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A novel combined process of MFPAC coagulation and mineralized refuse adsorption for landfill leachate pretreatment

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ABSTRACT

A novel composite coagulant of MFPAC was prepared from Fe_3O_4 nanoparticles and polyaluminum chloride (PAC). Landfill leachate was pretreated by MFPAC coagulation combined with mineralized refuse adsorption. Higher COD and color removals were achieved by using the MFPAC magnetic coagulant than by adding the coagulant PAC alone. Under the working conditions of 1:3 Fe_3O_4/PAC mass ratios, 1.5 g/L MFPAC dosage, and pH 7.5, the removal rates of COD and color reached 63% and 67%, respectively. Infrared spectra showed that MFPAC is a type of hydroxyl-containing ligand with a nano-Fe_3O_4 multi-core and a hydroxyl polymer of aluminum and iron that is similar complex valence and crystal structure as that of PAC. The effluent of MFPAC coagulation was further treated using mineralized refuse adsorption. Under the working conditions of <2 mm particle size of mineralized refuse, 700°C roasting temperature, 40 mg/L adsorbent dosage, and pH 9.0, the removal rates of COD and ammonia nitrogen reached up to 57% and 68%, respectively, after 12 h of treatment. Infrared spectra analysis revealed that OH, C=O, and C–O played key roles in the adsorption process. After the landfill leachate was treated with the combined process, the removal rates of COD, color, and ammonia nitrogen were enhanced to 84%, 80%, and 74%, respectively. The encouraging results demonstrated that the combined process could provide a viable alternative to the pretreatment of landfill leachate.

Keywords: Adsorption; Coagulation; Landfill leachate; MFPAC; Mineralized refuse

1. Introduction

Landfill leachate contains huge amounts of organic matter, ammonia nitrogen, heavy metal, and other pollutants. If not properly collected and safely disposed, these materials may become potential sources of pollution to groundwater and surface water. Given its unique advantages, particularly, in operating costs, over other treatment methods, biological technology has become the most preferred and most widely used approach for landfill leachate treatment [1]. However, biological degradation alone cannot treat landfill leachate efficiently, and the effluent of such treatment does not always meet the national discharge standards. In addition, during operation of landfills, the COD value and ammonium nitrogen concentration increase and the biodegradability of organic pollutants decreases, and meanwhile the C, N, P ratio becomes imbalanced [1,2]. These would lead to the biological technology being more difficult to effectively treat landfill leachate alone. Therefore, biodegradation is usually used in combination with other technologies for the treatment of landfill leachate since it is difficult to obtain a satisfactory treatment efficiency using individual treatment methods [3,4]. In general, with biological process considered the main procedure, other physiochemical and chemical processes are also used as pretreatment or in-depth treatment to form combined processes for landfill leachate disposal [5,6].

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Coagulation and flocculation is a core environmental protection technology that has a wide range of applications in water and wastewater treatment projects [7,8]. When combined with other appropriate technologies, coagulation and flocculation is a viable option for the treatment of various types of wastewater due to its simplicity and cost-effectiveness [9,10]. For example, this method has been used in the pre- or post-treatment of landfill leachate to enhance the biodegradability of the leachate or to remove residual recalcitrant matter [11,12]. When used in pretreatment, this approach can effectively reduce the COD, color, and other pollutants in the landfill leachate, thus providing favorable conditions for the subsequent biological technology. The increase in the performance of the coagulation stage seems to be a key factor in enhancing the overall leachate treatment efficiency. Such enhancements can be achieved through the use of more effective coagulants since the coagulation efficiency is fundamentally determined by the inherent properties of the coagulants [13].

With the rapid development of nanotechnology, magnetic nanoparticles have been widely applied in the field of water and wastewater treatment. Fe_3O_4 nanoparticles are a type of material characterized by having a larger specific surface area, exhibiting a stronger adsorption capacity, and easy separation [14]. Composite magnetic coagulants are considered to behave better than traditional coagulants since their magnetic components may improve the coagulation behaviors. Zhang et al. [15] successfully synthesized a novel ferromagnetic nanoparticle composited polyaluminum chloride (PAC). The experiment shows that the addition of Fe_3O_4 can not only effectively increase COD removal but also significantly accelerate the sedimentation rate of particles during coagulation. A study conducted by Jiang et al. [16] shows that the coagulation performance is significantly better when a new type of composite flocculant prepared by introducing Fe_3O_4 nanoparticles into polyferric chloride is applied to algae removal than when polyferric chloride is used alone. Fe_3O_4 nanoparticles can improve the floc density and settling performance, thereby enhancing the removal of *Microcystis aeruginosa*. Fe_3O_4 nanoparticles and an organic coagulant (chitosan or polyacrylamide) are combined to prepare the inorganic–organic composite coagulant that is applied to the wastewater treatment [17,18]. Combination of these materials has been found to generate a strong synergistic effect that significantly can improve the coagulation performance.

