Advanced Treatment Process for Papermaking Wastewater by Composite Photoelectrocatalysis and Heterogeneous Photocatalysis of Nano-TiO_2 Colloid and its Pilot-scale System

Wenhao Shen, Jiao Li, Xiaoquan Chen,* Shibin Wu, Zhifeng Lin, and Xiaohang Tian

It is difficult for papermaking wastewater to reach the discharge standard with only a sequencing batch reactor activated sludge process (SBR). This study developed an advanced wastewater treatment system with nano-TiO_2 colloid photoelectrocatalysis and heterogeneous photocatalysis (PEPC). First, the performances of different flocculation processes and their influences on the subsequent PEPC process were studied. The recycling of the nano-TiO_2 colloid photocatalyst was further investigated. The results showed that the ternary composite flocculation process using both the inorganic flocculant and the nano-TiO_2 colloid (1×10^{-3} wt%) had the best flocculation effect with a suspended solid (SS) removal rate of 93.5% and a chemical oxygen demand (COD) removal rate of 66.9%. It also achieved the best PEPC treatment performance with a COD removal rate of 93.6% in 90 min with the 0.05 wt% dosage of the nano-TiO_2 colloid photocatalyst. Moreover, the COD removal rate reached 88.5% after four recyclings of the nano-TiO_2 colloid photocatalyst, which demonstrated the excellent reusability of the nano-TiO_2 colloid photocatalyst. Finally, based on the PEPC process, an automatic and continuous pilot-scale system was established. Its successful operation suggests the feasibility of operating PEPC technology at an industrial scale.

Keywords: Papermaking wastewater; Photoelectrocatalysis; Heterogeneous photocatalysis; Advanced treatment

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INTRODUCTION

The pulp and papermaking industry produces large amounts of wastewater, with consumption of 80 m^3/t to 150 m^3/t paper (Wen *et al*. 2016; Ginni *et al*. 2017), which accounts for 13.0% of the total industrial wastewater discharge in China (China Paper Association 2017). The main wastewater treatment method, in many cases, is the sequencing batch reactor activated sludge process (SBR). However, it is difficult to reduce the chemical oxygen demand (COD) of wastewater to the limit of 50 mg/L using only SBR technology (GB 3544-2008 2008; Hubbe *et al*. 2016; Subramonian *et al*. 2017). Due to the global water shortage, it is urgent to reduce freshwater consumption and wastewater discharge in the papermaking industry (Lucas *et al*. 2012). Hence, advanced treatment processes are necessary to meet the discharge standard and to include wastewater as recycling process water.

Several advanced treatment processes have been used to degrade the non-biodegradable pollutants in the SBR effluent, including adsorption, flocculation

precipitation, membrane separation, electrochemical, photocatalytic oxidation, Fenton oxidation, ozone oxidation, *etc.* (Kamali and Khodaparast 2015; Hubbe *et al*. 2016). Due to its mild reaction conditions and lack of secondary pollution, photocatalytic oxidation is a potential process for the advanced treatment of wastewater (Li *et al.* 2009; Zangeneh *et al*. 2015).

There are obstacles for the industrialization of wastewater treatment with nano-TiO_2 photocatalytic oxidation, including the separation of nano-TiO_2 from the treated wastewater for reuse, which reduces the production cost. Immobilization technology solves this problem; nano-TiO_2 is loaded onto activated carbon (Shi 2009), carbon fiber (Kim *et al*. 2012), or zeolite (Khodadoust *et al*. 2012). However, these methods reduce the specific surface area, causing decreases in photocatalytic efficiency. In this work, the nano-TiO_2 colloid was used as the photocatalyst. The pH was adjusted to separate the photocatalyst, and excellent photocatalytic activity was observed in the recovered product. This activity reflected its outstanding monodispersibility, which was due to its synthesis at low temperature (Chen and Shen 2008).

