

Treatment of phosphate-containing oily wastewater by coagulation and microfiltration

ZHANG Jin^{1,2}, SUN Yu-xin³, HUANG Zhi-feng⁴, LIU Xing-qin¹, MENG Guang-yao^{1,4,*}

(1. Department of Materials of Science and Engineering, University of Science and Technology of China, Hefei 230026, China. E-mail: mgym@ustc.edu.cn; jzmary@mail.ustc.edu.cn; 2. School of Chemistry and Chemical Engineering, Anhui University, Hefei 230039, China; 3. National Key Laboratory of Transient Physics, Nanjing 210094, China; 4. Great Wall New Century Membrane Technology Corporation, Hefei 230601, China)

Abstract: The oily wastewater generated from pretreatment unit of electrocoating industry contains oils, phosphate, organic solvents, and surfactants. In order to improve the removal efficiencies of phosphate and oils, to mitigate the membrane fouling, coagulation for ceramic membrane microfiltration of oily wastewater was performed. The results of filtration tests show that the membrane fouling decreased and the permeate flux and quality increased with coagulation as pretreatment. At the coagulant Ca(OH)₂ dosage of 900 mg/L, the removal efficiency of phosphate was increased from 46.4% without coagulation to 99.6%; the removal of COD and oils were 97.0% and 99.8%, respectively. And the permeate flux was about 70% greater than that when Ca(OH)₂ was not used. The permeate obtained from coagulation and microfiltration can be reused as make-up water, and the recommended operation conditions for pilot and industrial application are transmembrane pressure of 0.10 MPa and cross-flow velocity of 5 m/s. The comparison results show that 0.2 μm ZrO₂ microfilter with coagulation could be used to perform the filtration rather than conventional ultrafilter, with very substantial gain in flux and removal efficiency of phosphate.

Keywords: ceramic membrane; crossflow microfiltration; coagulation; phosphate removal; fouling mitigation; phosphate-containing oily wastewater

Introduction

The cleaning and pretreating of metal prior to the electrocoat bath are critical steps in the process providing a high-performance paint finish. Alkaline cleaners are used to remove dirt and oils in industrial metal parts, and phosphate pretreatments are used to enhance corrosion protection. The effluents produced from these processes, oil-in-water emulsion, contain oils, phosphate, organic solvents, surfactants, etc. (Oravitz, 1999). The main problem of the effluents is that they become contaminated, losing their properties, and have to be replaced by new emulsions, thus yielding an oily waste (Rios *et al.*, 1998). The presence of emulsified oil, phosphate, etc. contributes to the toxic and hazardous properties of these wastes (Knoblock *et al.*, 1994; Liu, 2001). Environmental impact of oily wastewater from electrocoating industry has recently attracted much attention in China.

The traditional process for the treatment of oily wastewater consists of a series of physical and chemical steps, namely, free oil removal, suspended solids removal, chemical emulsion break, dissolved air floatation, clarification, and filtration (Knoblock *et al.*, 1994; Liu, 2001).

Stricter environmental regulations and increasing consciousness towards wastewater reuse lead to reconsideration of the conventional treatment processes (Chang *et al.*, 2001). Environmental regulations require that the concentrations of oils and phosphate in receiving waters must be below 10 and 0.5 mg/L,

respectively. Many studies have reported the application of membrane filtration for the treatment of oily wastewater. Typical processes of the treatment included ultrafiltration (UF) (Zhang *et al.*, 1996), and UF combined with ozone (Chang *et al.*, 2001), however, the relatively low flux limits the large-scale application of them. Furthermore, the present membrane processes employ polymeric membranes. Polymer membranes are sensitive to both polar and chlorinated solvents, as well as to high oil fractions, which limit the application range of them. The ceramic membranes, particularly zirconia(ZrO₂) membranes show a better separation performance such as higher flux, less fouling and higher oil rejection (Higgins *et al.*, 1994; Zhong *et al.*, 2003). Therefore, ceramic membranes have been widely used as a separation technique in many fields (Afonso *et al.*, 2002), but few focused on the oily wastewater containing phosphate from pretreatment unit of electrocoating industry.

Preliminary studies showed that microfiltration (MF) with zirconia membranes could decrease the oil content and chemical oxygen demand (COD) value of the wastewater. However, we met two main problems in MF process: one was how to improve the removal efficiency of phosphate (PO₄³⁻); another was how to mitigate the membrane fouling. In order to solve these problems, traditional chemical method-coagulation was chosen as pretreatment. So, the aim of present work was to study the performance of MF using ZrO₂ membranes combined with coagulation as pretreat-

ment. The effects of coagulation on filtration flux and permeate quality were investigated. The optimal operation parameters of the membrane process for pilot plant were also determined. The results obtained from coagulation and MF were compared with those of UF.