Although coagulation can considerably remove COD, color, and other pollutants, its removal on ammonia nitrogen is unsatisfactory. In landfill sites, refuse becomes partly or fully stabilized after years of placement; this type of refuse is called mineralized refuse and could be safely excavated. Many scholars have investigated the adsorption properties of mineralized refuse, and they have found that mineralized refuse exhibits good adsorption properties [19]. In view of these good COD and ammonia nitrogen adsorption effects, mineralized refuse can thus be used as a low-price new adsorption material that can increase its adsorption properties to wastewater through modification. In the treatment of landfill leachates, mineralized refuse is widely used in the form of mineralized refuse bioreactors [20,21]. Adopting mineralized refuse to adsorb wastewater can achieve the purpose of "disposing waste with waste." This treatment method effectively improves landfill capacity, facilitates waste resourcization, and reduces the operation costs of landfill site [22].

In this study, the combined process of MFPAC coagulation and mineralized refuse adsorption is used to pretreat mature landfill leachate. The effects of various operating factors for the two processes will be optimized and determined. The proposed combined process may be an effective technical choice for the pretreatment of landfill leachate.

2. Experiment

2.1. Chemicals

Fe_3O_4 magnetic nanoparticles were purchased from Aladdin Biochemical Technology Co., Ltd. (Shanghai, China). NaH_2PO_4 was obtained from Xilong Chemical Co., Ltd. (Shantou, China). PAC was provided by Tianjin Damao Chemical Co., Ltd. (Tianjin, China). All the chemicals were analytical grade and were used as received without further purification.

2.2. Wastewater samples

The experimental wastewater samples were taken from the equalization storage pond in Maiyuan sanitary landfill. The sanitary landfill was established in 1997, sites in Nanchang, the capital of Jiangxi Province, China. The total area of the landfill is 10^7 ha and about 2,200 t of municipal solid waste is disposed daily. About 800 m^3/d landfill leachate is generated in the landfill that was collected into an equalization storage pond with 50,000 m^3 capacity. During each sampling, 60 L of the leachate was collected, put in acid pretreated polyethylene bottles, transported to the laboratory, and then stored at 4°C. The landfill leachate was dark brown and contained some suspended materials. Typical characteristics of the wastewater are as follows: COD 5,180~6,560 mg/L, pH 7.3~8.1, color 1,320~2,060 times, ammonia nitrogen 960~1,450 mg/L, alkalinity 7,200~8,400 mg/L.

2.3. Preparation of the MFPAC magnetic coagulant

The MFPAC coagulants were prepared in the laboratory. A measured quantity of magnetic Fe_3O_4 nanoparticles was added into a triangle flask containing 300 mL of distilled water. A magnetic stirrer was used to rapidly stir until the magnetic particles were completely mixed in the distilled water. After a measured amount of PAC solution was injected slowly, 20 mL NaH_2PO_4 (10 mg/L) was dropped as a stabilizing agent for 20 min while stirring thoroughly. After 2 h of rapid stirring, slow stirring was carried out until it was absolutely mixed with the solution to prepare the MFPAC reagents.

2.4. Coagulation experiments

Coagulation experiments were carried out by jar test in a six-gang stirrer at room temperature. The time and speed of mixing for rapid and slow mixing were set automatically by means of a controller. The pH values of samples were adjusted to the desired levels by the addition of appropriate amounts of H_2SO_4 or NaOH solution. Briefly, 500 mL of landfill leachate was added into beaker with a predetermined amount of coagulant, after which the test was conducted by subjecting the solution to 2 min of rapid mixing at 300 rpm followed by 15 min of slow mixing at 70 rpm. After the mixed samples settled without any agitation for 30 min, the supernatant was withdrawn from the beakers and used for chemical analysis and further treatment by mineralized refuse adsorption. Each coagulation test was run in parallel and the result reported in this paper was the arithmetic average result of the two tests.

2.5. Adsorption experiments

The landfill leachate treated by coagulation was further subjected to adsorption with mineralized refuse. All the mineralized refuse used in this study was excavated from the Nanchang Maiyuan landfill disposed in 1999. The mineralized refuse was naturally air-dried at room temperature in a laboratory, and large inorganic substances, including stones, glass, and bottles, were separated and removed. After screening, aged refuse less than 15 mm in diameter was selected as adsorbent material. In the mineralized refuse adsorption test, 20 mL of landfill leachate treated by coagulation and mineralized refuse were mixed in a 100 mL conical flask. Adsorption test was conducted at 150 rpm of oscillating velocity in a constant temperature oscillator (Haerbin Dongming medical instrument factory, Haerbin, China). Then, the mixed liquor was centrifugalized at 3,000 rpm for 10 min. The supernatant was collected for subsequent analysis. Each adsorption test was run in parallel and the result reported in this paper was the arithmetic average result of the two tests.

2.6. Analysis of wastewater quality

COD, ammonia nitrogen, and color were measured according to the Standard Methods for the Examination of Water and Wastewater established by the Ministry of Environmental Protection of China. The pH was measured by using a pH meter (PHS-3C, Shanghai Leici Instrument, Shanghai, China).

