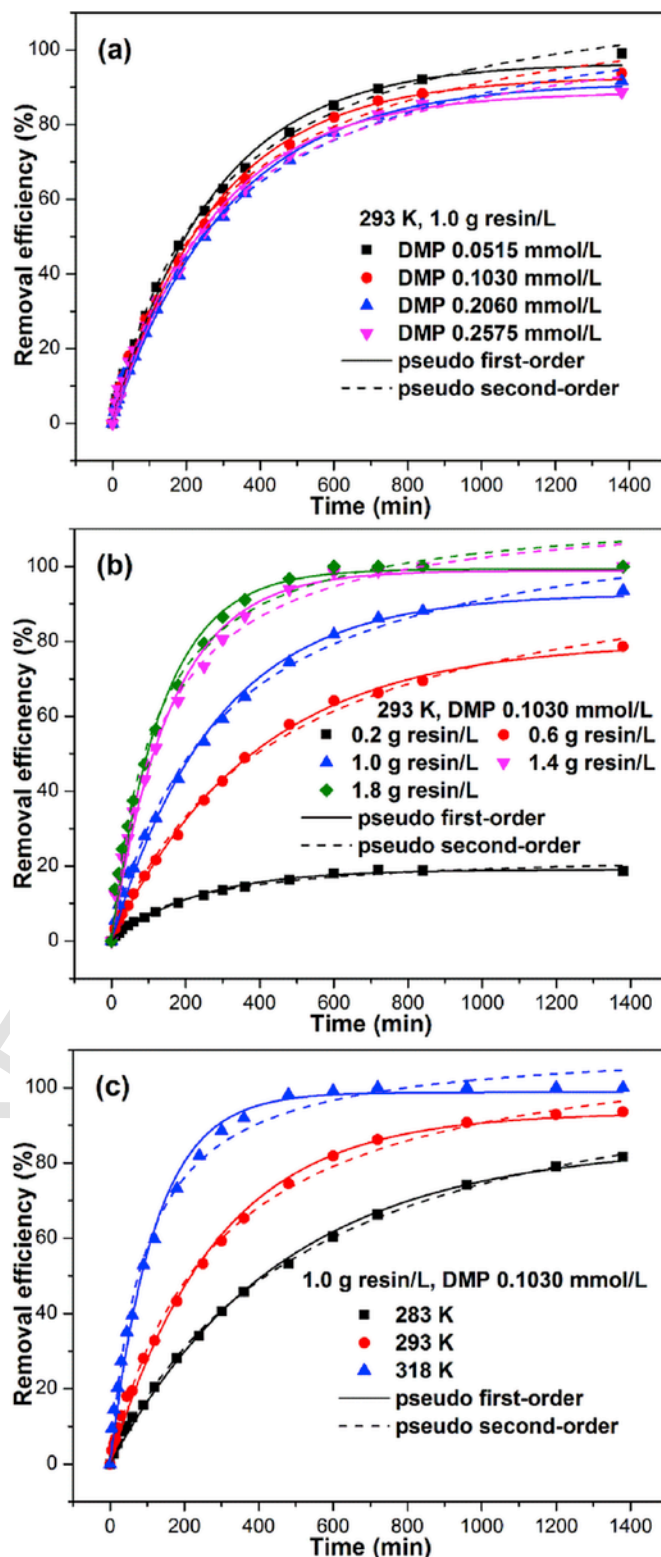


Fig. 3. Removal kinetics of DMP using MAER-OH and their modeling by pseudo-first-order and pseudo-second-order model with different (a) resin dosage, (b) initial DMP concentration, and (c) reaction temperature.

second-order kinetic model at most experimental conditions, which were in accordance with their chemisorption nature (Özer et al., 2012b; Wang et al., 2015). However, the theoretical REs calculated by the pseudo-first-order kinetic model were more close to the experimental results. On the other hand, it was found in Supplementary Fig. S2 and Table S4 that the removal kinetics of PA and MMP by the MAER-OH were also more favorably described by the pseudo-second-order kinetic model. Especially, the initial adsorption rates h for PA and MMP removal were about two orders of magnitude larger than that for DMP removal (complete removal of MMP and PA within 30 min), confirming that hydrolytic degradation was the rate-controlling step.

