



Zero discharge process for dyeing wastewater treatment



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ARTICLE INFO

Article history:

Received 13 January 2016

Received in revised form 24 March 2016

Accepted 28 March 2016

Available online 6 April 2016

Keywords:

Reverse osmosis

Electrochemical oxidation

Bipolar membrane electro dialysis

Zero discharge

Reuse

ABSTRACT

The feasibility of a novel zero discharge process for dyeing wastewater depth treatment after biochemical processes was investigated in this study. The novel process was integrated with reverse osmosis (RO) technology, electrochemical oxidation (EO) and bipolar membrane electro dialysis (BMED). The fresh water generated from the RO and BMED processes and the mixed acid and base solutions regenerated from BMED could be reused as resources. No pollutants or wastewater were discharged into the environment during dyeing wastewater depth treatment. The effects of operation parameters, such as recovery ratio, specific current and input power on RO/EO/BMED performance were explored and discussed. The experimental results indicated that the recovery ratio of wastewater by this RO/EO/BMED process reached 97%, as compared with 70% achieved by RO or nanofiltration (NF); more than 83% of the total dissolved solids (TDS) in wastewater were desalinated and converted into mixed acid and base solutions. The total operating power requirement was 24.6 kWh to treat one cubic meter of wastewater, 0.97 tons fresh water and 1.31 kg mixed acid (0.12 mol/L) and 2.16 kg base (0.18 mol/L) were produced. This work has demonstrated proof of concept for the RO/EO/BMED process; further optimization remains to be carried out.

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1. Introduction

The dyeing industry is characterized by high water consumption and high discharge volumes of colored wastewater with high chemical oxygen demand (COD) and inorganic loads, making it one of the main sources of severe pollution worldwide. The conventional methods for treating dyeing wastewater combine of biological and chemical processes [1]. Although more than 90% of pollutants can be removed from dyeing wastewater by these conventional processes, considerable amounts of COD and total dissolved solids (TDS) remain in the effluents after the biochemical processes [2,3]. More stringent criteria [4] are being introduced to reduce pollutant discharges into the environment and these oblige dyeing factories to upgrade their existing waste treatment systems. Furthermore, dyeing companies may face shortages of available water resources due to water scarcity and limitations for ground water use. In the near future, many dyeing companies will have to reuse secondary effluents to achieve environmental and economic benefits [2,3]. A more sustainable solution may be to consider the wastewater as a 'renewable resource' from which water and other valuable

substances can be reused or recovered for economic reasons and environmental protection. Madsen et al. [5] reported that combining membrane filtration with electrochemical oxidation could effectively remove most pollutants from wastewater and reduce energy consumption. Xu et al. [6] also presented an integrated system coupling nanofiltration with electrolytic oxidation for treating dyeing wastewater. Although these integrated systems are novel, they are not able to achieve high reuse/recovery rates because of the residual TDS in the effluent. Finding a zero discharge process for dyeing wastewater treatment is therefore imperative to the future sustainability of the dyeing industry.

Reverse osmosis (RO), a widely used and rapidly growing desalination technology, can efficiently remove TDS from wastewater and produce fresh water to meet the reuse requirements of secondary effluents [4,7,8]. Although RO has become a viable technology for wastewater reclamation, further biological treatment of the concentrated water, with upgraded of chromaticity, COD, salts, and other contaminants, is difficult [9].

Electro-oxidation (EO) is considered environmentally compatible because its main reagent is the electron, which is a clean reactant [10,11]. Scientists and engineers have selected EO and other technologies to reduce chromaticity, COD, and other contaminants [12–14]. The concentrated water also has high conductivity owing to its high concentration of salts, which benefits the process

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Table 1
The main compositions of the dyeing wastewater after biochemical processes.

Parameters	Units	Raw wastewater
Na ⁺	mg/L	589.80 ± 0.50
Mg ²⁺	mg/L	15.95 ± 0.30
Mn ²⁺	mg/L	1.43 ± 0.05
Fe ³⁺	mg/L	0.25 ± 0.01
SO ₄ ²⁻	mg/L	958.12 ± 3.0
NO ₃ ⁻	mg/L	342.28 ± 0.8
Cl ⁻	g/L	3.48 ± 0.01
Conductivity	mS/cm	12.0
Chromaticity	times	25
COD _{Cr}	mg/L	160 ± 5

by reducing the electrolytic cell voltage and thereby reduces energy consumption.

Bipolar membrane electrodialysis (BMED) can split salts in an aqueous phase into acid and base [15,16]. It has been developed as an environmentally friendly technology with a wide range of industrial applications, including clean chemical production, resource reclamation, energy recovery and environmental preservation [17,18]. BMED not only offers environmental benefits and reduces water pollution, but also regenerates valuable products for sustainable development [18]. However, pollutants, such as organic matters in wastewater, affect the performance of BMED.