2.7. FTIR spectroscopy

The coagulants (PAC and MFPAC), and the mineralized refuse (before and after modification) were analyzed by FTIR using a FTIR spectrophotometer (model Tensor27, Germany). Briefly, a small amount of sample was mixed with certain amount of KBr (5% of the mixture), and subsequently the mixtures were pressed using a hydraulic press at 10 MPa for 5 min to form 10 mm diameter pellets that was suitable for FTIR analysis. 128 scans were taken at a resolution of 4 cm^{-1}. FTIR spectra were then conducted and the spectra were in the range of 4,000–400 cm^{-1}.

3. Results and discussion

3.1. Coagulation test

3.1.1. Effect of mass ratio of Fe_3O_4/PAC in MFPAC on coagulation performance

When a total of 1.2 g/L Fe_3O_4 magnetic nanoparticles and PAC are added, the mass ratio of Fe_3O_4/PAC is changed. The effect of MFPAC on the coagulation performance under different mass ratios is shown in Fig. 1.

With an increase in the mass ratio of Fe_3O_4 magnetic nanoparticles/PAC, the removal rates of COD and color gradually increase. The color removal rate reaches its highest value (64%) when the mass ratio is 1:4. When the mass ratio is increased to 1:3, the COD removal rate reaches its highest value (56%), and the color removal rate reaches 63%. As the mass ratio continues to increase, the removal rates of COD and color become reduced to a certain degree. When the mass ratio is 1:1, the removal rates of COD and color are only 36% and 42%. The COD removal rate is the highest under the mass ratio of 1:3. Even if color removal is reduced slightly, the removal ratio is still high. Therefore, the optimum mass ratio of Fe_3O_4/PAC for preparing MFPAC is 1:3.

3.1.2. Coagulation performance of PAC and MFPAC at different dosage

The coagulation performance of PAC and MFPAC at different dosage is shown in Fig. 2. As shown in Fig. 2, the coagulation performance of MFPAC prepared from Fe_3O_4 nanoparticles and PAC is obviously better than that of PAC under the same conditions. The removals of COD and color have been greatly improved by the introduction of Fe_3O_4 nanoparticles.

As the dosages of PAC and MFPAC increase, the removal rates of COD and color tended to initially increase fast and subsequently decrease slightly. When the dosage is 1.5 g/L, the COD removal rate with the MFPAC coagulant reaches its

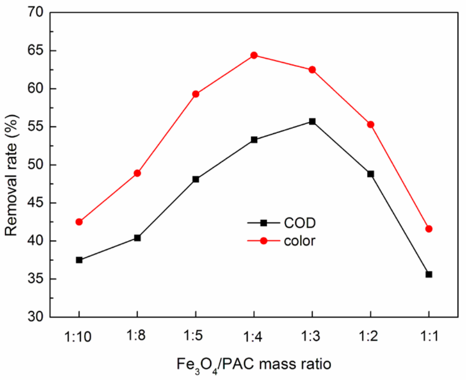

Fig. 1. Removal rates of COD and color at different mass ratios of Fe_3O_4/PAC.

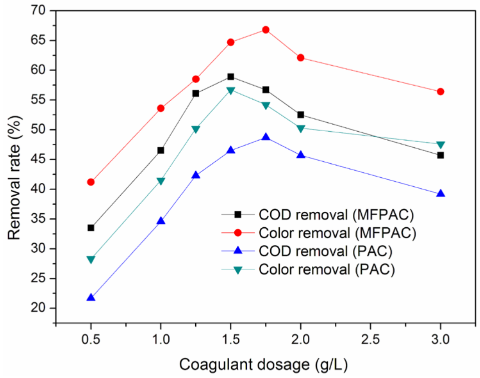

Fig. 2. Removal rates of COD and color at different dosage of PAC and MFPAC.

maximum (59%). By contrast, COD removal rate with PAC alone is only 47%. The COD removal rate when MFPAC is added is 12% higher than when only PAC is added. When the dosage of MFPAC increases to 1.75 g/L, the color removal rate reaches its maximum (67%). The color removal rate when MFPAC is added is 13% higher than when only PAC is added. The reason is that, first, the larger specific surface area and adsorption capacity of Fe_3O_4 nanoparticles have become the cores of floc in the flocculation process, playing the role of heterogeneous nucleation [16]. Consequently, the density and settling property of the flocculation body are improved, and the floc formation, aggregation, and settling time are shortened, thereby enhancing the flocculation of PAC [15]. Second, Fe_3O_4 is magnetic. With increased dosage, Fe_3O_4 becomes easier to combine with the flocculation body of the coagulant to form a more compact magnetic flocculation. Moreover, mutual attraction between magnetic particles is enhanced, thus increasing the number of particles that aggregate into large aggregates and ultimately leading to a good coagulation effect [23].

