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Optimization of demulsification-coagulation-adsorption parameters for the treatment of wastewater with fluorescent permeating agent from a Chinese machinery plant

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ABSTRACT

Fluorescent penetrant is used for the cleaning process of precision machine parts in non-destructive testing (NDT). Wastewater will be produced in that course with high chemical oxygen demand (COD) (1000–15,000 mg/L), high mineral oil (300–3000 mg/L) and high chroma (600–2000). This liquid waste has a serious influence on the environment due to its' stronger biological toxicity and higher virulence. When the oil content exceeds 0.01 mg/L in water, the water will lack oxygen and lead aquatic plants and animals to die, thus create badly water pollution. How to treat this polluted water is a difficult task in sewage treatment. The demulsification-coagulation-adsorption process was adapted for conducting this emulsifying wastewater. This research has compared the demulsification effects between the nonionic surfactant demulsifier of AR and the electrolyte demulsifier of $CaCl_2$ and $MgCl_2$ as well as the coagulation performance between the polymeric aluminum chloride (PAC) and the polyaluminium chloride sulfate (PACS). Effects of the types of demulsifier and coagulant, dosage, pH, static duration, absorbing time and other process parameters have been investigated. Based on this, the process parameters have been optimized. The results shown that the best treatment condition was using AR as demulsifier, PACS as flocculant, and vermiculite as adsorbent, which resulted in higher quality and efficiency in removal of 97.87% COD, 99.62% oil and 99.22% colority. This could meet the first grade standard of the national integrated wastewater discharge standard (GB8978-1996). Thus, the integration method of demulsification-coagulation-adsorbtion is a practicable way to solve this kind of sewage.

Keywords: Emulsifying wastewater; Demulsification-coagulation-adsorbtion; Fluorescent penetrant

1. Introduction

The emulsifying wastewater is a type of high concentration wastewater which comes from the cleaning process after NDT of precision parts with the fluorescence penetrant as tracer. The composition of emulsifying wastewater is complicated and greatly harmful to the environment [1–3]. That is, high concentration of organic matter, high oil content, high colority and high biotoxicity even in small quantities. In addition, it is intermittently discharged. The COD value of this kind of liquid waste is 1000–15,000 mg/L, the mineral oil it contains is 300–3000 mg/L, and the colority value is 600–2000. If this wastewater is discharged directly, it will have unimaginable consequences on the global ecosystem: plants, soil, water and humanity itself [4–6].

The disposal of emulsified wastewater is not only a major problem, but also a new subject in the field of wastewater treatment. And, less research has been done on its effective treatment. The difficulties of liquid waste disposal are demulsification and sediment as well as decoloration and removing COD. Thus, such wastewater is difficult to treat using conventional wastewater processes. Various demulsification treatment methods for wastewaters have been reported to remove more persistent pollutants relative

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to traditional physical and chemical methods such as acidification demulsification [7], chemical agent demulsification [8], microbiological method [9], ultrasonic demulsification [10], ultrafiltration demulsification [11], etc. And as for decoloration and removal of COD, the main methods are coagulation [12], gas flotation method [13], adsorption [14], magnetic separation [15], extraction [16], deep oxidation [17] and biochemical processes [18].

However, these single treatment methods have defects, such as poor treatment efficiency and inability to meet the demands of environmental protection, high treatment costs, complicated treatment processes and not being conducive to the needs of large-scale processing, etc. Despite the development of various technologies for water treatment and reclamation, economic, effective, and rapid water treatment and reclamation at a commercial level is still a challenging problem. So, it is of great significance to study a set of efficient and feasible methods to treat emulsified wastewater.

In view of the characteristics of wastewater with NDT of precision parts in this mechanical company, the COD removal process provided the criteria chosen to evaluate the treatment efficiency. The present study compared demulsification effects between the nonionic surfactant demulsifier of AR, the electrolyte demulsifier of $CaCl_2$ and $MgCl_2$, and the coagulation performance between PAC and PACS. Effects of the types of demulsifier and coagulant, dosage, pH value, static duration, absorbing time, and other process parameters have been investigated. Based on that, the process parameters have been optimized. Vermiculite was used for deep deprivation in the last stage to investigate its potential for effective post-treatment of the coagulation–flocculation effluent and if the discharged sewage could meet integrated wastewater discharge standards (GB8978-1996). The results have already been used in the wastewater treatment project of this company. The authors hope that this research can provide a new solution for the disposal of this kind of high concentration, low biodegradation wastewater.

