Modification of natural zeolite and its application to advanced recovery of organic matter from an ultra-short-SRT activated sludge process effluent
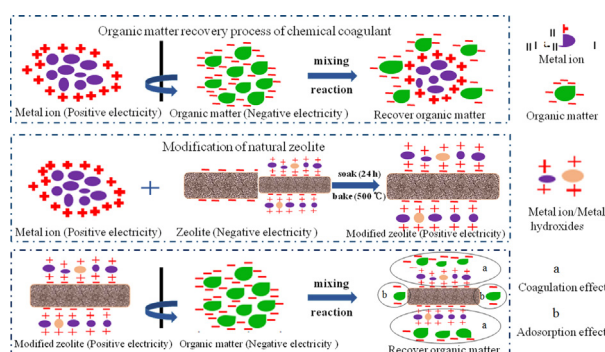
Guo-hua Liu, Yuanyuan Wang, Yuankai Zhang *, Xianglong Xu, Lu Qi, Hongchen Wang *

School of Environment & Natural Resource, Renmin University of China, No. 59 Zhongguancun Street, Haidian District, Beijing 100872, China

HIGHLIGHTS

- Natural zeolite was successfully modified through loading the traditional chemical coagulants.
- The organic recovery ability of natural zeolite was improved evidently after modification.
- The MZs can allow a lot of dissolved organic matter (SCOD) recovery from effluent.
- The recovery mechanism for the MZs mainly included the coagulation effect and adsorption effect.

GRAPHICAL ABSTRACT

ABSTRACT

Natural adsorbent was optimized from four natural adsorption materials (kaolin, bentonite, diatomite, and natural zeolite) through the comparison of their ability to recover organic matter from an ultra-short-sludge-retention-time (ultra-short-SRT) activated sludge process effluent. Natural zeolite was modified by the loading of three types of chemical coagulants ($Fe_2(SO_4)_3$, $Al_2(SO_4)_3$, and $ZnSO_4$) and was used for the study of the advanced recovery of organic matter. The results of Brunauer–Emmett–Teller surface area (S_{BET}) measurements, scanning electron microscopy (SEM), and X-ray diffraction (XRD) analyses showed that natural zeolite was successfully modified, with decrease in the specific surface area of the modified zeolite (MZ), but some metal ions/metal oxides were loaded onto the surface of natural zeolite. Compared with chemical coagulant and natural zeolite, the organic recovery efficiency from the effluent of the MZs improved, and after the optimization process, the organic recovery efficiency of MZ4 (Zeolite:$Fe_2(SO_4)_3$ = 4:1), MZ9 (Zeolite:$Al_2(SO_4)_3$ = 4:1), and MZ13 (Zeolite:$ZnSO_4$ = 2:1) reached 72.0%, 67.6%, and 61.2%, respectively. The MZs can allow a significant amount of recovery of soluble chemical oxygen demand (SCOD) from the effluent, with SCOD recovery efficiencies for MZ4, MZ9, and MZ13 of 44.8%, 44.3%, and 39.4%, respectively. The E_4/E_6, UV_{253}/UV_{203}, and SUVA analyses after the organic recovery experiments indicated that the generation potential of disinfecting byproducts or halogenated products was reduced in the treated effluent by the MZs. The mechanism can be considered in two ways: the coagulation effect of the loaded metal ions/metal oxides and the physical and chemical adsorption effect based on the hydrogen bond and π—π bond between the MZ and organic matter. This study facilitated the application of organic recovery from wastewater and the advanced treatment of effluent.

© 2018 Elsevier B.V. All rights reserved.

* Corresponding authors.
  E-mail addresses: zyk11@ruc.edu.cn (Y. Zhang), whc@ruc.edu.cn (H. Wang).

1. Introduction

It is estimated that wastewater contains around 1.5–1.9 kWh·m^{-3} organic chemical energy, which is approximately 10-fold greater than the energy consumption during the treatment of wastewater (Bowen et al., 2014; Mccarty et al., 2011). However, this energy was wasted mostly in the current form of energy-destroy-energy wastewater treatment. Therefore, increasing attention to energy recovery from wastewater will be paid in the future, and some investigations have already begun to consider the ultra-short-sludge-retention-time (ultra-short-SRT) activated sludge process (Ge et al., 2015; Meerburg et al., 2016; Ge et al., 2013). Since the ultra-short-SRT activated sludge system cannot fully reclaim organic matter from wastewater, it is necessary to conduct organic advanced recovery from the ultra-short-SRT activated sludge process effluent to meet the discharge standard.

Organic advanced recovery can be realized through physical and chemical methods such as adsorption, coagulation, and membrane filtration (MF). Compared with the MF method, adsorption and coagulation techniques are easier to implement and more cost-effective.

Adsorbents include two major categories of natural and synthetic material. Natural adsorbents have advantages such as low cost, large storage capacity, and environmental friendliness (Gupta et al., 2009). Zeolite as a natural adsorbent has been widely used in the field of wastewater treatment (Moreno et al., 2001; You et al., 2017; Camacho et al., 2010). However, the adsorption ability of organic matter by natural zeolite without modification is limited due to the inhomogeneous porous structure of zeolite. Currently, most studies of natural zeolite have focused on its modification for enhancing its adsorption capacity (Minato et al., 2004; Alver and Metin, 2012); few studies have reported on improving its ability to recover organic matter by combining the effects of adsorption and coagulation.

The objective of the present study was to improve the ability of modified zeolite (MZ) to recover organic matter by both the adsorption and coagulation effects. Natural zeolite was modified by loading the chemical coagulant onto its surface, and the modification conditions of natural zeolite and its performance in the recovery of effluent organic matter from the ultra-short-SRT activated sludge process were studied.

2. Materials and methods

2.1. Natural zeolite

Zeolite is a silicate mineral that is formed by volcanic eruption crystals, with high mechanical strength and porosity. It has a specific gravity of 2.0–2.6 g·cm^{-3}, bulk density of 1.6 g·cm^{-3}, clay content of <1%, moisture content of <1.5%, and wear rate of <1%. Zeolite powder was washed three times with distilled water to clean its surface impurity, dried in a muffle furnace (MF-1200C, Shanghai), and was sieved to ensure that the particle size was <0.074 mm.

2.2. Source effluent used in the experiment

Source effluent used in the organic advanced recovery experiments was derived from the effluent of a lab-scale sewage treatment system with an ultra-short-SRT activated sludge process (SRT = 2d), and its chemical oxygen demand (COD) and pH were 60–80 mg·L^{-1} and 8.0, respectively. Three liters of source effluent (pH = 8) were collected and used in each batch experiment.

2.3. Modification of natural zeolite

A kilogram of natural zeolite powder was washed with distilled water three times and then dried and powdered (size < 0.074 mm). Three chemical coagulant solutions (ZnSO$_4$, Fe$_2$(SO$_4$)$_3$, and Al$_2$(SO$_4$)$_3$) were prepared and thoroughly mixed with the natural zeolite powder. The zeolite loaded with each chemical coagulant was separated into

Table 1
Comparison of the properties of the MZs prepared by different methods.

