Desalination and Water Treatment
www.deswater.com

34 (2011) 382–388
October

1944-3994/1944-3986
doi: 10/5004/dwt.2011.2883

Fouling and cleaning of gas-filled membrane for cyanide removal from acrylonitrile wastewater

Jinling Wu*, Jianlong Wang, Haiyang Liu, Shijun He

Laboratory of Environmental Science and Technology, Institute of Nuclear and New Energy Technology, Tsinghua University, Beijing, China
Tel. +86-10-62796856; Fax: +86-10-62771150; email: jinlingwu@tsinghua.edu.cn

Received 3 September 2010; Accepted 3 January 2011

ABSTRACT

Gas-filled membrane absorption process is a safe, effective and economic method for acrylonitrile wastewater treatment. However, membrane fouling is a serious problem affecting proper operation of gas-filled membrane system. This study investigated the fouling characteristics in a 72 h continuously operating gas-filled membrane, and proposed an effective method to clean the membrane modules. In the gas-filled membrane system for acrylonitrile wastewater treatment, HCN transfer through gas-filled membrane stopped in two hours because of fouling. Cyanide removal rate achieved 82.0%. Permeation caused by hydrophilization occurred when gas-filled membrane absorption period was long enough, which led to operation failure of the whole treatment system. Inorganic fouling caused by Fe was found as the predominant reason. Four cleaning agents and three cleaning modes were applied for the fouled membrane to recovery mass transfer coefficient (*K*). The four-step cleaning (tap water-HCl-NaOH-EDTA) was recommended for the hydrophobic membrane system. The recovery of *K* value reached 95% for each cleaning cycle, which was confirmed in the pilot study as well. The results showed that it is feasible to reuse membrane modules during gas-filled membrane process for acrylonitrile wastewater treatment.

Keywords: Gas-filled membrane; Fouling, Cyanide; Acrylonitrile wastewater

1. Introduction

Acrylonitrile is an important chemical for petrochemical industry. The wastewater from acrylonitrile plants contains high concentration cyanide, which is high toxic. Because of the potential hazards associated with cyanide, cyanide removal from acrylonitrile wastewater is therefore essential. The adopted methods for cyanide-contaminated effluent treatment include the alkaline-chlorination-oxidation process, copper-catalyzed hydrogen peroxide oxidation, ozonation, electrolytic decomposition, biodegradation, etc [1,2]. Gas-filled membrane absorption process is a promising process for cyanide removal from some kinds of industrial wastewater with its advantages over other processes [3]: (1) wide applicability; (2) high cyanide recovery efficiency; (3) no production of secondary pollutants; (4) low energy consumption; and (5) convenient operation. However, little information and inadequate experience are available on removing cyanide from acrylonitrile wastewater using gas-filled membrane in previous investigations.

In our previous study, we applied gas-filled membrane to acrylonitrile wastewater treatment. The operational conditions were optimized and the pre-treatment strategies were proposed to enhance HCN removal. The overall removal rate has been significantly increased to 87.1%. However, membrane fouling was found to be an important problem affecting proper operation of gas-filled membrane system. In other previous studies, little information is available on membrane fouling and

*Corresponding author.

Presented at the AMS6/IMSTEC10, The 6th conference of the Aseanian Membrane Society in conjunction with the 7th International Membrane Science and Technology Conference, Sydney Australia, November 22–26, 2010

appropriate cleaning strategies. Membrane cleaning will be essential in the design of a process for acrylonitrile wastewater treatment [3–13].

In this paper, the fouling characteristics of long-term running gas-filled membrane for cyanide removal from acrylonitrile wastewater were studied. Various cleaning strategies were investigated. A pilot-scale study was conducted further to confirm effectiveness of the cleaning strategies and stability of gas-filled membrane system performance.

