Chinese Chemical Letters 34 (2023) 108379

Contents lists available at ScienceDirect

Chinese Chemical Letters

journal homepage: www.elsevier.com/locate/cclet

An enhanced coagulation using ferric chloride and poly-ferric chloride coagulant assisted by polyamidine: Performance and mechanisms

Bo Guo[a,b], Sen Zhang[a], Xing Xu[b], Baoyu Gao[b,*], Qian Li[b], Qinyan Yue[b]

[a] Shandong Institute of Metrology, Ji'nan 250014, China
[b] Shandong Key Laboratory of Water Pollution Control and Resource Reuse, School of Environmental Science and Engineering, Shandong University, Ji'nan 250100, China

ARTICLE INFO

Article history:
Received 31 October 2022
Revised 27 February 2023
Accepted 23 March 2023
Available online 24 March 2023

Keywords:
Coagulation performance
Polyamidine
Ferric chloride
Poly-ferric chloride

ABSTRACT

The deterioration of water caused by industrial production is a thorny problem. Solving the problem cogently through innovative coagulationstrategies has been recognized of important practical significance. In this work, a simple enhanced coagulation by using ferric chloride (FC) and poly-ferric chloride (PFC) coupled with polyamidine (PA) were tried to remove the toxic organics. The results shown that PA addition could obviously enhance coagulation performances of the iron-based coagulants. The synergic coagulation process and mechanism were studied and discussed in detail based on the coagulation behaviors, flocs properties, removal efficiency and zeta potentials. FC and PFC remove organics mainly through charge neutralization and adsorption-bridging, resulting in a good purification performance. While PA with a higher charge density showed better purification performance due to enhanced charge neutralization. It is worth mentioning that the addition of PA could make the coagulants adapt to a wider pH range, and remove the toxic organics more effectively. That is to say, the practical adaptability of the coagulant was enhanced. This work thus provides a simple strategy to effectively purify wastewater and further improve the water safety.

© 2023 Published by Elsevier B.V. on behalf of Chinese Chemical Society and Institute of Materia Medica, Chinese Academy of Medical Sciences.

As the legislation related to environment is becoming stricter in many countries due to an increase of public consciousness, treatment of wastewater requires much effort from scientists and public. For common water pollution, the removal of toxic organics from textile printing and dyeing industries has received much attention and investigation [1–4]. The presence of these toxic organics from textile printing and dyeing industries is aesthetically unfriendly in surface water and could cause disaster toward the aquatic biosphere due to reduction of sunlight penetration and depletion of dissolved oxygen. Furthermore, these toxic organics are mutagenic and have the potential to cause cancer. However, toxic organics removal from industrial wastewater by means of cheap and environment-friendly technologies is still a major challenge. Recently, various methods have been tried to remove these toxic organics from textile printing and dyeing industries, and the common approaches include microbiological decomposition, enzymatic decomposition, photocatalytic degradation, adsorption, and so on [5–7].

The application of microorganisms for the biodegradation of these toxic organics is an efficient method by operation. Ali and El-Mohamedy reported that six fungal isolates belong to *Aspergillus niger*, *Penicillium* spp. and *Pleurotus osstreatus*, which had good effect for decolorization activities of some toxic organics [8]. Baeta *et al.* reported an anaerobic-aerobic combined system that could be efficient in removing aromatic amines, volatile fatty acid, soluble microbial products and color from azo dye effluents [9]. However, the biological mechanisms are very complex and expensive. Moreover, the majority of these compounds are chemically stable and resistant to microbiological attack. Enzyme preparations are often combined with other methods to remove these toxic organics from textile printing and dyeing industries more efficiently because that the employment of enzyme preparations and nanomaterials shows considerable benefits over the direct use of it. A novel promiscuous enzyme was covalently immobilized on the functionalized magnetic graphene oxide for synergistic adsorption-degradation of organics by Ariaeenejad *et al.* [10]. Base on the high laccase loading and improved activity, biocatalytic nanoflower was used by Li *et al.* to remove organic dye and micropollutant effectively [11]. In addition to the biodegradation of these toxic organics, other physicochemical methods, *e.g.*, adsorption, and coagulation, have also attracted much attentions because they are feasible, efficient, easy

---

[*] Corresponding author.
E-mail addresses: baoyugao_sdu@aliyun.com, bygao@sdu.edu.cn (B. Gao).

https://doi.org/10.1016/j.cclet.2023.108379
1001-8417/© 2023 Published by Elsevier B.V. on behalf of Chinese Chemical Society and Institute of Materia Medica, Chinese Academy of Medical Sciences.