Chemical coagulant	Type	Mass ratio (zeolite:chemical coagulant)	S_{BET} (m^2·g^{-1})
–	MZ0	Natural zeolite	217.2
Fe$_2$(SO$_4$)$_3$	MZ1	1:2	45.5
	MZ2	1:1	75.0
	MZ3	2:1	98.9
	MZ4	4:1	153.0
	MZ5	6:1	176.0
Al$_2$(SO$_4$)$_3$	MZ6	1:2	38.5
	MZ7	1:1	55.7
	MZ8	2:1	82.3
	MZ9	4:1	134.8
	MZ10	6:1	169.1
ZnSO$_4$	MZ11	1:2	32.9
	MZ12	1:1	54.1
	MZ13	2:1	142.2
	MZ14	4:1	156.1
	MZ15	6:1	171.4

five types of modified zeolites (MZs), whose mass ratio of natural zeolite to chemical coagulant were 1:2, 1:1, 2:1, 4:1, and 6:1, respectively. First, the chemical coagulant and zeolite powder were mixed evenly and sealed for 24 h at about 25 °C. Then, the mixtures were baked in a muffle furnace (MF-1200C, Shanghai) in the following procedure: heated from 25 °C to 500 °C at a rate of 15 °C·min^{-1}, kept at 500 °C constantly for 1 h under an N$_2$ atmospheric pressure of 0.2 psi, and finally cooled to 25 °C. The MZ was powdered to a size < 0.074 mm. The main modification conditions for different chemical coagulant-based MZs were listed in Table 1.

2.4. Effluent organic advanced treatment experiment by MZs

Effluent organic advanced treatment experiments by different MZs were carried out in a six-kneading mixer instrument (ZR4-6, Beijing). To compare the ability to remove COD of effluent, effluent organic advanced treatment experiments for three types of chemical coagulants (ZnSO$_4$, Fe$_2$(SO$_4$)$_3$, and Al$_2$(SO$_4$)$_3$) and four natural adsorption materials (zeolite, diatomite, bentonite, and kaolin) were also conducted. The concentration gradients of the three chemical coagulants were 0.01, 0.05, 0.1, 0.15, 0.2, 0.25, and 0.30 g·L^{-1}, and that of both the four natural materials and five different MZs were 0.1, 0.3, 0.6, 1, 1.5, 2, and 2.5 g·L^{-1}.

The experimental procedure includes two steps: stirring and sedimentation. Specifically, different materials and chemicals were added into 500-mL of effluent and then mixed by stirring. The stirring was
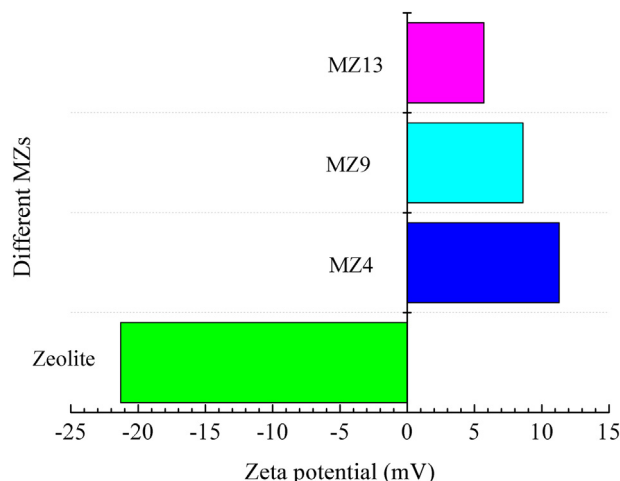

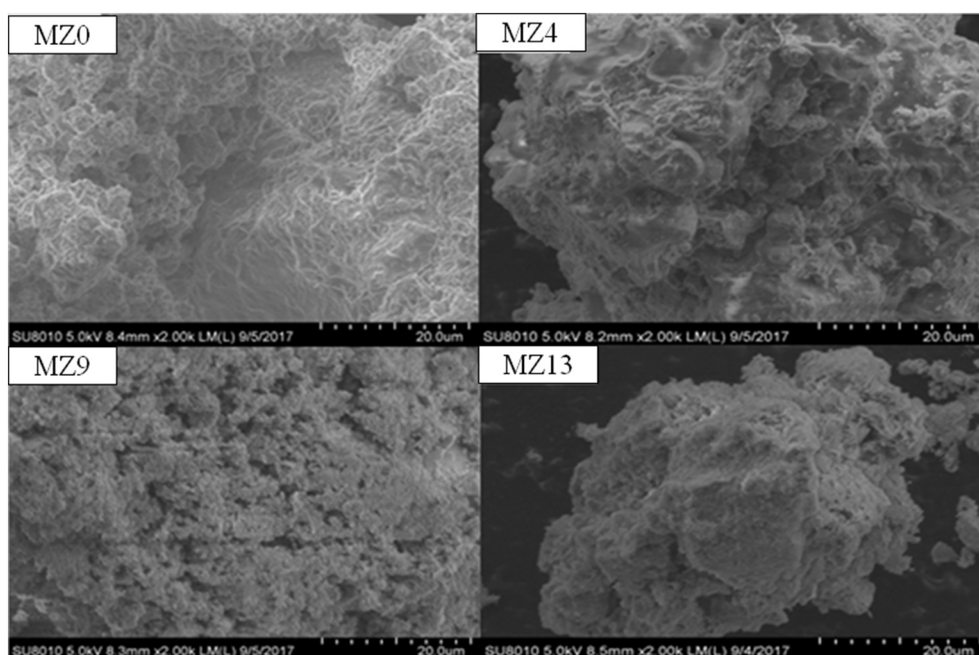**Fig. 1.** Zeta potential of zeolite and MZ solution.

Fig. 2. Scanning electron microscopy (SEM) observations of MZ0, MZ4, MZ9, and MZ13.

done for 15 min at a speed of 124 rev·min^{-1}. Then, the turbid solution was kept stationary for 30 min, and the supernatant was collected for subsequent analysis. The batch test was performed at 20–25 °C, and the pH of the reaction solution was controlled at 8.0.

2.5. Characterization of the modified zeolite properties

The Brunauer-Emmett-Teller surface areas (S_{BET}) of MZs were analyzed using a CA-1115A specific surface analyzer (Tristar 3020 II, Micromeritics, USA). The surface structure of MZs was observed by scanning electron microscopy (SEM, CA-1115A, Hitachi, Japan). X-ray diffraction (XRD) measurements were performed by X-ray diffractometer (Smartlab, Rigaku, Japan).

2.6. Characterization of effluent

Three-dimensional fluorescence of advanced treated effluent was measured by a fluorescence spectrophotometer (F-7000, Hitachi, Japan). COD was measured by the intelligent multi-parameter digestion instrument (LH-25A, China) and multi-parameter water quality analyzer (LH-3B, China) (Jimenez et al., 2003). Total COD (TCOD) was divided into three forms: soluble, colloidal, and particulate COD (SCOD, CCOD, and PCOD, respectively). The SCOD was determined through measuring the COD of the filtration solution using a 0.45-μm filter; the PCOD was calculated from TCOD minus the COD of the solution filtrated using a 1.5-μm filter, and the CCOD was calculated from PCOD minus SCOD. The degree of substitution on benzene rings by carbonyl, hydroxyl, and carboxyl groups was calculated based on the UV_{253}/UV_{203} value, measured by a spectrophotometer (UV-6100, China) (Korshin and Li, 1997). The specific UV absorbance (SUVA, $100 \times UV_{254}/DOC$) can also reflect the potential generation of halogenated compounds, which are preferentially derived from aromatics (Weishaar et al., 2003). The ratio of E_4/E_6 (UV_{465}/UV_{665}) reflecting the relative molecular weight of organic matter in water was measured with a UV–visible spectrophotometer (Chen et al., 1977). The zeta potentials of zeolite and MZ solution were determined by a zeta potential analyzer (DelsaNano C, Beckman, America) at 25 °C (Kirby and H. Jr., 2010).