As shown in Fig. 2, when the dosage of MFPAC exceeds 1.75 g/L, COD and color are gradually slowly decreased as the coagulant dosage is increased. When the dosage of MFPAC is 3 g/L, COD and color decrease to 46% and 56%, respectively. The reason is that an increased dosage of MFPAC causes a greater dosage of Fe_3O_4. Thus, self-coagulation would occur between Fe_3O_4 nanoparticles, which would no longer combine with the flocculation body of the coagulant to form a more compact magnetic flocculation. As such, these nanoparticles can no longer facilitate heterogeneous nucleation, resulting in poor flocculation performance. In addition, according to the charge neutralization theory, hydrolyzed products of the added coagulant can interact with negative colloids and neutralize their charges, which made the colloids destabilization and then removal. Over the appropriate dosage than the amount required for coagulation, the colloids can absorb the cations and become positively charged, resulting in stable again because of electrical repulsion, thus leading to poor coagulation performance [24]. Overdosing of coagulant not only weakened the flocculation efficiency but also increased the cost. Although not at its highest, the color removal rate still reaches up to 65% when the dosage of MFPAC is 1.5 g/L, which is therefore considered the best dosage of MFPAC.

3.1.3. Effect of the pH on the coagulation performance

The pH of the wastewater is an important parameter in coagulation process. The effect of different pH values on the coagulation performance is shown in Fig. 3.

As the pH increases, the COD and color removal rates by MFPAC tended to initially increase and then subsequently decrease. When the pH of the landfill leachate is increased from 4 to 7, the COD and color removal rates are significantly increased. When the pH level is 4, the COD and color removal rates are the lowest at 33.6% and 36.9%, respectively. When the pH level is 7, the color removal rate reaches its highest (66.3%). When the pH level is 7.5 (nearly to the initial pH value of the leachate), the COD removal rate reaches its highest (61%), and the color removal rate is 64%. When the pH is increased from 7.5 to 9, the COD and color removal rates decrease with an increase in pH. When the pH level is 9, the COD and color removal rates decline to 47% and 54%, respectively. In consideration of the effects of pH value on COD and color removals, pH 7.5 is selected as the optimum pH. This pH value is close to the initial pH of the leachate. The pH of the leachate does not need any adjustments.

3.1.4. Effect of flocculation time on the coagulation performance

The effect of different flocculation time on the coagulation performance is shown in Fig. 4. As shown in Fig. 4, the removal rate of COD initially increases and then decreases with the flocculation time, which greatly improved when the flocculation time increased from 0 to 30 min. At the flocculation time of 30 min, the removal rate of COD increases to the maximum (63%). This is probably due to the fact that magnetic Fe_3O_4 nanoparticles as a core of the floc is combined with the floc of the flocculation to form a more complex magnetic flocculation. The magnetic flocculation is rapidly formed into large aggregates and settled down with the flocculation time increasing, thereby the concentration of COD is significantly reduced. As the flocculation time prolonged, the COD removal tends to be declined, which decrease to 54.8% at the flocculation time of 40 min. A short flocculation time cannot reach a better flocculation performance, while a longer one may destroy the generated flocs. Moreover, the reason why the COD removal does not have a obvious decline from 30 to 60 min is that the magnetic Fe_3O_4 nanoparticles as a core of the floc alum can play a role of heterogeneous

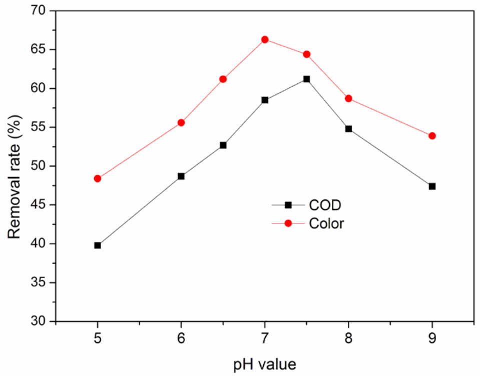

Fig. 3. Removal rates of COD and color at different pH.

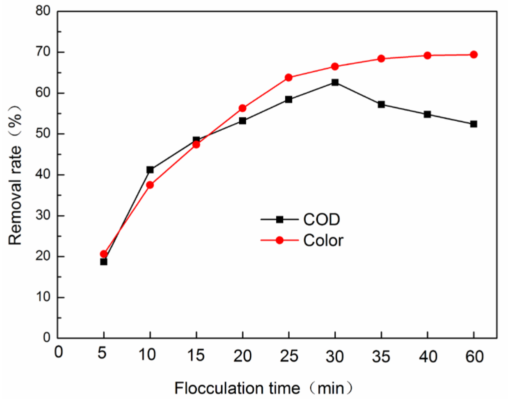

Fig. 4. Removal rates of COD and color at different flocculation time.

nucleation, improve the density and the capability against breaking of the floc, so the removal rate of COD decreased slightly. The removal efficiency of color increased with the flocculation time. At the flocculation time of 30 min, the color removal rate reaches 67%. At the flocculation time of 40 min, the color removal rate reaches the maximum (70%). Taking COD and color removal into consideration, it is suggested that the application of flocculation time 30 min would be appropriate for the landfill leachate treatment.