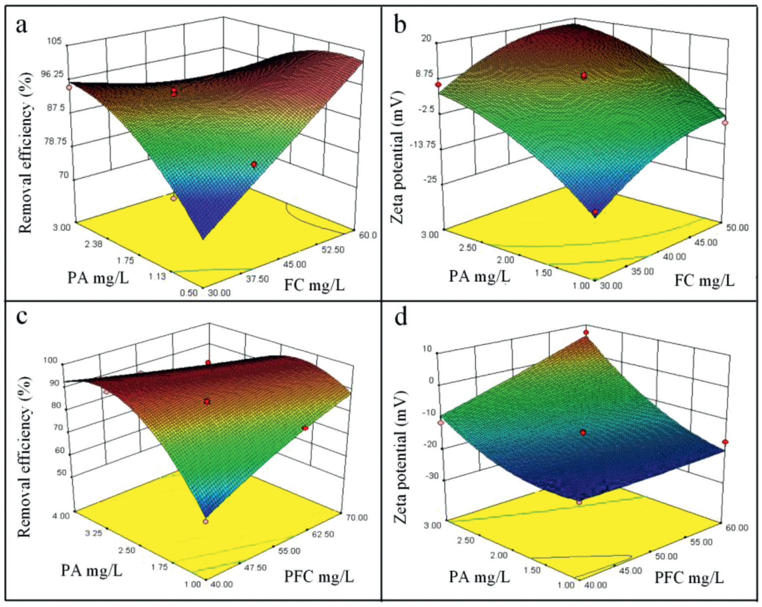

Fig. 1. Response surface diagram of the effect of dosage on removal efficiency (a) FC-PA, (c) PFC-PA. Response surface diagram of the effect of dosage on zeta potential (b) FC-PA, (d) PFC-PA.

to implement and low cost. For adsorption, a series of nanomaterials and natural materials were used to adsorb the toxic organics from aqueous solutions, such as carbonaceous, metallic, magnetic, bionanomaterials, cellulose [12,13]. Moreover, the application of coagulation for the treatment of toxic organics wastewater has also been emphasized and encouraged as the viable alternative [14]. Some novel pre-hydrolysed coagulants such as polyaluminium chloride, polyaluminium ferric chloride, polyferrous sulfate, polyferric chloride (PFC) and natural coagulants have been found to be more effective than traditional metal coagulants for toxic organics removal [15].

As the most common coagulants, ferric chloride (FC) and PFC have been widely used in wastewater treatment plants for many years [16,17]. As a novel macromolecular polymer with amidine units on its molecular chains, polyamidine (PA) has attracted more attention in coagulation process. Generally, circular PA contains high cationic density due to the amino groups with five membered rings on its chains. However, the usage of PA combined with ferric salt is rarely discussed in coagulation process and needed to be improved in the future research. In this study, PA as a dual-coagulation was combined with FC and PFC to remove the typical toxic organics in textile printing and dyeing industries (reactive turquoise blue K-GL, RTB). A series of controlled parameters were conducted, and the effects of solution pH, dosage of coagulant of PA on RTB removal were studied. Finally, the principle of coagulation was also investigated.