3.3. Mechanism

The FTIR spectra could shed light on the nature of adsorptive interactions between DMP and MAER-OH. The fresh and exhausted resins were examined by FTIR characterization and shown in Fig. 4a. An obvious peak belongs to carboxylic group is observed at 1562 cm^{-1} for the saturated resin, which directly confirms the electrostatic interactions between the carboxylic group of hydrolytic intermediates (MMP and PA) and quaternary ammonium group of MAER-OH (Fu et al., 2015). Furthermore, the peak intensity in the range of $1400\sim 1500\text{ cm}^{-1}$ attributed to the C—N stretching vibration is obviously weakened for the saturated resin, which also demon-

strates the variation of electron cloud density for the quaternary ammonium group.

Meanwhile, XPS characterizations of virgin and saturated resin were also conducted to elucidate the removal mechanism. The wide scan of XPS spectra was shown in Fig. S3 and the high-resolution N1s spectra of resin samples were presented in Fig. 4b. The N1s spectrum of fresh MAER-OH has a single peak at 401.77 eV for the quaternary ammonium group ($-\text{N}^+(\text{CH}_3)_3$). As the quaternary ammonium type-N maintains stable during the ion exchange process, the shift of this peak is negligible, confirming the electrostatic attraction mechanism of resultant intermediates removal.

Based on above discussion, it can be reasonably proposed that the DMP was removed via an MAER-OH induced hydrolytic degradation and simultaneous ion-exchange process. The removal mechanism was shown in Fig. 5. In the basic resin phase, the DMP was first de-esterified to MMP and methanol, and then further decomposed to PA and another methanol. As the pH in resin phase (>13) was much higher than the pK_a of MMP (5.41) and PA (2.95, 5.41), the hydrolytic intermediates MMP and PA were in negative form and had high adsorption affinity to the anion exchange resin, and thus could be easily removed through a preferable anion exchange process, which was similar to the adsorption of fulvic acid (Jutaporn et al., 2016), humic acid (Li et al., 2014) and other organic acids (Kanazawa et al., 2004) by using anion exchange resin.

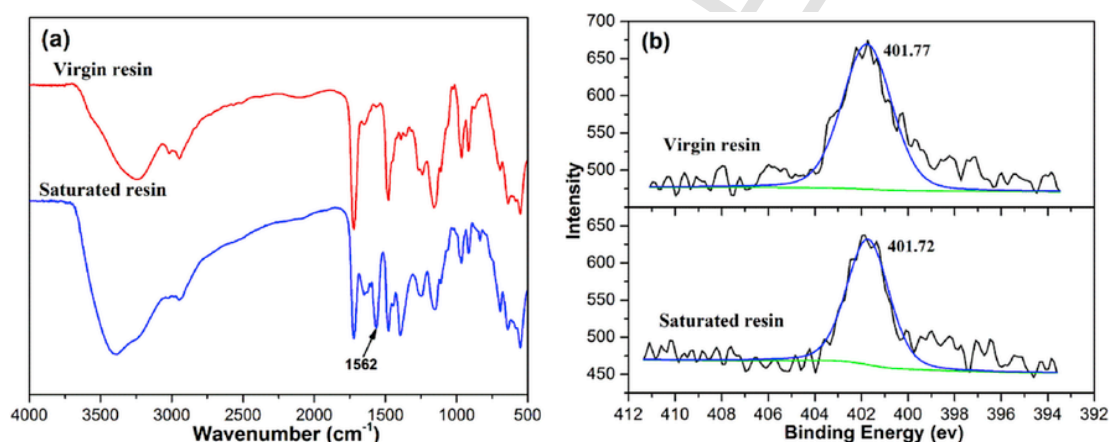


Fig. 4. The FTIR spectra (a) and N1s XPS spectra (b) of virgin and saturated MAER-OH.

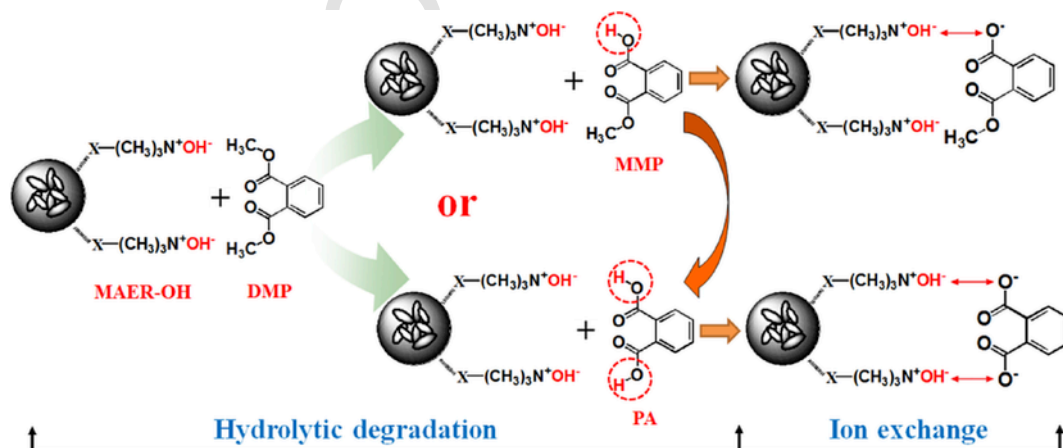


Fig. 5. Proposed mechanisms for the DMP removal by using MAER-OH.