Another weakness of this process is the easy recombination of photo-generated carriers, which leads to low photocatalytic efficiency. To overcome this defect, photoanode materials are used in the reaction system for photoelectrocatalytic oxidation to promote the separation of photo-generated electrons and holes, thereby improving the efficiency of photocatalytic reaction. Ward and Bard (1982) employed an external voltage to increase the photocatalytic activity, and photoelectrocatalytic oxidation technology has been shown to be an effective method for wastewater treatment (Meng *et al*. 2015; Cao *et al*. 2017; Garcia-Segura and Brillas 2017). The applied photoanode materials with this technology include TiO_2, ZnO, WO_3, $ZnWO_4$, $BiPO_4$, Bi_2WO_6, Bi_2MoO_6, and organic semiconductors (such as g-C_3N_4). Among these, TiO_2 has been applied as a common photoanode material due to its advantages of non-toxicity, high stability, and high oxidation resistance (Zhang *et al*. 2012; Garcia-Segura and Brillas 2017; Zhang *et al.* 2017). Most recent studies focus on the various preparations of photoanode, including electrophoretic deposition (Liu *et al*. 2016), dip-coating (Tang *et al*. 2018), *in situ* anodic oxidation of titanium (Turolla *et al*. 2018), *etc*., where loading is often followed by calcination. However, the complexity and energy consumption of these preparations limit their industrial applications.

Photoelectrocatalysis and heterogeneous photocatalysis (PEPC) of anatase nano-TiO_2 colloid have a synergistic effect on the degradation of Rhodamine B, when a porous metal substrate is immersed in the reaction system (Wu and Chen 2015). This method simplifies the preparation of the photoelectric working electrodes and preserves the large specific surface area of the photocatalyst. However, there has been a lack of studies applying the PEPC process in the advanced treatment of papermaking wastewater.

In the present study, the PEPC system with nano-TiO_2 colloid was applied to the advanced treatment of papermaking wastewater, and the aluminum honeycomb net was used as the porous metal substrate. First, a ternary composite flocculant was used for the flocculation of papermaking wastewater to remove the suspended solids (SS), and the effects of different flocculation processes on the flocculation efficiency and on the subsequent PEPC advanced treatment efficiency were investigated. By adjusting the pH of the composite system to neutrality for separating the photocatalyst, the recycling efficiency of the nano-TiO_2 colloid photocatalyst was studied. Finally, to test the possible industrialization of PEPC technology, an automatic continuous pilot-scale system was established. The high COD removal rate, excellent reusability of nano-TiO_2, and pilot-scale results were obtained with PEPC technology.

EXPERIMENTAL

Materials

The nano-TiO_2 colloid (anatase, solid content of 20%, particle size of 5 nm) was obtained from Hunan Taitang Nano Science & Technology Co., Ltd (Hunan, China). The papermaking wastewater of SBR effluent was collected from a secondary fiber paper mill (Guangzhou, China), whose COD, pH, and SS were 359.7 mg/L, 8.0, and 78.0 mg/L, respectively. The aluminum honeycomb net was bought from Dongguan Xionglin New Material Technology Co., Ltd. (Dongguan, China), and the sponge nickel network was purchased from Shenzhen Zibo Environmental Protection Equipment Co., Ltd (Shenzhen, China). Polyaluminum chloride (PAC) and polymeric ferric sulfate (PFS) were purchased from Tianjin Guangfu Fine Chemical Research Institute (Tianjin, China). Hydrogen peroxide (H_2O_2) and all other reagents were analytical grade.

Flocculation Pre-treatment of Papermaking Wastewater

To ensure the PEPC treatment efficiency, the SBR effluent with high SS content was flocculated. A certain amount of flocculant was added to 1 L of SBR effluent, and the mixture was stirred for 30 min at 250 rpm. The three flocculation processes were inorganic (PAC: PFS = 3:2, 0.025 wt%), nano-TiO_2 colloid (0.025 wt%, pH 5), and ternary composite (0.025 wt% PAC and PFS, 0.01 wt% nano-TiO_2 colloid, pH 5). The reasons for choosing the three flocculation were as follows. The PFS and PAC are widely used inorganic flocculants. Nano-TiO_2 colloid with positive charge and high specific surface area is a potential excellent capturing flocculant. A ternary composite combining the inorganic flocculants with the nano-TiO_2 colloid might reduce the cost of usage of nano-TiO_2 colloid.

Determinations of SS and COD

Determination of SS

The 100 mL flocculated wastewater sample was passed through a filter membrane of 0.45 μm, which was washed 3 to 5 times with 10 mL of deionized water. The filter membrane with SS and weighing bottle was dried at 103 ºC to 105 ºC for 2 h until it reached a constant weight. A blank filter membrane and the weighing bottle were dried under the same conditions. The SS content of the wastewater sample was calculated with Eq. 1,

$$SS = \frac{(m_2 - m_1) \times 10^6}{V} \quad (1)$$

where m_1 is the weight (g) of the blank filter membrane and weighing bottle, m_2 is the weight (g) of filter membrane, weighing bottle, and V is the volume (mL) of the flocculated papermaking wastewater sample.