2. Materials and method

2.1. Chemicals

All the purity specifications of materials in the experiments are analytically pure. AR type demulsifier, $CaCl_2$ and $MgCl_2$ were used as the demulsifier, PAC and PASC as the coagulant, polyacrylamide (PAM) as the coagulant aids, and vermiculite as the adsorbent.

Raw wastewater was obtained from the cleaning process of precision parts in NDT of a machine factory in Hunan province, and samples were collected at the storage tank. The emulsified wastewater appears fluorescent green, ropey and has an unpleasant smell. The composition of the pollutants is mainly of fluorescence powder, mineral oil, surfactant and other chemical additives such as fluorescent dyes, fluorescent bleacher, #5 machine oil, dibutyl phthalate (DBP) and ether. The physical and chemical properties of the raw emulsifying wastewater were analyzed and are listed in Table 4. It shows that the characteristics are high COD, high oil, high colority and acidic pH.

2.2. Analytical methods

COD was determined by dichromate method, colority was determined by dilution multiple method, oil containing was determined by ultraviolet spectrophotometer method, and pH was measured by a PHS-3C pH meter [19].

2.3. Experiment method

Single factor variable and orthogonal experiment method were used to conduct the experiments. Take 100 mL wastewater in a 500 mL beaker, add 1–12 mL reagent, mix 1–5 min, stand 5–35 min according to the experiment design. Then take 10 mL liquid supernatant for water quality analysis. In order to improve accuracy of the single factor variable experiments, duplicate analyses were conducted for each treatment condition and the arithmetic average of the two measurements was used as the final result.

2.3.1 Demulsification experiment

Effect of pH value on COD removal in the emulsified wastewater with different demulsifiers was carried out at room temperature. Adding 0.2 mL demulsifier solution with mass concentration of 45%, slowly stirring at 50 rpm for 5 min, and then rapidly stirring at 300 rpm for 3 min was performed followed by sedimentation for 10 min. Experiments were also conducted at the same operating conditions by varying the demulsifier dose and static duration while keeping the pH constant to assess the effect of the demulsifier dose and static duration on the process efficiency. The demulsification process was optimized by an orthogonal experiment.

2.3.2 Coagulation experiment

Take the supernatant of the demulsification experiment to perform the coagulation experiment. Add 0.3 mL of 10% coagulation solution, slowly stir at 50 rpm for 3 min, and then rapidly stir at 300 rpm for 1 min. Add 0.1% PAM solution in proportion to 4 mL/L wastewater, rapidly stir at 300 rpm for 3 min, and let stand for 15 min. Then evaluate the influence of pH value, coagulation dosage and coagulation aids dosage and static duration. The coagulation process was also optimized by an orthogonal experiment.

2.3.3. Adsorption experiment

The effect of adsorbent dosage on COD removal was studied through static experiments. Take 100 mL liquid supernatant after coagulation treatment, manipulate the amount of adsorbent by raising from 1 to 7 g/L, rapidly stir at 300 rpm for 30 min, and then filter and separate.

Use the pseudo-first-order kinetics model and the pseudo-second-order kinetics model to simulate kinetics process of vermiculite adsorbtion on emulsification wastewater at the best suitable added amount. The adsorption capacity in equilibrium (q_e, mg/g) and the adsorbed amounts of COD (q_t, mg/g) at different intervals were calculated by the following equations:

$$q_e = \frac{V(C_o - C_e)}{W} \tag{1}$$

$$q_t = \frac{V(C_o - C_t)}{W} \tag{2}$$

where C_o is the initial solution concentration (mg/L), and C_t is the solution concentration at time t (mg/L), V is the volume of solution (L), C_e is the COD equilibrium concentration and W is the mass of the adsorbent used (g).

3. Results and discussion

3.1. Effect of pH, demulsifier and static duration on demulsification process of wastewater with fluorescent permeating agent

Demulsification is a crucial step in the success of the experiment. At the initial stage of the investigation, the experiment was designed to determine the optimum type and amount of demulsifier in the demulsification reaction. After that, the static duration was examined in order to simplify the process.