On the basis of the above analysis, the optimum conditions for the treatment of landfill leachate by MFPAC coagulation are at 1:3 mass ratio of Fe_3O_4/PAC in MFPAC, approximately 1.5 g/L MFPAC dosage, the pH level of 7.5 (7.5 is the initial pH of the landfill leachate, without adjusting pH), and the flocculation time of 30 min. Under these conditions, the removal rates of COD and color reaches up to 63% and 67%, respectively.

3.1.5. Infrared analysis of MFPAC

FTIR is to study the relationship between molecular structure and infrared adsorption curve. An infrared adsorption curve can be described by the position and strength of the adsorption peak. The FTIR spectra of PAC and MFPAC are shown in Fig. 5.

As shown in Fig. 5, the absorption peaks at 3,435 and 1,635 cm^{-1} observed in the FTIR spectra of PAC are related to the O–H stretching vibration and the flexural vibrations of water absorbed or complexed in the reagent [25]. The vibrational absorption peak of the Al–OH–Al group appears at 2,362 cm^{-1}. The absorption peak at 1,028 cm^{-1} was attributed to the flexural vibration of Al–O–Al caused by the polymerization of aluminum ions [26]. Additionally, characteristic absorbance bands appearing at approximately 624 ~600 cm^{-1} are attributed to the vibrations of water–chloride.

The main absorption peaks of the FTIR spectra of MFPAC appeared at 3,428, 2,345, 1,635, 980, and 580 cm^{-1}, respectively. The bands near 3,400~3,500 cm^{-1} are stretching vibrations of hydroxyl or carboxyl, while those near 1,635 cm^{-1} bands correspond to C=C vibration peaks [27]. Among them, the absorption peak at 3,428 cm^{-1} is attributed to the stretching vibration of –OH linked with Fe or Al. It can be seen that the peak width approximately 3,428 cm^{-1} in the FTIR spectra of MFPAC is slightly higher than that of in PAC, indicating a higher content of O–H in MFPAC than in PAC. Similar to the FTIR spectra of PAC, the adsorption peak at 1,635 cm^{-1} can be assigned to the H–O–H flexural vibrations of water absorbed or complexed in the MFPAC. The adsorption peak at 2,345 cm^{-1} can be assigned to the vibration of the Al–OH–Al group in the MFPAC. The absorption peak at 580 cm^{-1} in the spectra of MFPAC indicates that the vibrational peak of water–chloride of PAC is overlapped by the characteristic peak of Fe–O–Fe stretching vibrations in Fe_3O_4. On the whole, the spectrum of MFPAC is similar to that of PAC. This indicates that almost no new chemical bonds were generated during the preparation of MFPAC with Fe_3O_4 nanoparticles and PAC, and also illustrates that the MFPAC is mainly a physical mixture.

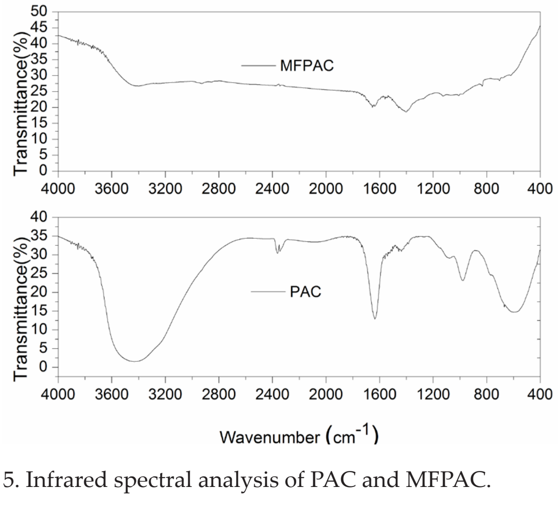

Fig. 5. Infrared spectral analysis of PAC and MFPAC.

3.2. Mineralized refuse adsorption

After treatment by MFPAC coagulation, the typical parameters of the wastewater are as follows: COD 1,760~2,570 mg/L, pH 6.5~7.8, color 450~750 times, ammonia nitrogen 824~1,380 mg/L. The landfill leachate treated by MFPAC coagulation was further subjected to adsorption with mineralized refuse.

3.2.1. Effect of the particle size of mineralized refuse on the adsorption performance

Under the conditions of mineralized refuse dosage of 40 g/L and treatment time of 12 h, the effect of different particle sizes of mineralized refuse on the COD and ammonia nitrogen removals is shown as Fig. 6.

