Advanced treatment of textile wastewater for reuse using electrochemical oxidation and membrane filtration

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Abstract

The treatment of textile wastewater for reuse using an electrochemical oxidation step combined with a membrane filtration step is reported in this paper. The electrolytical process is a traditional one, which is easy to scale up and to apply in practice. This paper proposes a modification of the transfer-flow membrane (TFM) module with fibres welded in an arc-shape to enhance the mechanical properties of the fibres and to increase the specific membrane surface of TFM modules. The goal of this research was to study the performance of the arc-shaped TFM module to demonstrate these sequences of electrochemical oxidation coupled with membrane filtration processes and to develop a potential dyehouse wastewater treatment system for reuse. Two testing sequences of electrochemical oxidation and membrane filtration were studied in a sequential batch order. The results show clearly that fibres welded in an arc-shape can enhance the mechanical properties of the fibres effectively and that electrochemical oxidation and membrane filtration as sequential processes are feasible. Electrochemical oxidation has a high removal (89.8% efficiency) of the chemical oxygen demand (COD) of the wastewater while the membrane filter can almost totally remove the total suspended solids (TSS) (nearly 100% reduction) and turbidity (98.3% elimination) in it. Coincidentally, their advantages make up for their disadvantages. After these two steps, all the wastewater indices decrease to low levels; in particular, COD levels are reduced to 18.2 mg·ℓ^{-1}. The treated water can be reused in many production areas of the textile dyehouse factory. To take best advantage of this disposal system, the two processes should run in a rational sequence, with membrane filtration following the electrochemical oxidation process. With widely studied electrodes, this research offers a promising way for recycling textile wastewater.

Keywords: electrolysis, oxidation, membrane, dye, wastewater treatment

Introduction

Increasingly stringent effluent discharge permit limitations have been put into effect (Defazio and Lemley, 1999). The textile industry generally has difficulty in meeting wastewater discharge limits, particularly with regard to dissolved solids, ionic salts, pH, COD, colour, and sometimes, heavy metals (Author: This is a consulting firm and the name has to be written out in full: Steffen, Robertson and Kirsten, 1993; Lin and Peng, 1996; Vlyssides et al., 1999)

The problem of colour in textile dyehouse effluent and the possible problems associated with the discharge of dyes and dye degradation products are of concern. Traditional methods for dealing with this kind of wastewater are usually the biological, physical and chemical techniques as well as the various combinations of theses. It has been widely reported that many dye chemicals are difficult to degrade using conventional biological treatment processes. It is more important to reuse this kind of wastewater than to discharge it after treatment in that the costs of chemicals, energy and water continually increase.

Many advanced treatments have been studied and electrochemical oxidation has been applied to many kinds of wastewater (Naumczyk et al., 1996; Simonsson, 1997). It is presented as an effective, selective, economical, and clean alternative for dealing with wastewaters bearing high loads of organic compounds, especially some bio-refractory organic pollutants. Such treatment produces total degradation of compounds to CO_2 and H_2O or at least a considerable decrease in toxicity. A direct anodic process or an indirect anodic oxidation via the production of oxidants such as hydroxyl radicals, ozone, etc. usually destroys the organic and toxic pollutants present in wastewater such as dyes and phenols. Titanium electrodes covered with very thin layers of electrodeposited noble metals have recently been used for electro-oxidation. Electrodes can also be coated with ruthenium, rhodium, lead and stannum oxide (Vlyssides and Israilides, 1998; Chen et al., 2003; Taghizadeh et al., 2000). By means of electrochemical oxidation, pollutants in wastewater can be completely mineralised by electrolysis using high oxygen over-voltage anodes such as PbO_2 and boron-doped diamond. (Nicola and Badea, 1996; Tezuka and Jwasaki, 1996; Casado and Brillas, 1996). Naohide et al. (1998) treated dyestuff using PbO_2 anode. In their study, Orange II was decolourised completely by a 120 min electrolysis procedure using a PbO_2 anode at current density of 0.2 A cm^{-2}. Polcaro et al. (1999) studied the performance of the Ti/PbO_2 anode during electrolysis of 2-cholorophenol in terms of faradic yield and fraction of toxic intermediates removed. Ti/PbO_2 anode was used as the anode in this experiment, since it has been widely studied and used in some electrolysis industries, such as chlorine producing factories.