3.4. Effects of co-existing anion

As electrostatic attraction is the main driving force to remove negatively charged hydrolysis intermediates in our experiments, the co-existing anion may seriously hamper the DMP removal (Deng et al., 2010; Li et al., 2017b). As can be seen in Fig. S4a, the presence of NaCl in solution could substantially quicken the DMP removal rate with the NaCl concentration increasing from 0 to 150 mg L⁻¹. However, a further increase in NaCl concentration did not bring about any improvement. These results were associated with the variation of solution pH. It was evident in Fig. 6a that the pH enhanced quickly with the increase of NaCl concentration and the maximum pH maintained stable at near 11. This was because the additive Cl⁻ in solution could quickly ion-exchange with OH⁻, leading to an increase of solution pH. However, when the concentration of NaCl was higher than 150 mg L⁻¹, the hydroxyl counter-anion in resin phase was completely transferred into the solution, thus the solution pH changed slightly with further Cl⁻ addition.

On the other hand, in the presence of NaCl, the hydrolytic intermediate MMP was detected and increased with time in the initial stage and then decreased gradually to near zero, as shown in Fig. S4b. Furthermore, the concentration of MMP increased with the increasing Cl⁻ in solution, which was because the co-existing Cl⁻ could compete with MMP for adsorption and decrease its adsorption speed. As the DMP removal by the use of MAER-OH was a base-promoted hydrolysis reaction, the increasing Cl⁻ concentration could result in a burst of OH⁻ in solution, which helped to hydrolyze the DMP and result in the formation of more MMP. Notably, nearly no PA was found in solution, which might be due to the fact that the relatively lower solution pH cannot further convert the MMP to PA. The total removal kinetics of DMP and its hydrolytic products were shown in Fig. 6b. A continuous increase in total removal efficiency was observed with the NaCl concentration increasing from 0 to 150 mg L⁻¹. However, further increase of NaCl concentration led to a decline in total removal efficiency. This phenomenon may be explained as the competitive adsorption between co-existing chloride and hydrolytic intermediates, and was consistent with their respective initial removal rate, as shown in Fig. S5. Similar results were also reported in other literature (Jing et al., 2017; Xu et al., 2010).

As real effluents often contain a large amount of salt and this point is primordial for a potential application in real condition, the effects of ionic strength were further investigated at high concentration levels (500–5000 mg L⁻¹). At such high NaCl concentrations, the hydroxyl counter-anion in resin matrix was completely ion-exchanged with Cl⁻

and transferred into the solution, resulting in a quick increase of solution pH (from neutral to nearly 11.0) within 30 min and fast removal of DMP in solution, which could be seen in Fig. S6a. However, the total removal efficiencies of DMP and its hydrolytic intermediates were greatly decreased with increasing NaCl concentration due to the competition adsorption between high concentration of co-existing anion and hydrolytic products. As shown in Fig. S6b, within 12 h, the total removal efficiency decreased from 99.85% (with 50 mg L⁻¹ NaCl) to 56.62% and 24.73% in the existence of 1000 mg L⁻¹ and 5000 mg L⁻¹ NaCl, respectively. Therefore, high ionic strength was considered as the limiting factor for a wide application of this method.

3.5. Desorption and reusability

From the viewpoint of large-scale applications, the reusability of MAER-OH was considered as one of the most important criteria (Wan Ngah et al., 2008; Wang et al., 2010). In this study, NaOH solution was utilized for the regeneration of exhausted resin as it can replace the adsorbed anionic adsorbates. As can be seen in Fig. S7, the *DE* of the resins enhanced gradually with the increase of NaOH concentration and kept stable at concentrations higher than 8.0%. More importantly, only PA was detected in the desorption agent, suggesting all DMP was converted to much less toxic PA at the final treatment stage. Such high conversion efficiency was explained by the fact that hydroxyl anion was highly concentrated in the resin phase and desorption solution. Hence, 8.0% NaOH solution was used as the desorption agent in adsorption-desorption experiments.