3.1.1. Selection of the optimum pH

pH value is of vital importance to the effect of demulsifiers and conditions were optimised primarily to achieve minimum COD. As shown in Fig. 1, the COD removal efficiency of AR demulsifier in strong acid and strong alkali conditions were lower than that of weak acid and weak alkali conditions. Comparing the efficiency of three kinds of demulsifiers for COD removal, AR proved to be better than $CaCl_2$ and $MgCl_2$ within pH 3–10, and got the best removal rate of COD for 73.54% at pH 6–9. However, $CaCl_2$ and $MgCl_2$ had a better performance at pH 11–12 with the best results being 63.70% and 71.48% respectively. The better results might account for the AR demulsifier being susceptible to hydrolysis in a weak acid or a weak alkali medium, but being unfavourable to sufficient hydrolysis in a strong acid or a strong alkali medium. COD removal effects of $CaCl_2$ and $MgCl_2$ also showed an upward trend with increasing pH in a range of 3–11 and had the best removal effect of COD under strong alkali. Because the wastewater was slightly acidic with H^+, $CaCl_2$ and $MgCl_2$ hydrolyzed in the solution and produced a hydroxide polymer or a complex ion that created strong charge neutralization and produced flocculent settling that could remove COD. If pH is too low, it can inhibit the hydrolysis of the demulsifiers to produce such substances and weaken their demulsification effect.

3.1.2. Selection of the optimum demulsifier

Manipulate demulsifier dose from 1 to 6 mL/L, the result is shown in Figs. 2 and 3. When demulsifier was added to the wastewater, the stratification of oil and water was destroyed and the upper wastewater gradually became clear. With the increase of three kinds of demulsifier dosage, the COD removal efficiency gradually increased. In this case, the oil-water interfacial tension decreased with the concentration of demulsifier, but the dehydration rate kept increasing. When the amount of demulsifier was over 4 mL/L, demulsifier dosage had no obvious effect on COD removal rates and the color of wastewater did not change significantly. At this point, the oil-water interface of emulsifying oil adsorption tended to balance and the oil-water interfacial tension didn't decrease anymore and the COD

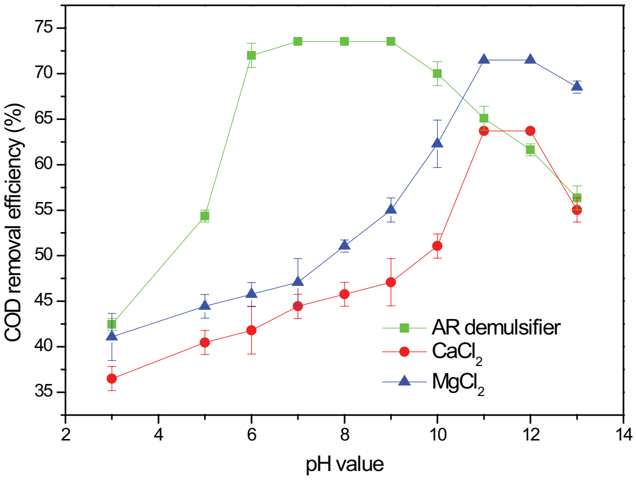


Fig. 1. Effect of pH on the removal efficiency of COD in demulsification process.

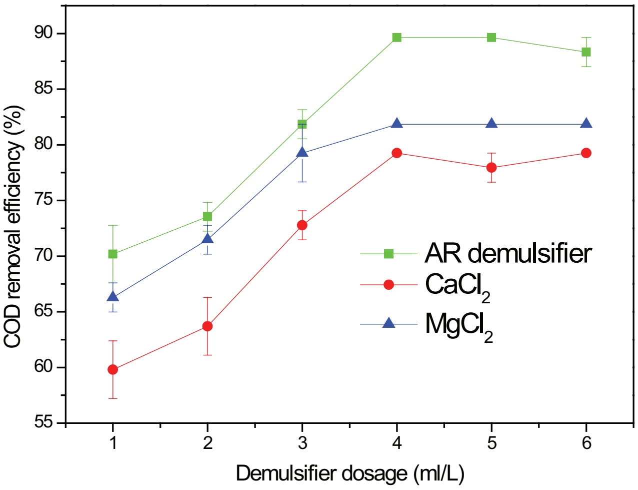


Fig. 2. Effect of dosage on the removal efficiency of COD in demulsification process.

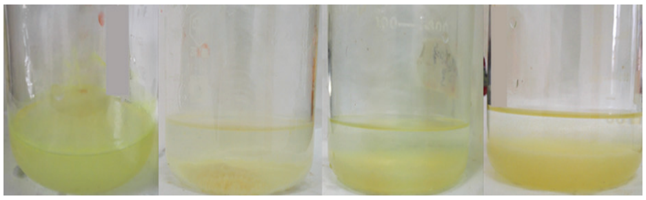

(a) (b) (c) (d)

Fig. 3. The effect of wastewater with fluorescent permeating agent demulsification using different demulsifier. (a) Before demulsification; (b) Demulsified by $CaCl_2$; (c) Demulsified by $MgCl_2$; (d) Demulsified by AR type demulsifier.

removal rate reached its maximum. When more demulsifier was added, it changed little or even worsened. Therefore, the best dosage for demulsifiers was 4 mL/L and the highest removal efficiency of AR type, $MgCl_2$ and $CaCl_2$ were 89.63%, 81.85% and 79.25% respectively.