Membrane systems have also been reported in dyehouse wastewater treatment (Jadwiga et al., 1998; Wu et al., 1998 and Grimm et al., 1998). Membrane systems can successfully remove the large amount of suspended solids (SS) in wastewater. The aim of introducing membrane filtration is not only to reduce water

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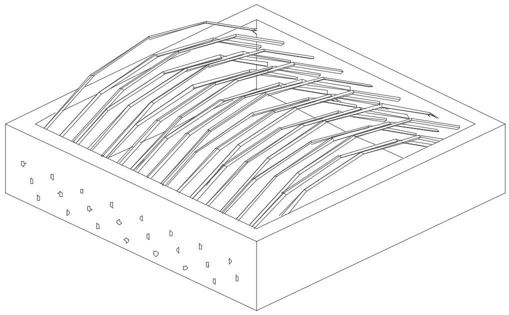

Figure 1
Transfer-flow membrane module with fibre welded in an arc-shape

consumption and wastewater effluents, but also to reduce the consumption of energy as the warm water can be recovered. Crossflow filtration was one of the most important methods proposed to overcome concentration polarisation and membrane fouling. Different from classical dead-end filtration, the suspension flow in crossflow microfiltration system is tangential to the filter surface and the wall with a velocity ranging from 1 to 4 $m \cdot s^{-1}$ in order to control and limit the development of the coating on the membrane (Bailey et al., 1994). In addition to the ratio of circulating wastewater to permeate flux being as high as 10~20:1, its power consumption of water treatment varies between 5 $kWh \cdot m^{-3}$ and 8 $kWh \cdot m^{-3}$ (Van Dijk and Ronken, 1997; Kim et al., 2002).

To lessen fibre contamination and polarity, Triqua (Knops et al., 1992) first researched a new type of membrane separator, the TFM separator. Influent flow is not parallel to the axis of the module as it is in crossflow membrane, but perpendicular to the fibre. It strengthens mass transfer in boundary layer, resulting in the fibres themselves serving as turbulence promoters. High-feed flow velocities or auxiliary turbulence promoters are not necessary. Therefore, compared with crossflow modules, transverse flow modules require less membrane area and consume less energy to produce a given amount of permeate. Energy requirements for this type of membrane filtration are about 0.1 to 0.5 $kWh \cdot m^{-3}$ (Van Dijk and Ronken, 1997).

However, the end-fibres tend to leak with sustained high stress caused by recycling wastewater (Sakellariou, 1998; Zhang, 2000). To overcome these shortcomings, a modification of the transfer-flow membrane module with the fibre welded in an arc-shape to enhance the mechanical properties of the fibres and to increase the specific membrane surface of TFM modules is proposed in this paper. This type of fibre arrangement can efficiently decrease the stress of the end-fibres and make the membrane tough, highly tenacious and strongly resistant to bending fatigue. This arc-shaped fibre is longer than a linear fibre in the same scale module, which increases the specific membrane surface of TFM modules to more than that of the normal transfer-flow membrane module.

Membrane-wet oxidation, an integrated process, has been demonstrated by Dhale and Mahajani (2000) to treat the disperse dye bath waste. Li and Zhao (1999) have developed an advanced treatment process for dyestuff wastewater treatment. A TiO_2 photo-catalytic reactor ran as advanced treatment for complete decolourisation and high COD removal. Suspended TiO_2 powder used in photo-oxidation was separated from the slurry by a membrane filter and treated wastewater was continuously recycled to the photo-reactor.

However, as yet, there has not been a method employing the electrochemical oxidation process combined with the membrane filtration process for the treatment and reuse of textile dyehouse wastewater. The goal of this research is to study the performance of the arc-shaped transfer-flow membrane module, at the same time, to demonstrate these processes and to develop a potential dye-wastewater treatment system for reuse.