As shown in Fig. 6, the removal rates of COD and ammonia nitrogen decrease with an increase in the particle size of mineralized refuse. When the particle size of mineralized refuse is 0~2 mm, the removal rates of COD and ammonia nitrogen reach their maximum at 39% and 54%, respectively. When the particle size of mineralized refuse is 7~15 mm, the removal rates of COD and ammonia nitrogen decline to 32% and 49%, respectively. The reason is that, first, the specific surface area of mineralized refuse increases as particle size decreases, thus improving the adsorption rate on the surface of the adsorbent. Second, the surface of mineralized refuse contains some organic matters. These organic matters contain chemical functional groups with good adsorption

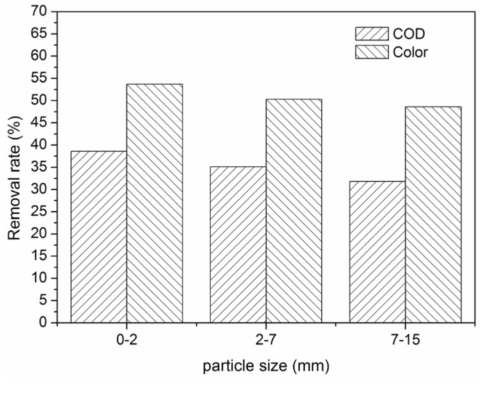

Fig. 6. Removal rates of COD and ammonia nitrogen at different particle size of mineralized refuse.

performance, which improve the adsorption performance of mineralized refuse. In fact, these substances are more abundant on the surface of the small-size mineralized refuse than that of large-size mineralized refuse. Organic pollutants in landfill leachate are dispersed into the adsorbent from the outer surface. Diffusion path and mass transfer resistance increase as particle size increases. Large-size adsorbents cannot facilitate adsorption on its internal surface, thus reducing adsorption effect. Mineralized refuse demonstrates good COD and ammonia nitrogen adsorption efficiencies when the particle size of the adsorbent is 0~2 mm.

3.2.2. Effect of roasting temperature on the adsorption performance

Mineralized refuse is modified under different roasting temperature. The effect of roasting temperature on COD and ammonia nitrogen removals is shown in Fig. 7.

The COD and ammonia nitrogen removals first increase and then decline with an increase in roasting temperature. When the roasting temperature is 700°C, the removal rates of COD and ammonia nitrogen reach their maximum at 56% and 64%, respectively. As roasting temperature continues to increase, the COD and ammonia nitrogen removal rates slightly decrease. When the roasting temperature is 800°C, the COD and ammonia nitrogen removal rates decline to 44% and 61%, respectively. The reason is that the increase in roasting temperature leads to the formation of more channels in the mineralized refuse, resulting in a larger specific surface area. However, when the roasting temperature exceeds 700°C, the increasing roasting temperature would easily cause the loss of the structural water in mineralized refuse. Consequently, the structure of the mineralized refuse is destroyed, the internal micropore is blocked, and the specific surface area is decreased. At the same time, the activity of a certain content of oxide in mineralized refuse is sintered to disappear, thus greatly reducing the adsorption performance of mineralized refuse. Therefore, the optimal roasting temperature is 700°C.

3.2.3. Effect of dosage of mineralized refuse on adsorption performance

Adopting the modified mineralized refuse as adsorbent, the effects of dosages on the adsorption performance are shown in Fig. 8. As the dosage of mineralized refuse is increased, the removal rates of COD and ammonia nitrogen removal rates gradually increase and tend to be balanced in the end. The reason is that the increased dosage of the adsorbent increases the surface area of adsorption, causing a growth in the functional groups involved in the adsorption and ultimately providing more active sites for adsorption. An increased dosage of the adsorbent can effectively improve the removals of COD and ammonia nitrogen. When the adsorbent dosage reaches a certain degree, the adsorption of the adsorbent to pollutants gradually reaches a saturated status. Therefore, COD and ammonia nitrogen adsorption finally reaches a balance.

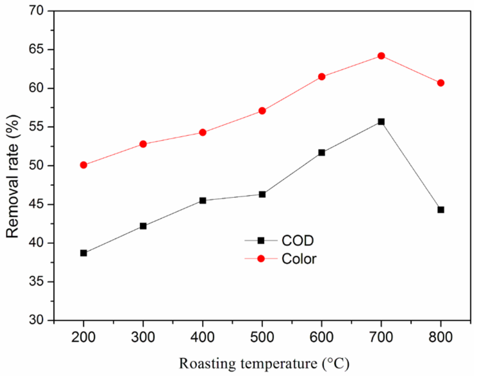

Fig. 7. Removal rates of COD and ammonia nitrogen at different roasting temperature.

