



Analysis and selection of powdered zeolite dosing point in enhanced coagulation–sedimentation for treating micro ammonia polluted raw water

Zhen Liang Liao¹, Hao Chen¹, Bai Rong Zhu, Huai Zheng Li*

Shanghai Engineering Research Center of Sewerage System, College of Environmental Science and Engineering, Tongji University, 1239 Siping Road, Shanghai 200092, China, Tel. +86 187 0197 4804; email: zl_liao@tongji.edu.cn (Z.L. Liao), Tel. +86 131 6255 6627; email: chenhao_722@163.com (H. Chen), Tel. +86 138 1674 9336; email: 380078303@qq.com (B.R. Zhu), Tel. +86 181 2113 3128; email: lihz@tongji.edu.cn (H.Z. Li)

Received 19 January 2014; Accepted 24 October 2014

ABSTRACT

Ammonia pollution occurs frequently in urban water supply systems. Zeolite is a kind of promising adsorbent for ammonium removal. In an actual running water work, different zeolite dosing points should have various influences on the effluent, which, however, draws insufficient attention. This paper focuses on the analysis and selection of powdered zeolite (PZ) dosing point in enhanced coagulation-sedimentation for treating micro ammonia polluted raw water. We investigate the variations of effluent ammonium concentration, turbidity, COD_{Mn} and UV_{254} of the coagulation-sedimentation schemes which have different PZ dosing points and we also analyse the relevant causes. PZ dosing can induce extra turbidity and the existing turbidity can inhibit ammonium removal to certain extent. In COD_{Mn} and UV₂₅₄ removal process, both synergistic effect and antagonistic effect exist, and PZ dosing point determines which effect it is. PZ dosing has a significant synergistic effect on promoting poly aluminium chloride to remove ammonium. Among the four PZ dosing points, i.e. the suction well, the pipeline mixer, the early step of coagulation and the middle step of coagulation, (1) when turbidity, COD_{Mn} and UV_{254} need to be removed effectively and simultaneously, the suction well is the best PZ dosing point, and the PZ dosage must exceed 1 g/L for removing $COD_{Mn'}$ (2) when it is required that ammonium be removed in priority, the early step of coagulation is the optimal point.

Keywords: Ammonium removal; Powdered zeolite (PZ); Coagulation–sedimentation process; Dosing point

1. Introduction

Ammonia pollution occurs frequently in many developing countries. Strategies have been developed to remove this harmful chemical [1]. Conventional

*Corresponding author.

biological treatments have limited efficiency on the removal of ammonium. Among the materials or processes proposed to reduce ammonium, zeolite is considered to be promising in laboratories or commercial plants [2–5].

Natural zeolite is considered to be a certain type of crystalline hydrated aluminosilicate with a framework

¹United Nations Environment Program, Tongji Institute of Environment for Sustainable Development, Tongji University, 1239 Siping Road, Shanghai 200092, China.

^{1944-3994/1944-3986 © 2014} Balaban Desalination Publications. All rights reserved.

structure containing pores [6]. For the hydrophilic surface and cationic exchange ability, as well as its similar pore diameters to that of ammonium ions, zeolite has strong selective adsorption capability to ammonium.

In a conventional raw water purification treatment, coagulant is mainly applied to remove turbidity and natural organic matter (NOM) [7], and zeolite is particularly efficient for removing ammonium [8,9]. Unknown synergistic or antagonistic effects may occur in between. In another aspect, all the steps in purification treatment are crucially important. If coagulation or sedimentation fails, a large number of pollutants with previous effluent including disinfection by-products (DBPs) precursors will penetrate the sand filter blanket of filter basin and discharge into subsequent chlorination process. As a result, a number of DBPs will generate, and the problem is that a large portion of those are cancerogens. Besides, zeolite particles may be enmeshed by the flocs in the coagulation process and it will impact ammonium removal efficiency greatly. From the perspective of avoiding or alleviating the above influences, zeolite dosing point should not be chosen before or in the coagulation process. For ensuring sufficient stirring time and adsorption time, zeolite dosing point should be arranged at the beginning of the treatment process. These may be the difficulties in practical operation of zeolite enhanced coagulation, which, however, draw insufficient attention.

