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Advanced treatment of biologically treated coking wastewater by membrane distillation coupled with pre-coagulation

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HIGHLIGHTS

- Membrane distillation was developed for advanced treatment of coking wastewater.
- Pre-coagulation with PACl significantly reduces the solids and organic loadings.
- Small amount of low molecular weight aromatic substance presents in the MD permeate.
- PACl coagulation prevents the formation of calcium carbonate on membrane surface.
- PAM increases organic removal but causes aggregate accumulation and severer fouling.

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ABSTRACT

In this study, a laboratory-scale membrane distillation (MD) system was developed for advanced treatment of biologically treated coking wastewater (BTCW), while the effect of pre-coagulation was also investigated. Results showed that membrane distillation could effectively reject the salts (>99.1%) and organic pollutants in BTCW (>96.2%) and no membrane wetting was observed. The remaining organics in distillate was largely determined by the amount of volatile substances in the feed. Pre-coagulation with poly-aluminum chloride (PACl) was found to be effective for significantly reducing the contaminant level in BTCW. This in turn significantly reduces the propensity of membrane fouling. Use of polyacrylamide (PAM) as a coagulant aid could further decrease the contaminant level in BTCW, but it may lead to even severer membrane fouling. Scanning electron microscopy (SEM), energy-dispersive spectrometer (EDS) and fluorescence spectra analyses revealed that the interaction between PACl and remaining organics could prevent the formation of calcium carbonate on the membrane surface, whereas the addition of PAM facilitated the accumulation of aggregates on membrane surface, leading to serious membrane fouling. This study shows that membrane distillation coupled with pre-coagulation could serve as a potential alternative for advanced treatment of biologically treated coking wastewater.

1. Introduction

In China, pollution caused by coking wastewater remains a severe problem as China produces about 470 million tons of coke per year [1]. Coking wastewater is often generated during high-temperature carbonation, coal gas purification, and chemical refining in coke plants. It is a complex industrial wastewater comprising hundreds of organic pollutants and inorganic pollutants, which usually contains ammonia, phenol, benzene, nitrogen heterocyclic compounds (e.g., quinoline, pyridine, and indole), and polycyclic aromatic hydrocarbons [2–4]. Many of these compounds are refractory, toxic, mutative, and/or carcinogenic [5,6].

Conventional treatment of coking wastewater includes physio-chemical technologies (e.g. solvent extraction of phenolic compounds and steam stripping of ammonia), and biological treatment prior to discharge to the receiving water bodies. Activated sludge system, such as anoxic/oxic (A/O) or anaerobic/anoxic/oxic (A^2/O) processes, is the dominant biological process in China for coking wastewater treatment because of its low cost, simple operation and maintenance [5,7,8]. Unfortunately, due to the presence of refractory and inhibitory contaminants, the effluents from these systems still contain relatively high concentration of non-biodegradable organic pollutants [2,3,9]. With the raised concerns of these hazardous effluents, China has recently

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strengthened the national discharge standard of coking wastewater (GB16171-2012). In addition, a new revised regulation on coking industry access requirements issued by Chinese government states that the discharge of production wastewater from any newly built coking plants is completely prohibited [8]. As a result, advanced treatment and zero discharge of the biologically treated coking wastewater (BTCW) are becoming increasingly important.

Currently, various technologies have been proposed for advanced treatment of BTCW, such as advanced oxidation processes, adsorption technologies and membrane filtrations. The advanced oxidation processes like Fenton, ozone and electrochemical oxidation have the ability to remove or even mineralize the organics by generating hydroxyl radicals, but the cost is usually high due to the large consumption of oxidants and/or the use of energy intensive equipments [2,4,10,11]. Adsorption is a promising method, but the activated carbon or other polymers have difficulties in regeneration, and the disposal of the exhausted adsorbents remains a challenge [3,12,13]. Membrane filtration including microfiltration and ultrafiltration is effective in removing the biorefractory organics, however membrane performance can dramatically decrease as a consequence of membrane fouling due to the presence of the refractory organics in BTCWs [8,14,15]. In addition, the effluent of abovementioned systems often requires further desalination process such as nano-filtration (NF) and reverse osmosis (RO) to meet the reusing water standard [3,8].

Membrane distillation (MD) is a technology with the hydrophobic membrane which itself acts as a barrier to hold the liquid/vapor interfaces at the entrance of the pores, and the driving force is a vapor pressure difference across the membrane. It has the advantages of theoretically 100% salt rejection, lower operating temperature than conventional distillation processes, less requirements of membrane mechanical strength, and lower operating pressure compared to conventional pressure-driven membrane processes such as RO [16]. The first patents on MD were granted in the late 1960s, but it wasn't technologically feasible until ultrafiltration membranes in recent years enabled sufficiently high trans-membrane fluxes [17]. Since then, MD has regained extensive interests on membrane development, configuration design and application exploring [16–19].