The SS removal rate (R_{SS}) was calculated with Eq. 2,

$$R_{SS} = \frac{(SS)_0 - (SS)_t}{(SS)_0} \quad (2)$$

where $(SS)_0$ and $(SS)_t$ are the SS values (mg/L) of the wastewater samples before and after the flocculation process, respectively.

Determination of COD

The flocculated wastewater sample was centrifuged at 4500 rpm for 10 min, and the COD of the supernatant was measured with a DR1200 COD tester (HACA, Loveland, USA). The COD removal rate (R_{COD}) was calculated with Eq. 3,

$$R_{COD} = \frac{(COD)_0 - (COD)_t}{(COD)_t} \quad (3)$$

where $(COD)_0$ and $(COD)_t$ are the COD values (mg/L) of the wastewater sample before and after flocculation process, respectively.

PEPC Treatment of Papermaking Wastewater

The 1 L flocculated papermaking wastewater sample was poured into a beaker, and the pH was adjusted to 5 with 1 M diluted nitric acid, followed by adding 0.5 g/L sodium sulfate as the electrolyte and a certain amount of nano-TiO_2 colloid as the photocatalyst. As shown in Fig. 1, two pieces of the porous aluminum honeycomb nets and one UV lamp (CN-SZU15, 15 W, 254 nm, Foshan, China) were placed into the system and fixed with iron wire. The aluminum honeycomb nets were impregnated into the system for 15 min to adsorb the nano-TiO_2 colloid for forming a photoelectric working electrode, and another small sponge nickel net was put on the inside edge of the beaker without impregnating into the system as a counter electrode. A 0.8 V DC power supply (TASI-1305, Suzhou, China) was applied on the two electrodes, followed by adding 2 mL/L H_2O_2. The PEPC oxidation reaction was performed under the magnetic stirring and UV irradiation. Every 15 min during the PEPC treatment, a wastewater sample of 5 mL was taken and centrifuged at 4500 rpm for 10 min to measure the COD of the supernatant.

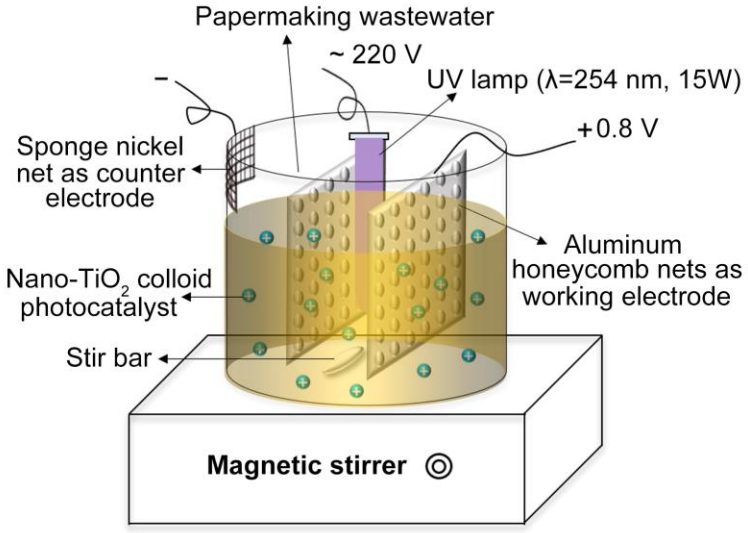

Fig. 1. Schematic diagram of experimental device of PEPC treatment of papermaking wastewater

Recycling and Residual Amount Measurement of Nano-TiO_2 Colloid Photocatalyst

After the PEPC treatment, sodium hydroxide was added into the beaker to adjust pH to 7.0 for the sedimentation and collection of the nano-TiO_2 colloid photocatalyst. The collected nano-TiO_2 colloid was applied as the photocatalyst to the next PEPC treatment process, and the recycling process of the nano-TiO_2 colloid was repeated to examine the performance of the recycled nano-TiO_2 colloid.

After the PEPC treatment, the residual amount of nano-TiO_2 colloid photocatalyst in the PEPC effluent was measured in the supernatant according to the diantipyryl methane spectrophotometric method (GB-T 6609.7-2004 2004). The Ti^{4+} reacts with diantipyryl

methane to form a stable yellow complex with an absorption peak at 390 nm. After digestion by microwave and aqua regia, the decomposed Ti^{4+} concentration in the supernatant was calculated by its linear relationship with the absorbance.