A statistical experimental design based on "central composite design (CCD)" was planned [18,19]. The removal efficiency or zeta potential was measured for different variables such as dosages of FC and PA or PFC and PA. The dosage was written as x_1 and x_2, respectively. These variables were investigated at five levels (−2, −1, 0, 1, 2) and the dependent variables was Y. We used the Design Expert software (version 8.0.5.0) to design and evaluate these two independent variables at five levels on the responses according to Eq. 1 and Eq. 2. The ranges for the selected levels of the four variables are shown in Tables S1 and S2 (Supporting information). The theoretically predicted values of removal efficiency and zeta potential for different selected levels of variables are shown in Tables S3 and S4 (Supporting information) for 13 runs, respectively.

$$Y = \beta_0 + \sum \beta_j \cdot X_i + \sum \beta_{jj} \cdot X_j^2 + \sum \beta_{jk} \cdot X_j \cdot X_k \tag{1}$$

where Y = response, β_0 = intercept, β_j = linear coefficients, β_{jj} = squared coefficients, β_{jk} = interaction coefficients, X_i, X_j^2, X_j, X_k = level of independent variables, and

$$\begin{aligned} \alpha &= \text{star point} \\ &= \pm\left(2^{\text{No. of parameters}}\right)^{1/4} \\ &= \pm\left(2^4\right)^{1/4} \\ &= \pm 2 \end{aligned} \tag{2}$$

The smaller the P-value, the more significant is the corresponding coefficient. The results of statistical analysis are shown in Tables S5 and S6 (Supporting information). Based on the statistical results with confidence level of 95%, the effect of each term in the models could be significant provided that its P-value be smaller than 0.05 ($P < 0.05$). The results showed that the model met the significance test, and the design was reliable.

Effect of different dosages of FC and PA on the removal of RTB was shown in Fig. 1a. As the dosage of PA increases, two distinguished trends of the removal efficiency can be observed. In the range of 0∼1.24 mg/L, the removal efficiency increases with a prominent slope until it reaches its maximum value (99.9%) and further increasing PA dosage causes a mild decrease in removal efficiency (96%). The effect of FC dosage is also demonstrated in Fig. 1a for the range of 30∼60 mg/L. The enhancement of removal efficiency is observed as the dosage of FC is increased from 30 mg/L to 56.6 mg/L and the maximum removal efficiency of 99.9% is reached. Combined with the results in Table S5, it can be seen that the P-value of dosage of PA (0.0089) is significantly less than the result of FC (0.0217). This indicates that both FC and PA play a significant role on removal efficiency, and PA turns out to be the more important factor.

Effect of coagulant dosage on zeta potential was given in Fig. 1b. The zeta potential increased as the dosages of PA and FC increased. The isoelectric point was obtained when the dosage of FC and PA were 31 mg/L and 2.1 mg/L, or 51 mg/L and 1.2 mg/L, respectively. Fairly small numbers of P-value of zeta potential suggest that they played an equally important role in electrical neutralization. Considering removal efficiency and zeta potential, the optimal dosage of FC and PA was selected at 55 mg/L and 1 mg/L, respectively.

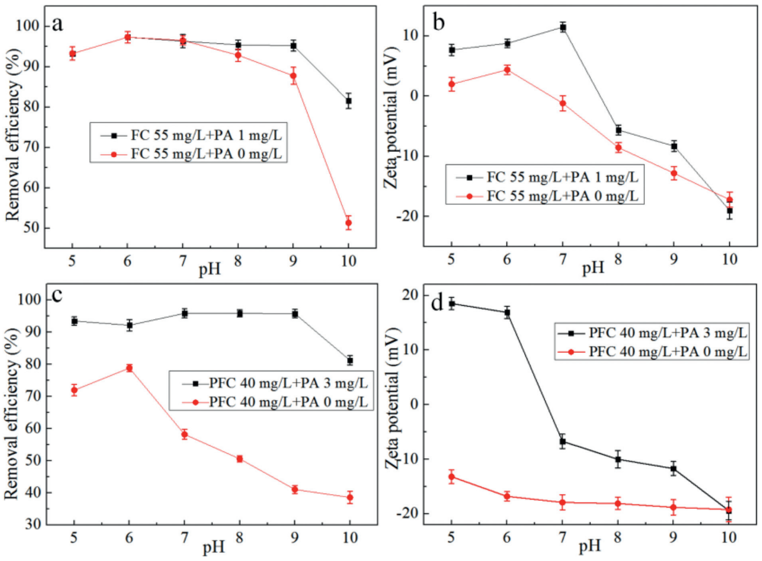

Fig. 2. Effect of pH condition on removal efficiency (a) FC-PA, (c) PFC-PA and zeta potential (b) FC-PA, (d) PFC-PA.

