Nitrate-Reducing Magnetic Hybrid Coagulant for Rapid and Advanced Wastewater Treatment and its Mechanistic Investigation

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Abstract

Dissolved contaminants (NO_3^--N, etc.) in municipal sewage effluent and polluted water resources need to be further removed, but common advanced water treatment technologies usually have unsatisfactory performance and large process footprints. Magnetic seeding coagulation (MSC) has a rapid settling speed; however, it is less effective for removing dissolved contaminants and cannot recovers effective components. Herein, a novel covalently bound magnetic hybrid coagulant (MHC) was synthesized and used to treat secondary biological effluent. MHC settling time was 2/3 shorter than traditional MSC and showed high removal efficiencies for conventional coagulation indicators and dissolved contaminants such as NO_3^--N and organic nitrogen. The NO_3^--N removal mechanisms included NO_3^--N capture through the electrostatic attraction and the collision efficiency enhancement. MHC integral structure can be bioregenerated for multiple cycles. Because of its effectiveness in removing dissolved contaminants rapidly, MHC has potential application in advanced water treatment, especially in land-scarce areas.

Introduction

When municipal sewage and polluted natural waters have been treated by aerobic biological techniques, some dissolved contaminants such as nitrogen, phosphorus, and organic pollutants will not be fully removed and thus remain in the effluent.[1] Nitrogen-containing contaminants mainly exist in the form of NO_3^--N.[2] After being discharged into natural water bodies, these contaminants may pose a threat to ecological safety and human health.[3] Advanced water treatment technologies including biological denitrification,[4] adsorption,[5] and ion exchange[6] usually exhibit unsatisfactory removal efficiencies and occupy a large land area. In many urban areas, high population density leaves almost no space to adopt additional advanced water treatment technologies. Therefore, developing a small-footprint, effective water treatment technology is required to control water pollution in urban areas.

Coagulation is one of the most widely-used technologies for conventional water treatment and is also the basis for some of the most-preferred advanced treatment processes.[7] Magnetic seeding coagulation (MSC) has attracted attention because it settles faster than conventional coagulations,[8] resulting in smaller treatment footprints. MSC is generally carried out by adding magnetic seeds (usually Fe_3O_4 particles), inorganic coagulants (polyaluminum salt/polyferric salt), and/or organic polymer flocculants (usually polyacrylamide) to water.[9] Contaminants, coagulants, and magnetic seeds mix to form magnetic flocs, which quickly aggregate and precipitate with an applied magnetic field. The magnetic seeds can be recovered after magnetic separation.[10] Similar to conventional coagulation, MSC can effectively remove particulate and colloidal pollutants, but it shows lower efficacy in removing dissolved contaminants with higher risks, including NO_3^--N and dissolved organic nitrogen (DON).[11, 12]

In our previous work, we prepared inorganic-organic covalently bound hybrid coagulants with a capacity to remove typical dissolved contaminants by introducing organic groups into inorganic coagulants.[13, 14] If

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special functional groups can be introduced into magnetic seeding components, the novel magnetic coagulants have the potential to remove dissolved contaminants that are difficult to be removed by conventional coagulants. Covalent bonds between magnetic components and coagulants are beneficial because they form tighter magnetic flocs, which precipitate more easily and further shorten the settling time. In addition, the integral magnetic coagulants can be recovered, overcoming the disadvantage of MSC, which can recover the magnetic seeds and not the coagulants (Figure 1).

In this study, we synthesized a novel inorganic-organic covalently bound magnetic hybrid coagulant (MHC) in one step by using silane coupling agents with quaternary ammonium groups and iron salts. Secondary biological effluent was used as raw water to test the performance of MHC. We focused on removal efficacy and mechanism of nitrogen-containing contaminants, including NO_3^--N and DON. The NO_3^--N adsorption site and removal pathway were elucidated by molecular dynamics (MD) simulations. The effect of applied magnetic field strength on NO_3^--N removal was modeled using MATLAB (MathWorks, Natick, MA, USA). The feasibility of MHC recovery and regeneration was also explored.