In the previous researches of our group (Li et al., 2014, 2017a; Wang et al., 2012), the magnetic strongly basic anion-exchange resin (NDMP-2) and magnetic weak acidic cation-exchange resin (MCER) have been successfully applied in the advanced treatment of domestic sewage and electroplating effluent (Fig. S8) due to their excellent treatment performance and simple operation, as well as recovery of valuable compounds from wastewater. To access the reusability of MAER-OH for DMP treatment, continuous 20 cycles of DMP removal and resin regeneration were conducted. As can be seen in Fig. 7, the exhausted MAER-OH could be regenerated and repeatedly used with negligible efficiency loss, which greatly facilitate the scale-up of resin applications.

As depicted in Fig. 8a, an efficient removal of DMP was observed within more than 5000 bed volume (BV) before a significant breakthrough occurred. The gradual loss of removal efficiency (2% per 100 BV on average) was attributed to the progressive loss of resin capacity during multiple cycles of DMP removal. Furthermore, the pH val-

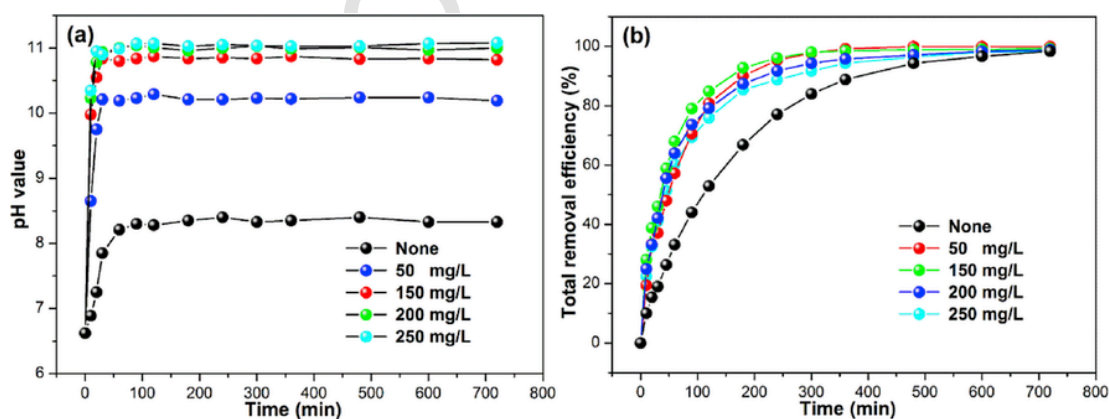


Fig. 6. Effects of NaCl concentration on (a) solution pH and (b) total removal efficiency at different time intervals.

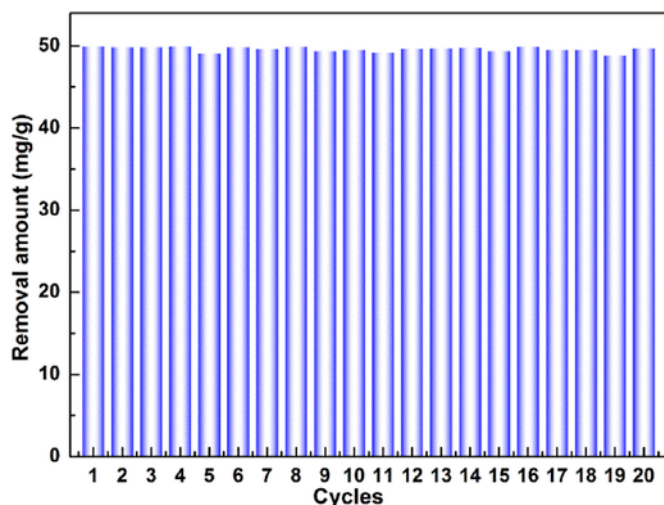


Fig. 7. Effects of adsorption-desorption cycles on the removal amount of DMP for 20 times (1.0 g L^{-1} MAER-OH, 50 mg L^{-1} of DMP solution, 318 K).

ues of resultant solution maintained stable at near 8.0, suggesting no need of further neutralization process. More importantly, the MMP and PA were undetected in the supernatant, confirming that hydrolytic products were simultaneously adsorbed by the resin. The saturated capacity of MAER-OH for DMP removal was 134.9 mg g^{-1} . On the other hand, as shown in Fig. 8b, the treated volume declined substantially (lower than 20% of previous volume) in the presence of chloride, while the saturated capacity for DMP removal was only 30.2 mg g^{-1} . These results were in accordance with the increasing solution pH (higher than 10) during the DMP removal process, which meant most of the active sites were ion-exchanged by the co-existing chloride.