Compare the effect of three kinds of demulsifiers for demulsification, although $MgCl_2$ and $CaCl_2$ are metal ions with the same valency, but the metal ionic radius of the two cases are different. The radius of Mg^{2+} is less than Ca^{2+}, however the electric field intensity of Mg^{2+} is larger. It has the effective thickness of an oil droplet diffused by an electric double layer, reducing it further. The demulsification is easier when the potential distribution of the width and the gradient of electric double layer become lower. AR demulsifier has the best COD removal efficiency and the yielding water is clean with fewer suspended substances in it. The molecular weight of AR demulsifier is greater than that of electrolyte demulsifiers, but it is not a high polymer. So, the effect of AR demulsifier is better than that of $MgCl_2$ and $CaCl_2$, and AR is the best demulsifier.

Stand and observe effects of demulsification treated by AR demulsifier. The flocculation sank slowly and the COD removal rate gradually increased during the early first 10 min. After that, COD did not show any significant change and remained in 89.63%. The optimum static duration for this wastewater was 10 min.

3.1.3. The orthogonal experiment of demulsification process

The demulsification process was optimized by an orthogonal experiment. This experiment consisted of taking COD removal efficiency as examination indexes. Three factors were then used to investigate the demulsification process: pH, dosage of AR demulsifier and static duration.

The L_9 (3^4) orthogonal test was designed by the factor level in Table 1. The results are shown in Table 1: $R_A > R_B > R_C$. pH > dosage > static duration were the effects of these three factors on COD removal of wastewater. Among the 3 factors, pH had the most obvious effects on demulsification. The optimum demulsification condition was $A_2B_2C_3$ (within the designed range of the experiments). That was, adding 4 mL/L AR in wastewater, pH = 7, and allowing to stand for 15 min.

Table 1
Design and results of orthogonal demulsification test

Serial number	A pH	B Dosage (mL/L)	C static duration (min)	COD removal efficiency (%)
1	3	2	5	41.79
2	3	4	10	53.70
3	3	6	15	55.02
4	7	2	10	73.54
5	7	4	15	89.63
6	7	6	5	80.35
7	11	2	15	70.90
8	11	4	5	72.22
9	11	6	10	77.51
k_1	150.51	186.23	194.36	
k_2	243.52	215.55	204.75	
k_3	220.63	212.88	215.55	
K_1	50.17	62.08	64.79	
K_2	81.17	71.85	68.25	
K_3	73.54	70.96	71.85	
R	93.01	29.32	21.19	

3.2. Effect of pH, coagulant, PAM dosage and static duration on coagulation process

Coagulation is the most suitable method for COD, mineral oil and colority deprivation for pretreatment of emulsifying wastewater. So, coagulation was used to treat the wastewater after demulsification. Also, the impact of pH and coagulant dose were investigated.

3.2.1. Selection of the optimum pH

The coagulation experiment results at pH value 3–11 for PAC and PACS are shown in Fig. 4, the best COD removal rate was 50.10% at pH value 7–8 for PAC. It produces the best coagulation morphology $Al_{13}[AlO_4Al_{12}(OH)_{24}(H_2O)^{7+}{}_{12}]$ due to the hydrolysis of PAC which is affected greatly by pH. Adding the appropriate amount of alkali, it can hydrolyze and produce Al_b, basically equal to Al_{13}, which has the best flocculent effect. But it is difficult to spontaneously hydrolyze and produce Al_{13} for aluminum salt solution when pH is too low. Generated Al_b is dominated by Al_{b1} and the removal rate is not ideal as it results in a lower COD removal rate [20,21].

PACS had a wider pH adaptability and a better removal effect than PAC because PACS combines the advantages of PAC with quick precipitation speed, big floc and a stronger ability to adapt to the change of wastewater quality. The maximum rate of 62.58% COD at pH 7–9 was found to be removed. Compared with the highest removal rate of PAC, it was 12.48% higher.