Experimental Section

Materials

Secondary biological effluent and synthetic aqueous solution were used in experiments. More details are in the Supporting Information (SI). Ferric chloride ($FeCl_3 \cdot 6H_2O$), ferrous chloride ($FeCl_2 \cdot 4H_2O$), polyferric chloride (PFC), polyacrylamide (PAM), ferroferric oxide (Fe_3O_4), potassium nitrate (KNO_3), and potassium sulfate (K_2SO_4) were obtained from Sigma-Aldrich (St. Louis, USA). 3-(trimethoxysilyl) propyl-n-octadecyldimethyl ammonium chloride (TPODAC) was purchased from Bailingwei (Beijing, China). Potassium dihydrogen phosphate (KH_2PO_4) was purchased from Macklin (Shanghai, China).

MHC synthesis

MHC was synthesized by combining co-precipitation and slow alkalinity titration method into one step. First, 150 mL deionized water was added to a three-necked flask and deoxygenated by bubbling N_2 gas for 5 min. Under a nitrogen atmosphere, 32.5 g $FeCl_3 \cdot 6H_2O$ and 4.8 g $FeCl_2 \cdot 4H_2O$ were added, and the mixture was stirred at room temperature for 5 min until dissolved. Then the mixture was gradually heated to 80 , and TPODAC was added at the Si/Fe molar ratio of 1/6. The mixture was titrated by 1 mol/L NaOH (270 mL) for 3 h under rapid stirring. After cooling to room temperature, the product aged for 12 h to obtain MHC.

Jar tests

Coagulation performance was evaluated using a programmable TA6-1 jar test apparatus (Wuhan, China). MHC or conventional coagulants were added to raw water, mixed rapidly at 250 rpm for 1.5 min, mixed slowly at 50 rpm for 20 min, and settled for 30 min with applied magnetic field. For MSC, Fe_3O_4 and PFC were added before stirring, and PAM was added after rapid mixing. During the settling period, samples were collected from 2 cm below the water surface at regular intervals. Turbidity was analyzed, and then samples were filtered through 0.22 μm nylon membrane filters before analyzing TP, NO_3^--N, UV_{254}, dissolved organic matter (DOM), and N-containing compounds in DOM. The secondary biological effluent was used to explore the coagulation performance, and the synthetic aqueous solution was used to evaluate factors affecting coagulation.

Analytical methods

The morphology and chemical structure of MHC were analyzed by transmission electron microscopy (TEM; Hitachi, H-9000NAR, Tokyo, Japan) and Fourier-transform infrared spectroscopy (FTIR; Nicolet iS50, Madison , USA), respectively. TP, NO_3^--N, and UV_{254} were determined by an ultraviolet-visible 1800 spectrophotometer (Shimadzu, Kyoto, Japan). Turbidity was measured by a turbidimeter (2100 N Turbidimeter, Hach, Loveland, USA). To measure DOM and DON concentration and type in the coagulated water by MHC, a Bruker Apex (Madison, USA) ultra Fourier-transform ion cyclotron resonance mass spectrometer (FT-ICR MS) equipped with a 9.4 T superconducting magnet was used. More details are in SI.

MD simulations

Partial charges for MHC atoms and NO_3^- ions were obtained from density functional theory (DFT) calculations using Gaussian 09 program. The Becke three parameters hybrid exchange-correlation functional (B3LYP)[15] and the standard Gaussian-type basis set 6-311 G* were employed. All other force field parameters for atoms were extracted from PLOS-AA force field[16]. The initial configuration was solvated into a cubic water box with 63 Å on each side, containing 8,000 water molecules. The simple point charge (SPC) water model as explicit solvent was used for solvation[17]. Then 15 Cl^- were added to balance system charges. The system energy was minimized for 500 steps using steepest descending method. The initial velocities were assigned to produce a Maxwell distribution at 298 K. After a 0.2 ns equilibrium, a 1 ns simulation was carried out with the NO_3^- ion frozen so that the MHC carbon chains would reach a balance. Finally, this system perform a 3 ns MD simulation. More details are in the SI.