The objective of this paper is the analysis and selection of powdered zeolite (abbreviated as PZ) dosing point in enhanced coagulation-sedimentation for treating micro ammonia polluted raw water. Effluent ammonium concentration variation of each scheme is studied comprehensively. Since, water matrix like colloids or organic matters have a tendency to interfere with ammonium removal [10,11], three other typical contamination indexes are also measured to evaluate their influences, i.e. turbidity, COD_{Mn} (chemical oxygen demand, oxidant is potassium permanganate) and UV₂₅₄ (ultraviolet absorbance under 254 nm wavelength). COD_{Mn} is used to measure the oxidisable organic matter in water. Source water absorption of UV light is widely attributed to the aromatic chromophores present in NOM molecules dissolved in the water [12]. Because of the good correlation to the dissolved part of NOM, UV₂₅₄ is used as surrogate parameter to dissolved NOM [7]. The water industry also uses it to monitor sites for DBPs precursors caused by NOM [13]. The different dosing points (spatial and temporal), i.e. the suction well, the pipeline mixer, the early step of coagulation and the middle step of coagulation are set up for comparison. We employ a sequence of jar tests as the main approach. An analysis of removal effects of PZ and poly aluminium chloride (abbreviated as PAC, coagulant) is given. Finally, a brief summary of PZ dosing point selection for different removing targets is drawn.

2. Methodology

2.1. Materials

Natural PZ used in the study were purchased from Jinyun, China. These samples are grinded to become 200 mesh (70–77 μ m) before use. Two hundred mesh is the optimal grain size for achieving the best ammonium removal efficiency in a certain condition [14]. Afterwards, the samples are washed with de-ionised water and dried at 105°C for 24 h [15]. The chemical composition of natural PZ is shown in Table 1.

Micro ammonia polluted raw water samples were collected from Lingqiao water work, which is located near Yangtze River. All the ammonium present is expected to be in ionic form and available for ion exchange [16]. The general contamination index values of these raw water samples and the relevant water quality requirements in National Drinking Water Standard are listed in Table 2 [17]. Coagulant used here is PAC (10% Al₂O₃, kept in 4°C). This soluble aluminium polymer has been used to remove colour and DBPs precursors caused by NOM [18]. PAC can hydrolyse and form complexes possessing high positive charges [19]. Its dosing concentration is 18 mg/L (18 mg PAC dosed into 1 L raw water).

2.2. Coagulation-sedimentation process

2.2.1. Batch study of different dosing points

A sequence of jar tests is employed as a successive coagulation-sedimentation process, i.e. the suction well, the influent pipeline, the pipeline mixer, coagulation and sedimentation [21,22]. This batch adsorption experiment is widely used for environmental purposes [9]. Settings of dosing points of PZ and PAC in

Table 1				
Chemical	composition	of natural	Jinyun	PZ (wt%)

Constituent	Value (%)	
SiO ₂	69.58	
CaO	2.59	
Na ₂ O	2.59	
MgO	0.13	
Al ₂ O ₃	12.20	
K ₂ O	1.12	
Fe ₂ O ₃	0.87	
Loss of ignition	10.91	

Note: Provided by Jinyun zeolite company.

Table 2 General contamination index values of raw water sample and relevant water quality requirements in National Drinking Water Standard

	Raw water	Standard requirements
pН	7–8	6.5–8.5
Turbidity (NTU)	296	≤1
COD_{Mn} (mg/L)	7.04	≤3
UV ₂₅₄	0.082	_
Ammonium (mg/L)	2.13	≤0.5

Note: Under normal conditions, COD_{Mn} is required to be below 3 mg/L; COD_{Mn} concentrations in source water are above 6 mg/L, the COD_{Mn} values should be lower than 5 mg/L [17,20]. There is no clear requirement on UV₂₅₄ at present.

coagulation-sedimentation process are demonstrated in Table 3. All steps and parameters refer to conventional treatment scheme [20], as shown in Fig. 1. Both PZ and PAC are dosed in the beginning of each step, respectively. In our primary experiments, the early

Table 3 Settings of PZ dosing point and PAC dosing point

step of coagulation shows a colloid destabilisation and flocs forming stage. In the middle step of coagulation, flocs are agglomerating and precipitating. This coagulation–sedimentation process is consistent with the actual running purification scheme in water works of Shanghai, despite the lack of sand filtration and postchlorination (after sedimentation). We do not set these two steps because we need to analyse the effluent quality of PZ enhanced coagulation–sedimentation procedure immediately.