2. Theory

Gas-filled membrane is a process of using hydrophobic micro-porous membrane and chemical absorbents to remove and recover volatile substances from wastewater. The removal and recovery of cyanide from wastewater is a typical gas-filled membrane absorption process. As illustrated in Fig. 1a, acidified cyanide-containing wastewater (the form of cyanide here is HCN) and NaOH absorption solution are separated by a polypropylene (PP) micro-porous membrane. Due to the hydrophobic nature of PP, aqueous solution cannot wet the membrane. Both wastewater and absorption solution can flow individually in two sides of the membrane without mixing. There is partial concentration (or vapour pressure) gradient of HCN between two sides of the PP membrane. Under the driving of this gradient: (1) HCN evaporates on the inter-surface of membrane pores and wastewater; (2) the evaporated gaseous HCN diffuses through membrane pores from wastewater to NaOH solution; (3) the penetrated gaseous HCN is immediately absorbed by and reacted with NaOH on the inter-face of membrane and NaOH solution. Finally, the volatile HCN is recovered in the non-volatile form of NaCN [3].

Since the HCN concentration at the NaOH solution side is always zero, it could be considered that there is no difference in HCN concentration along membrane fibers at the NaOH solution side. Therefore, flow arrangement has little effect on the mass transfer of HCN. In our study, the counter-current was applied as Fig. 1b.

According to the mass transfer process, the overall mass transfer resistance can be expressed as

$$R = \frac{1}{K} = \frac{1}{k_w} + \frac{1}{Hk_m} + \frac{1}{k_a} \quad (1)$$

where R is the overall mass transfer resistance, K, k_w, k_m and k_a are the mass transfer coefficients of the overall, the wastewater, the membrane and the absorption solution, respectively. H is the Henry's constant [4].

The mass transfer equation in the gas-filled membrane has following form:

$$In\frac{C_0}{C_t} = \frac{KA}{V}t \quad (2)$$

where C_0, C_t are cyanide concentrations of the wastewater at time $t = 0$ and $t = t$, respectively. K is the overall mass transfer coefficient, A is the membrane area, and V is the feed volume [8].

Like in other membrane technologies, membrane fouling is an unavoidable problem in gas-filled membrane. Membrane fouling in gas-filled membrane could be divided into three types: (1) plugging fouling caused by suspended particles, microorganisms and others; (2) prompting fouling caused by the affinity adsorption of organic compounds and colloids to fibers; (3) cumulative fouling caused by the slow deposition of the inorganics [8]. Any type of fouling will increase R, and decrease K, therefore reduce the overall removal rate for the pollutant.

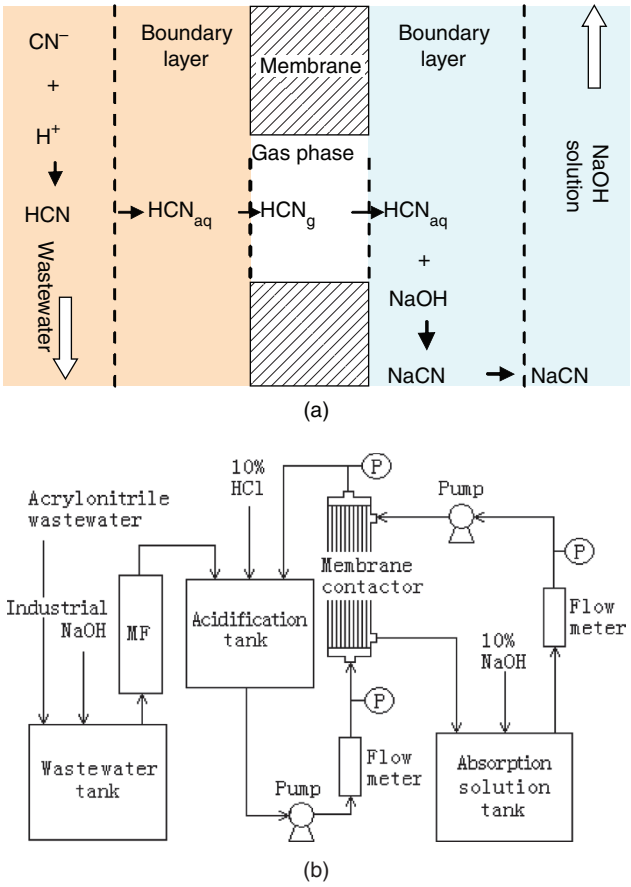

Fig. 1. Schematic representation of HCN removal by gas-filled membrane: (a) illustration of the mass transfer of HCN; (b) schematic process for the lab-scale and pilot experiments.