Fig. 1c shows the effect of different dosage of PFC and PA on RTB removal efficiency. The removal efficiency increased to the maximum value of 95.9% with the increasing PFC dosage to 65 mg/L and then reached to the equilibrium. It can be seen from Table S6 that the *P*-value of PFC and PA are all less than 0.0001, which shows that PFC and PA played an equally important role for RTB removal due to their strong synergistic effects.

Fig. 1d shows the effect of different dosages of PFC and PA on zeta potential. The zeta potential increased obviously with the increase of PA content. However, there was no significant rise in the zeta potential as the PFC dosage increases. The reason might be that PFC has less positive charge than FC. The isoelectric point can be obtained when the dosage of PFC and PA were 62 mg/L and 2.6 mg/L, or 40 mg/L and 3.5 mg/L, respectively. It can be seen from Table S6 that the *P*-value (zeta potential) of PFC is 0.0012, while that of PA is 0.0001, indicating that PA played a more important role to the surface charge as compared with PFC. Considering the both indexes, *i.e.* removal efficiency and zeta potential, the optimal dosage of PFC and PA can be selected at 40 mg/L and 3 mg/L, respectively.

Effect of pH condition on removal efficiency of RTB and zeta potential by FC and PFC in the presence or absence of PA was investigated by adjusting the primitive pH of RTB solution, which was settled in the range of pH 5.0∼10.0 (Fig. 2). When FC was used alone, the removal efficiency was improved with pH increasing in the range of 5∼6. Then the removal efficiency decreased slowly and maintained at around 90% in the pH range of 6∼8. Finally, the removal efficiency reduced greatly (50%) when pH exceeded 9.0. The removal efficiency of RTB was quite different when PA was added in the system. The RTB removal efficiency changed gently at pH 5∼9, showing a gradual and slow decrease. It decreased significantly above pH 9 but remained above 80%. As shown in Fig. 2b, in the FC alone system, the zeta potential of floc increased sharply at pH 5.0∼6.0 and then decreased gradually with the increasing of pH from 6.0 to 10.0. In acidic condition, the hydrolyzation of Fe was limited to the positive electricity due to the lack of OH^-. As a result, decoloration mechanism was based on the charge neutralization in this condition. However, the zeta potential trended to decline with the further increase of pH, which suggested that charge neutralization was weakened at pH from 6.0 to 9.0.

When PFC was used alone, the RTB removal efficiency was improved with pH increasing in the range of 5∼6 (Fig. 2c). Whereafter, the removal efficiency decreased dramatically when pH exceeding 6.0. When PA was used as coagulant aid with PFC, the removal efficiency changed gently at pH 5∼9. The removal efficiency decreased to 80% when pH was higher than 9. The zeta potential decreased with the increase of pH regardless of PFC alone or PA combined with PFC (Fig. 2d). Especially when PA was used together with PFC as a coagulant aid, zeta potential decreased sharply when pH was higher than 6.