MHC bioregeneration

Donnan dialysis coupled with bio-denitrification was used to regenerate MHC. Before bioregeneration, MHC was saturated by NO_3^--N in repeated coagulation processes. Then the bioregeneration was carried out at room temperature and under anaerobic conditions in a Donnan dialysis setup. The setup was made of Plexiglas (Beijing, China), divided into two chambers by a JAM-I homogeneous anion exchange membrane. The spent MHC was added into the desorption chamber. Sludge, 0.3 mol/L NaCl, and 12.9 mol/L ethanol (as carbon source) were added to the stripping chamber. The solution pH in both chambers was adjusted to 7.0 $\pm$ 0.2. The solution was stirred continuously at 400 rpm. Throughout the 30 h regeneration process, samples were collected at regular intervals from both chambers and filtered through 0.22 μm nylon membranes for analysis of residual NO_3^--N. The sludge cultivation method is in the SI.

Results and Discussion

MHC synthesis and characterization

The MHC synthesis steps and structure are shown in Figure 2. Briefly, the organic-inorganic covalently bound MHC was synthesized in one step by mixing Fe^{3+}, Fe^{2+}, and silane coupling agents in proportion, slowly titrating alkalinity, and ageing. The TEM image (Figure 3a) shows that MHC has an irregular shape. Comparing to the Fe_3O_4 TEM image (Figure 3b), it can be seen that the black component in MHC is Fe_3O_4. The periphery of Fe_3O_4 is the highly-crosslinked polymer of the organic silane coupling agent. It shows that MHC is a cross-linked integral structure consisting of magnetic components and organic compounds.

The presence of silane coupling agents will form Si-O-Si bonds. Generally, the asymmetric stretching peak of Si-O-Si is at 1046 cm^{-1}.[18] Shown in the infrared absorption spectrum of MHC (Figure 3c), there is a clear absorption peak at 1028 cm^{-1}. It may be related to red shift of the Si-O characteristic peak induced by Fe replacing Si in Si-O-Si.[19] This indicates that the inorganic Fe components in MHC are coupled to organic components through covalent bonds of Si-O-Fe, which is different from MSC that simply physically mixes magnetic seeds and coagulants. Other absorption wavenumbers are listed in Table S1. In addition, MHC has a high zeta potential (>25 mV) over a wide pH range of 3–11 (Figure S1), which can be attributed to the introduction of positively-charged quaternary ammonium groups.

Coagulation performance

Secondary biological effluent from a municipal wastewater treatment plant was used as raw water (the raw water quality is shown in Table S2) to test the coagulation performance. The MHC settling time (5 min) was shorter than conventional coagulations (20 min) (Figure S2, close to previous reported results[8, 20]). The MHC settling time was also shorter than MSC (15 min), especially for UV_{254}, TP, and NO_3^--N (Figure 4 b, c, d). The settling time of the two coagulants for turbidity removal is similar, which is because particulate contaminants are easier to aggregate into large complexes and can quickly precipitate under gravity. The rapid settling speed of MHC can be attributed to the covalent bonds between magnetic components and coagulants. Magnetic flocs formed when MHC combined with contaminants, which settled rapidly by both magnetic force and gravity. Moreover, the MHC flocs have higher density, which are easier to settle than

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flocs formed by physical mixing. For MSC, however, the lack of covalent bonds means some flocs are not combined with magnetic seeds. These flocs have smaller density and can only settle slowly by gravity rather than by magnetic force.