3. Materials and methods

3.1. Lab-experiment

3.1.1. Gas-filled membrane set up

The membrane contactor employed in the lab-experiment is an acrylonitrile butadiene styrene (ABS) cylinder with the outside diameter of 4.0 cm and the length of 40 cm. There are 300 hydrophobic symmetric PP hollow fibers (nominal pore size: 0.16 μm; inner/outer diameter: 0.38/0.50 mm) in the membrane module and the effective length of 30 cm. The total membrane area of this contactor is 0.14 m^2. The experimental flow configuration is schemed in Fig. 1b. According to our previous study [14], the optimal operational conditions were applied in this study: The temperature was set at 40˚C. The raw wastewater was first introduced into the wastewater tank. Industrial alkali powder (NaOH) was directly added in the tank to increase the pH of wastewater to 12.0. The produced sediments by alkali addition were then removed by microfiltration. After the microfiltration, the wastewater was acidified by 10% HCl to adjust the pH to 5.0. The acidified wastewater was then pumped into the gas-filled membrane contactor. The acidified wastewater and the absorption solution (10% NaOH solution) were counter-current flowed in lumen side and shell side of hollow fibers, respectively. The wastewater stream velocity was 0.14 ms^{-1}. The gas-filled membrane absorption process was continuously conducted for 72 h. The long-term fouling characteristics were analysed.

3.1.2. Acrylonitrile wastewater

The raw wastewater used in this study was collected from Acrylonitrile Plant, Jilin Chemical Group, China, which consisted of 80% acrylonitrile manufacturing wastewater and 20% ammonium sulphate, acetone cyanohydrin and butanone production wastewater. The constituents were complicated with the main components of acrylonitrile, ammonia, cyanide, acetonitrile, acetone cyanohydrin, acrylic acid and so on. It contained CN^- 800–4500 mg l^{-1}, COD 20000–60000 mg l^{-1}, pH 6–8, salinity 20000–22000 mg l^{-1} and with a dark brown colour. Its main metal element compositions were shown in Table 1.

3.1.3. Analysis of wastewater and membrane foulants

Cyanide concentration analysis was followed by standard method [15]. Elemental composition of membrane foulants was analysed by field emission scanning electronic microscope-energy dispersive spectrometer (FESEM-EDS, JSM−6310F, link ISIS EDS, oxford).

Table 1
Element compositions in raw wastewater

Element	Concentration (mg l^{-1})
Na	1,300
Mo	100
Si	44
Fe	30
Ni	26

3.1.4. Cleaning strategies

Three runs were operated to obtain fouled membranes at different fouling degrees. By the end of absorption, four cleaning agents were applied to recover mass transfer coefficient for gas-filled membrane: tap water, 1% HCl, 5% NaOH and 3% EDTA. This so-called four-step cleaning was applied in three modes as follows: 1) immersing modules in cleaning agents for 1 h, 2) recycling cleaning agents at the shell and lumen sides for 20 min and, 3) pumping cleaning agents from the shell side to the lumen side through membrane for 10 min. After each cleaning step, the overall mass transfer resistance (R) for pure KCN solution was calculated as Eq. (1). The recovery of mass transfer coefficient (K) could be therefore calculated. The four cleaning solutions produced by four-step cleaning (tap water-HCl-NaOH-EDTA) were analysed in terms of total organic carbon concentration (Shimadzu, TOC−5000A, Japan) and element composition. The element composition was analysed by atomic absorption spectrum (Jena, AAS6, Germany).

3.2. Pilot experiment

The pilot sale experimental set up is shown in Fig. 1b. The system was located in an acrylonitrile plant of China National Petroleum Corporation Jilin Chemical. Two membrane modules were applied with the area of 1.4 m^2 for each, to treat the same real wastewater as that in the lab-experiment. Based on the lab scale experiments, the effect of the optimal cleaning strategy was verified at the pilot study.