Pilot-scale System for the PEPC Treatment

To achieve industrialization of the developed PEPC technology, an automatic pilot-scale system based on the optimum conditions of the PEPC treatment process was established. The pilot-scale system was a continuous system integrating the flocculation process, PEPC treatment process, and nano-TiO_2 colloid recycling process.

RESULTS AND DISCUSSION

Flocculation Pre-treatment of Papermaking Wastewater

Flocculation efficiency of different flocculants

Because the SBR effluents of papermaking wastewater contain large quantities of SS, the SBR effluent was flocculated prior to the PEPC treatment to ensure the photocatalytic efficiency. Three flocculation processes (inorganic, nano-TiO_2 colloid, and ternary composite) were compared. The measured SS and COD of the flocculated papermaking wastewater and the removal rates of SS and COD are listed in Table 1, and the flocculated papermaking wastewater samples are shown in Fig. 2.

Table 1. Comparisons of SS and COD of the Papermaking Wastewater after Pre-treatments with Different Flocculants

Flocculants	Dosage (wt%)	SS (mg/L)	SS Removal Rate (%)	COD (mg/L)	COD Removal Rate (%)
PAC/PFS	0.010/0.015	21.0	73.1	256.6	28.7
Nano-TiO_2 colloid	0.025	13.4	82.8	241.8	32.8
Nano-TiO_2/PAC/PFS	0.001/0.010/ 0.015	5.1	93.5	119.0	66.9

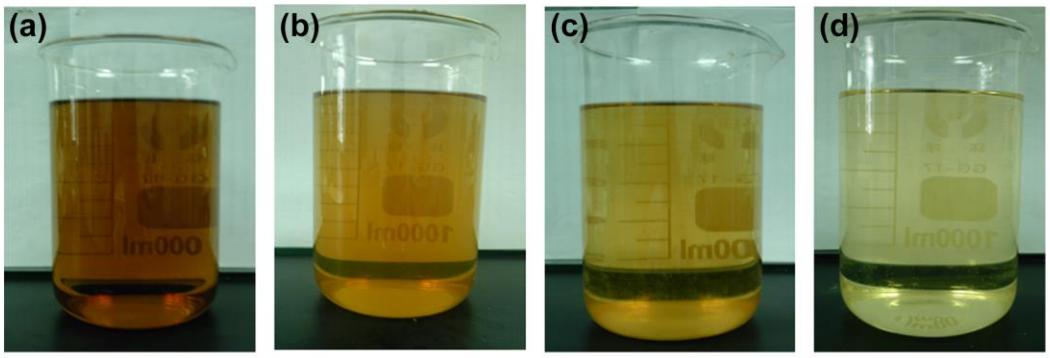

Fig. 2. Samples of papermaking wastewater before and after the different flocculation processes; (a) before flocculation; (b) inorganic flocculation; (c) nano-TiO_2 colloid flocculation; (d) ternary composite flocculation

The original COD and SS of the SBR effluent (Fig. 2a) were 359.7 mg/L and 78.0 mg/L, respectively. As shown in Table 1, the removal rates of SS and COD of papermaking wastewater pre-treated with the ternary composite flocculation process reached 93.5% and 66.9%, respectively, which were higher than those of the inorganic flocculant and the nano-TiO_2 colloid. From the appearance of the wastewater samples in Fig. 2, the ternary composite flocculation process using both the inorganic flocculant and the nano-TiO_2 colloid had the best flocculation effect, while the inorganic flocculant demonstrated the worst.

The synergistic flocculation effect of the ternary composite flocculation could be analyzed as follows. The papermaking wastewater is a stabilizing colloidal dispersion system with negative charge (Shen *et al*. 2011), while the inorganic flocculant (PAC/PFS) produces positively charged metal oxide colloid, and the nano-TiO_2 colloid also has a positive charge. These positively charged flocculants could neutralize the negative colloidal charge in the papermaking wastewater, reduce the zeta potential of the reaction system, destroy the colloidal stability in the flocculation system, and result in the agglomeration of SS in the wastewater. The function of inorganic flocculants is mainly to remove dissolved substances, while the nano-TiO_2 colloid with the large specific surface area is mainly to remove nano-microfibers dispersed in wastewater. In addition, the nano-TiO_2 has also the ability to remove the dissolved colloidal substances (Chen *et al*. 2009).