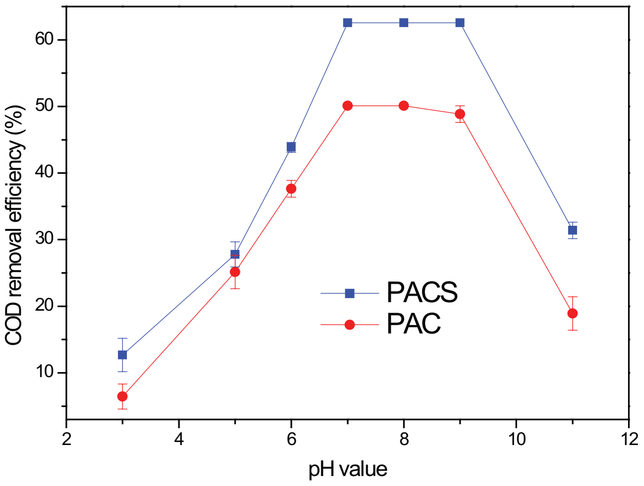


Fig. 4. Effect of pH on the removal efficiency of COD in coagulation process.

3.2.2. Selection of the optimum coagulant

The effect of coagulant dosage on the removal of COD from wastewater is shown in Fig. 5. When the dosage of coagulant was less than 3 mL/L, the removal rate of COD increased with the increase of PAC and PACS dosages. When 3 mL/L coagulant was added into wastewater, the COD removal rates were 50.10% and 62.58% respectively (It was the best proportion). However, continuing to increase the coagulant dosage did not enhance the coagulation effect but restrained it. According to the theory of adsorption/charge neutralization, a large number of positively charged polymeric ions are produced by the hydrolysis of aluminum salts when the aluminum salt added dosage is beyond a certain amount in the water. They will be directly adsorbed by negatively charged colloid nuclei, thereby making the emulsifying oil of flocculate become stable again and produce the best coagulation effect. Alumina content and base saturability of PACS, which are obviously lower than those of PAC, is a kind of polyaluminium chloride with divalent ligand SO_4^{2-}. It has better floc cohesion ability than pure polymerized aluminum. So, PACS has a wider pH adaptability and better removal effect than PAC. Chen et al. [22] also reported comparable results during their investigation for the treatment of twin screw extrusion pulping waste liquor. The coagulation property of PACS is better than PAC and it can adapt pH better. Thus, PACS may be more appropriate as a coagulant for treating this wastewater.

3. 2.3. Selection of the optimum PAM dosage

PAM has an ideal flocculent and aid flocculent ability which makes it a good coagulant aid in typical sewage treatment. The results of COD removal while varying the PAM dosage from 2 to 12 mL/L are found in Fig. 6. When PAM dosage was lower than 4 mL/L, the more dosage added, the better the results got. At this time, PAM formed a bridge between colloid particles and alum to produce big and tough flocs to lead a better coagulant effect. When the dosage of PAM is over 4 mL/L, the COD removal rate decreased inversely to the dosage increase of PAM. This is because that the concentration of PAM increases to a certain degree, different degrees of re-stabilization may occur in water. The active points on the surface of colloidal particles in wastewater are wrapped by organic flocculation molecules which make them difficult to bridge and the flocculation effect worsens. So, 4 mL/L PAM dosage was the suitable dosage for this process.

After coagulation, the wastewater stood for settling tests. When the static duration reached 15 min, the suspended particles were almost completely settled and the removal rate of COD was stable at about 62.58% (determined to be the best value).

3.2.4. The orthogonal experiment of coagulation process

Effects of pH, dosage of coagulant, dosage of coagulant aid and static duration on COD removal rate were investigated by three levels of orthogonal experiment for each factor. L_9 (3^4) table was applied to design the orthogonal test. The results in Table 2 show that $R_B > R_C > R_A > R_D$. It is indicated that their effects were coagulant dosage > coagulant aid dosage > pH > static duration in turn. Among the 4 factors, both coagulant dosage and coagulant aid dosage had the obvious effects on COD removal. The optimum coagulation condition was $A_2B_3C_1D_2$ within the designed range of the experiments.

3.3. Adsorption

The demulsification-coagulation process had achieved good results, but the water quality after demulsification-coagulation treatment did not meet the first grade standard of national integrated wastewater discharge standards (GB8978-1996). It still needs advanced treatment. Following analysis on the economic benefits and industrialized feasibility, the wastewater was deep treated with vermiculite as adsorbent.

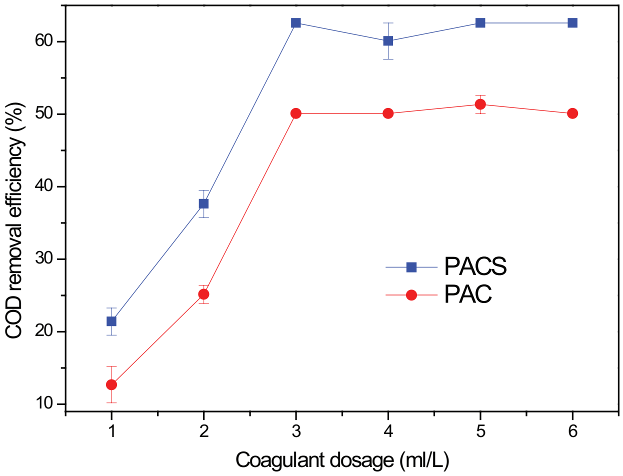


Fig. 5. Effect of coagulant dosage on the removal efficiency of COD.