1 Materials and method

1.1 Materials

The wastewater tested in this work was obtained from an automobile plant (Anhui, China). The

relevant characteristics of the wastewater are shown in Table 1.

The asymmetric ZrO₂ membranes were provided by Great Wall New Century Membrane Technology Corporation (Hefei, China). The nominal pore size was 0.2 μm for microporous membrane, and the UF membrane with the molecular weight cut-off (MWCO) of 80000 Daltons was used. The average membrane layer was about 20 μm thick and the effective membrane area was about 0.05 m² for both of them.

Table 1 Characteristics of the wastewater in experiments

Parameter	COD _{Cr} , mg/L	PO ₄ ³⁻ , mg/L	Oil, mg/L	Ca ²⁺ , mg/L	Mg ²⁺ , mg/L	Zn ²⁺ , mg/L	Turbidity, NTU	pH
Value	16000—16200	60—62	4800—4950	19.38	4.75	1.71	1170—1200	9.5—10.0

1.2 Experimental methods

The coagulation tests were performed in seven 20 kg buckets and conditions in each bucket were identical. A different volume of lime slurry (written as Ca(OH)₂) was injected into the bucket. The corresponding dosage of Ca(OH)₂ was 0, 100, 200, 350, 500, 720 and 900 mg/L, respectively. After the addition of Ca(OH)₂, the mixture was intensely stirred for 3 min. Then polyacrylamide (PAM) was introduced into each bucket and slowly stirred for another 5 min. Allow the mixture to stand for a certain time, then take the supernatant for characterization.

After coagulation, the mixture was filtered through the membrane for 120 min or longer. During each test run, a known volume of the feed solution was processed through the membrane module at a suitable transmembrane pressure and cross flow velocity. Schematic diagram of the MF system with pretreatment process is shown in Fig. 1.

the oil content of permeate was analyzed by UV spectrophotometry (Zhong *et al.*, 2003). The COD values were determined by conventional potassium dichromate oxidation process. The concentrations of the cations (Ca²⁺, Mg²⁺ and Zn²⁺) were analyzed by inductively coupled plasma atomic emission spectrometer (ICP-AES, USA). Turbidities were measured by UV spectrophotometry. All chemicals used are analytical grade, obtained from Shanghai No.1 Reagent Factory (China).

Membrane performance refers to the percentage rejection of a particular component, as defined in the equation:

$$\text{Rejection (\%)} = \left(1 - \frac{C_p}{C_f}\right) \times 100 \quad (1)$$

where C_f and C_p are the component concentrations in the feed and permeate, respectively.

2 Results and discussion

2.1 Effect of coagulation on filtration flux

The effect of coagulant dosage on filtration flux was investigated under the conditions of transmembrane pressure of 0.1 MPa and cross flow velocity of 5 m/s. Fig.2 shows the flux values for different concentrations of Ca(OH)₂ over a period of 2 h. Flux declines sharply at the beginning, and then decreases gradually after 20 min. When Ca(OH)₂ was not used, the flux decreased to about 150 L/(m²·h) after 120 min of running time. Using 200 mg/L of Ca(OH)₂, the flux was 180 L/(m²·h) after 120 min, which is about 20% greater than that without coagulant. Increasing Ca(OH)₂ dosage to 900 mg/L, the flux was found to decay at a smoother rate; the value was about 260 L/(m²·h) after 120 min of running time and tended to stabilize around the same value with time. The improvement of filtration flux after coagulation may be attributed to coalescence between the droplets in an aggregate and the consequent the size of emulsion in wastewater increased, then the extent of internal

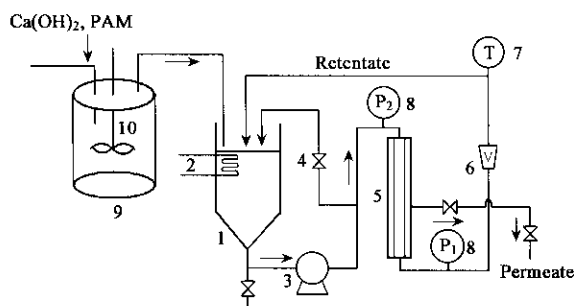


Fig.1 Flow schematic sketch of a combined coagulation and microfiltration process

1. feed tank; 2. heat exchanger; 3. centrifugal pump; 4. by-pass valve; 5. tubular MF module; 6. flow meter; 7. temperature controller; 8. pressure gauge; 9. coagulation bucket; 10. stirrer