Turbidity removal was high for both MHC and MSC (>97.1%) (Figure 4a). For UV_{254} and TP (Figure 4b, c), removal efficiency was much higher with MHC (78.3% for UV_{254}, 98.8% for TP and from 0.55 mg/L to 0.0065 mg/L) than MSC (67.5% for UV_{254}, 78.2% for TP and from 0.55 mg/L to 0.12 mg/L). The TP removal efficiency by MSC was relatively low, which may be related to the low initial TP concentration. More importantly, MSC (Figure 4d) and conventional coagulations (Figure S2) were comparatively ineffective for removing NO_3^--N, whereas NO_3^--N concentration decreased from 11.3 mg/L to 3.1 mg/L (72.2% removal) with MHC coagulation (Figure 4d). In conclusion, for contaminants that can be removed by traditional MSC, MHC had a higher removal efficiency and settling speed. MHC was also effective for removing contaminants that cannot be removed by conventional coagulations and traditional MSC (e.g., NO_3^--N).

We investigated DOM removal at the molecular level when using MHC. According to the element composition, DOM is divided into CHO, CHON, CHOS, and CHONS. After coagulation by MHC, above four types DOM decreased significantly, especially CHON compounds (Figure 5a). However, the relative abundance of CHON did not change obviously after conventional coagulants treatment (Figure S3). This shows that MHC is significantly different from conventional coagulants. MHC can remove DOM, especially DON that is resistant to conventional coagulants.

Van Krevelen diagrams[21] (see the SI for the Van Krevelen diagram method) were applied to further elucidate the performance of MHC for removal of DON with different element ratios. Based on the H/C and O/C element ratios, DON can be divided into seven compound classes, including lipids (Lip), aliphatic/proteins (Ali/Pro), lignins/carboxylic rich alicyclic molecules-like (CRAM), carbohydrates (Car), unsaturated hydrocarbons (UH), aromatic (Aro), and tannin (Tan). DON in raw water was distributed centrally in the CRAM region (Figure 5b), and the relative abundance of CRAM was the highest (Figure 5d), indicating that these components had a high contribution to the DON in the raw water. Other researches have had similar results.[22, 23] It may be related to CRAM's resistance to biodegradation and the refractory nature caused by the structural diversity found within CRAM and its substantial content of alicyclic rings and branching.[24] However, the dots in the CRAM region disappeared partially after MHC coagulation (Figure 5c), and the relative abundance reduced by about 2/3 (Figure 5d), revealing that MHC coagulation can effectively reduce the number of CRAM contaminants species and concentration of DON. Nitrogen-containing organic compounds are toxic, and various nitrogen compounds can be converted between each other, such as NO_3^--N and DON.[25, 26] MHC can effectively remove DON in water, reducing the possibility of DON transformation to NO_3^--N.

Factors affecting nitrate removal

We next studied influence factors in nitrate removal through MHC coagulation using synthetic aqueous solutions. The nitrate removal efficiency remained almost unchanged when initial NO_3^--N ranged from 15 to 25 mg/L (Figure 6a; all are above 69.2%), demonstrating that MHC is suitable for the treatment of wastewater with varying pollutant concentrations. Across the pH range of 5–9, there was no substantial effect on the NO_3^--N removal efficiency (Figure 6b). When pH > 10, the removal efficiency decreased substantially (Figure S4), which can be attributed to the competing adsorption of OH^-.

Using typical anions in natural water (i.e., sulfate and phosphate), we investigated the effect of competing ions on nitrate removal when using MHC. As molar ratio of sulfate and phosphate to NO_3^- increased, the NO_3^--N removal efficiency gradually decreased (Figure 6c). To further quantify the effect of competition, the selectivity coefficient $K_{NO_3^-/X^{n-}}$ (calculation formula is in SI) was applied to characterize the affinity of MHC to NO_3^- and coexisting ions. K values greater than one means that the affinity for NO_3^- is stronger than X^{n-}, lower than one means that the affinity for NO_3^- is weaker than X^{n-}. When phosphate and sulfate are present, the selectivity coefficients of MHC for NO_3^- are 3.19 and 0.77 respectively (Figure 6d), revealing that the affinity order of MHC for the three ions is phosphate < nitrate < sulfate.