TABLE 1
Arc-shaped transfer-flow membrane module specifications and operating conditions

Manufacturer	Centres of Zhongke membrane technology
Membrane material	PAN
Weight cut-off	500.00
Outer diameter	1 mm
Length	16 cm
The total membrane area	0.23 m^2
Suction pressure	0.03 MPa
Circulating flux	40 $\ell \cdot h^{-1}$
Aeration rate	0.2 $m^3 \cdot h^{-1}$

TABLE 2
Characteristics of wastewater used

Character	Value
pH	7.2
COD, $mg \cdot \ell^{-1}$	178.5
Turbidity, NTU	18.5
TSS ($mg \cdot \ell^{-1}$)	285
ADMI colour unit	1 520

Materials and methods

Electrode preparation

A titanium plate (8cm×3cm) was galvanized with PbO_2. A Ti/PbO_2 plate was used as an anode while stainless steel meshwork of the same dimensions served as a cathode in this system.

Membrane filter

Figure 1 shows the transfer-flow membrane module with the arc-shaped welded fibre. Its specifications and operating conditions are given in Table 1. The dimension of the arc-shaped transfer-flow membrane module is $150 \times 150 \times 100$ mm^3.

Materials

The wastewater sample used was collected after a bio-filter treatment from a textile dyehouse in Beijing. It looked red. The composition of the sample is shown in Table 2.

Instrumentation

Solution pH values were detected by a pH/mV meter (COLE PARMER, USA). Samples' colour was analysed by U-3010

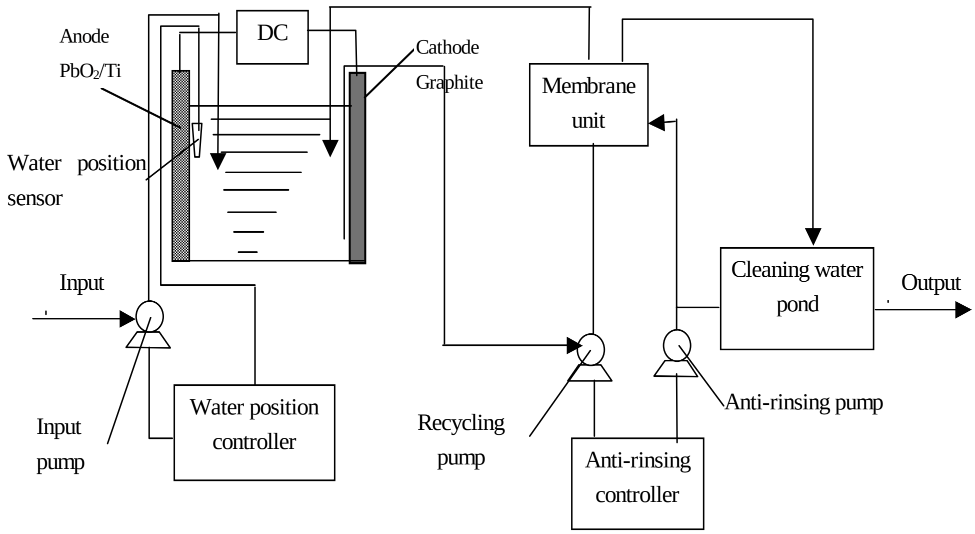

Figure 2
Schematic diagram of electrochemical oxidation experimental set-up

Spectrophotometer (Hitachi, Japan). Each dye solution was scanned and its maximum absorbency visible wavelength was detected. The colour unit was detected by a standard method (Author: specify and refer to the method) COD and the colour remains ratio was calculated as follows:

$$\text{Remains}_{colour}\ \% = ABS/\ ABS_0 \times 100\% \quad (1)$$

(ABS_0: ABS value before electrolysis)
(ABS: ABS value after electrolysis)

$$\text{Remains}_{COD}\ \% = COD/\ COD_0 \times 100\% \quad (2)$$

(COD_0: COD value before electrolysis)
(COD: COD value after electrolysis)

Methods

Electrochemical oxidation of wastewater was conducted in an undivided reactor of 1.2dm^3 volume. The overall experimental set-up mainly consists of a cell unit, water position control system, a set of recycling system and a membrane unit, as shown in the following Fig. 2. Electrolysis was conducted at 8V DC and electric current density was kept at 124 $A \cdot m^{-2}$. After electrolysis, COD_{Cr} and the colour of the solution are determined by a U-3010 Spectrophotometer, respectively.