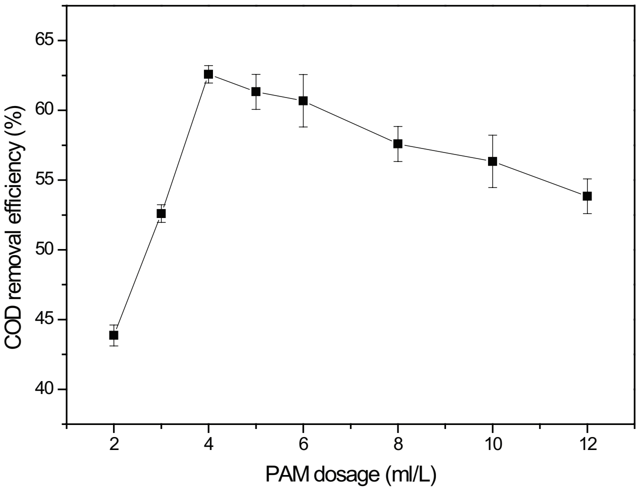


Fig. 6. Effect of PAM dosage on the removal efficiency of COD in the coagulation process

Table 2
Orthogonal test results of coagulation process

Serial number	A pH	B Coagulant dosage (mL/L)	C Dosage of coagulant aid (mL/L)	D Static duration (min)	COD removal efficiency (%)
1	6	1	2	5	28.90
2	6	2	4	10	36.37
3	6	3	6	15	33.88
4	8	1	4	15	21.41
5	8	2	6	5	18.91
6	8	3	2	10	42.61
7	10	1	6	10	16.41
8	10	2	2	15	31.38
9	10	3	4	5	36.37
k_1	99.15	66.72	102.89	84.18	
k_2	82.93	86.66	94.15	95.39	
k_3	84.16	112.86	69.2	86.67	
K_1	33.05	22.24	34.30	28.06	
K_2	27.64	28.89	31.38	31.80	
K_3	28.05	37.62	23.07	28.89	
R	16.22	46.14	33.69	11.21	

3.3.1. Effect of adsorbent dosage on COD removal from wastewater with fluorescent permeating agent

The effect of vermiculite dosage on COD removal was also investigated in the present study. As can be seen from Fig. 7, the COD removal efficiency changed from 21.79 to 45.60% when the vermiculite dosage was manipulated by increasing it from 1 to 5 g/L. After that, the COD removal efficiency remained practically unchanged, even if the amount of vermiculite continued to increase. Although the total amount of absorbed COD increased, the concentration of COD dropped with the increasing of vermiculite dosage. So, the effect of collision and aggregation between vermiculite particles increased when the vermiculite dosage was increased to a certain amount. The surface adsorption of vermiculite was blocked and the adsorption was in dynamic equilibrium.

3.3.2. Kinetics of adsorption of COD in wastewater by vermiculite adsorption

Fig. 8 shows the COD removals of vermiculite at different reaction times which were at optimum dosage with 5 g/L vermiculite. The removal rate increased rapidly during the initial five minutes. When the adsorption time was between 5 min and 30 min, the adsorbing COD rate grew slowly. However, there was no significant change in COD removal rate and adsorption tended to be in equilibrium when it was more than 30 min. At the same time, the removal rate of COD to vermiculite was 45.60% and the adsorption capacity was 10.574 mg/g, and indicated the suitable adsorption time was 30 min.

In order to explore the kinetics characteristics of the COD adsorption of vermiculite in the oil emulsion wastewater, the kinetics models, including the pseudo-first-order kinetics model and the pseudo-second-order kinetics model, were applied to fit the experimental data.

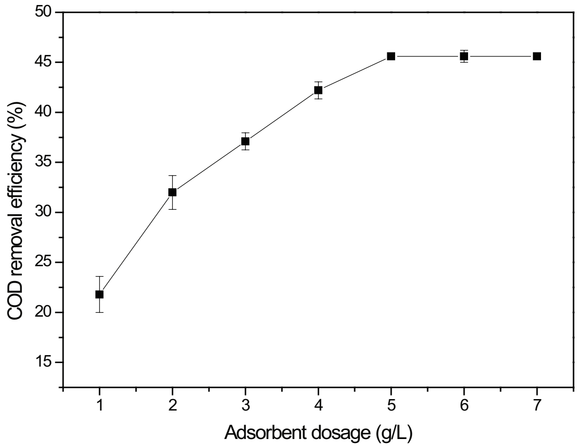


Fig. 7. Effect of adsorbent dosage on COD removal.