4. Results and discussion

4.1. HCN removal by gas-filled membrane

Fig. 2a shows the cyanide concentration variation of wastewater during the 72 h continuous absorption by gas-filled membrane. The operational parameters were achieved according to our previous investigation as acidified pH of 5.0, wastewater velocity of 0.14 m s^{-1}, NaOH concentration of 10%, temperature of 40˚C and

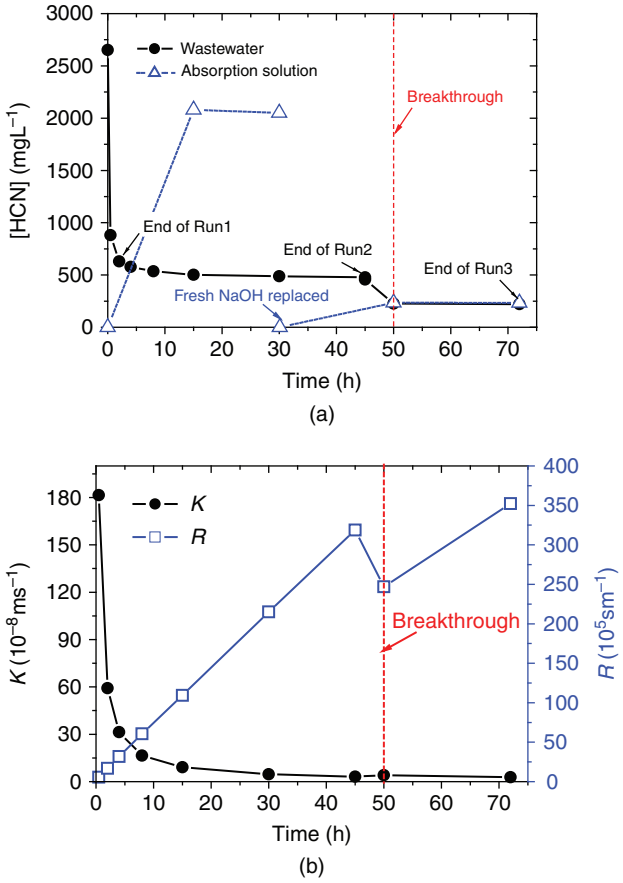

Fig. 2. HCN transfer in gas-filled membrane: (a) HCN concentration in the wastewater and the absorption solution with time; (b) mass transfer coefficient (K) and resistance (R) with time.

alkalization as pre-treatment [14]. Under this condition, the cyanide concentration in the wastewater was quickly reduced from 2653 mg l^{-1} to 630 mg l^{-1} in two hours. The cyanide removal efficiency reached 76.3%. During the following absorption, the cyanide concentration gradually decreased and reached 478 mg l^{-1} in 45 h. A high removal in 45 h was achieved as 82.0%, which proved proper operation of the gas-filled membrane system. After 50 h, the cyanide concentration suddenly decreased to only 420 mg l^{-1}, which was caused by a breakdown of the whole system.

The cyanide concentration in the absorption solution was simultaneously examined as well. From Fig. 2a, the cyanide concentration in absorption solution kept stable at about 2000 mg l^{-1}, when HCN transfer reached balance. In order to enhance HCN transfer, absorption solution was changed as fresh 10% NaOH. However, in the following 5 h, the absorption solution turned to brown colour. Furthermore, the cyanide concentrations at both wastewater and absorption solution sides became exactly the same. The gas-filled membrane was penetrated by both streams. The wastewater and the absorption solution mixed up. The reason for breakthrough was membrane hydrophilization, which would be discussed as below.

According to changes of the cyanide concentration in the wastewater (Fig. 2a), three new runs were conducted to study the fouling process. The end of each run was marked in Fig. 2a. At the each end point, fouling and cleaning characteristics were analysed. The results are as below.