In this study, we aimed to develop a novel zero discharge process for dyeing wastewater depth treatment and investigate its feasibility. The process integrates RO, EO and BMED. RO removes pollutants from the wastewater and produces fresh water, which is recycled as a water resource, and concentrated water. EO decomposes organic pollutants in the concentrated water and avoids the negative effect of organics on the subsequent BMED step. BMED splits the salts remaining in the concentrated wastewater into mixed acid and base solutions, which can be reused in wastewater pretreatment and other suitable applications, while the water produced by splitting of the salts can also be reused as a water resource. In summary, no pollutants or wastewater are discharged into the environment during dyeing wastewater depth treatment by this novel RO/EO/BMED process. Here, the effects of operation parameters such as recovery ratio, specific current and input power on RO/EO/BMED performance are discussed.

2. Experimental

2.1. Wastewater characteristics

The dyeing wastewater was collected from the secondary sedimentation tank of the wastewater treatment process at a dyeing factory located in the Shaoxing region of Zhejiang Province, China. The compositions of the effluents after the various biochemical processes are shown in Table 1. The secondary effluent still contained high levels of COD, TDS and chromaticity, so it was not permitted to be directly discharged or recycled as a water resource.

2.2. Zero discharge system

The novel zero discharge system for the depth treatment of dyeing wastewater after biochemical processes, consists of reverse osmosis (RO) technology, electrochemical oxidation (EO) and bipolar membrane electrodialysis (BMED), is shown in Fig. 1.

The RO membrane (Model: SG1812), supplied by GE Power & Water Technologies, comprised an aromatic polyamide composite crosslinked with polysulfone. The surface area of membrane was 0.32 m². The electrolytic cell was made of polypropylene with an effective volume of 4 L. Mesh-plate titanium-based lead dioxide electrode (Ti/PbO₂) and titanium mesh-plate were selected as

the anode and cathode, respectively, each with a working area of 0.15 m² and an interelectrode distance of 2 cm. The BMED consisted of four compartments: electrode, salt, acid and base compartments. Membranes used in the BMED experiments were cation exchange membranes (FKB, Germany), anion exchange membranes (FAB, Germany) and bipolar membranes (BMP), each with an effective area of 189 cm².

Raw wastewater from the secondary sedimentation tank of the biochemical processes was pumped into the RO apparatus to produce fresh and concentrated water at a pressure of 12 bar and temperature of 25 °C. The fresh water permeating the osmosis membrane was collected for reuse.

The concentrated water intercepted by the RO membrane flowed into the EO device. Using a direct current (DC) power supply and current density of 15 mA/cm², the EO process decomposed the organic pollutants and reduced the COD concentration.

When the COD_{Cr} value was below 60 mg/L, the concentrated water was fed into the BMED unit. The mixed acid and base solutions were collected in the acid and base compartments, respectively. The desalinated wastewater, also called fresh water, was collected for reuse.

2.3. Analysis and calculation methods

All industrial wastewater samples were preserved in sealed polyethylene containers and kept at room temperature before analysis. The concentrations of the cations in the wastewater were determined by inductively coupled plasma spectroscopy with mass-spectrometric detection (ICP-MS); the anions concentrations were determined by ion chromatography. The concentrations of acid and base from BMED were respectively determined by titration with standard sodium hydroxide and hydrochloric acid solutions using phenolphthalein and methyl orange as indicators. TDS, conductivity and pH of the feed wastewater were monitored throughout the process using conductivity and pH meters, respectively.

The removal efficiency R (%) of the RO process was determined during membrane filtrations and quantified as the percentage rejection of a particular component:

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

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

The desalination ratio γ (%) of the process was calculated using Eq. (2)

$$\gamma = \frac{C_{in} - C_{ef}}{C_{in}} \times 100\% \quad (2)$$

where C_{in} and C_{ef} are the salt concentrations in the feed and permeate (g/L), respectively.

The BMED input power was calculated using Eq. (3):

$$P = IU \quad (3)$$

where U (V) is the voltage drop across the BMED stack; I (A) is the current.

The energy consumption E (kWh/kg) of BMED was calculated using Eq. (4) [19]:

$$E = \int \frac{UIdt}{(C_t - C_0)VM} \quad (4)$$

where U (V) is the voltage drop across the BMED stack; I (A) is the current; C_t and C_0 are the concentrations of acid/base (mol/L) at time t and 0, respectively; V is the volume of the acid/base cycle (500 mL); and M is the molar mass of the acid/base.

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