In terms of COD adsorption in leachate, when the adsorbent dosage is 40 mg/L, the COD removal rate reaches the highest (57%), and the ammonia nitrogen removal rate is 67%. When the adsorbent dosage is increased from 40 to 60 mg/L, the removal rate of ammonia nitrogen reaches its maximum (71%). Although the removal rate of ammonia nitrogen is slightly increased, the increment is insignificant. When the adsorbent dosage is 20 mg/L, the adsorption capacity to COD and ammonia nitrogen reach the maximum at the same time with 20.85 and 22.95 mg/g, respectively. When the adsorbent dosage exceeds 20 mg/L, the adsorption capacity to COD and ammonia nitrogen decrease as the adsorbent dosage is increased. The reason is that the coalescence caused by increasing adsorbent dosage would reduce the total specific surface area of the adsorbent and increase the diffusion path of the organic pollutants to the adsorbent. In addition,

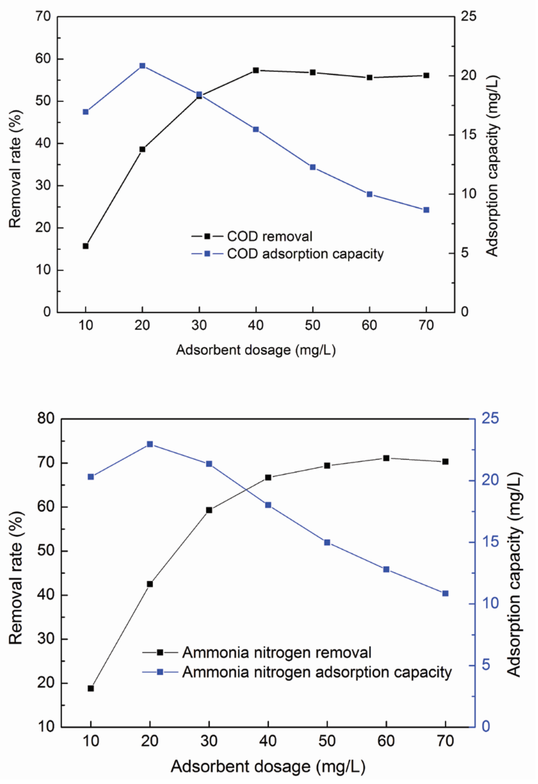

Fig. 8. (a) Adsorption performance of COD at different adsorbent dosage. (b) Adsorption performance of ammonia nitrogen at different adsorbent dosage.

the unsaturated adsorption point would diminish the unit adsorption amount.

3.2.4. Effect of initial pH values on adsorption performance

The adsorption behavior of mineralized refuse at different initial pH values was investigated. The effect of initial pH values on COD and ammonia nitrogen removals is shown in Fig. 9.

As is shown in Fig. 9, with the pH value gradually increasing, the removals of COD and ammonia nitrogen primarily increase and then subsequently decrease. When the pH value is 9, the removals of COD and ammonia nitrogen reach their maximum at the same time, 57% and 68%, respectively. That is because the proper alkalinity is beneficial to improve the absorbent activity of chemical functional groups of the mineralized refuse and then enhance the adsorption efficiencies of COD and ammonia nitrogen onto the absorbent. Furthermore, the ammonia nitrogen on the landfill leachate mainly exists through the balance of NH_3 and NH_4^+, which can be described as following: $NH_3 + H_2O = NH_4^+ + OH^-$. Increasing pH value would benefit the balanced relationship to move to the left, which resulted in the existence of ammonia nitrogen in the landfill leachate mainly in the form of NH_3, the ammonia nitrogen content was reduced because of the ammonia escaping. When the pH value increased from 9 to 11, the removal rate of COD and ammonia decreased. When the pH value increases to 11, the removal rates of COD and ammonia nitrogen decreased to 45.6% and 53.3%, respectively. In the high alkalinity conditions, some substances contained in the mineralized refuse may generate hydroxide precipitation on its surface. In addition, some heavy metal ions adsorbed into the mineralized refuse will generate a hydroxide precipitation too. These hydroxide precipitations can block the adsorption channel of mineralized refuse, decrease the specific area, and result in deterioration of adsorption performance.

On the basis of the above analysis, the optimum conditions for mineralized refuse adsorption are at <2 mm particle size of mineralized refuse, 700°C roasting temperature, 40 mg/L adsorbent dosage, and pH of 9. Under these working conditions, the removal rates of COD and ammonia nitrogen reached 56.7% and 68.4%, respectively, after 12 h of treatment. By combining MFPAC coagulation with mineralized refuse adsorption, the removal rates of COD, color, and ammonia nitrogen could be enhanced to 84%, 80%, and 74%, respectively.

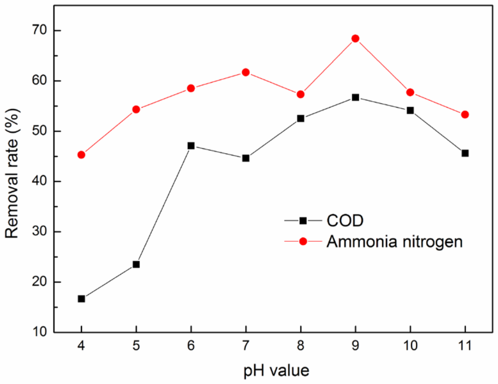

Fig. 9. Removal rates of COD and ammonia nitrogen at different pH values.