Following the principle of consistency or closest to the practical running condition in water works, ambient temperature (25°C) and intrinsic pH (7–8) of raw water are kept in the experiment. Moreover, when a temperature is close to 25°C and pH is between 7 and 8, ammonium removal efficiency is relatively good, as additional studies have reported [3,5]. Dry-type PZ dosing pattern is employed because it has an equal effect on the effluent compared to wettype dosing pattern, and it is more convenient in lab. Actually in water works, wet-type dosing pattern

	Suction well	Pipeline mixer	Early step of coagulation	Middle step of coagulation
Scheme I	PZ	_	_	_
Scheme II	-	PZ	-	_
Scheme A	PZ	-	PAC	_
Scheme B	-	PZ	PAC	_
Scheme C	-	_	PZ/PAC	_
Scheme D	-	_	PAC	PZ
Reference I	-	_	PAC	_
Reference II	1,000 mL raw w	ater sample precipitate	e for 30 min	

Note: PAC dosage 18 mg/L is constant in each scheme and reference sample.



Fig. 1. Schematic sketch of coagulation-sedimentation process.

would be more reasonable, as this dosing pattern could reduce the raising dust.

The variation tendency of ammonium removal efficiency using PZ is quick-increasing and slow-equilibrating [23,24]. Thus, the contacting and stirring time in above process are rather short [25], which is beneficial to the emergency treatment of ammonia pollution in water works. The dosage range of PZ in this study is 0.2-4 g/L (0.2-4 g PZ dosed into 1 L raw water), for the reason that our preparation experiment indicates that more dosage (>4 g/L) cannot significantly improve the ammonium removal efficiency, but increases the material's cost.

A series of 1,000 mL micro ammonia polluted raw water samples are added to stirring beakers. Correspondingly, quantities of PZ and PAC are dosed in each point referring to Fig. 1. Effluent contamination indexes of ammonium, turbidity, COD_{Mn} and UV_{254} are measured. Under the same condition, 1,000 mL raw water sample is coagulated (added with equal quantities of PAC) and precipitated as Reference I. In addition, another beaker of 1,000 mL raw water sample is precipitated for 30 min as Reference II, as listed in Table 3.

2.2.2. Measurement of effluent contamination indexes

Turbidity is measured by HACH 2100P portable turbidity metre [26]. Ammonium concentration is measured through the standard nesslerisation method using Shimazu UV-2550 spectrophotometer [27,28]. COD_{Mn} is measured through the acid titration method using potassium hypermanganate [29]. UV₂₅₄ is measured by Shimazu UV-2550 spectrophotometer [30]. Effluent samples are filtrated by 0.45 μ m filter membrane to eliminate the disturbance of turbidity before measuring UV₂₅₄. Unless specifically noted, all reagents used in this study are analytically pure.

3. Results and discussion

In Table 4, compared to the single sedimentation in Reference II, coagulation–sedimentation in Reference I

remove turbidity almost completely. Turbidity is usually derived from colloids and some solid particles suspended in water. Colloids cannot precipitate during sedimentation, but they can be destabilised and precipitated during coagulation through charge neutralisation and enmeshment by Al³⁺ and hydrolysed aluminium flocs (most efficient component is $Al_{13}O_4(OH)_{24}^{7+}$) from PAC [31,32]. Sedimentation hardly has removal effects on ammonium and UV_{254} . It indicates that the organic matter in which UV₂₅₄ presents are dissolved, while the proportion of COD_{Mn} which is removed through single sedimentation may be adsorbed on solid phase particles. However, coagulation-sedimentation has better removal efficiencies on UV_{254} and COD_{Mn} . It verifies that the coagulation-sedimentation method is more effective on removing turbidity and as many organic materials as possible [33,34]. Both single sedimentation and coagulation-sedimentation (only dose PAC) have a limited efficiency on ammonium removal. This phenomenon is consistent to some running cases in water works of Shanghai.

3.1. Turbidity

Fig. 2(a) shows that the effluent turbidity values in schemes I and II ascend rapidly with the increasing dosage of PZ, till a high level. The turbidity values are approximate. A same phenomenon also exists in schemes C and D. However, their effluent turbidity values will increase to relatively stable levels when the PZ dosage is in excess of 3 g. Even when PZ is largely dosed, all the effluent turbidity values of schemes A to D are relatively smaller than the initial ones (296 NTU).

In schemes I and II, only PZ is dosed. When the PZ dosage is less than 1 g/L, the effluent turbidity values are all below initial ones, which indicate that a small amount of PZ has limited removal effects on turbidity. It may be attributed to simple physical adsorption [16]. When the PZ dosage is close to or above 2 g/L, the effluent turbidity values are all more than initial ones, which means an overdose of PZ can also induce

Table 4

Turbidity, COD_{Mn}, UV₂₅₄ and ammonium removal rate variation in single sedimentation and coagulation-sedimentation

	Coagulation-sedimentation in Reference I	Single sedimentation in Reference II
Turbidity (%)	99.9	69.1
COD _{Mn} (%)	60.2	32.4
UV ₂₅₄ (%)	26.8	0
Ammonium (%)	1.6	1.4

Note: Settings of References I and II are listed in Table 3.