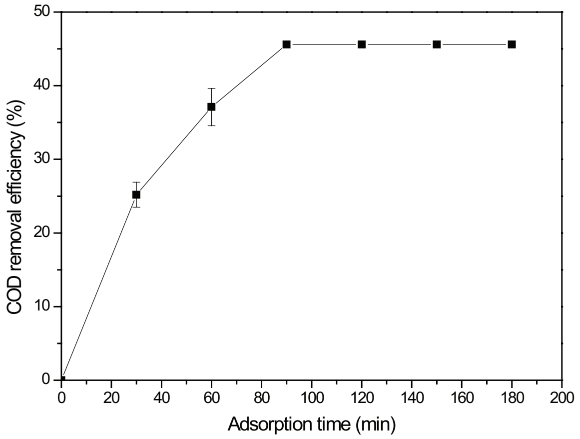


Fig. 8. Effect of adsorption time on COD removal.

The linear form of the pseudo-first-order equation can be described as [23]:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{3}$$

where q_e is the adsorption capacity in equilibrium (mg/g), q_t is the amount of adsorbate adsorbed at time t (mg/g), k_1 is the pseudo-first-order kinetic rate constant (min^{-1}), and t is the time (min).

The experimental data were also tested by the pseudo-second-order kinetics model [24]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{4}$$

where k_2 is the pseudo-second-order kinetic rate constant, g/(mg·min).

According to Fig. 9 and Table 3 with the regression coefficient values ($R^2 = 0.9953$), the fitting results of pseudo-second-order kinetics model to vermiculite adsorption COD removal data are much better than pseudo-first-order kinetics model. The regression coefficient values of the pseudo-second-order kinetics model is $R^2 = 0.9953 > 0.8483$. The absolute error between experimental data ($q_{e,max;\,exp}$ = 10.899 mg/g) and values calculated by pseudo-second-order kinetic model ($q_{e,max;\,cal}$ = 11.455 mg/g) is very small, of which the percentage is less than 5%. However, it is 7.143 mg/g ($q_{e,max;\,cal;}$) of the pseudo-first-order kinetics model, further study is required regarding both the physical adsorption process and chemical adsorption process.

4. Optimization of treatment process for wastewater with fluorescent permeating agent

According to the above orthogonal experiments and analysis of operational factors, the optimum conditions for the treatment process are recommended as follows: use AR demulsifier as de-emulsifier, add 4 mL/L (1.8 g/L) in wastewater, adjust the suitable pH to 7–9, and stand for 10 min. Then, use PACS coagulant dose of 3 mL/L (300 mg/L), adjust pH at 7–9, use PAM dose of 4 mL/L (4 mg/L) as coagulant aid and lay aside for 15 min. Finally, treat the wastewater with vermiculite as adsorbent with the best dosage of 5 mg/L for 30 min adsorption time.

After demulsification-coagulation-adsorbtion treatment, the discharged sewage can meet the first grade standard of national integrated wastewater discharge standards (GB8978-1996). The quality parameters of treated wastewater are shown in Table 4 and the effect of treatment of each stage is shown in Fig. 10.

Table 4
The parameters of the treated wastewater

Parameter	Raw wastewater	Treated wastewater	Rejection (%)	Standard[25]
COD (mg/L)	3048 ± 4	65.02	97.87	100
Oil (mg/L)	1170 ± 1.2%	4.45	99.61	5
Colority	1024 ± 10	8	99.22	50
pH	5.45 ± 0.01	7.15	–	6–9