The above results show that the pH can affect the hydrolysis behavior of FC and PFC in water. The polynuclear hydroxy complexes of iron or polyferricpolymers are a system of intermediate compounds produced in the Fe(III) solution by the continual processes of hydrolysis, complexation, polymerization, solation, precipitation and gelation. In the hydrolysis of Fe(III), Fe can be divided into three morphologies: Fe(a), Fe(b), Fe(c) [20,21]. Among them, Fe(a) and Fe(b) are active components, especially Fe(b) is the most effective component which has stronger coagulation performance. Fe(c) is chemically inert and has poor coagulation effect. Lower pH results in lower OH^- concentration in water, Fe(a) cannot be converted into highly positive hydrolysate Fe(b) and then contact with the organics, thus leading to poor coagulation effect. Then, the increase of pH led to the increase of OH^- concentration in water, followed by a gradual increase in the yield of Fe(b), so the coagulation effect becomes better. In this process, both charge neutralization and adsorption-bridge play important roles in the removal of organics. Finally, Fe(III) hydrolyzes rapidly as the pH of the water becomes alkaline [22]. As is known to all, PFC is a forced hydrolysis product of FC. The increasing concentration of OH^- cause more precipitation of $Fe(OH)_3$ and great reduce of positive charge density. At this time, the zeta potential becomes negative, both FC and PFC lose the ability of charge neutralization, which led to a sharp decrease in coagulation effect. In the presence of PA, however, its long-chain structure increases its adsorption-bridge capacity. Even when the pH is high for invalidation of Fe(III), the positively charged PA acts through both charge neutralization and adsorption-bridge, keeping the removal efficiency at a high level. It can be seen that the addition of PA can make the coagulants adapt to a wider pH range, and can remove the organics more effectively. To better understand the mechanism of organics removal by coagulation taking place between coagulants and RTB, a preliminary depiction of the process is proposed in Fig. 3. It is well known that the coagulants can induce coagulation through charge neutralization [23]. RBT with negatively charged reacts easily with PA, which is cationic. Iron salt coagulants exhibited strong

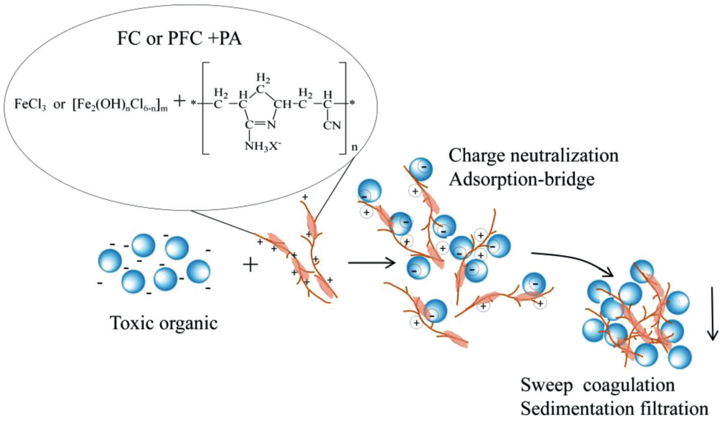

Fig. 3. Scematic representation of the coagulation principle using FC or PFC with PA to remove the RTB.

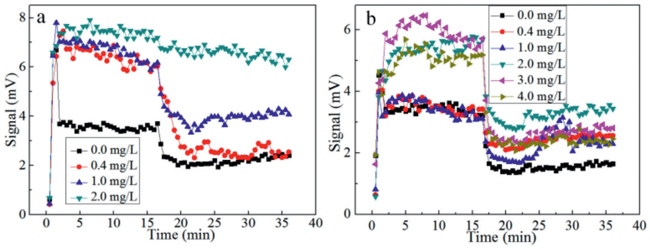

Fig. 4. Growth, breakage and regrowth of flocs for different dosages of PA: (a) FC-PA as coagulant, (b) PFC-PA as coagulant.

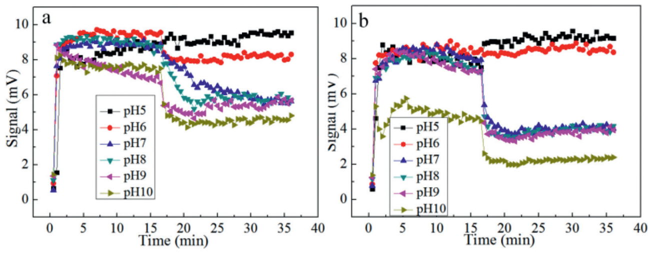

Fig. 5. The breakage and regrowth curves of flocs for different pH of PA: (a) FC-PA as coagulant, (b) PFC-PA as coagulant.

bridge adsorptive performance. The structure consists of polynuclear hydroxy complexes with variable morphology; thus, it reacts easily with the reactive groups (–Cl and –SO_3Na) in RBT [24]. Finally, because of the polymeric properties of the hydrolysis of iron salts coagulants and the macromolecular structure of PA, sweep coagulation and sedimentation filtration mechanism could be the dominant mechanism.