Fig. 2. Turbidity (NTU) of effluent as a function of PZ dosage (g/L). (a) From each scheme; (b) from schemes A and B. The black short dash line presents the effluent turbidity of coagulation–sedimentation which only doses PAC (Reference I), as in Tables 3 and 4.

extra turbidity, and this can be resulted from the colloids which induced by PZ cannot be precipitated. Comparing scheme A to I, or scheme B to II, we can find that either initial turbidity or induced turbidity can be removed effectively when PAC is added. Under the condition of pH > 4, colloids of clay minerals like PZ are negatively charged [35–37], while the hydrolysed aluminium cations or flocs are positively charged. As a result, the colloidal particles are electrostatically attached to the flocs (mainly in early step of coagulation) [32]. This should be the reason, why turbidity induced by PZ can be removed by PAC effectively.

Turbidity values of effluent from schemes A and B in Fig. 2(b) are quite low and they present a linear growth with the increasing of PZ dosage. In these two schemes, a longer time of stirring promotes PZ to remove more turbidity. When PZ is dosed in the middle step of coagulation, as in scheme D, the turbidity removal efficiency is worse than the dosed in the early step of coagulation. In the middle step of coagulation, PAC has already hydrolysed to become flocs, and the flocs are agglomerating and precipitating subsequently. Hence, the PZ colloidal particles' removal through charge neutralisation or enmeshment by Al³⁺ and PAC hydrolysate is incomplete (these two physical reactions mainly take place in the early step of coagulation), which results in higher effluent turbidity in scheme D [31,32].

Furthermore, another phenomenon needs the attention. Compared with the 99.9% of turbidity removal efficiency of coagulation–sedimentation which only dose PAC, as in Table 4, even the highest turbidity removal efficiency (0.49 NTU, 99.8%) in the PZ enhanced coagulation–sedimentation process (0.2 g/L dosage of PZ, suction well, scheme A) is still slightly lower, let alone more PZ dosage or other dosing points. It reveals that PZ dosing is hardly conducive to PAC removing turbidity. However, if the dosing point is optimised, its effluent turbidity can reach the water quality requirement.

Even turbidity can continue to be removed during the subsequent filtration in water works effectively [38], it is more reasonable to dose PZ into the suction well, and simultaneously, its effluent turbidity reaches the water quality requirement of National standard in Table 2.

3.2. COD_{Mn}

In Fig. 3, all the effluent COD_{Mn} are less than the standard requirement 5 mg/L. PZ dosing points have a distinct impact on the effluent COD_{Mn} , which is shown among schemes A, B and schemes C, D. For the early step and middle step of coagulation, their influence on COD_{Mn} removal seems similar.

Moreover, schemes A and B can get better removal efficiencies, and their effluent COD_{Mn} values reach the stringent standard requirement 3 mg/L when PZ dosage is more than 0.5 g/L. We compare the effluent COD_{Mn} of each scheme to the black short dash line of Reference I. When PZ is dosed in the early step or middle step of coagulation, as in scheme C or scheme D, their effluent COD_{Mn} values are higher than the effluent from Reference I. It reveals that PZ dosed in these two steps can inhibit PAC from removing COD_{Mn} . When PZ is dosed in the suction well or pipeline mixer, the dosage is equal to or more than 1 g/L, their COD_{Mn} removal efficiencies can reach or become



Fig. 3. COD_{Mn} (mg/L) of effluent as a function of PZ dosage (g/L). The black short dash line presents the effluent COD_{Mn} of coagulation–sedimentation which only doses PAC (Reference I), as in Tables 3 and 4.

greater than 62.1 and 60.4%, respectively, which is higher than the 60.2% of COD_{Mn} removal efficiency of Reference I in Table 4. It indicates that PZ dosing can promote PAC to remove COD_{Mn} under that dosing point and dosage condition. These phenomena demonstrate that PZ dosing can either promote PAC to remove COD_{Mn} or inhibit to it, which means that synergistic effect and antagonistic effect all exist, and the PZ dosing point determines which effect it is.

Moreover, a longer stirring time can promote PZ to remove more COD_{Mn} . Both chemical adsorption (dominant) and physical adsorption are involved in the adsorption of organic constituents on zeolite, and longer stirring time obviously promotes its adsorption [16]. It is optimal to dose PZ in the suction well, and the dosage needs to exceed 1 g/L.