1.3 Analytical methods

The phosphate contents of feed and permeate were analyzed by ammonium molybdate spectrophotometry. The oil contents of feed and supernatant were analyzed by petroleum ether extraction test, but

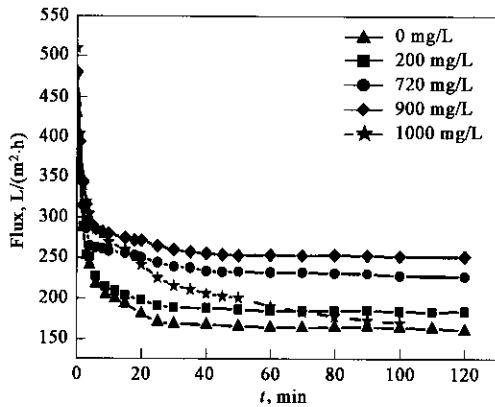


Fig.2 Effect of Ca(OH)₂ dosage on filtration flux

plugging of the membrane decreased and the void of sedimentation layer on membrane surface increased after coagulation (Al-Malack and Anderson, 1996; Kim *et al.*, 2005; Peuchot and Aim, 1992; Wiesner *et al.*, 1989; Zhong *et al.*, 2003).

When the coagulant concentration increases further (1000 mg/L), the flux decreases. This result might be due to an excess of coagulant altered the aggregates (Peuchot and Aim, 1992).

Therefore, the recommended Ca(OH)₂ dosage for

pilot and industrial application is 900 mg/L: the flux is important and the turbidity of permeate is low (1.3 NTU).

2.2 Effect of Ca(OH)₂ dosage on water quality

Figs.3a, 3b, and 3c show the effects of Ca(OH)₂ dosage on phosphate, COD, and oil removal by coagulation and combined coagulation with microfiltration (coagulation-MF), respectively. Fig.3d shows the effect of Ca (OH)₂ dosage on turbidity. According to Fig. 3, when the coagulant dosage increased, the phosphate, COD and oil removal increased by coagulation, and the values further increased by membrane filtration. The increase is perhaps because the coagulation broke the stability of colloid particles and emulsified oils in wastewater by double layer compression, enmeshment in precipitate, adsorption, and interparticle bridging due to the action of PMA. The destabilized colloid particles and oils aggregated, increasing their sedimentation rate (Zhong *et al.*, 2003). It is followed by microfiltration, and the aggregates will be retained by membrane surface due to their size (Peuchot and Aim, 1992; Wiesner *et al.*, 1989).

Using 900 mg/L of Ca(OH)₂, the phosphate con-

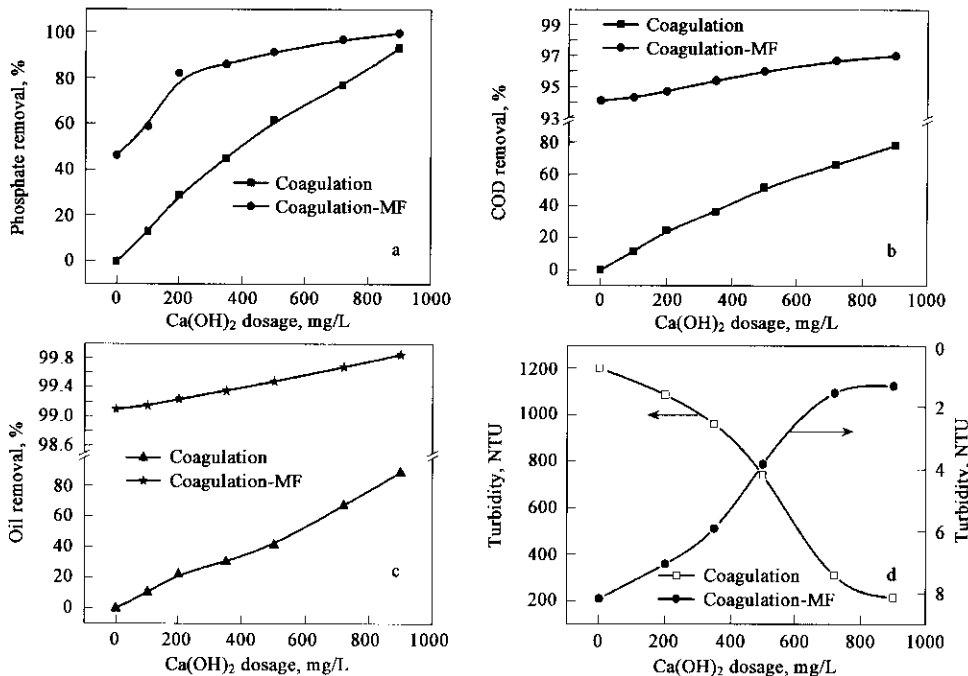
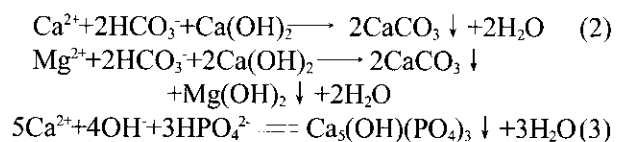