Results and discussion

Electrochemical oxidation process prior to membrane filtration process

To test these processes, the two processes were run in sequential batch order. Firstly, electrochemical oxidation was performed in a cubic reactor and followed by a membrane filtration process. The results of the former step are given in Table 3. It is seen from the table that electrochemical oxidation can more efficiently remove colour than turbidity and SS. The remaining ratio of colour is 145: 1 520 (9.5%), which is less than the TSS ratio. The reason is that it is difficult for the oxidative radicals, $\cdot O_2$ or HO· to break the large amount of solids particles in the sample.

Table 4 shows that the second step can make up the deficiency of the first one. Membrane filtration can remove almost all the TSS and the turbidity, which is difficult for a chemical oxidation system to achieve. These two processes work well together for textile wastewater treatment. After the two steps, the COD remains at a low level, only 18.2 $mg \cdot \ell^{-1}$, and so do other indices. The treated water can be reused in many production areas of the textile dyehouse factory. It is reported that Ti/RuO_2, Ti/SnO_2 and Ti/SnO_2+Sb_2O_5 electrodes have better ability to oxidize toxic compounds and are more efficient than our Ti/PbO_2 anode. If these more efficient electrodes are used in this system, the wastewater can be treated more effectively, and can be used in all production areas of the textile factory. It can therefore be deduced that this system provides a promising way to treat textile dyehouse wastewater for reuse.

The wavelength scan result in Fig. 3 confirms the above conclusion. After both steps, the absorption among visible wavelength scope is decreased to a low level.

TABLE 3
Treatment effect of electrochemical oxidation as a first step

Character	30 min		50 min	
	Value	Remains/%	Value	Remains/%
pH	7.0		6.9	
COD, $mg \cdot \ell^{-1}$	78.6	44.0	46.0	25.8
Turbidity, NTU	9.8	53	8.7	47
TSS ($mg \cdot \ell^{-1}$)	260	91.2	245	86
ADMI colour units	395	26.0	145	9.5

TABLE 4
Treatment results of membrane filtration as a second step

Character	Value	Remains /%
pH	7.6	
COD, $mg \cdot \ell^{-1}$	18.2	10.2
Turbidity, NTU	0.32	1.7
TSS ($mg \cdot \ell^{-1}$)	0	0
ADMI colour units	135	8.9

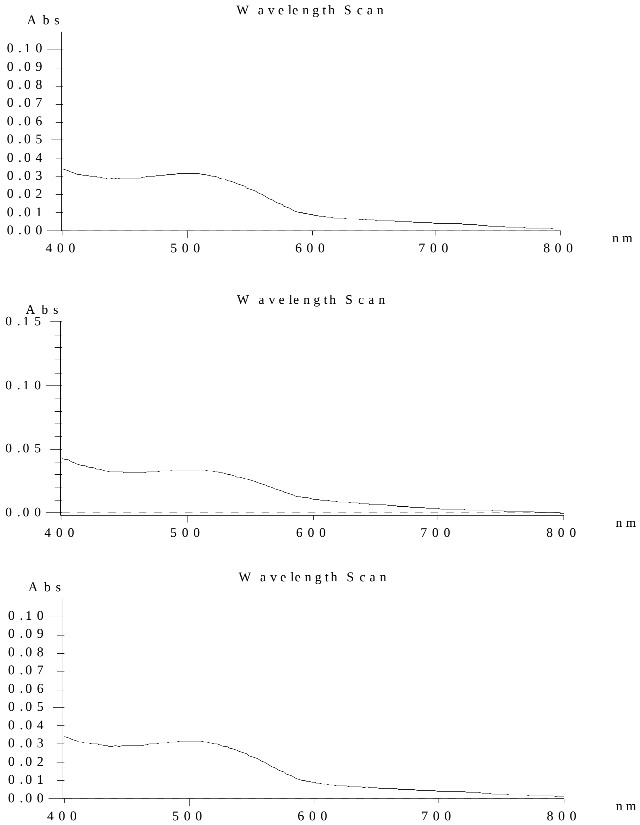

Figure 3
Wavelength scan of textile wastewater of raw sample (upper), sample after electrochemical oxidation as a first step (middle) and sample after both the two steps (lower)