3.3. UV₂₅₄

Effluent UV_{254} of all the schemes are shown in Fig. 4. Compared to the initial UV_{254} 0.082 of raw water, single PAC has a favourable removal effect on this contamination index, as in Reference I. However, possible maximum UV_{254} removal efficiency of PAC may be more than that. Several studies confirmed that coagulation pH appeared to be a determining factor for maximum NOM removal, and the removal of DBPs precursors was significantly enhanced at pH 5.5. Hence, the initial pH 7–8 may not be appropriate for PAC to become fully effective, though it is beneficial for PZ to remove ammonium [39,40].



Fig. 4. UV_{254} of effluent as a function of PZ dosage (g/L). The black short dash line presents the effluent UV_{254} of coagulation–sedimentation which only doses PAC (Reference I), as in Tables 3 and 4.

Similar to the phenomena in COD_{Mn} removal, synergistic effect and antagonistic effect also exist in PΖ enhanced coagulation-sedimentation process when removing UV₂₅₄. In schemes I and II, PZ dosing can synergistically promote PAC to remove UV₂₅₄. In these two schemes, PZ is dosed in the suction well and pipeline mixer, respectively. The mechanisms through which NOM is removed include a combination of charge neutralisation, entrapment, adsorption and complexation with coagulant metal ions into insoluble particulate aggregates [7]. Adsorption may be the major cause when PZ removes the organic constituent such as dissolved NOM [16]. Other studies proved that larger molecular mass and hydrophobic components of NOM can be removed efficiently, whereas low molecular mass and hydrophilic compounds are observed to be resistant to removal in coagulation [41-43]. As the raw water sample is micro polluted, aluminium coagulant is not efficient to remove trace NOM [44]. Therefore, PZ may perform more efficiently to remove the trace quantity, low molecular mass and hydrophilic compounds than PAC, and positively, its dosing point is a particularly important influencing factor.

 UV_{254} content decline means effective reduction of DBPs precursors' risk, as DBPs precursors is caused by NOM [18]. Among these schemes, suction well also is the best dosing point for removing UV_{254} , and its effluent UV_{254} will descend with the increasing dosage of PZ till a rather low level.

3.4. Ammonium

Effluent ammonium concentrations of all the schemes are shown in Fig. 5. Compared with the 1.6% of ammonium removal efficiency of single PAC in Reference I, PZ dosing has a significant synergistic effect on promoting PAC by removing ammonium in all the enhanced coagulation–sedimentation schemes. Effluent ammonium concentration increases to a rather stable value when the PZ dosage is in excess of 3 g, and this may be attributed to the formation of aggregates at a higher solid/liquid ratio of PZ particles [5].

Since PZ also has a capability to adsorb organic matters, as confirmed by the results of COD_{Mn} experiment and UV₂₅₄ experiment in this study, PAC removing a fair amount of organic matters can allow PZ to retain a more adsorption capability for ammonium removal because the adsorption capability of zeolite is limited during an adsorption equilibrium [2,45]. Moreover, organic matters like NOM can disrupt PZ's adsorption, but PAC dosing can reduce this interference [46]. When PZ is dosed in the suction well or pipeline mixer, it will adsorb organic matters and ammonium simultaneously, and the adsorption will reach equilibrium in a short contact time during the pre-process [23-25]. Hence, even adding PAC to the post-process cannot promote PZ to remove more ammonium. When PZ is dosed in the early step or middle step of coagulation, PZ adsorption and PAC hydrolysis proceed simultaneously, and PAC removes NOM through charge



Fig. 5. Ammonium concentration (mg/L) of effluent as a function of PZ dosage (g/L). The black short dash line presents the effluent ammonium concentration of coagulation–sedimentation which only doses PAC (Reference I), as in Tables 3 and 4.

neutralisation, entrapment, adsorption and complexation. It can allow PZ to remain more absorption-capable for removing ammonium [7,38]. This should be the reason as to why the ammonium removal efficiencies of scheme C and D are higher in comparison to schemes A and B.

In scheme C, colloids including the negatively charged clay materials' colloids in raw water can be destabilised by positive charged Al³⁺ and PAC hydrolysate through charge neutralisation or enmeshment [35–37]. Hence, dosing PZ in middle step of coagulation can avoid these negative effects to some extent, because in the middle step, charge neutralisation is almost over, and flocs are agglomerating and precipitating. It can reduce the destabilisation of PZ colloids and retain more available PZ for ammonium removal [31,32]. This has been identified as the reason to which the ammonium removal efficiency of scheme D is slightly higher than scheme C.