To analyze the influence of PA on properties of flocs formed in FC-PA and PFC-PA systems, PA with different dosages were selected as (0.0∼2.0) mg/L for FC-PA system and (0.0∼4.0) mg/L for PFC-PA system. The dosage of FC and PFC was 55 mg/L and 40 mg/L, respectively. The performance of flocs was monitored online by PDA 2000, and the flocs size expressed as ratio was plotted in computer. The signal of instrument measurement was used to characterize the size of the flocs and reflect the floc growth trend of the test process.

It can be seen from the Fig. 4 that the particle size of flocs increased, and the maximum particle size was obtained when the dosage of PA was 2.0 mg/L in FC-PA system. When the flocs were subjected to shear force, the degree of fragmentation was small, and the particle size decreased slightly. This indicated that the flocs bond closely after adding PA, and the shear force was not enough to destroy the flocs structure. With the increase of the PA dosage, the particle size of flocs increased first and then decreased, and reached the maximum value when the dosage of PA was 3.0 mg/L in PFC-PA system. This indicated that PA provided adsorption-bridge capacity and could effectively increase the particle size of flocs as a polymer. However, large concentration of PA would lead to too much positive charge, which not only affected the aggregation of colloids, but also led to the reduction of particle size of flocs.

In order to figure out the effect of PA working with FC or PFC on floc properties, three parameters (strength factor, recovery factor and TWV) after coagulation were investigated by different PA dosages (Table S7 in Supporting information).

It can be seen from Table S5 that, at the same dosage, the flocs produced by FC coagulation were generally stronger than PFC in terms of strength and recovery capacity after fragmentation. From the perspective of FC-PA system, the intensity of the formed flocs was increased with the increase of PA dosage. There was a very small change in the particle size of flocs before and after shearing, so there was no recovery process in the system. From the perspective of PFC-PA system, S_f was increased first and then decreased with the increase of PA dosage. The main reason was that a large amount of positively charged PA changed the electrical properties of the flocs, making the flocs with the same charge repulsive to impede the growing up. However, FC and PFC represented different characteristics in TWV. For PFC-PA system, the TWV_2 value of the flocs in the regeneration stage was generally smaller than that in the stable stage, which indicated that the flocs structure in the regeneration stage was more compact than that in the stable stage. This was also due to the different dominant mechanisms of coagulation leading to different flocs strength.

Flocs performance as a function of pH (5.0∼10.0) was presented in Fig. 5. FC-PA exhibited the best floc structure at pH 6.0, and also achieved a good resilience at pH 5.0. In contrast, PFC-PA gained the biggest floc size and recovery at pH 5.0 and 6.0. In the two systems, with the increase of pH value, the particle size of the flocs gradually decreased, and the shear resistance became worse, which are matched with the trend of organics removal.

The calculated S_f, R_f, TWV_1 and TWV_2 as well as flocs characteristics expressed under different pH were given in Table S8 (Supporting information). S_f showed the same trend in FC-PA and PFC-PA systems. R_f expressed a negative correlation with pH, because the large flocs have a looser structure and the recovery ability against breakage tend to be impaired. TWV tended to be in a random pattern in FC-PA system. PFC-PA system showed a more pronounced pattern: TWV_2 was always less than TWV_1; this reflected the smaller and denser properties of flocs after breakage.