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MHC has a stronger affinity for sulfate than nitrate. Sulfate contains more charges than nitrate, and the hydrated radius for sulfate (0.300 nm)[27] is smaller than nitrate (0.335 nm)[28], which are both beneficial for electrostatic interaction with quaternary ammonium. For the secondary biological effluent, the molar ratio of sulfate to nitrate is mostly lower than 1.5,[29-31] and the nitrate removal efficiency can still reach more than 65% (Figure 6c). Therefore, although sulfate will reduce nitrate removal to a certain extent when using MHC, sulfate has little effect on practical applications. MHC has weaker affinity for phosphate than nitrate, probably because phosphate Gibbs hydration energy (-1125.3 kJ/mol for HPO_4^{2-} and -465 kJ/mol for $H_2PO_4^-$, the two main form of phosphate under neutral pH conditions)[32, 33] are lower than nitrate Gibbs hydration energy (-306 kJ/mol)[33]. Thus phosphate only has a slight effect on the NO_3^--N removal. In conclusion, MHC has strong adaptability to the change of water quality.

Removal pathway of nitrate by MHC

NO_3^- was taken as an example to explore the mechanism of dissolved contaminants removal by MHC using MD. First, the adsorption site was determined by the relationship between the total interaction potential (V_{total}) and relative positions of MHC and NO_3^-. NO_3^- positions were classified into three categories according to V_{total}: strongly attracted (V_{total} < -80 kJ/mol, purple dots in Figure 7a, configuration i in Figure 7b), weakly attracted (-40 kJ/mol < V_{total} < 0, green dots in Figure 7a, configuration ii in Figure 7b) and almost no interaction (V_{total} = 0, yellow dots in Figure 7a, configuration iii in Figure 7b). It can be seen that NO_3^- that has strongest interaction with MHC was distributed around quaternary ammonium N atoms. The contact area with quaternary ammonium N atoms was large (S_{buried} > 1.5 nm^2) and the distance to the N plane was 0 (Figure 7a). However, NO_3^- have weak interaction with MHC were distributed around carbon chains. The above results show that the N atom of the positively-charged quaternary ammonium group is the main adsorption site, and the carbon chains only have very weak attraction to NO_3^-.

To investigate NO_3^- removal pathway and driving force, representative trajectory and time evolution of van der Waals (vdW) and electrostatic interaction energies between NO_3^- and quaternary ammonium N atom were analyzed. Electrostatic interaction energy changed rapidly with NO_3^- adsorption compared with vdW interaction energy (fluctuating at ~ 0), indicating that electrostatic attraction is the main driving force for adsorption. At t = 1000 ps, the electrostatic interaction energy decreased, but it immediately increased and fluctuated at ~ 0 (Figure 7c), which suggests that the electrostatic interaction at 1000 ps was weak and unstable. Configuration i in Figure 7e illustrates that NO_3^- was outside the methyl groups of quaternary ammonium at 1000 ps, which hindered the interaction of positive N atom and NO_3^-.

After t = 2000 ps, the electrostatic interaction energy decreased and stabilized at ~ -100 kJ/mol (Figure 7c). At the same time, hydrogen bonds between NO_3^- and coordinating water molecules decreased from ~ 7.9 (before 2000 ns) to ~ 6.7 (after 2000 ns) (Figure 7d), indicating NO_3^- dehydrates during adsorption. As shown in Figure 7e, NO_3^- will first adjust its configuration to enter into the methyl groups (Configuration ii) and then will interact closely with the quaternary ammonium N atom (Configuration iii) to achieve stable adsorption. The above results revealed that during NO_3^- removal, NO_3^- will dehydrate and penetrate methyl groups of quaternary ammonium and interact strongly with quaternary ammonium N atom by electrostatic attraction.