However, all the effluent ammonium concentrations do not reach the ammonium requirement of National Drinking Water Standard (0.5 mg/L). It should be noted that PZ enhanced coagulation–sedimentation process in this study is not a complete process as in actual running water works. There are two additional processes following sedimentation, i.e. sand filtration and post-chlorination in actual water works. Ammonium will continue to be removed effectively during these two processes in water works.

Considering ammonium removal separately, the middle step of coagulation is the best PZ dosing point for ammonium removal. However, dosing PZ in the middle step of coagulation can cause distinctly higher turbidity in comparison to the early step of coagulation (Fig. 2). As the ammonium removal efficiencies of scheme D and scheme C are rather similar, it is optimal to dose PZ in the early step of coagulation for better comprehensive efficiencies.

3.5. Influence of turbidity, COD_{Mn} and UV_{254} on ammonium removal

Figs. 6 and 7 reveal the influence of turbidity, COD_{Mn} , UV_{254} on ammonium removal.

In schemes I and II of Fig. 6(a), turbidity almost has the same impact on ammonium removal. Higher turbidity relates to higher effluent ammonium compared to the schemes C and D. The descended turbidity promotes the decreasing ammonium concentration. In other words, the existing turbidity may inhibit ammonium removal to a certain extent. Nevertheless, as the effluent ammonium concentration ranges of



Fig. 6. Influence of turbidity (NTU) on ammonium concentration (mg/L). (a) In schemes I, II, C and D; (b) in schemes A and B.

schemes I, II, A and B present few changes, much lower turbidity cannot promote PZ to remove more ammonium. The causes of this phenomenon are complicated, which involves the adsorption characteristics and dosing point of PZ [5,7].

PAC dosing barely presents apparent removal on ammonium in the same experimental conditions, which is depicted in schemes I, II, A and B of Fig. 7(a) and (b). The ammonium removal efficiency range of Y axis is nearly not changed, but COD_{Mn} and UV_{254} removal efficiencies improve significantly after dosing PAC. PZ dosing point in coagulation process promotes the ammonium removal efficiency while decreasing the removal efficiency of COD_{Mn} and UV_{254} , which can be drawn from comparing schemes C and D to schemes A and B of Fig. 7(a) and (b).



Fig. 7. Ammonium removal efficiency variation in each scheme. (a) Influenced by COD_{Mn} removal efficiency; (b) influenced by UV_{254} removal efficiency.

4. Conclusions

An analysis and selection of PZ dosing point in enhanced coagulation–sedimentation treatment is obtained through a sequence of jar tests, which provides a valuable reference for practical application of PZ in water works.

PZ dosing can cause extra induced turbidity, and it is not beneficial for PAC to remove turbidity. Worse, existing turbidity can inhibit ammonium removal to a certain extent. Dosing PZ in the suction well can minimise this adverse impact, and consequently, the effluent turbidity can reach the standard requirement. PZ dosing can either promote PAC to remove COD_{Mn} and UV_{254} or inhibit to it, which means both synergistic effect and antagonistic effect exist, in the meantime, the PZ dosing point determines which effect it is. It is optimal to dose PZ in the suction well for removing COD_{Mn} and UV₂₅₄ simultaneously. The PZ dosage must exceed 1 g/L when removing COD_{Mn}. Compared to the much limited ammonium removal efficiency of single PAC, PZ dosing has a significant synergistic effect to promote PAC to remove ammonium. When ammonium needs to be removed in priority, the early step of coagulation should be the optimal point, but it can decrease the removal efficiencies of COD_{Mn} and UV₂₅₄ on contrary. Furthermore, only PZ enhanced coagulation-sedimentation process cannot reach the effluent ammonium requirement in National Drinking Water Standard. Ammonium will continue to be removed effectively during sand filtration and post-chlorination processes in actual running water works.

Acknowledgement

This study was financially supported by Science and Technology Commission of Shanghai Municipality (Project No. 13DZ2251700).