4.2. Fouling characteristics of gas-filled membrane

4.2.1. HCN transfer coefficient (K)

The mass transfer coefficient, i.e., K, is an important index to evaluate the system performance for gas-filled membrane because it is directly related to the evolution of membrane fouling. Fig. 2b shows K value and the membrane resistance of R with time during continuous absorption. K decreased fast during the first 10 h, while R increased accordingly. Fig. 2b shows that R increased linearly over time during the initial 40 h, which indicates that membrane fouling occurs during operation. In addition, at 50th h, R suddenly decreased from 4.9×10^{6} m s^{-1} to only 3.3×10^{6} m s^{-1}, where breakthrough occurred.

4.2.2. Foulants on membrane surface.

Elemental composition of membrane foulants for the three runs were analysed by FESEM-EDS and compared. Table 2 shows the data of elemental composition. It could be found that both inorganics and organics existed on the whole membrane surface. In Run 1, great amount of carbon and oxygen representing organic foulants could be observed with small amount of several kinds of inorganics as shown in Fig. 3a. The relative amount of inorganics kept increasing with time during absorption. In Run 3, the inorganic matters contributed more than organic ones to membrane fouling. The predominant metal element of foulants was Fe as shown in Fig. 3b. The differences in Fe content between the three runs were significant, which caused membrane hydrophilized and breakthrough occurred.

4.3. Membrane cleaning for gas-filled membrane

4.3.1. Effect of four-step cleaning

Aiming to remove the organic foulants on membrane surface, NaOH was applied as a cleaning agent. For the inorganic foulants, HCl and EDTA were applied as cleaning steps. Firstly, tap water was applied to remove the attached solids on membrane. Tap water was also used to save other cleaning agents. This so-called

Table 2
Element composition of the membrane foulants for the three runs

Element	Run 1	Run 2	Run 3
C	86.39	76.56	33.60
O	11.82	5.24	–
Fe	1.44	12.21	55.58
Cl	0.11	2.43	4.13
Cu	0.08	1.23	2.41
Ca	–	2.33	2.34
Ba	–	–	0.36
P	–	–	0.17
Na	0.14	–	–
Mg	0.09	–	–
Total	100	100	100

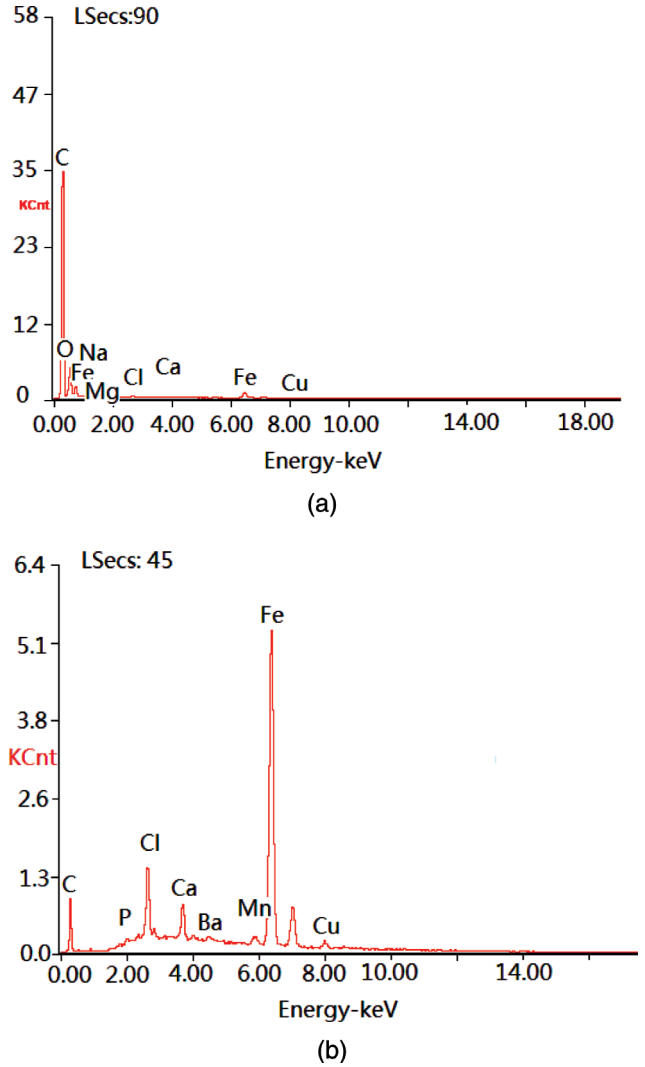

Fig. 3. Spectrometer of element composition in the membrane foulants by FESEM-EDS: (a) Run 1; (b) Run 3.