Fig.3 Effect of Ca(OH)₂ dosage on water quality
a. phosphate removal; b. COD removal; c. oil removal; d. turbidity

centration, COD, oil content, and turbidity of supernatant are 4.29 mg/L, 3550.9 mg/L, 550.6 mg/L and 216 NTU, respectively. It is followed by microfiltration, the corresponding values are 0.24 mg/L, 484.2 mg/L, 8.283 mg/L and 1.3 NTU. Furthermore, the removal efficiency of PO₄³⁻ is increased from 46.4% (without coagulation) to 99.6%. The removal principle of phosphate is as follows:



When added to wastewater, hydrated lime increases pH and reacts with carbonate hardness as shown in Eq.(2). The calcium ion also combines with

orthophosphate in the presence of hydroxyl ion to form gelatinous calcium hydroxyapatite as shown in Eq.(3) (Hammer, 1986).

If sufficient $\text{Ca}(\text{OH})_2$ is added, precipitation softening continues with the formation of magnesium hydroxide (Hammer, 1986). It is found that the pH value was 11.4 at $\text{Ca}(\text{OH})_2$ dosage of 900 mg/L. At such a pH, magnesium and calcium precipitates are complete and aggregation of particles takes place by adsorption and/or enmeshment mechanisms (Almalack *et al.*, 1989).

The parameters of water quality with and without

coagulation are listed in Table 2. The results show that the oil and phosphate contents of permeate after microfiltration (MF) were still high, so the MF with coagulation was done in this study. After coagulation and MF, the oil and phosphate contents of permeate decreased, this met the request of environmental regulations. Furthermore, the concentrations of Ca^{2+} , Mg^{2+} and Zn^{2+} decreased evidently.

The results (Figs. 2, 3 and Table 2) indicate that the coagulation as pretreatment could decrease the membrane fouling and increase the filtration flux, and coagulation was beneficial to water quality improve-

Table 2 Comparison results of different treatment methods

Method	COD _{co} , mg/L	Oil, mg/L	PO ₄ ³⁻ , mg/L	Ca ²⁺ , mg/L	Mg ²⁺ , mg/L	Zn ²⁺ , mg/L	Flux, L/(m ² ·h)
Feed	16140.3	4872.5	61.2	19.38	4.75	1.71	
Microfiltration	952.3	43.9	32.8	13.07	4.12	1.23	153.7
Coagulation-MF*	484.2	8.283	0.24	0.91	0.031	0.018	261.1
Ultrafiltration	469.5	7.801	22.7	13.06	4.11	1.20	65.3

Notes: After microfiltration (MF) 30 min permeate for COD, PO₄³⁻, Ca²⁺, Mg²⁺ and Zn²⁺ content analysis; for MF and coagulation-MF, the operation conditions are transmembrane pressure of 0.1 MPa, cross-flow velocity of 5 m/s, and temperature of 35°C; * $\text{Ca}(\text{OH})_2$ dosage: 900 mg/L

ment of the membrane system.

However, MF membranes do not retain small dissolved molecules such as surfactant, so the COD removal of permeate does not increase evidently with coagulation in spite of the value of 97.0%. The main components of the MF permeates are water and surfactant. Thus it can be reusable as make-up water in the pretreatment unit of electrocoating industry (Chang *et al.*, 2001).

2.3 Comparison with ultrafiltration

The molecular weight cut-off of the ultrafiltration (UF) membrane used in this study was 80000 Daltons, and UF was investigated under the conditions of transmembrane pressure of 0.18 MPa and cross flow velocity of 5 m/s. The comparison results between UF and coagulation-MF are also listed in Table 2. It was shown that 0.2 μm ZrO₂ microfilter with coagulation could be used to perform the filtration rather than conventional ultrafilter, with very substantial gain in flux (Bhave, 1991). In addition, the removal efficiency of PO₄³⁻ is 62.9% with UF, which is much lower than that of coagulation-MF.

