Chemical Engineering Journal 306 (2016) 186–192

Contents lists available at ScienceDirect

Chemical Engineering Journal

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

Removal of polyacrylonitrile oligomers from acrylic fiber wastewater using two-stage flotation

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HIGHLIGHTS

- The SS in acrylic fiber wastewater were PAN oligomers.
- A two-stage flotation was developed using CTAB as collector and foaming agent.
- The PAN oligomers in the foamate were easily removed by free setting.
- The SS and COD were significantly decreased.
- 82.1 ± 4.1% of CTAB could be reused.

ARTICLE INFO

Article history:
Received 9 June 2016
Received in revised form 16 July 2016
Accepted 18 July 2016
Available online 18 July 2016

Keywords:
Two-stage flotation
Polyacrylonitrile oligomers
Acrylic fiber wastewater
Suspended solids
Chemical oxygen demand

ABSTRACT

It is a very interesting work to sufficiently treat the industrial wastewaters containing the suspended solids (SS) which are difficultly removed and biodegraded. The SS of acrylic fiber wastewater were polyacrylonitrile (PAN) oligomers from FTIR analysis and they were one of the most bio-refractory contaminants. For effectively removing PAN oligomers and then greatly decreasing chemical oxygen demand (COD) from the wastewater, a two-stage flotation was developed using cetyl trimethyl ammonium bromide (CTAB) as a collector. In the first stage, a high volume ratio 8.3 ± 0.4 was obtained and the PAN oligomers in the foamate were easily precipitated. In the second stage, the recovery percentage of CTAB reached 66.8 ± 3.3% by using the residual solution of the first stage as the feeding solution of the second stage. At last, 82.1 ± 4.1% of CTAB could be reused by recovering CTAB from the supernatant solution after the free setting of the first stage and the foamate of the second stage. Furthermore, the total removal efficiencies of SS and COD reached 98.2 ± 4.9% and 81.0 ± 4.1%, respectively, under the suitable conditions of two-stage flotation. This work was aimed at removing PAN oligomers cost-effectively from the wastewater and supplying a new method for removing other refractory SS of industrial wastewaters.

1. Introduction

Acrylic fiber is one of important synthetic fibers and it is commonly produced by polymerizing acrylonitrile (AN) monomers. Because of its excellent dyeability, high strength and good elasticity [1], acrylic fiber is widely used in the production of blankets, artificial furs and plush toys [2]. At present, the annual production of acrylic fiber is approximately 0.7 million tons and however, the annual discharge of acrylic fiber wastewater is more than 9.35 million tons correspondingly [2]. Acrylic fiber wastewater contains large quantities of polyacrylonitrile (PAN) oligomers and other organic contaminants such as N,N-dimethylformamide (DMF), cyanide, heterocyclic nitrogen compounds and inorganic contaminants (mainly sulfates and sulfites) [3], which are toxic, bio-refractory and environmentally harmful. So the wastewater may cause serious environmental pollution and health risks if it is discharged directly without appropriate treatment.

Presently, most acrylic fiber manufacturing companies have adopted anaerobic and aerobic biological techniques for treating acrylic fiber wastewater [4]. However, the effluents after the biological treatment still have a high concentration of chemical oxygen demand (COD) [5] and are hard to meet increasingly strict environmental standard [6]. The above biological techniques were not efficient enough, mainly because high quantities of PAN oligomers in acrylic fiber wastewater are recalcitrant to be biodegraded and seriously affect the microbial activity of anaerobic tank and aerobic pool. For this reason, an effective pretreatment must be adopted prior to the biological treatment to remove PAN oligomers and then to improve COD removal efficiency and biodegradability of the wastewater [4].

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http://dx.doi.org/10.1016/j.cej.2016.07.069
1385-8947/

The removal of PAN oligomers from acrylic fiber wastewater faces two major challenges. One is that they are difficult to be removed by free setting and coagulating sedimentation due to their small particle size (50–80 μm), low density and high dispersity in the wastewater. Thus electrocoagulation (EC) technique was used to pretreat acrylic fiber wastewater because it is more effective than the chemical coagulation one [7]. Nevertheless, this technique has not yet been widely accepted by reason of its high initial capital cost and large power consumption although its COD removal efficiency could reach 60% [7]. The other challenge is that PAN oligomers are recalcitrant to be biodegraded [4] and seriously affect the biological treatment. For example, the COD removal efficiency was only 51% because PAN oligomers influenced the sludge activity in a two-stage UASB (up-flow anaerobic sludge blanket) reactor for pretreating acrylic fiber wastewater [8]. Therefore, some researchers focused their attention on the degradation of bio-refractory substances via advanced oxidation techniques, such as photocatalytic oxidation [9] and Fenton oxidation [10]. However, it was still difficult for these techniques to be used in commercial size due to their higher operating cost and larger oxidizing agent consumption. Besides, ultrafiltration (UF) and reverse osmosis (RO) were employed to treat acrylic fiber wastewater [11], and the removal efficiency of COD was above 92%. But the application of membrane separations was limited because PAN oligomers could plug the membrane pores, resulting in serious membrane fouling and then increasing separation cost. Thereby, it is necessary to develop a cost-effective technique for effectively removing PAN oligomers and then greatly decreasing COD from acrylic fiber wastewater.