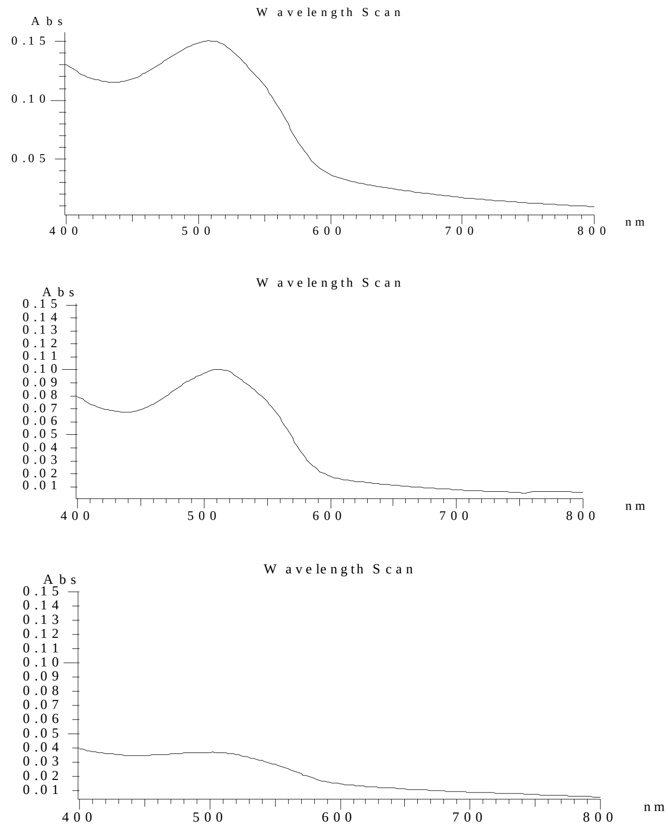

Figure 4
Wavelength scan of textile wastewater of raw sample (upper), sample after membrane filtration as a first step (middle) and sample after both the two steps (lower)

TABLE 5
Treatment results of membrane filtration as a first step

Character	Value	Remains /%
pH	7.1	
COD, mg·ℓ$^{-1}$	67.4	37.8
Turbidity, NTU	0.40	2.2
TSS (mg·ℓ$^{-1}$)	0	0
ADMI colour units	942	62

TABLE 6
Treatment effect of electrochemical oxidation as a second step

Character	Value	Remains /%
pH	7.1	
COD, mg·ℓ$^{-1}$	24.7	13.8
Turbidity, NTU	0.9	4.9
TSS (mg·ℓ$^{-1}$)	—	—
ADMI colour units	225	14.8

Membrane filtration process prior to electrochemical oxidation process

Secondly, another order of the two processes was also performed. Electrochemical oxidation was conducted after membrane filtration. Table 5 and Table 6 show the experimental results of this testing sequence. The advantages and disadvantages of membrane filtration are indicated in Table 5. Its poor decolourisation effect must be because most the dyestuffs are small molecules. In general, the smaller the size of a molecule, the higher the passing rate through the membrane. Figure 3 gives the absorption states in this experimental order and shows that most of the colour is disposed of in the second step.

However, even after being treated by a second electrochemical oxidation process, the colour unit of the solution is no less than 500 in the latter test order and the COD removal is not as effective as in the previous experiment. This may be attributed to lower SS in the wastewater after the filtration. Some particles in the solution may serve as catalyst, accompanied by many kinds of ions. Many form-changeable ions, such as Ag^{2ÿ}0Co^{3ÿ} and Fe^{3ÿ}, can be oxidative intermediates and accelerate the degradation of organic pollutants. The function of these ions has been confirmed in the oxidation of benzene, phenol and oil.

By contrast, the change in sequence of these two steps leads to a variation in the result. Author to check The former method with electrochemical oxidation being the first step is prior to the latter one. In order to make full use of this disposal system, it is important that the two processes should run in a rational sequence.