2.4 Effect of transmembrane pressure on filtration flux

Prior to filtration, 900 mg/L of $\text{Ca}(\text{OH})_2$ was introduced into the feed and pH value was adjusted to about 11.4. After coagulation, the mixture was filtered through the membrane.

The effect of transmembrane pressure on filtration flux is shown in Fig.4. It can be seen that the pseudo-steady flux increased with pressure at 0.055—0.10 MPa transmembrane pressure, and approximately was constant at 0.10—0.12 MPa. This trend can be attributed to the competition between the permeability

and resistance of cake layer that both of them increased with pressure. When permeability increases more than resistance, the flux will increase as the pressure less than 0.10 MPa. When the competition reached equilibrium, the flux tends to constant (Zhao *et al.*, 2002). The increase of hydraulic resistance with pressure is due to compressibility of cake and the thickening of the cake layer (Defrance and Jaffrin, 1999). Therefore, the transmembrane pressure of 0.10 MPa was recommended for pilot and industrial application.

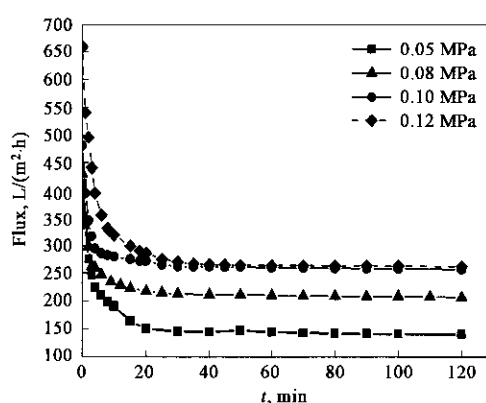


Fig.4 Effect of transmembrane pressure on filtration flux

2.5 Effect of crossflow velocity on filtration flux

Generally, the filtration flux increases with the increase of cross-flow velocity since the increase of crossflow velocity leads to an increase of shear stress on membrane surface and decrease the height of sedimentation layer (Bhave, 1991). The results reported in Fig.5 illustrate the effect of crossflow velocity on flux. An increase in the crossflow velocity

results in higher flux, but the increase extent is not proportional to the crossflow velocity. A crossflow velocity of 5 m/s is recommended since higher velocities are at the expense of substantially higher energy costs (Bhave, 1991). Stable flux values of about 260 L/(m²·h) were obtained at a transmembrane pressure of 0.10 MPa and cross-flow velocity of 5 m/s.

2.6 Membrane cleaning

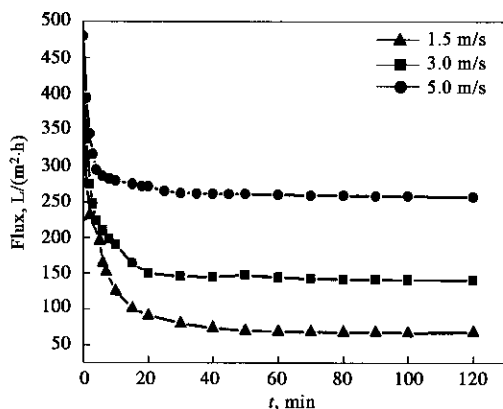


Fig.5 Effect of cross-flow velocity on filtration flux

The investigation of membrane fouling has indicated that the main foulants are oils, Ca(OH)₂ particles, calcium precipitates, and a little amount of organic matter, etc. According to the chemical properties of foulants, some agents that can dissolve foulants were chosen to clean the fouled membranes. The effective cleaning procedure for fouled membranes is: (1) deionized water rinsing 15 min (40°C, ΔP=0.05 MPa, circulating velocity 8 m/s); (2) 0.2 mg/L HNO₃ and surface active agent solution cleaning 20 min (30°C, ΔP=0.10 MPa, circulating velocity 4 m/s); (3) deionized water rinsing thoroughly until the pH value of the permeate approximate to 7. The flux recovered to 90% of the initial value after the cleaning of the membrane.

3 Conclusions

In order to improve the removal efficiencies of phosphate and oils, mitigate the membrane fouling, coagulation as pretreatment for ceramic membrane microfiltration of oily wastewater containing phosphate was performed. The recommended Ca(OH)₂ dosage for pilot and industrial application is 900 mg/L, and an excess of coagulant will decrease filtration flux. The membrane fouling decreased and

the permeate flux and permeate quality increased with coagulation as pretreatment. Compared with UF, the coagulation and MF with 0.2 μm ZrO₂ membrane is much appropriate to perform the filtration, which shows substantial gain in flux and removal efficiency of phosphate.

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