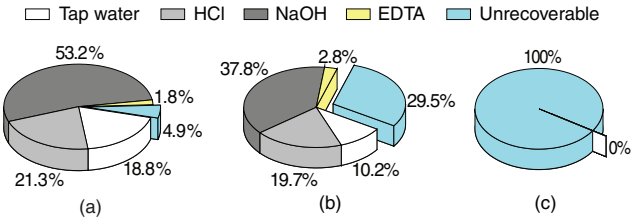

Fig. 4. Recovery of *K* by four-step cleaning: (a) Run 1; (b) Run 2; (c) Run 3.

four-step cleaning (tap water-HCl-NaOH-EDTA) was applied to recover mass transfer coefficient in gas-filled membrane. Three modes were applied as 1) immersing modules in cleaning agents 2) recycling cleaning agents at the shell and lumen sides and 3) pumping cleaning agents from the shell side to the lumen side through membrane.

The three runs represent different fouling degrees. Four-step cleaning was conducted for the three fouled membrane respectively. Fig. 4 shows the recovery of *K* by four-step cleaning in the three runs. In Run 1, the four-step cleaning was able to recover *K* value to 95.1%. Among the four solutions, NaOH contributed most to *K* recovery. Tap water, HCl and EDTA were effective in recovering *K* as well. In Run 3, *K* could not be recovered at all. Here new membrane modules should be considered to replace. Therefore, the absorption should be performed within two hours for one cleaning cycle, and all the four agents in four-step cleaning were recommended for gas-filled membrane.

4.3.2 Foulants removed by cleaning agents

The major element contents in the cleaning solution were analysed by atomic absorption spectrum, as shown in Figs. 5a, b and c. It was confirmed that Fe was the predominant foulant on the membrane surface. Besides Fe, Ni was an important foulant as well. HCl was effective for Fe removal. NaOH removed most Ni. EDTA was also an effective cleaning agent for the metal foulants.

Fig. 5d exhibits the organic contents in the cleaning solutions. It was found that the organic foulants continuously accumulated on the membrane surface. The TOC concentration for Run 3 was much higher than that in Run 1. NaOH removed most organic foulants from the membrane. HCl was also an effective cleaning agent for the organics foulants.

4.4. Frequent cleaning in pilot study

The four-step cleaning was applied in the pilot study. For each cleaning cycle, the mass transfer coefficient *K* could be recovered by 95%, as shown in Fig. 6.