Effect of nano-TiO_2 colloid amounts on flocculation efficiency

Because the ternary composite flocculation process had the best performance, the effect of its nano-TiO_2 colloid dosage on the flocculation efficiency was investigated. The COD removal rates with different amounts of nano-TiO_2 colloid are listed in Table 2.

Table 2. COD Removal Rate of the Papermaking Wastewater by the Ternary Composite Flocculation with Different Amounts of Nano-TiO_2 Colloid

Amount of nano-TiO_2 colloid in the ternary composite flocculation (wt%)	5×10^{-5}	1×10^{-4}	1×10^{-3}	1×10^{-2}
COD removal rate (%)	33.1	45.6	66.9	56.0

From the value of COD removal rate, the optimal applied amount of nano-TiO_2 colloid in the ternary composite flocculant (nano-TiO_2/PAC/PFS) was 1×10^{-3} wt%. Due to its small particle size and abundant surface electronic charges, the nano-TiO_2 colloid particles in the ternary composite flocculant can bridge the hydrated condensation polymers from the hydrolysis of PAC or PFS, which increased the density of the incompact hydrated polymers and favored the flocculating process. Conversely, the excessive nano-TiO_2 colloid particles increased the surface charges of the flocs and inhibited its precipitation, which resulted in the decreased COD removal rate accordingly.

Based on these results, the ternary composite flocculation process had the best flocculation performance, and the optimum amount of the nano-TiO_2 colloid in the ternary composite flocculation process was 1×10^{-3} wt%.

PEPC Treatment of Papermaking Wastewater

As shown in Fig. 1, the application of a weak DC voltage (0.8 V) to the working electrode (single electrode), without the electrolysis of aluminum (redox potential: 1.66 V) and the formation of an electrical circuit, was to form a micro potential on the surface of

the nano-TiO_2 colloid photocatalyst adsorption film to hinder the photogenerated carrier recombination. Therefore, the developed nano-TiO_2 colloid PEPC process consisted of photoelectrocatalysis on the surface of porous aluminum honeycomb nets adsorbed nano-TiO_2 colloid and the heterogenous photocatalytic oxidation in the wastewater with the dispersed nano-TiO_2 colloid, simultaneously. In this study, the applied nano-TiO_2 colloid was anatase nanocrystal obtained by the acid hydrolysis of the titano-oxygen organic compound. Due to its outstanding mono-dispersity obtained by the low temperature synthesis method, the nano-TiO_2 colloid has excellent dispersion stability (below its isoelectric point of 6.67) and photocatalytic activity (Chen and Shen 2008). The effects of the different factors on the PEPC treatment of papermaking wastewater were considered.

Effect of nano-TiO_2 colloid photocatalyst

Having conducted the PEPC treatments for 80 min with dosages of 0.01 wt% to 0.08 wt%, the effect of nano-TiO_2 colloid photocatalyst dosage on the COD removal rate is shown in Fig. 3. With the increase of nano-TiO_2 colloid dosage, the COD removal rate rose gradually, and then it decreased after the 0.05 wt% nano-TiO_2 dosage. This result could be explained as follows. With the low nano-TiO_2 colloid dosage, there were not enough reaction centers in the reaction system to convert the photons into the chemical energy, whereas the excessive applied nano-TiO_2 colloid particles were also unfavorable to the photocatalytic reaction due to its impeding the transmittance of the UV-light (Ghaly *et al*. 2011).

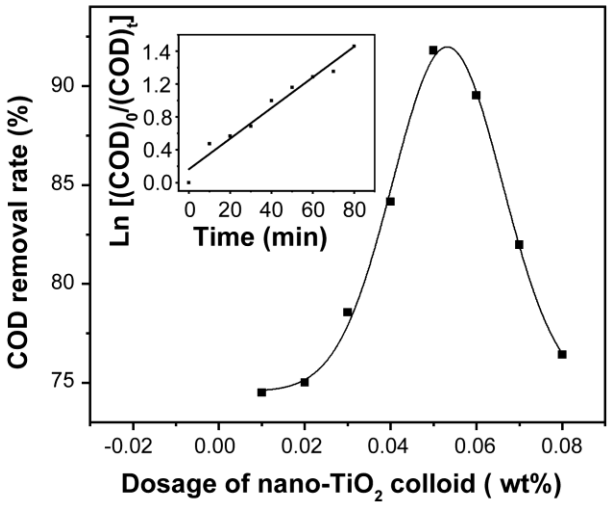

Fig. 3. COD removal rate of the papermaking wastewater by the PEPC treatment with different nano-TiO_2 colloid dosage. Correlations of $Ln[(COD)_0/(COD)_t]$ with the reaction time (top left corner).