Overall, the process can satisfactorily fulfill the objective of simultaneous DMP degradation and immediate pollutant removal in aqueous matrices. With the advantages of superior reusability and convenient separability, the MAER-OH could be considered as a good candidate and provide a sustainable and environmentally-friendly option to deal with PAEs wastewater.

4. Conclusions

In this study, a highly efficient procedure for catalytic degradation of DMP and simultaneous removal of intermediate products from aqueous solution by using self-prepared magnetic resin MAER-OH as the solid basic catalyst and adsorbent was performed. The MAER-OH was about $50\text{--}150 \mu\text{m}$ in size with uniform grain diameter and exhibited high rate of settlement in aqueous solution due to its superior magnetic characteristics. Batch kinetic studies showed that the DMP removal process was limited mainly by DMP hydrolysis. The DMP removal performance and solution pH were seriously affected by the co-existing chloride content, while a satisfactory degradation and removal efficiency was also achieved. At the final treatment stage, all DMP was converted to far less toxic PA. The proposed mechanism responsible for DMP removal relies on its catalytic degradation by MAER-OH combined with selective adsorption of the intermediates MMP and PA through a preferable anion exchange process. The exhausted MAER-OH was easily regenerated by 8.0% NaOH solution, and could be reused during 20 cycles with negligible capacity loss. More than 5000 BV DMP solution (10 mg L^{-1}) was efficiently treated in sequencing batch jar test, and the saturated capacity of MAER-OH for DMP removal was 134.9 mg g^{-1} . Overall, MAER-OH was proved to be a viable approach for effectively degrading and removing potential PAEs from contaminated waters, and importantly, the satisfactory reusability of MAER-OH could considerably extend the lifetime of resin for real applications. This technique had advantages of less investment in equipment (minimal cost) and simple operation, which made it possible to industrialize the techniques with economic and environmental benefits.

Competing financial interests

The authors declare no competing financial interests.

Acknowledgements

The authors would like to express appreciation for the generous support provided by the National Natural Science Foundation of China (51438008, 51678289), Natural Science Foundation of Jiangsu Province (BK20140608) and Postgraduate Research & Practice

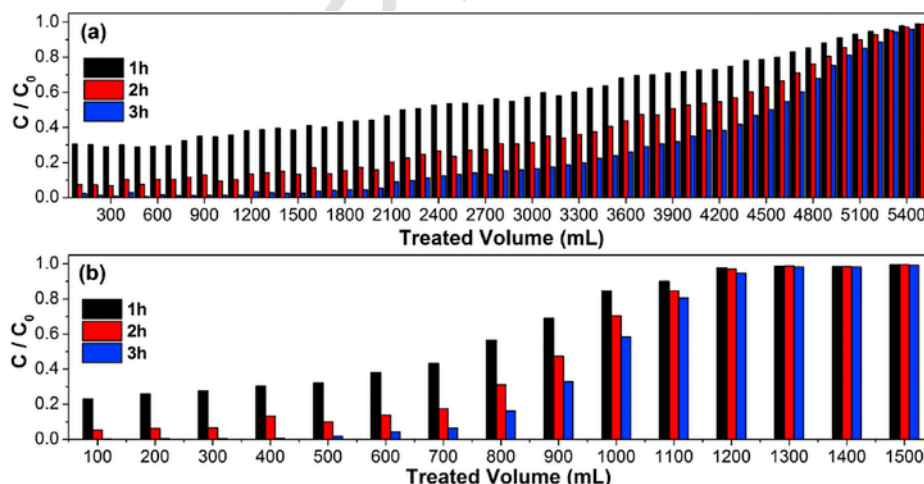


Fig. 8. The DMP removal performance by using MAER-OH in sequencing batch mode: (a) without co-existing anion and (b) in the presence of 50 mg L^{-1} NaCl in solution (1.0 mL resin, 318 K , 10 mg L^{-1} DMP).

Innovation Program of Jiangsu Province (KYCX17_0032). The authors also thank the Joint Innovation Project for Production-Study-Research in Jiangsu Province (BY20160608-06), China, National Key R&D Program, China (No. 2016YFE0112300) and the European Union's Horizon H2020 Research and Innovation program MAD-FORWATER (No. 688320)

Appendix A. Supplementary data

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.jclepro.2017.11.121>.

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