References

- S. Ringuet, L. Sassano, Z.I. Johnson, A suite of microplate reader-based colorimetric methods to quantify ammonium, nitrate, orthophosphate and silicate concentrations for aquatic nutrient monitoring, J. Environ. Monit. 13 (2011) 370–376.
- [2] R. Malekian, J. Abedi-Koupai, S.S. Eslamian, S.F. Mousavi, K.C. Abbaspour, M. Afyuni, Ion-exchange process for ammonium removal and release using natural Iranian zeolite, Appl. Clay Sci. 51 (2011) 323–329.
- [3] Q. Du, S.J. Liu, Z.H. Cao, Y.Q. Wang, Ammonia removal from aqueous solution using natural Chinese clinoptilolite, Sep. Purif. Technol. 44 (2005) 229–234.
- [4] A.A. Zorpas, Recycle and reuse of natural zeolites from composting process: A 7-year project, Desalin. Water Treat. 52 (2014) 37–39.
- [5] K. Saltalı, A. Sarı, M. Aydın, Removal of ammonium ion from aqueous solution by natural Turkish (Yıldızeli) zeolite for environmental quality, J. Hazard. Mater. 141 (2007) 258–263.
- [6] S.B. Wang, Y.L. Peng, Natural zeolites as effective adsorbents in water and wastewater treatment, Chem. Eng. J. 156 (2010) 11–24.
- [7] D. Ghernaout, B. Ghernaout, A. Kellil, Natural organic matter removal and enhanced coagulation as a link between coagulation and electrocoagulation, Desalin. Water Treat. 2 (2009) 203–222.
- [8] N. Widiastuti, H.W. Wu, H.M. Ang, D.K. Zhang, Removal of ammonium from greywater using natural zeolite, Desalination 277 (2011) 15–23.
 [9] S. Eturki, H. Kallali, N. Jedidi, H.B. Ben Dhia,
- [9] S. Eturki, H. Kallali, N. Jedidi, H.B. Ben Dhia, Ammonium nitrogen removal from synthetic water by treatment with Tunisian natural clay, Desalin. Water Treat. 49 (2012) 227–233.

- [10] I.R. Bautitz, R.F.P. Nogueira, Degradation of tetracycline by photo-Fenton process-Solar irradiation and matrix effects, J. Photochem. Photobiol., A 187 (2007) 33–39.
- [11] W.W. Ben, Z.M. Qiang, X. Pan, M.X. Chen, Removal of veterinary antibiotics from sequencing batch reactor (SBR) pretreated swine wastewater by Fenton's reagent, Water Res. 43 (2009) 4392–4402.
- [12] J.A. Leenheer, J.P. Croué, Peer reviewed: Characterizing aquatic dissolved organic matter, Environ. Sci. Technol. 37 (2003) 18A–26A.
- [13] J.P. Croué, G.V. Korshin, M. Benjamin, Characterization of Natural Organic Matter in Drinking Water, American Water Works Association Research Foundation, Denver, CO, 2000.
- [14] H.M. Huang, X.M. Xiao, B. Yan, L.P. Yang, Ammonium removal from aqueous solutions by using natural Chinese (Chende) zeolite as adsorbent, J. Hazard. Mater. 175 (2010) 247–252.
- [15] A. Peter, L. Mihaly-Cozmuta, A. Mihaly-Cozmuta, C. Nicula, E. Indrea, H. Tutu, Calcium- and ammonium ion-modification of zeolite amendments affects the metal-uptake of *Hieracium piloselloides* in a dose-dependent way, J. Environ. Monit. 14 (2012) 2807–2814.
- [16] A.A. Halim, H.A. Aziz, M.A.M. Johari, K.S. Ariffin, Comparison study of ammonia and COD adsorption on zeolite, activated carbon and composite materials in landfill leachate treatment, Desalination 262 (2010) 31–35.
- [17] Sanitary standard for drinking water, Ministry of health of PR China and standardization administration of P.R. China (GB5749-2006), 2007.
- [18] J.E. Smith Jr., R.C. Renner, B.A. Hegg, J.H. Bender, Upgrading Existing or Designing New Drinking Water Treatment Facilities, Noyes Data Corporation, Park Ridge, NJ, 1991.
- [19] A. Matilainen, M. Vepsäläinen, M. Sillanpää, Natural organic matter removal by coagulation during drinking water treatment: A review, Adv. Colloid Interface Sci. 159 (2010) 189–197.
- [20] H.J. Liu, R.P. Liu, C. Tian, H. Jiang, X.L. Liu, R. Zhang, J.H. Qu, Removal of natural organic matter for controlling disinfection by-products formation by enhanced coagulation: A case study, Sep. Purif. Technol. 84 (2012) 41–45.
- [21] H.E. Hudson, E.G. Wagner, Conduct and uses of tests, J. Am. Water Works Assoc. 4 (1981) 218–223.
- [22] Standard Practice for Coagulation–Flocculation Jar Test of Water, Annual Book of ASTM Standards, West Conshohocken, PA, 1995, pp. 71–74.
 [23] M. Sarioglu, Removal of ammonium from municipal
- [23] M. Sarioglu, Removal of ammonium from municipal wastewater using natural Turkish (Dogantepe) zeolite, Sep. Purif. Technol. 41 (2005) 1–11.
- [24] L.C. Lei, X.J. Li, X.W. Zhang, Ammonium removal from aqueous solutions using microwave-treated natural Chinese zeolite, Sep. Purif. Technol. 58 (2008) 359–366.
- [25] M. Rožić, S. Cerjan-Stefanović, S. Kurajica, V. Vančina, E. Hodžić, Ammoniacal nitrogen removal from water by treatment with clays and zeolites, Water Res. 34 (2000) 3675–3681.
- [26] Water quality—Determination of turbidity, The State Environmental Protection Administration of China (SEPA) (GB 13200-91), Beijing, 1991.