3. Results and discussion

3.1. Characterization of the surface properties of zeolite and MZs

To explain the different COD recovery effects from effluent, the surface properties of zeolite and MZs (M4, M9, and M13) including S_{BET}, zeta potential, SEM, and XRD were measured. Their results are shown in Table 1 and Figs. 1–3, respectively.

As can be seen from Table 1, the specific surface area of the natural raw zeolite (MZ0) was 217.2 m^2·g^{-1}, but the specific surface area of the three modified zeolites—M4, M9, and M13—decreased to 153.0 m^2·g^{-1}, 134.8 m^2·g^{-1}, and 142.2 m^2·g^{-1}, respectively. These results showed that the chemical coagulant causes a partial blockage to the pore structure of natural raw zeolite. However, the zeta potential of the MZs increased from −21.3 mV (MZ0) to 11.3 mV (MZ4), 8.6 mV (MZ9), and 5.7 mV (MZ11) (Fig. 1). Generally, organic matter in the effluent has a negative charge; therefore, increasing the zeta potential will improve the adsorption ability of zeolite for organic matter due to the effect of the electrostatic force.
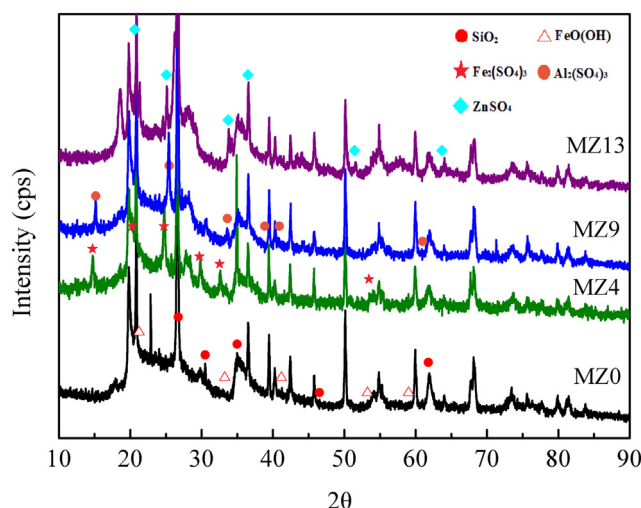

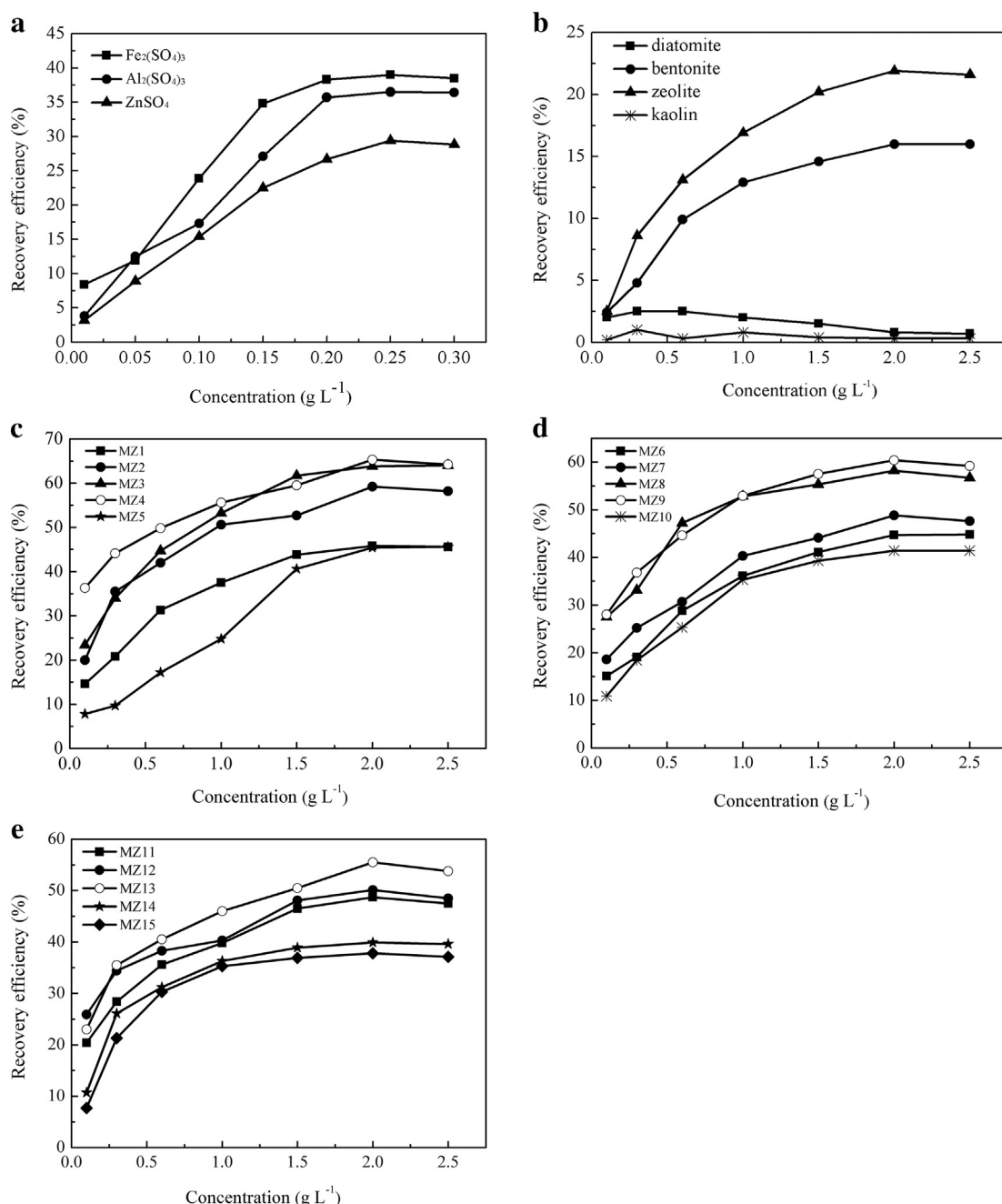**Fig. 3.** X-ray diffraction of MZ0, MZ4, MZ9, and MZ13.

Fig. 4. COD recovery efficiency of different materials towards source water, (a) three activators, (b) four natural materials, (c) five different $Fe_2(SO_4)_3$-modified zeolites, (d) five different $Al_2(SO_4)_3$-modified zeolites, (e) five different $ZnSO_4$-modified zeolites.

The SEM images for the MZ0, MZ4, MZ9, and MZ13 samples presented in Fig. 2 show that the surface micropores of modified zeolite was loaded with the chemical coagulant. Moreover, the XRD patterns (Fig. 3) of different MZs indicated that the composition of MZ4, MZ9, and MZ13 changed in comparison with MZ0, mainly through combining the composition of the chemical coagulant ($Fe_2(SO_4)_3$, $Al_2(SO_4)_3$, and $ZnSO_4$) to the surface composition of MZ0. This may improve the COD recovery capacity of the zeolite due to the added coagulation effect from the three chemical coagulants.