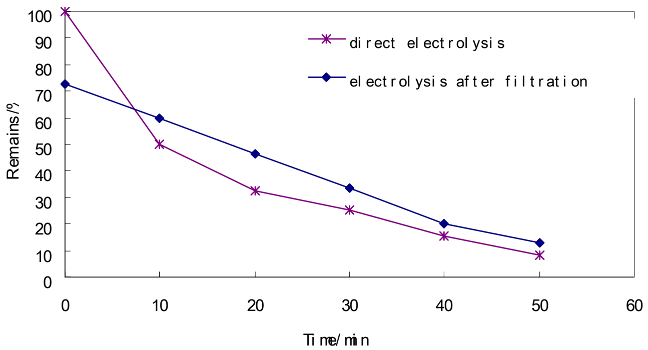

Figure 5
Colour removal of wastewater with the time, at 8V D.C., electric current density 124 mA cm^{-2}

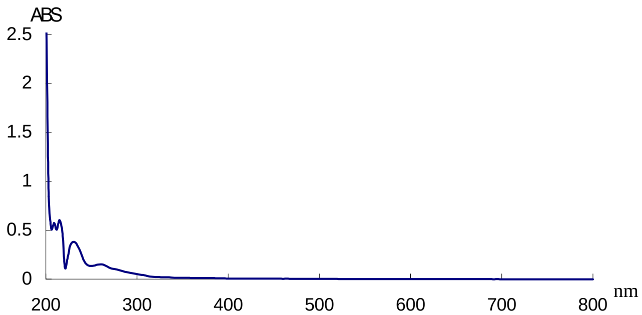

Figure 6
Spectrum of wastewater extraction by CH_2Cl_2 before treatment

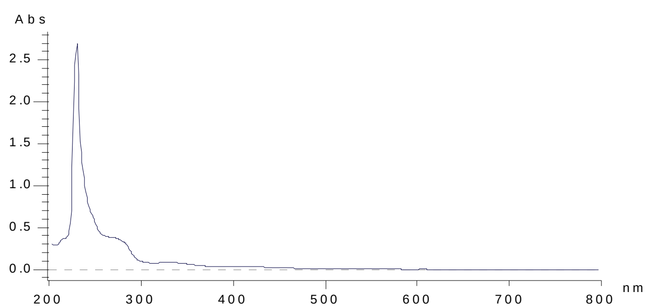

Figure 7
Spectrum of wastewater extraction by CH_2Cl_2 after treatment

Contrast of the UV-Vis spectrum of wastewater before and after treatment

Figure 6 is the UV-Vis spectrum of the primary solution extracted by CH_2Cl_2. The primary solution extracted by CH_2Cl_2 is colourless and its absorption is not obvious in UV-Vis. It indicates the strong polarity of the dye, only a faint absorption front in 234nm. Because the purity of the dye on sale is not very high, the dye contains some decomposed products, which are affected by sunlight and UV. In comparison with Fig. 6, Fig. 7 is the UV-Vis spectrum of the electrolysed wastewater extracted by CH_2Cl_2 (colour removal >95%).The maximum absorption front is stronger after treatment, and this may be attributed to the faint polarity or non-polarity of the decomposed products. The maximum absorption front in 234nm shows there are still aromatic compounds in the residual solution.

Conclusions

Transfer-flow membrane modules with arc-shaped welded fibres can enhance the mechanical properties of the fibres and increase the specific membrane surface of TFM modules. The phenomenon of fibres leaking did not occur during the experiment. Two testing sequences of electrochemical oxidation and membrane filtration were studied. The two processes treated textile dyehouse wastewater samples in turn. The results clearly show the feasibility of these two sequential processes. Electrochemical oxidation effectively removes the colour of the wastewater while the membrane filter almost totally removes the TSS in it. It is obvious that their advantages can make up for the disadvantages of each. After both steps, all the wastewater indices decrease to low levels. The treated water can be reused in many production areas of the factory. To make the most of this disposal system, it is important that the two processes should run in a rational sequence. It is indicated that the membrane filtration process should follow the electrochemical oxidation process. As electrolysis is a traditional method, it is easy to operate an electrochemical oxidation process and to apply it. With more efficient electrode materials, this system will provide us with a more effective method for recycling textile dyehouse wastewater.

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