- [27] A.D. Eaton, L.S. Cleceri, A.E. Greenerg, Standard Methods for the Examination of Water and Wastewater, ninetieth ed., American Public Health Association, Washington, DC, 1995.
- [28] Editorial Committee of "Monitoring and Analytical Methods of Water and Wastewater", Monitoring and Analytical Methods of Water and Wastewater, fourth ed., The State Environmental Protection Administration of China (SEPA), Beijing, 2002.
- [29] Water quality–Determination of permanganate index, The State Environmental Protection Administration of China (SEPA), (GB 11892-89), Beijing, 1989.
- [30] Determination of total organic carbon and specific UV absorbance at 254 nm in source water and drinking water, Method 415. 3. 600, The US Environmental Protection Agency (USEPA), USA, 2005.
- [31] J.Q. Jiang, Development of coagulation theory and pre-polymerized coagulants for water treatment, Sep. Purif. Methods 30 (2001) 127–141.
- [32] D. Ghernaout, B. Ghernaout, Sweep flocculation as a second form of charge neutralisation—A review, Desalin. Water Treat. 44 (2012) 15–28.
- [33] N.Z. Almutairi, M.F. Hamoda, I.A. Al-Ghusain, Coagulant selection and sludge conditioning in a slaughterhouse wastewater treatment plant, Bioresour. Technol. 95 (2004) 115–119.
- [34] A. Mahtab, M. Tariq, T. Shafiq, A. Nasir, Coagulation/ adsorption combined treatment of slaughterhouse wastewater, Desalin. Water Treat. 12 (2009) 270–275.
- [35] C. Rattanakawin, Aggregate size distributions in sweep flocculation, Songklanakarin J. Sci. Technol. 27 (2005) 1095–1101.
- [36] M.A. Yukselen, J. Gregory, The reversibility of floc breakage, Int. J. Miner. Process. 73 (2004) 251–259.
- [37] P.D. Patel, W.B. Russel, A mean field theory for the rheology of phase separated or flocculated dispersions, Colloids Surf. 31 (1988) 355–383.

- [38] B. Eikebrokk, T. Juhna, S.W. Østerhus, Water treatment by EnC—Operational status and optimisation issues, Techneau, D 5.3.1., December, 2006 (accessed June 2007).
- [39] A. Mesdaghinia, M.T. Rafiee, F. Vaezi, A. Mahvi, A. Torabian, A. Ghasri, Control of disinfection by products formation potential by enhanced coagulation, Int. J. Environ. Sci. Technol. 2 (2006) 335–342.
- [40] P. Jarvis, B. Jefferson, S. Parsons, Characterising natural organic matter flocs, Water Sci. Technol. 4 (2004) 79–87.
- [41] C.W.K. Chow, R. Fabris, J.V. Leeuwen, D. Wang, M. Drikas, Assessing natural organic matter treatability using high performance size exclusion chromatography, Environ. Sci. Technol. 42 (2008) 6683–6689.
- [42] Y.Ć. Soh, F. Roddick, J.V. Leeuwen, The impact of alum coagulation on the character, biodegradability and disinfection by-product formation potential of reservoir natural organic matter (NOM) fractions, Water Sci. Technol. 58 (2008) 1173–1179.
- [43] C.W.K. Chow, J.A. van Leeuwen, R. Fabris, M. Drikas, Optimised coagulation using aluminium sulfate for the removal of dissolved organic carbon, Desalination 245 (2009) 120–134.
- [44] J.T. Alexander, F.I. Hai, T.M. Al-aboud, Chemical coagulation-based processes for trace organic contaminant removal: Current state and future potential, J. Environ. Manage. 111 (2012) 195–207.
- [45] Y.F. Wang, F. Lin, W.Q. Pang, Ammonium exchange in aqueous solution using Chinese natural clinoptilolite and modified zeolite, J. Hazard. Mater. 142 (2007) 160–164.
- [46] S.A. Baghoth, S.K. Sharma, G.L. Amy, Tracking natural organic matter (NOM) in a drinking water treatment plant using fluorescence excitation–emission matrices and PARAFAC, Water Res. 45 (2011) 797–809.