3.2. Comparison of organic recovery effect by different materials

The COD recovery efficiency of the three chemical coagulants ($Fe_2(SO_4)_3$, $Al_2(SO_4)_3$, and $ZnSO_4$) and the four natural absorption materials

are shown in Fig. 4(a) and (b), respectively. The COD recovery effects of the $Fe_2(SO_4)_3$-, $Al_2(SO_4)_3$-, and $ZnSO_4$-based MZs are shown in Fig. 4(c), (d), and (e), respectively.

A chemical coagulant concentration of 0.25 $g \cdot L^{-1}$ corresponded to the maximum organic recovery efficiency, 39% for $Fe_2(SO_4)_3$, 36.5% for $Al_2(SO_4)_3$, and 29.4% for $ZnSO_4$. For the four natural absorption materials, natural zeolite had a maximum COD recovery efficiency of 21.9% from the source effluent for a concentration of 2.0 $g \cdot L^{-1}$, which could be related to their specific surface area differences (zeolite: 217.2 $m^2 \cdot g^{-1}$, bentonite: 116.4 $m^2 \cdot g^{-1}$, diatomite: 34.6 $m^2 \cdot g^{-1}$, and kaolin: 11.7 $m^2 \cdot g^{-1}$).

After the modification of zeolite by the three chemical coagulants ($Fe_2(SO_4)_3$, $Al_2(SO_4)_3$, and $ZnSO_4$), the COD recovery efficiency by the MZs was improved, reaching maximum COD recovery efficiencies of
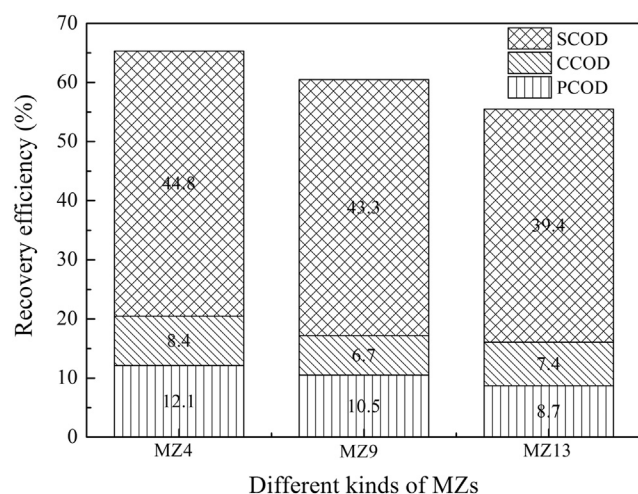
Fig. 5. Recovery efficiency of three types of COD by different MZs.

65.3% for the Fe$_2$(SO$_4$)$_3$-based MZ (4:1), 60.5% for the Al$_2$(SO$_4$)$_3$-based MZ (4:1), and 55.5% for the ZnSO$_4$-based MZ (2:1), respectively, for a concentration of 2.0 g·L^{-1}.

The above results, show that the COD recovery ability of the MZs is related to the chemical coagulant type and mass ratio of zeolite to chemical coagulant. In the present study, the Fe$_2$(SO$_4$)$_3$-based MZs exhibited better COD recovery ability than Al$_2$(SO$_4$)$_3$- and ZnSO$_4$-based MZs. The mass ratio of zeolite to chemical coagulant affected COD recovery. The mass ratio for the optimal effect was 4:1 for Fe$_2$(SO$_4$)$_3$-based MZs (MZ4), 4:1 for Al$_2$(SO$_4$)$_3$-based MZs (MZ9), and 2:1 for ZnSO$_4$-based MZs (MZ13). This may be because the valence of the key cation

was different, as the recovery ability of the ferric iron and aluminum ion was higher than the zinc ion.

Fig. 3 shows that the characteristic peak of FeO(OH) in MZ4 was strengthened, suggesting that new FeO(OH) is generated on the surface of raw zeolite through modification with Fe$_2$(SO$_4$)$_3$. Because of the high specific surface area and stable physical and chemical properties, the ability of FeO(OH) to remove pollutants in the environment is considered to be strong (Fortin and Langley, 2005; Wang et al., 2012). This may be why the Fe$_2$(SO$_4$)$_3$-based MZ has a better COD recovery effect than the Al$_2$(SO$_4$)$_3$- and ZnSO$_4$-based MZs.

3.3. Water quality characteristics analysis

3.3.1. Three types of COD analysis in the treated effluent

The recovery efficiency of three types of COD was evaluated by measuring SCOD, CCOD, and PCOD values. As shown in Fig. 5, the recovery efficiencies of TCOD for MZ4, MZ9, and MZ13 were 65.1%, 60.5%, and 55.5%, respectively. For the three types of COD (SCOD, CCOD, and PCOD), the recovery efficiencies of MZ4 were 44.9%, 8.1%, and 12.1%, respectively; the efficiencies of MZ9 were 43.3%, 6.7%, and 10.5%, respectively; and the efficiencies of MZ13 were 39.4%, 7.4%, and 8.7%, respectively. From the results, the MZs had the advantage in SCOD recovery from the source effluent; this may be the reason that the MZs had better organic recovery capacity than the chemical coagulant and natural zeolite alone.

3.3.2. Fluorescence analysis of wastewater SCOD

Dissolved organic matter (DOM) in wastewater contains a large number of organic compounds with fluorophores such as aromatics, tryptophan, humic acid, and fulvic acid (Mcknight et al., 2001; Hudson et al., 2010). When the fluorophores are excited, they will generate
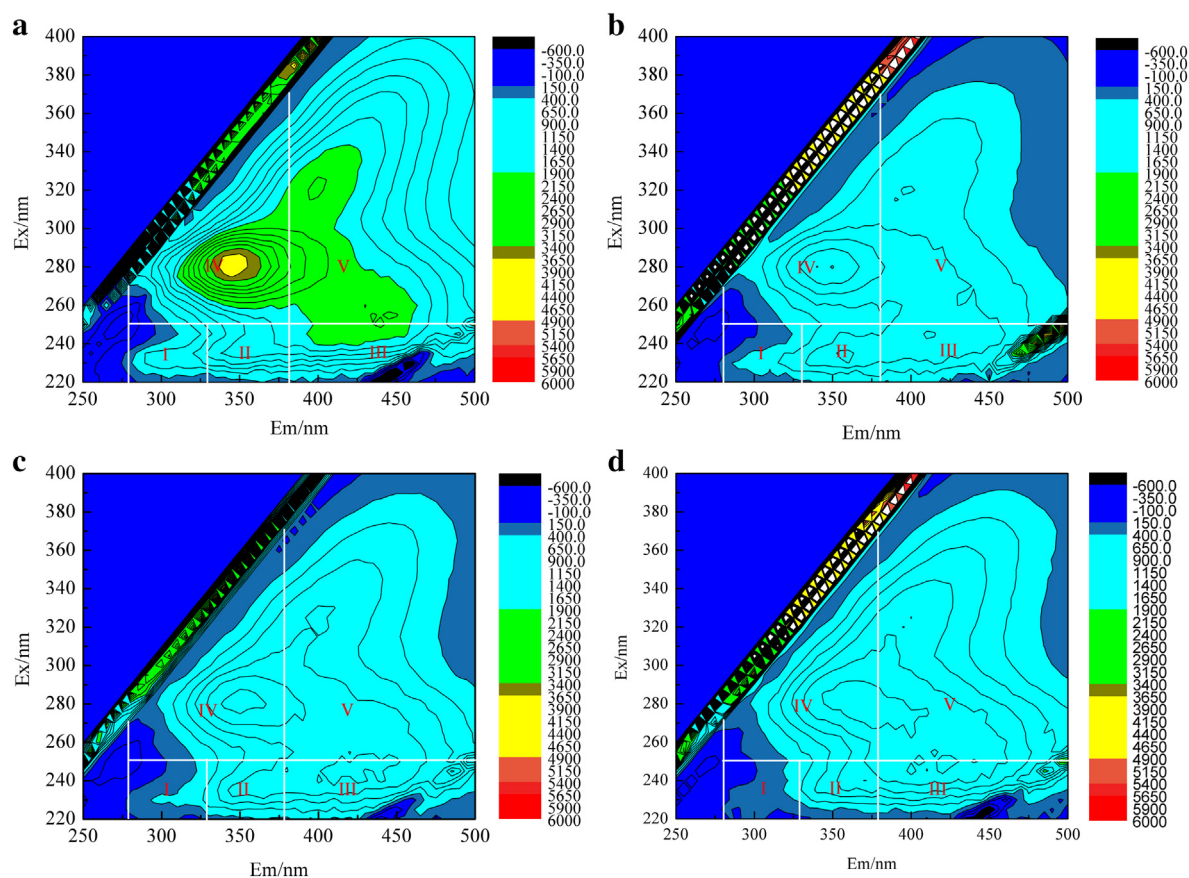