Removal mechanism by magnetic components

With the magnetic field, NO_3^--N removal was 71.3%, while without magnetic field, NO_3^--N removal was 58.1% (Figure 8a). The mechanism of enhancing NO_3^--N removal under magnetic field was explored using MATLAB. When the distance between magnetic particles was constant, the greater the applied magnetic field intensity, the greater the interaction potential. Furthermore, the interaction potential between magnetic particles with magnetic field was five orders of magnitude higher than that without magnetic field (Figure 8b). Without magnetic field, the particle interactions are only vdW and electrostatic . With the applied magnetic field, an additional magnetic interaction is generated among magnetic particles[34], which increases the total interaction potential. According to the collision efficiency formula and the classical flocculation model (SI), the higher the interaction potential, the higher the interparticle collision efficiency α_{ij} and the

coagulation efficiency.[35] Therefore, the applied magnetic field can increase the interaction potential between particles, thereby enhancing the contaminant removal when using MHC.

MHC bioregeneration

Donnan dialysis combined with bio-denitrification was applied to regenerate MHC (Figure 9a). Donnan dialysis (the principles are in SI) is a process that promotes migration of target ions across a membrane.[36] The transport of target ions is promoted by the electrochemical potential gradient caused by the ion composition on both sides of the membrane, while the transfer of co-ions is prevented by the ion exchange membrane. As shown in Figure 9b and c, during the regeneration process, the NO_3^--N concentration in the two chambers first increased, then decreased after ~ 5 hours, and reached equilibrium after 10 hours. It shows that NO_3^- was firstly desorbed from the MHC into the desorption solution, then transported across the membrane to the stripping solution driven by the electrochemical potential produced by NaCl, and finally denitrified by microorganisms. After three cycles of coagulation and regeneration, the NO_3^--N removal using MHC decreased from 72.2% to 61.8% (Figure 9d). This shows that the Donnan dialysis combined with bio-denitrification method can be used for MHC multiple regeneration cycles without significant reduction in contaminants removal efficiency. The method minimizes chemical reagent use and does not generate secondary high-concentration wastewater. The ion exchange membrane separates microorganisms from flocs, thereby preventing the microorganisms from attaching to the floc surface and thus avoid biofilm fouling.[37] Magnetic components and coagulant components are covalently bound in MHC, which allows effective recovery of the integral structure.

Conclusions

In order to achieve rapid and advanced wastewater treatment in areas with limited space, we synthesized a novel magnetic hybrid coagulant. MHC settling time was 2/3 shorter than traditional magnetic seeding coagulation. MHC improved the removal efficiency of contaminents that can be removed by traditional MSC and also efficiently removed dissolved contaminents that are difficult to remove using most conventional coagulants, especially NO_3^--N and DON. MHC peformed well over wide ranges of initial NO_3^--N concentration, pH, and coexisting ions, reducing the need for costly chemical pre-treatments. Although sulfate slightly reduced NO_3^--N removal, it has little effect on the practical water treatment porformance. The efficient NO_3^--N removal by MHC stems from the electrostatic adsorption of quaternary ammonium N atoms, which can promote nitrate dehydration and stable adsorption to quaternary ammonium N atoms. The applied magnetic field can also increase the interaction potential and collision efficiency between particles to promote the combination, precipitation, and removal of dissolved water contaminents such as NO_3^--N. In addition, components of used MHC can be recovered through magnetic separation and regenerated multiple times through Donnan dialysis combined with bio-denitrification. MHC can improve the effluent water quality with a short hydraulic retention time, threreby reducing treatment footprint compared with other technologies. As such, MHC has broad application potential in the land-scarce areas for treating black odorous water bodies, secondary biological effluent, and other similar water quality challenges.

Acknowledgments

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FIGURE CAPTIONS

Figure 1. Schematic illustration showing the structure, coagulation and regeneration of MHC.