With the optimal nano-TiO_2 colloid dosage of 0.05 wt%, the kinetic behavior of the PEPC treatment process was investigated, and the result is embedded in the top left corner of Fig. 3. The $Ln[(COD)_0/(COD)_t]$ had a linear relationship with the reaction time, which indicated that the PEPC reaction followed pseudo first-order reaction kinetics. During the PEPC reaction, the amount of the organic matter in the papermaking wastewater decreased gradually, leading to reduced COD in the papermaking wastewater.

Effects of different flocculants

Although the ternary composite demonstrated the best flocculation result, it did not mean that it also had the best PEPC behaviour. Thus, the effects of all three flocculants on the PEPC treatment of papermaking wastewater were further studied. As shown in Fig. 4, after the PEPC treatment for 90 min, the COD removal rate of the wastewater pre-treated with the ternary composite flocculation process reached 91.6%, which was higher than those of the other two processes. For the wastewater pre-treated with the nano-TiO_2 colloid flocculation process, the COD removal rate was high at 84.6%. This result might be attributed to residual nano-TiO_2 colloid in the flocculation process, which increased the photocatalyst dosage in the subsequent PEPC treatment stage, leading to degrading wastewater. However, for the wastewater pre-treated with inorganic flocculation, the residual inorganic flocculant would bond to the TiO_2 photocatalyst in the PEPC treatment system, pollute the nano-TiO_2 colloid photocatalyst to some extent, and lead to the low COD removal rate of 47.9%. Therefore, the best flocculation occurred with the ternary composite, which achieved both the optimal flocculation and the PEPC treatment results.

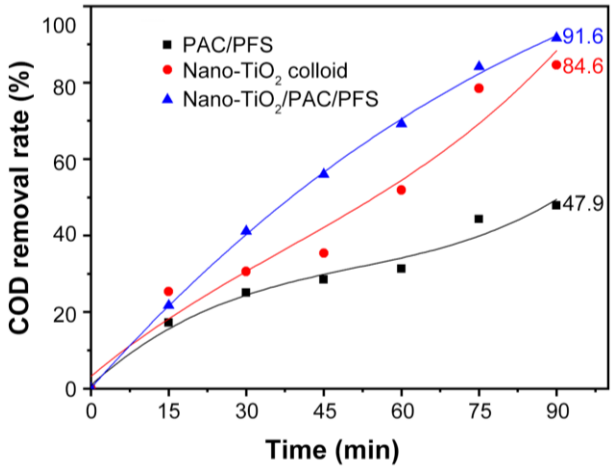

Fig. 4. Effects of different flocculation processes on the COD removal rate by the PEPC treatment of papermaking wastewater

Effects of different TiO_2 dosages in the ternary flocculation process

To evaluate the effect of the nano-TiO_2 colloid dosages in the ternary composite flocculation process on the subsequent PEPC treatment process, different dosages (equal to 5×10^{-5}, 1×10^{-4}, 1×10^{-3}, and 1×10^{-2} wt%) of the nano-TiO_2 colloid were employed in the ternary composite flocculation pre-treatment of papermaking wastewater.

Figure 5(a) shows that when the amount of nano-TiO_2 colloid in the ternary composite flocculation process increased from 5×10^{-5} wt% and 1×10^{-4} wt% to 1×10^{-3} wt%, the COD removal rate of papermaking wastewater by the PEPC treatment process also increased from 76.4% and 83.6%, respectively, to 93.6%. However, when the nano-TiO_2 colloid dosage was further increased to 1×10^{-2} wt%, the COD removal rate decreased to 91.6%. As displayed in Fig. 5(b), the kinetic behavior of the COD removal in the PEPC treatment process conformed to pseudo first-order reaction kinetics. With the increased TiO_2 dosage in the flocculation process from 5×10^{-5}, 1×10^{-4}, 1×10^{-3}, to 1×10^{-2} wt%, the corresponding first-order kinetic constant varied from 0.017, 0.021, 0.028, to 0.024 min^{-1}, respectively.