Fig. 6. Three-dimensional excitation-emission matrix fluorescence spectra for five dissolved organic matter fractions in water samples collected from different effluents: (a) source effluent, (b) effluent treated by MZ4, (c) effluent treated by MZ9, (d) effluent treated by MZ13.
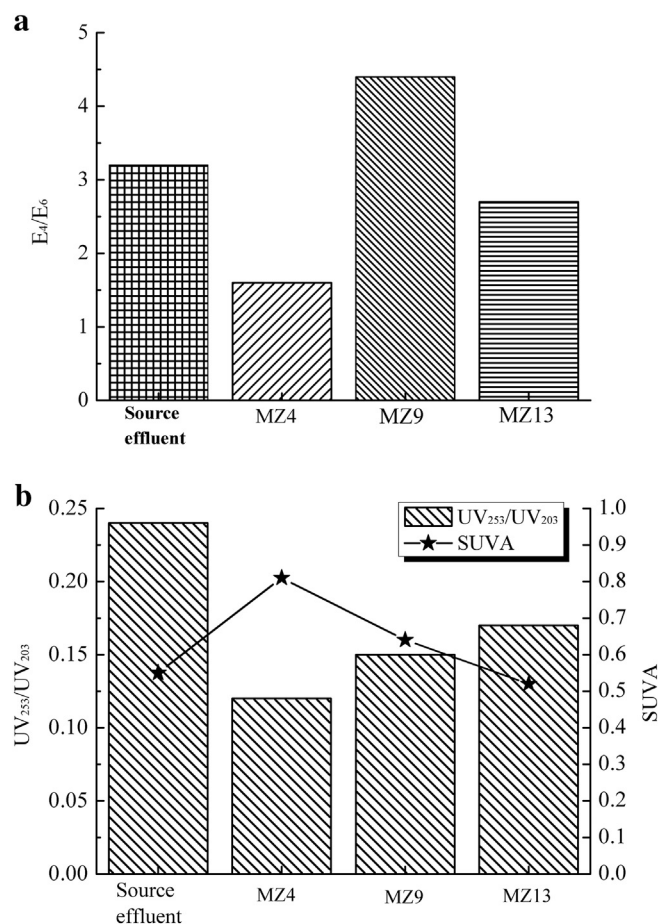
Fig. 7. (a) E_4/E_6 analysis for UV_{253}/UV_{203} and (b) SUVA analyses of effluent treated by MZs.

fluorescence with different wavelengths. Generally, DOM in wastewater can be determined through the relationship between organic matter and fluorescence regional integration (FRI). Chen et al. (Chen et al., 2003) studied organic matter in wastewater using the FRI method, including region I and II (aromatic protein such as tyrosine, $\lambda_{Ex}/\lambda_{Em}$ = 220–250 nm/280–380 nm), region III (fulvic-like, $\lambda_{Ex}/\lambda_{Em}$ = 220–250 nm/380–480 nm), region IV (soluble microbial by-product-like material, $\lambda_{Ex}/\lambda_{Em}$ = 250–280 nm/290–380 nm), and region V (humic-acid-like organics, $\lambda_{Ex}/\lambda_{Em}$ = 250 nm/380–480 nm) organic matter.

As shown in Fig. 6, all organic compounds in the effluent, including aromatic protein, fulvic-acid-like matter, soluble microbial by-product-like matter and humic-acid-like matter, decreased significantly after treated using MZs. In the source effluent, organic compounds mainly contain fulvic-like matter, soluble microbial by-product-like matter, and humic acid-like matter. After treatment by MZ4, most of the organics were recovered except a small amount of soluble microbial by-product-like material, and the treated effects from MZ9 and MZ13 were a little worse than MZ4.

3.3.3. E4/E6, UV₂₅₃/UV₂₀₃, and SUVA analysis of effluent treated by MZs

The E_4/E_6 value reflects the relative molecular weight of organic matter in wastewater. There is a larger proportion of low-molecular-weight organic matter in wastewater when the E_4/E_6 value is greater; however, there is a larger macromolecular organic proportion when the E_4/E_6 value is smaller (Yang, 1981; Zalba et al., 2016). Fig. 7(a) shows that the E_4/E_6 value changed significantly after treatment by MZs. In particular, more low-molecular-weight organic matter was recovered after treatment by MZ4 and MZ13, indicating that there is better bio-stability for the treated effluent.
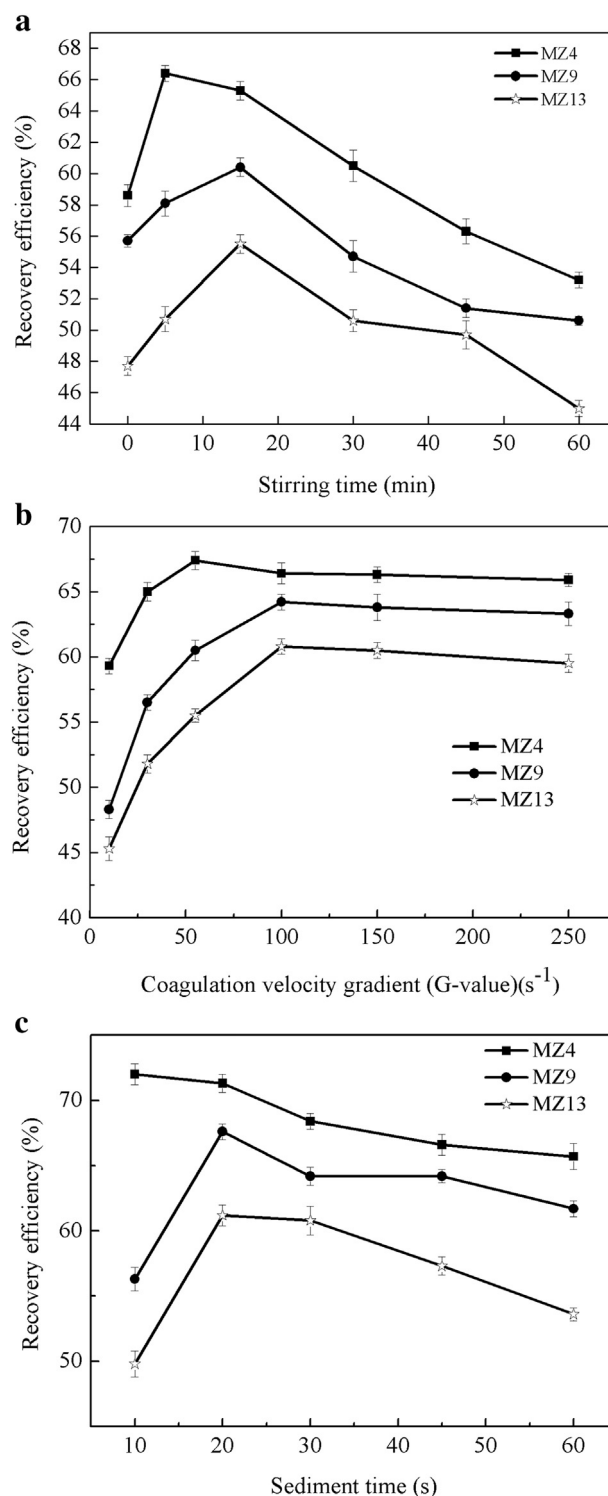