Due to the effectiveness on rejection of non-volatile substances, membrane distillation has also been applied in advanced treatment of industrial wastewaters including petrochemical wastewater, olive mill wastewater, as well as radioactive wastewater [20–22]. In these systems, MD has demonstrated good distillate water quality and less fouling propensity than pressure-driven membrane processes. Therefore, it is suggested that MD will be a potential alternative for advanced treatment of BTCW, and it also could significantly reduce the volume of RO concentrates or other wastes. In addition, the coking plant often has a large amount of waste heat, which makes the MD process competitive in practice. However it should be noted that although MD requires less intensive pretreatment as compared to pressure-driven membrane processes, the importance of pretreatment in MD cannot be underestimated as BTCW remains containing a relatively high concentration of pollutants.

In this regard, the present paper aims to determine the performance of advanced treatment of BTCWs with a laboratory direct contact membrane distillation (DCMD) system for a relatively long period (72 h). Furthermore, the effect of the different coagulation pretreatment methods on distillate quality and membrane fouling was investigated comprehensively. It is expected that this study would promote the application of MD in BTCW treatment.

2. Materials and methods

2.1. Wastewater characteristics

The biologically treated coking wastewater (BTCW) was collected from the effluents of a coking wastewater treatment plant based on anaerobic/anoxic/oxic (A^2/O) process in Shanxi, China. The effluent quality of the A^2/O process is given in Table 1.

2.2. Coagulation pretreatment

The coagulation experiments were conducted in 500 mL beakers using conventional Jar-test apparatus at room temperature. In the jar tests, analytical-grades of poly-aluminum chloride (PACl, hydrogen ratio of 40%) and nonionic polyacrylamide (PAM) (>300 kDa) were applied as coagulant and coagulant aid respectively. Samples were mixed at 250 r/min initially for 30 s before PACl or PACl/PAM was added. Then they were mixed with the coagulants at 200 r/min for another 90 s before reduced to 40 r/min for 30 min. When the coagulation was completed, the samples taken from each jar tests were centrifuged for 15 min and stored in a 4 °C refrigerator before conducting an analysis. The optimum dosages of PACl (175 mg/L) and PAM (2 mg/L) were determined by the removal of pollutants in the coagulated wastewater. In the pretreatment of PACl/PAM, PAM was added 10 s after dosing of PACl. The optimal dosage was used in all subsequent tests involving PACl and PAM.

2.3. DCMD experiment

A microporous hydrophobic flat membrane was used in this work, which was provided by Sumitomo Electric Industry Ltd Corp (Japan). The membrane consists of a thin porous polytetrafluoroethylene (PTFE) active layer (35 μm) and a polypropylene non-woven fabric net support layer (152 μm). The active layer has a 0.22 μm nominal pore size and 82% porosity. The membrane module was made of nylon fiberboard and the effective membrane area is 14.4 cm^2. The details of the membrane module can be found elsewhere [23].

The experiment set-up is shown schematically in Fig. 1. BTCWs were heated to 50 °C in a 1 L three-neck flask by a thermostatic water-circulator bath (HH-501A, Jiangsu, ±0.1 °C). MilliQ water was used as the cooling agent of DCMD, which was maintained at 20 °C in the entire experimental period by a precise low-temperature thermostat bath (DS-2006, Ningbo, ±0.1 °C). The BTCW and MillQ water were circulated at 0.3 m/s by two independent peristaltic pumps (WT600-2J, Baoding, China) in countercurrent directions. The water overflowed from the distillate reservoir (0.8 L) to a conical flask, which was continuously weighed by an electronic balance (DJ-1000J, Shanghai) and recorded every 10 min. The membrane flux was calculated by dividing the weight of overflow water and membrane effective area. The flow rate was measured with rotometers on each side of the membrane. The inlet and outlet temperatures of feed and permeate streams were measured using mercury thermometers. Conductivity in the BTCW and distillate was continuously examined by a conductivity meter (SevenMulti, Mettler Toledo, Germany). Concentration factor (CF) of feed was calculated by dividing the initial weight by the final weight of the feed as the distillates only contain little contaminants.

2.4. Analytical methods

COD, ammonia nitrogen (NH_4-N) and color were measured using standard method [24]. Turbidity was analyzed by a turbidity meter

Table 1
Characteristics of biologically treated coking wastewater.

Parameter	Unit	BTCW
pH		7.8 ± 0.3
BOD_5	mg/L	35 ± 5
COD	mg/L	315 ± 20
NH_3-N	mg/L	7.1 ± 0.5
Turbidity	NTU	33.3 ± 3.8
Color	°	361 ± 7
Conductivity	μs/cm	6092 ± 23