In summary, the addition of PA could greatly improve the coagulation performance of FC and PFC under the investigated dosages and pH conditions. The optimal coagulation performance was achieved at the two dosage conditions (*e.g.*, 55 mg/L of FC and 1 mg/L of PA, or 40 mg/L of PFC and 3 mg/L of PA). The introduction of PA could enhance the charge neutralization effect due to the high cationic degree of PA. In addition, the long chain of PA could provide a function of adsorption bridging in coagulation process. These compound coagulants showed excellent RTB removal efficiency in a wide pH range. Along with its excellent assisted removal capacity, the compound coagulants have great potential for wastewater treatment in the textile industry.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This work was financially supported by Taishan Scholar Foundation, China (No. ts201511003) and Major Technological Innovation Engineering Project of Shandong Province, China (No. 2020CXGC011204).

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.cclet.2023.108379.

References

[1] X.S. Wang, Y. Zhou, Y. Jiang, et al., J. Hazard. Mater. 157 (2018) 374–385.
[2] E. Erdem, G. Çölgeçen, R. Donat, J. Colloid Interface Sci. 282 (2005) 314–319.
[3] S. Natarajan, H.C. Bajaj, R.J. Tayade, J. Environ. Sci. 65 (2018) 201–222.
[4] K. Selvam, K. Swaminathan, K.S. Chae, World J. Microbiol. Biotech. 19 (2003) 591–593.
[5] D. Yuan, C. Zhang, S. Tang, et al., Chin. Chem. Lett. 32 (2021) 3387–3392.
[6] W. Peng, Y. Fu, L. Wang, et al., Chin. Chem. Lett. 32 (2021) 2544–2550.
[7] M. Tabatabaee, M. Roozbeh, M. Roozbeh, Chin. Chem. Lett. 22 (2011) 1501–1504.
[8] N.F. Ali, R.S.R. El-Mohamedy, J. Saudi Chem. Soc. 16 (2012) 117–123.
[9] B.E.L. Baeta, D.R.S. Lima, S.D.Q. Silva, et al., Chem. Eng. J. 259 (2015) 936–944.
[10] S. Ariaeenejad, E. Motamedi, G.H. Salekdeh, Bioresour. Technol. 319 (2021) 124228.
[11] H. Li, J. Hou, L. Duan, et al., J. Hazard. Mater. 338 (2017) 93–101.
[12] K.B. Tan, M. Vakili, B.A. Horri, et al., Sep. Purif. Technol. 150 (2015) 229–242.
[13] G. Annadurai, R.S. Juang, D.J. Lee, J. Hazard. Mater. 92 (2002) 263–274.
[14] J. Wu, Y. Liu, X. Yang, et al., Chin. Chem. Lett. 32 (2021) 2503–2508.
[15] A.K. Verma, R.R. Dash, P. Bhunia, J. Environ. Manage. 93 (2012) 154–168.
[16] T.H. Kim, C. Park, E.B. Shin, et al., Desalination 161 (2004) 49–58.
[17] Z. Yang, X. Lu, B. Gao, et al., J. Mater. Sci. 49 (2014) 4962–4972.
[18] H. Kamali, H.S. Ghaziaskar, J. Supercriti. Fluid. 54 (2010) 16–21.
[19] M. Daneshvar, H. Kamali, M. Masoomi, et al., J. Supercriti. Fluid. 70 (2012) 119–125.
[20] B. Tian, H. Tang, Environ. Chem. 8 (1989) 27–34.
[21] H.X. Tang, B.Z. Tian, Z.K. Luan, et al., Inorganic polymer flocculant polyferric chloride, its properties, efficiency and production, in: R. Klute, H.H. Hahn (Eds.), Chemical Water and Wastewater Treatment III, Eds., Springer, Berlin, Heidelberg, 1994, pp. 57–69.
[22] Y. Y. Wang, B. Gao, Q.Y. Yue, et al., Environ. Chem. 25 (2006) 730–734.
[23] Y. You, X. Sun, W. Yang, et al., Algal Res. 41 (2019) 101579.
[24] F. Mcyotto, Q. Wei, D.K. Macharia, et al., Chem. Eng. J. 405 (2021) 126674.