Fig. 8. Influence of (a) rapid stir time, (b) mixing intensity (G-value), and (c) sedimentation time on the COD recovery efficiency of the experiments.

The UV_{253}/UV_{203} value can reflect the substitution degree of —OH, —COOH, —C═O, and lipids to aromatic rings, and there is a greater tendency to produce disinfecting by-products when the substitution degree is greater. The SUVA not only reflects the aromatic and double-bond properties (e.g., humic substances) of dissolved organic matter in water but is also closely related to the formation potential of halogenated products (e.g., chloroform) (Ates et al., 2007; Vrijenhoek et al., 1998). As shown in Fig. 7(b), the UV_{253}/UV_{203} value decreased evidently after treatment by MZs, and the SUVA value increased after treatment

by MZ4 and MZ9, indicating that the generation potential of disinfecting byproducts or halogenated products was reduced after treatment by MZs when the chlorination disinfecting treatment of the effluent was carried out.

3.4. Condition optimization of effluent organic advanced recovery batch experiments

Based on the two steps of the batch experiments, the stirring time, turbulent G value, and sedimentation time were optimized, and the results are shown in Fig. 8. Fig. 4 shows that a dose of MZs (Fe$_2$(SO$_4$)$_3$-based MZs, Al$_2$(SO$_4$)$_3$-based MZs, ZnSO$_4$-based MZs) of 2 g·L^{-1} allowed the highest COD recovery efficiency. Therefore, the MZ dose used in other operating condition optimization experiments was chosen to be 2 g·L^{-1}. When the sedimentation time was set to be 20 min, as shown in Fig. 8(a), the most suitable stirring times for the MZ4, MZ9, and MZ13 samples were found to be 5 min, 15 min, and 15 min, respectively. Under the optimized stirring time condition, as shown in Fig. 8 (b), the most suitable stirring speeds (G value) for the MZ4, MZ9, and MZ13 samples were found to be 50 s^{-1}, 100 s^{-1}, and 250 s^{-1}, respectively. Moreover, under the optimized stirring time and speed conditions, as shown in Fig. 8(c), the most suitable sedimentation times for the MZ4, MZ9, and MZ13 samples were found to be 10 min, 20 min, and 20 min, respectively. Therefore, the highest COD recovery efficiency for MZ4, MZ9, and MZ13 under the optimized operating conditions, including the stirring time, stirring speed, and sedimentation time reached 72%, 67.6%, and 61.2%, respectively. During each condition optimization (stirring time, stirring speed, and sedimentation time), it was observed that MZ4, MZ9, and MZ13 indicated a similar tendency to recover organic matter from the effluent, but MZ4 had the best recovery efficiency. This may be because MZ4 had the larger specific surface area and higher zeta potential value compared with MZ9 and MZ13 (Table 1 and Fig. 1). According to AWWA (American Water Works Association (AWWA) and American Society of Civil Engineering (ASCE), 2012), the turbulent G values are 600–1000 s^{-1} in general coagulation tests, while MZs only required 55–250 s^{-1}, which demonstrated a large energy-saving potential for the application.

The stirring step in the traditional coagulation experiment includes rapid stirring and slow stirring (Matilainen et al., 2010; Komatsu, 2005). However, only one-step stirring was employed in the present study, mainly due to the abscission of the chemical coagulant from zeolite. In addition, the dispersing speed of the MZs was found to be remarkably high in wastewater, which may substitute for the fast stirring step. The coagulation and adsorption processes were often used as the recovery of organic matter from wastewater (Volk et al., 2000; Edzwald and Benschoten, 1990; Gu et al., 1994); however, the traditional coagulation agents and natural adsorbents contributed to low recovery efficiency of organic matter from wastewater (Suhas et al., 2007; Argun and Dursun, 2008). In our study, after the natural zeolite was loaded with the traditional coagulation agents, the COD recovery efficiency from wastewater was improved. This may be because the MZs simultaneously experienced the adsorption and coagulation effects.

3.5. Mechanism of organic matter recovery from effluent by MZs

Based on the above experimental results, the proposed mechanism for the organic recovery by MZ was shown in Fig. 9. When the chemical coagulant was used for organic recovery alone, the metal ions of the chemical coagulant formed a metal/metal oxide mixture in the water sample (positive charge) and recovered the organic substance (negative charge) through the coagulation effect. However, the efficiency was low because the metal/metal oxide mixture was not sufficiently dispersed in the water sample and could not effectively work in organic matter. Similarly, raw natural zeolite (negatively charged) has the ability to recover organics through the effect of adsorption due to its large specific surface area and good dispersity in water. However, the results showed that the organic recovery ability of raw natural zeolite was low, as well. Therefore, the organic recovery effect was improved when the metal ions were loaded onto the raw zeolite, reaching an organic recovery efficiency of 72%. The mechanism was considered in two ways: (1) the first way was the coagulation effect of zeolite surface metals (Fig. 9a), which could be identified by Figs. 1 and 3. That is to say, the metals loaded onto the surface of natural zeolite contributed to a good coagulation effect. This process is much more efficient than the use of chemical coagulant alone because the metal/metal oxide mixture is more uniformly distributed in the water sample due to the good dispersity of the zeolite; (2) the second way was the physical and chemical
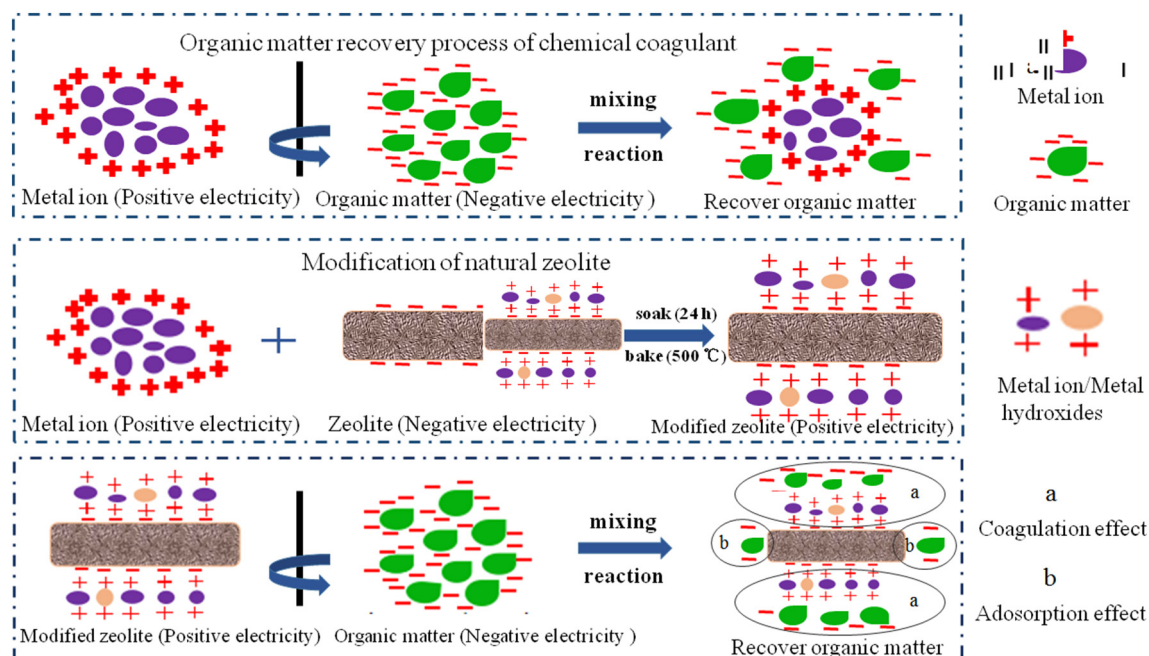