Figure 2. Synthesis and structure of MHC.

Figure 3. TEM images of MHC (a) and Fe_3O_4 (b), and FT-IR spectra (c) of MHC and Fe_3O_4. Scale bars, 50 nm.

Figure 4. Turbidity (a), UV_{254} (b), TP (c) and NO_3^--N (d) removal after the coagulation of the secondary biological effluent using MHC and MSC as a function of settling time with coagulant dosage of 0.8 mmol/L as total Fe and PAM dosage in MSC is 0.4 mg/L.

Figure 5. The relative abundance of CHO, CHON, CHOS, and CHONS in the raw water and MHC coagulated water (a). Van Krevelen diagrams of CHON of the raw water (b) and MHC coagulated water (c) with dosage of 0.8 mmol/L as total Fe. Colored dots express the relative abundance. The black lines in Van Krevelen diagrams divide CHON to seven major classes. The bar diagram shows the relative abundance of seven classes of CHON in the raw water and MHC coagulated water (d).

Figure 6. Effect of initial NO_3^--N concentration (a), pH (b), and ions (c) on the removal of NO_3^- and selectivity coefficient of NO_3^- to phosphate and sulfate (d). MHC dose in c and d was 0.8 mmol/L as total Fe.

Figure 7. Interaction energy between NO_3^- and N atom of quaternary ammonium group at different relative positions (a). Nitrate positions during removal categorized by total interaction potential (b). Van der Waals and electrostatic interaction energy between nitrate and MHC (c). Number of H bonds between NO_3^- and coordinating water molecules during removal process (d). Snapshots of nitrate removal pathway by quaternary ammonium groups (e). O, red; N, dark blue; H, gray; C, green. Methyl group C atoms on quaternary ammonium N atoms in (a) were highlighted in light blue.

Figure 8. Nitrate removal using MHC with and without magnetic field (a). The MATLAB simulation of interaction potential energy between magnetic particles under different magnetic field strengths (b). The parameters used in the modeling process are in Table S3, and the raw water quality is shown in Table S2.

Figure 9. MHC regeneration process schematic (a). NO_3^--N concentration variations in the desorption solution (b) and stripping solution (c) during regeneration. Nitrate removal after repeated MHC regeneration (d).

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Figure 1. Schematic illustration showing the structure, coagulation and regeneration of MHC.

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Figure 2. Synthesis and structure of MHC.

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Figure 3. TEM images of MHC (a) and Fe_3O_4 (b), and FT-IR spectra (c) of MHC and Fe_3O_4. Scale bars, 50 nm.

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Figure 4. Turbidity (a), UV_{254} (b), TP (c) and NO_3^--N (d) removal after the coagulation of the secondary biological effluent using MHC and MSC as a function of settling time with coagulant dosage of 0.8 mmol/L as total Fe and PAM dosage in MSC is 0.4 mg/L.

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Figure 5. The relative abundance of CHO, CHON, CHOS, and CHONS in the raw water and MHC coagulated water (a). Van Krevelen diagrams of CHON of the raw water (b) and MHC coagulated water (c) with dosage of 0.8 mmol/L as total Fe. Colored dots express the relative abundance. The black lines in Van Krevelen diagrams divide CHON to seven major classes. The bar diagram shows the relative abundance of seven classes of CHON in the raw water and MHC coagulated water (d).

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Figure 6. Effect of initial NO_3^--N concentration (a), pH (b), and ions (c) on the removal of NO_3^- and selectivity coefficient of NO_3^- to phosphate and sulfate (d). MHC dose in c and d was 0.8 mmol/L as total Fe.

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Figure 8. Nitrate removal using MHC with and without magnetic field (a). The MATLAB simulation of interaction potential energy between magnetic particles under different magnetic field strengths (b). The parameters used in the modeling process are in Table S3, and the raw water quality is shown in Table S2.

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