3.2.5. FTIR analysis of mineralized refuse

FTIR spectrums of mineralized refuse before and after modification are shown in Fig. 10. The mineralized refuse (before modification) contains the following functional groups: an adsorption peak occurring near 3,450 cm^{-1}, which corresponds to the –OH stretching vibration or the –NH stretching vibration; a stronger wide peak near 1,632 cm^{-1}, which corresponds to the aromatic ring C=C skeletal vibration peak, and an amide C=O stretching vibration peak. Among which, the C=C double bond is at 1,620 cm^{-1}, and the C=O stretching vibration peak is at 1,650 cm^{-1}. The adsorption peak in the mid strength near 1,386 cm^{-1} is a saturated hydrocarbon radical C–H in-plane bending vibration. A strong wide peak corresponding to the stretching vibration peak of ethers and aromatic ether compounds is found near 1,110 cm^{-1}. Among which, the peak at 1,109 cm^{-1} corresponds to the C–O–C stretching vibration peak of ether compounds, and the peak at 1,038 cm^{-1} is the =C–O–C stretching vibration peak of aromatic ether compounds. The stronger adsorption peak at 617 cm^{-1} corresponds to the benzene ring C–H wagging vibration peak, and the peak near 538 cm^{-1} is the Si–O–Mg bending vibration peak.

Comparing the FTIR spectrums of mineralized refuse (before and after modification), it can be seen that the structure of the main functional groups of mineralized refuse is unchanged, and only a slight displacement within 10 cm^{-1} occurred after modification at 700°C. The R–CH=CH_2 wagging vibration peak at 913 cm^{-1}, the Si–O stretching vibration peak near 797 cm^{-1}, and the C–H aromatic ring single substitution wagging vibration peak at 694 cm^{-1} become very weak, or even disappear, after modification. The reason may be that

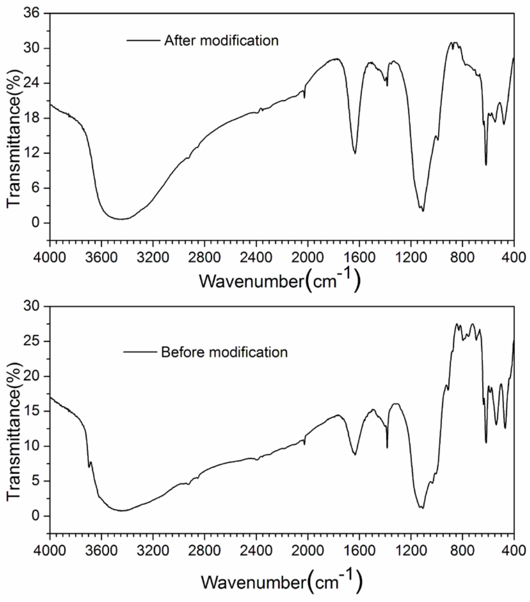

Fig. 10. FTIR spectrums of mineralized refuse before and after modification.

the roasting modification changes the existing forms of these functional groups, which may be the reason why modified mineralized refuse exhibit better adsorption performance.

4. Conclusion

The coagulation performance is significantly better when the new type of MFPAC magnetic coagulant prepared by introducing Fe_3O_4 nanoparticles into PAC is applied in treating landfill leachate than when PAC is used alone. Fe_3O_4 nanoparticles can improve the floc density and settling performance, thereby enhancing the pollutants removal from landfill leachate. The optimum mass ratio of Fe_3O_4/PAC for preparing MFPAC is 1:3. Under the operating conditions of MFPAC dosage of 1.5 g/L and pH of 7.5 (pH 7.5 is the initial pH of the landfill leachate, without adjusting pH), the removal rates of COD and color reaches up to 63% and 67%, respectively. FTIR analysis shows that the main characteristic groups of MFPAC are Fe(Al)–O, Fe–O–H–Fe, Al–O–H–Al, Cl–, O–H, and so on. The magnetic composite coagulant of MFPAC is a multi-core polymer possessing hydroxyl ligands and Fe_3O_4 nanoparticles, and has a complex valence and crystal structure.

The effluent of MFPAC coagulation was further treated by utilizing mineralized refuse as the adsorbent. Mineralized refuse has a good adsorption performance for COD and ammonia nitrogen removals from the effluent of MFPAC coagulation. Under the working conditions of <2 mm particle size of mineralized refuse, 700°C roasting temperature, and 40 mg/L adsorbent dosage, the removal rates of COD and ammonia nitrogen reached up to 57% and 68%, respectively, after 12 h of treatment. FTIR spectroscopy analysis shows that after the mineralized refuse is roasted at 700°C, the structure of the main functional groups of mineralized refuse is not significantly changed, although displacement occurs. Moreover, a small quantity of functional groups decrease or even disappear after modification.

Landfill leachate was treated by combining MFPAC coagulation with mineralized refuse adsorption, the removal rates of COD, color, and ammonia nitrogen were enhanced to 84%, 80%, and 74%, respectively. The encouraging results demonstrated that the combined process could provide a viable alternative to the pretreatment of landfill leachate.

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