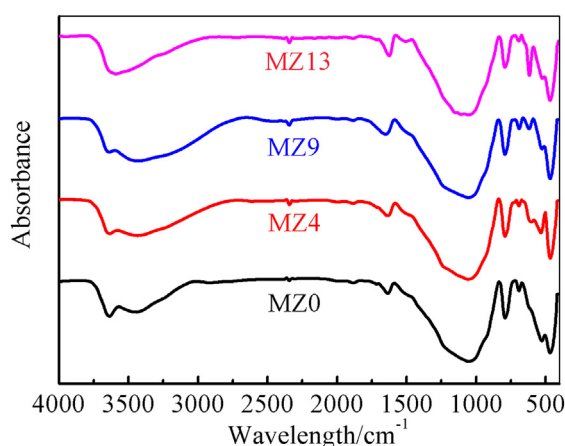**Fig. 9.** Proposed recovery mechanism of COD from effluent by MZs.

Fig. 10. Infrared spectrogram of natural raw zeolite and MZs.

adsorption effect (Fig. 9b), which could be identified by the large specific surface area (Table 1 and Fig. 1) and the result of the infrared spectrogram (Fig. 10). Physical adsorption worked based on the large specific surface area and positive charge of the MZ, and chemical adsorption worked based on the hydrogen bond and π—π bond between the MZ and organics. Fig. 10 showed that the infrared spectrogram for MZs was consistent with that of natural raw zeolite, suggesting that the functional groups on the zeolite (e.g., —OH at 3600 cm^{-1}, Si—O at 950–1200 cm^{-1} and 750–850 cm^{-1}, Al—O at 650–750 cm^{-1}) did not change significantly. The absorbents with the —OH group were reported to adsorb organic matter with —OH group or benzene ring through the hydrogen bond and π—π bond (Levine et al., 1991).

3.6. Operation mode of technological process in practice

The MZs allowed the organic recovery from the effluent with a recovery efficiency of >60% based on the process condition optimization, showing a great potential for application. When they will be used in practice, the technological process could be realized through coagulation and sedimentation operation (CSO) mode in a settling tank, or through filtration operation (FO) mode in a fixed-bed filtration apparatus. In the CSO mode, a high organic recovery efficiency can be achieved due to sufficient coagulation reaction, but the MZs are advised not to be regenerated or recycled due to high regenerating or recycling cost. Compared with the SCO mode, the organic recovery efficiency may decreased in the FO mode, but the service life of the MZs can be prolonged through regular backwashing operation.

4. Conclusions

The following conclusions could be drawn from this study of the modification of natural zeolite and its application to the advanced recovery of organic matter from an ultra-short-SRT activated sludge process effluent.

(1) Three types of chemical coagulants were successfully loaded onto the surface of natural zeolite. The specific surface area of the MZ decreased, but some metal ions/metal oxides were loaded onto the surface of nature zeolite, and the zeta potential increased significantly.

(2) Compared with the chemical coagulant and natural zeolite used, the organic recovery efficiency from the effluent by the MZs improved, and after the optimization, the organic recovery efficiency by the MZ4 (Zeolite:Fe$_2$(SO$_4$)$_3$ = 4:1), MZ9 (Zeolite:Al$_2$(SO$_4$)$_3$ = 4:1), and MZ13 (Zeolite:ZnSO$_4$ = 2:1) reached 72.0%, 67.6%, and 61.2%, respectively. Moreover, the MZs allowed significant dissolved organic matter (SCOD) recovery from the

effluent. The SCOD recovery efficiencies for MZ4, MZ9, and MZ13 were 44.8%, 44.3%, and 39.4%, respectively.

(3) The water quality analysis after the recovery experiments showed that the generation potential of disinfecting by-products or halogenated products was reduced in the treated effluent by the MZs.

(4) The mechanism can be considered in two ways: the coagulation effect of zeolite surface metals and the physical and chemical adsorption effects, based on the hydrogen bond and π—π bond between the MZ and organic matter.

References

Alver, E., Metin, A.Ü., 2012. Anionic dye removal from aqueous solutions using modified zeolite: adsorption kinetics and isotherm studies. Chem. Eng. J. 200-202 (34), 59–67. https://doi.org/10.1016/j.cej.2012.06.038.

American Water Works Association (AWWA), American Society of Civil Engineering (ASCE), 2012. Mixing, coagulation, and flocculation. In: Randtke, S.J., Horsley, M.B. (Eds.), Water Treatment Design, fifth ed. McGraw Hill, American Water Works Association and American Society of Civil Engineering, New York.

Argun, M.E., Dursun, S., 2008. A new approach to modification of natural adsorbent for heavy metal adsorption. Bioresour. Technol. 99 (7), 2516–2527. https://doi.org/10.1016/j.biortech.2007.04.037.

Ates, N., Kitis, M., Yetis, U., 2007. Formation of chlorination by-products in waters with low SUVA–correlations with SUVA and differential UV spectroscopy. Water Res. 41 (18), 4139–4148. https://doi.org/10.1016/j.watres.2007.05.042.

Bowen, E.J., Dolfing, J., Davenport, R.J., Read, F.L., Curtis, T.P., 2014. Low-temperature limitation of bioreactor sludge in anaerobic treatment of domestic wastewater. Water Sci. Technol. 69 (5), 1004–1013. https://doi.org/10.2166/wst.2013.821.

Camacho, L.M., Deng, S., Parra, R.R., 2010. Uranium removal from groundwater by natural clinoptilolite zeolite: effects of pH and initial feed concentration. J. Hazard. Mater. 175 (1), 393–398. https://doi.org/10.1016/j.jhazmat.2009.10.017.

Chen, Y., Senesi, N., Schnitzer, M., 1977. Information provided on humic substances by E4/E6 ratios. Soil Sci. Soc. Am. J. 41 (2), 352–358. https://doi.org/10.2136/sssaj1977.03615995004100020037x.

Chen, W., Westerhoff, P., Leenheer, J.A., Booksh, K., 2003. Fluorescence excitation-emission matrix regional integration to quantify spectra for dissolved organic matter. Environ. Sci. Technol. 37 (24), 5701–5710. https://doi.org/10.1021/es034354c.