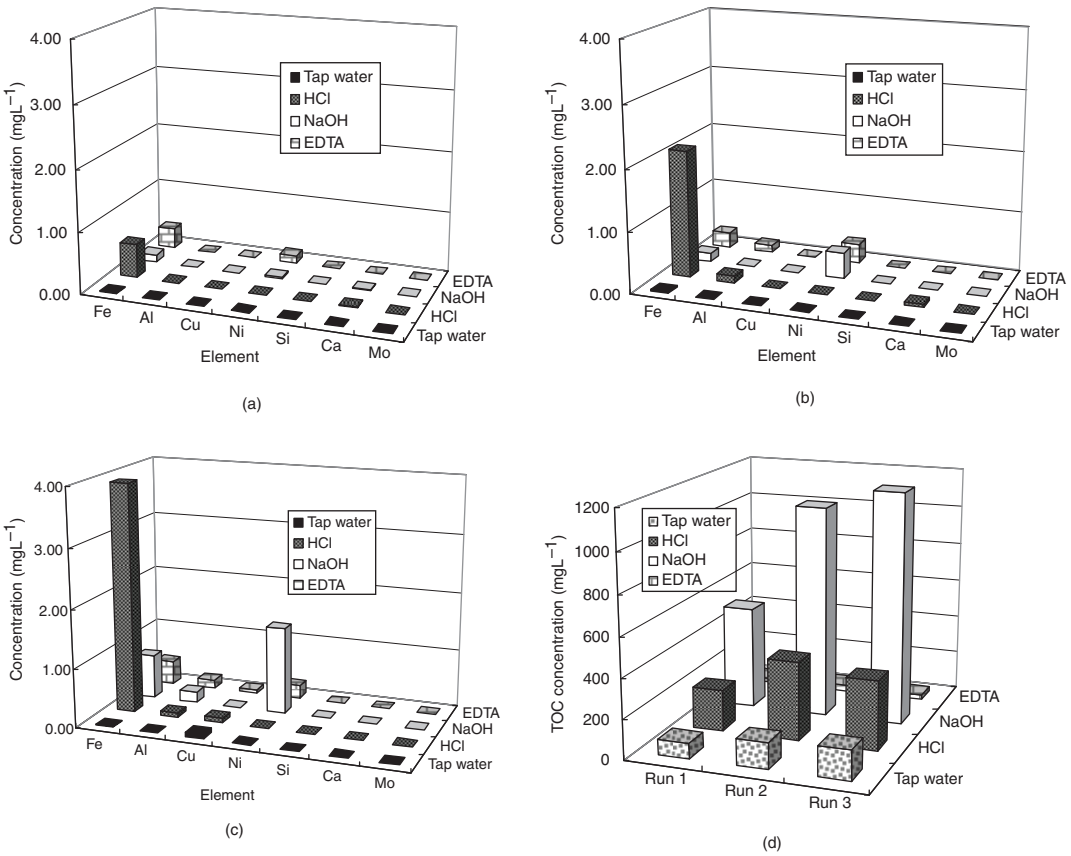

Fig. 5. Analysis of foulnts by four-step cleaning: element composition of inorganic foulants in (a) Run 1, (b) Run 2, (c) Run 3 and (d) total organic concentration.

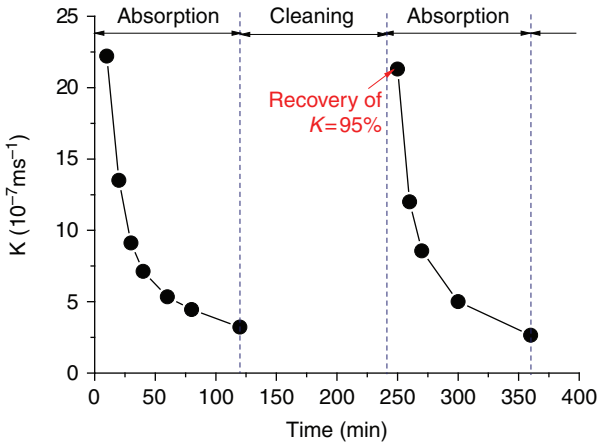

Fig. 6. *K* with time during one of cleaning cycles when four-step cleaning applied in pilot study.

Four-step cleaning provided the stable operation and proper performance of gas-filled membrane for refractory acrylonitrile wastewater.

5. Conclusions

In this study, the 72 h continuous performance of gas-filled membrane for cyanide removal from acrylonitrile wastewater was studied. HCN transfer through gas-filled membrane reached balance in two hours. Cyanide removal rate could reach 82%. Continuous operation for over 50 h caused a breakdown of the whole gas-filled membrane system because of membrane hydrophilized by great amount of inorganic foulants accumulating. Fe was the predominant element in the inorganic foulants on membrane. The four-step cleaning (tap water-HCl-NaOH-EDTA) was recommended for HCN transfer rate recovery. For each cleaning cycle, the mass transfer coefficient *K* could be recovered by 95%. This study provided the stable operation and proper performance of gas-filled membrane for refractory acrylonitrile wastewater.

Acknowledgement

This work was supported by the Major Projects on Control and Rectification of Water Body Pollution (No. 2008ZX07207–004).

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