Flotation is used to separate different minerals or solids based on the differences of their floatability by using stable froth as the separation medium [12]. It is generally acknowledged that flotation has been widely applied in the wastewater treatment [13] owing to its high efficiency, low energy consumption and simple operation process. Therefore, flotation has great potentials for pretreating acrylic fiber wastewater. Nevertheless, the performance of flotation is related with the type and the dose of surfactant [14]. Moreover, the volume of foamate and the process of foam drainage are always neglected in flotation because the targeted particles possess big particle size and high density and they are easily settled [15]. For pretreating acrylic fiber wastewater, the primary work was to select a suitable surfactant as the collector which was able to capture PAN oligomers and then make them hydrophobic. PAN oligomers were attached to gas bubbles and they could be floated. It was noted that although PAN oligomers could be separated from the wastewater by selecting the collector, they were still suspended in the foamate and hard to be removed. In order to overcome the separation difficulty of them from the foamate, a flotation column was used to enhance foam drainage and decrease the volume of the foamate. PAN oligomers were able to be greatly enriched in a small volume of the foamate and then easily removed by free setting, thereby largely reducing the cost of the subsequent separation. Furthermore, the additional collector should be recovered as far as possible from the supernatant solution after the free setting and the residual solution after flotation to realize the reusing of them. So another flotation was necessary to recover the collector by using the residual solution of the former flotation as the feeding solution and meanwhile, PAN oligomers in the residual solution of the former flotation could be further removed. Consequently, it is worthwhile to develop a new flotation technology to achieve the decrease of foamate volume and the increase of COD removal efficiency of acrylic fiber wastewater and the recovery of the collector.

In this work, a suitable surfactant was first determined and Fourier transform infrared spectroscopy (FTIR) was used to show that the suspended solids (SS) in the wastewater were PAN oligomers. Furthermore, a two-stage flotation technology was developed. In the first stage, the experiments were carried out in a flotation column and the effects of surfactant concentration, volumetric air flow rate and loading liquid volume on the removal efficiencies of SS and COD and the volume ratio were investigated, respectively. By using the residual solution of the first stage as the feeding solution of the second stage, the removal efficiencies of SS and COD were further improved and the surfactant was recovered as far as possible. Finally, the five-day biological oxygen demand/chemical oxygen demand (BOD_5/COD) biodegradability ratio was used to assess the biodegradability of the residual solution after the two-stage flotation. The objective of this work was to lay a foundation for the industrialization of removing PAN oligomers from acrylic fiber wastewater and supply a new method for removing other refractory SS of industrial wastewaters.

2. Materials and methods

2.1. Wastewater characteristics

The acrylic fiber wastewater used in this work was collected from a synthetic-fiber factory located at the city of Daqing, China. This wastewater had an extremely low degree of biodegradability and its characteristics are listed in Table 1.

2.2. Analytical methods

Dodecyl trimethyl ammonium bromide (DTAB), cetyl trimethyl ammonium bromide (CTAB), cetyl pyridinium bromide (CPB), sodium dodecyl sulfate (SDS) and tween 80 with analytical grade were purchased from Tianjin Chemical Reagent Co. Ltd., China. COD and BOD_5 were measured by a COD rapid digestion apparatus (DIS-1A, Tianjin Xingke Instrument Co. Ltd., China) and an OxiTop system (OxiTop, WTW, Germany) [2]. SS was measured in accordance with weight method [16]. pH was measured using a pH meter (pHS-25, Shanghai Jingke Instrument Co. Ltd, China).

2.3. Equipment

Fig. 1 shows the foam column used in this work. The flotation column constructed by transparent plexiglass had 1000.0 mm in height and 40.0 mm in inner diameter. At the bottom of the column, the air was bubbled through a gas distributor of sintered glass with the pore diameter of 100.0 ± 10.0 μm into the column by an air compressor (AC0-318, Guangdong Hailea Group Co. Ltd., China). Air flow rate was controlled by a rotameter (LZB-6T, Wuhuan Instrument Factory, China). A foam collector was attached to the top of the column, where the foam was collected and collapsed. The resultant liquid was called the foamate.

2.4. Experimental procedure

The schematic diagram of the two-stage flotation technology is presented in Fig. 1. All the flotation experiments carried out at room temperature 25.0 ± 2.0 °C. As shown in Fig. 1, CTAB was firstly added into a certain volume of the wastewater (between

Table 1
Characteristics of acrylic fiber wastewater.

Parameter	Unit	Value
COD	mg/L	605.0 ± 30.3
BOD_5	mg/L	30.2 ± 1.5
pH	–	6.6 ± 0.3
SS	mg/L	85.0 ± 4.3