Edzwald, J.K., Benschoten, J.E.V., 1990. Aluminum Coagulation of Natural Organic Matter [M]//Chemical Water and Wastewater Treatment. Springer Berlin Heidelberg, pp. 341–359 https://doi.org/10.1007/978-3-642-76093-8_22.

Fortin, D., Langley, S., 2005. Formation and occurrence of biogenic iron-rich minerals. Earth-Sci. Rev. 72, 1):1–19. https://doi.org/10.1016/j.earscirev.2005.03.002.

Ge, H.Q., Batstone, D.J., Keller, J., 2013. Operating aerobic wastewater treatment at very short sludge ages enables treatment and energy recovery through anaerobic sludge digestion. Water Res. 47 (17), 6546–6557. https://doi.org/10.1016/j.watres.2013.08.017.

Ge, H., Batstone, D.J., Keller, J., 2015. Biological phosphorus removal from abattoir wastewater at very short sludge ages mediated by novel PAO clade Comamonadaceae. Water Res. 69, 173–182. https://doi.org/10.1016/j.watres.2014.11.026.

Gu, B., Schmitt, J., Chen, Z., Liang, L., Mccarthy, J.F., 1994. Adsorption and desorption of natural organic matter on iron oxide: mechanisms and models. Environ. Sci. Technol. 28 (1), 38. https://doi.org/10.1021/es00050a007.

Gupta, V.K., Carrott, P.J.M., Ribeiro Carrott, M.M.L., Suhas, 2009. Low-cost adsorbents: growing approach to wastewater treatment—a review. Crit. Rev. Environ. Sci. Technol. 39 (10), 783–842. https://doi.org/10.1080/10643380801977610.

Hudson, N., Baker, A., Reynolds, D., 2010. Fluorescence analysis of dissolved organic matter in natural, waste and polluted waters—a review. River Res. Appl. 23 (6), 631–649. https://doi.org/10.1002/rra.1005.

Jimenez, J.A., Motta, E.J.L., Parker, D.S., 2003. Kinetics of removal of particulate COD in the activated sludge process. Proc. Water Environ. Fed., 759–780 https://doi.org/10.2175/193864703784755823.

Kirby, B.J., H. Jr., E., 2010. Zeta potential of microfluidic substrates: 1. Theory, experimental techniques, and effects on separations. Electrophoresis 25 (2), 187–202. https://doi.org/10.1002/elps.200305754.

Komatsu, K., 2005. Characterization of dissolved organic matter (DOM) removed by iron coagulation using spectrofluorimetry and pyrolysis GC/MS analysis. J. Water Supply 54 (3), 157–163. https://doi.org/10.2166/aqua.2005.0015.

Korshin, G.V., Li, C.W., Benjamin, M.M., 1997. Monitoring the properties of natural organic matter through UV spectroscopy: a consistent theory. Water Res. 31 (7), 1787–1795. https://doi.org/10.1016/s0043-1354(97)00006-7.

Levine, A.D., Tchobanoglous, G., Asano, T., 1991. Size distributions of particulate contaminants in wastewater and their impact on treatability. Water Res. 25 (8), 911–922. https://doi.org/10.1016/0043-1354(91)90138-G.

Matilainen, A., Vepsäläinen, M., Sillanpää, M., 2010. Natural organic matter removal by coagulation during drinking water treatment: a review. Adv. Colloid Interf. Sci. 159 (2), 189–197. https://doi.org/10.1016/j.cis.2010.06.007.

Mccarty, P.L., Jaeho, B., Jeonghwan, K., 2011. Domestic wastewater treatment as a net energy producer-can this be achieved? Environ. Sci. Technol. 45 (17), 7100–7106. https://doi.org/10.1021/es2014264.

Mcknight, D.M., Boyer, E.W., Westerhoff, P., Doran, P.T., Kulbe, T., 2001. Spectrofluorometric characterization of dissolved organic matter for indication of precursor organic material and aromaticity. Limnol. Oceanogr. 46 (1), 38–48. https://doi.org/10.4319/lo.2001.46.1.0038.

Meerburg, F.A., Boon, N., Winckel, T.V., Pauwels, K.T.G., Vlaeminck, S.E., 2016. Live fast, die young: optimizing retention times in high-rate contact stabilization for maximal recovery of organics from wastewater. Environ. Sci. Technol. 50 (17), 9781–9790. https://doi.org/10.1021/acs.est.6b01888.

Minato, J., Kim, Y.Jong., Yamada, H., Watanabe, Y., Tamura, K., Yokoyama, S., Cho, S.B., Komatsu, Y., Stevens, G.W., 2004. Alkali-hydrothermal modification of air-classified Korean natural zeolite and their ammonium adsorption behaviors. Sep. Sci. Technol. 39 (16), 3739–3751. https://doi.org/10.1081/ss-200041135.

Moreno, N., Querol, X., Ayora, C., Pereira, C.F., Janssen-Jurkovicovă, M., 2001. Utilization of zeolites synthesized from coal fly ash for the purification of acid mine waters. Environ. Sci. Technol. 35 (17), 3526–3534. https://doi.org/10.1021/es0002924.

Suhas, Carrott, P.J., Carrott, M.M.R., 2007. Lignin–from natural adsorbent to activated carbon: a review. Bioresour. Technol. 98 (12), 2301–2312. https://doi.org/10.1016/j.biortech.2006.08.008.

Volk, C., Bell, K., Ibrahim, E., Verges, D., Amy, G., Lechevallier, M.W., 2000. Impact of enhanced and optimized coagulation on removal of organic matter and its biodegradable fraction in drinking water. Water Res. 34 (12), 3247–3257. https://doi.org/10.1016/s0043-1354(00)00033-6.

Vrijenhoek, E.M., Childress, A.E., Elimelech, M., Tanaka, T.S., Beuhleret, M.D., 1998. Removing particles and THM precursors by enhanced coagulation. Journal 90 (4), 139–150. https://doi.org/10.1002/j.1551-8833.1998.tb08417.x.

Wang, B., Wu, H., Yu, L., Xu, R., Lim, T., Lou, X.W., 2012. Template-free formation of uniform urchin-like α-FeOOH hollow spheres with superior capability for water treatment. Adv. Mater. 24 (8), 1111–1116. https://doi.org/10.1002/adma.201104599.

Weishaar, J.L., Aiken, G.R., Bergamaschi, B.A., Fram, M.S., Fujii, R., Mopper, K., 2003. Evaluation of specific ultraviolet absorbance as an indicator of the chemical composition and reactivity of dissolved organic carbon. Environ. Sci. Technol. 37 (20), 4702–4708. https://doi.org/10.1021/es030360x.

Yang, T.W., 1981. An alternate interpretation about the plots of E4/E6 ratio vs. free radical concentrations for fulvic acid. Soil Sci. Soc. Am. J. 45 (4), 831–832. https://doi.org/10.2136/sssaj1981.03615995004500040035x.

You, X., Valderrama, C., Cortina, J.L., 2017. Simultaneous recovery of ammonium and phosphate from simulated treated wastewater effluents by activated calcium and magnesium zeolites. J. Chem. Technol. Biotechnol. 92 (9). https://doi.org/10.1002/jctb.5249.

Zalba, P., Amiotti, N.M., Galantini, J.A., Pistola, S., 2016. Soil humic and fulvic acids from different land-use systems evaluated by E4/E6 ratios. Commun. Soil Sci. Plant Anal. 47 (13–14), 1675–1679. https://doi.org/10.1080/00103624.2016.1206558.