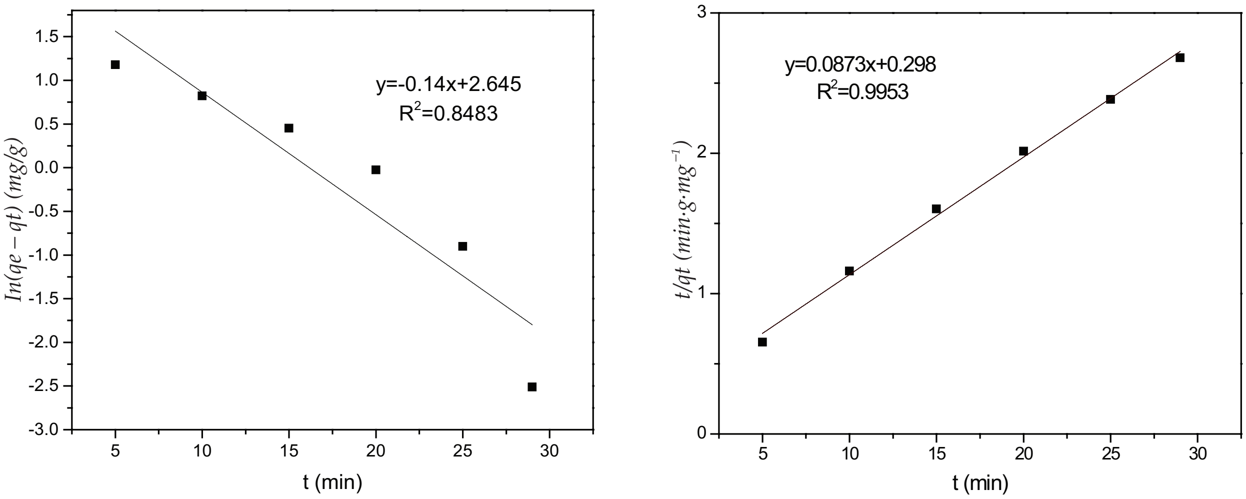
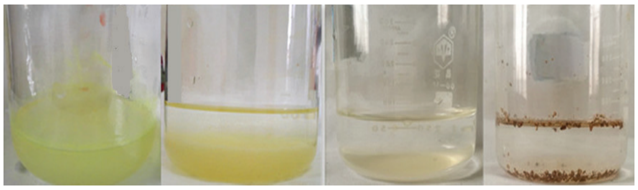


Fig. 9. Kinetic fits for COD removals. (a) The pseudo-first-order kinetics model; (b) The pseudo-second-order kinetics model.

Table 3
Adsorption kinetics parameters for vermiculite adsorption on COD

C_0 (g/L)	$q_{e;exp}$ (mg/g)	The pseudo-first-order kinetics model			The pseudo-second-order kinetics model		
		$q_{e;cal}$ (mg/g)	K_1 (min^{-1})	R^2	$q_{e;cal}$ (mg/g)	K_2 (g/mg min)	R^2
5	10.899	7.143	0.0355	0.8483	11.455	0.0570	0.9953



(a) (b) (c) (d)

Fig. 10. The effect of treatment. (a) Before treatment; (b) Demulsification efficiency; (c) Coagulation efficiency; (d) Adsorption effect.

5. Conclusions

In this study, an optimization group method of demulsification-coagulation-adsorption was applied to treat the wastewater with fluorescent permeating agent to provide an efficient and feasible process for the treatment of such wastewater. COD removal was selected as an evaluation index to evaluate the treatment effect of different conditions. The main conclusions are as follows:

Comparing AR demulsifier with the traditional demulsifier $CaCl_2$ and $MgCl_2$, AR demulsifier not only had better COD removal efficiency, but also had better adaptability to pH. What's more, the yielding water is clean with fewer suspended substances. PACS has a better coagulation property than PAC in the treatment of wastewater with fluorescent permeating agent.

Based on the results of orthogonal and single factor affecting experiments, the optimum operational conditions of demulsification were as follow: pH = 7, Dosage of demulsifier = 4 mL/L 45% AR, Static duration = 15 min. The optimum operational conditions of coagulation were as follow: pH = 8, Coagulant dosage = 3 mL/L 10% coagulation solution, Dosage of coagulant aid = 3 mL/L 0.1% PAM solu1tion, Static duration = 10 min.

When using the vermiculite to adsorb the wastewater after demulsification-coagulation treatment, only 5 g/L dosage and 30 min contacting time were needed. The pseudo-second-order kinetics model might explain the adsorption process, and the equilibrium adsorption capacity of the pseudo-second-order kinetics model was up to 11.455 mg/g which agreed well with the equilibrium adsorption capacity 10.899 mg/g of the test.

After treated by the integration method, the COD was 65.02 mg/L with 97.87% removal rate, oil was 4.45 mg/L with 99.62% removal rate, and colority was 8 with 99.22% removal rate. Thus, the quality of effluent could meet the first grade standard of national integrated wastewater discharge standards (GB8978-1996). Compared with other treatment technologies, the demulsification-coagulation-adsorption combined process had a very good effect on the wastewater with a fluorescent permeating agent. This treatment process had the advantages of simple operation and short treatment time. So, it has the potential to be the ideal treatment method of this kind of wastewater.

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