The above results can be explained as follows. When the nano-TiO_2 colloid amount was low, the efficiency of the ternary composite flocculation was limited, and the residual SS in the wastewater led to the photocatalyst poisoning in the PEPC process and low efficiency. Conversely, because the nano-TiO_2 colloid was more likely to flocculate with the SS in the wastewater, when its dosage was high, certain amounts of the redundant inorganic flocculant might be carried over into the subsequent PEPC process, bonded to the nano-TiO_2 colloid photocatalyst, which polluted the photocatalyst to a certain extent, and thereby decreased the PEPC efficiency.

Based on the above results of PEPC treatment of papermaking wastewater, the optimal conditions were as follows: the dosage of nano-TiO_2 colloid photocatalyst was 0.05 wt%, the wastewater pre-treatment with the ternary composite flocculation process had the highest PEPC performance, and the optimum amount of the nano-TiO_2 colloid in the ternary composite flocculation process was 1×10^{-3} wt%.

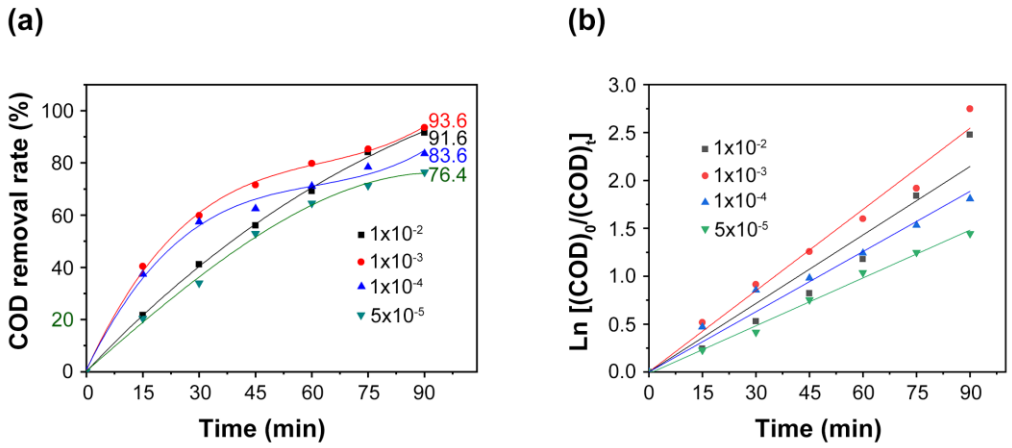

Fig. 5. Effects of different nano-TiO_2 colloid dosages (wt%) in the ternary composite flocculation process on the PEPC treatment of papermaking wastewater: (a) evolutions of COD removal rate with time; (b) correlations of $Ln[(COD)_0/(COD)_t]$ with time

Reusability of Nano-TiO_2 Colloid Photocatalyst

Based on the principle that the nano-TiO_2 colloid photocatalyst can be destabilized and settled under neutral conditions (above its isoelectric point of 6.67) (Chen and Shen 2008), the photocatalyst can be collected and recycled to overcome the difficulty of separating the photocatalyst from wastewater, whose property is different from that of nano-TiO_2 photocatalyst powder.

The reusability of the nano-TiO_2 colloid photocatalyst in the PEPC treatment process was investigated by recycling four times, and the result is shown in Fig. 6. The COD removal rates of the four recycles were similar. In the PEPC treatment process of 90 min, the COD removal rate increased rapidly in the early stage and increased slowly in the later stage. The overall COD removal rates during the first, second, third, and fourth recycles of the nano-TiO_2 colloid photocatalyst were 92.6%, 94.8%, 90.5%, and 86.2%, respectively, which revealed the excellent reusability of the nano-TiO_2 colloid photocatalyst and implied the cost-effectiveness of the PEPC technology. The small decline in COD removal rate in the next recycle could be due to loss of the photocatalyst during recycling and deactivation of the photocatalyst caused by the surface adsorption of the intermediate products in the liquid-solid photocatalytic reaction (Wang *et al*. 2005).

The wastewater samples after the PEPC treatments of the first round and the fourth

recycling of TiO_2 colloid photocatalyst were visually compared, as shown in Fig. 6. The two samples were similar in appearance, which demonstrated that the nano-TiO_2 colloid photocatalyst had very good photocatalytic performance even after being recycled four times.

These excellent treatment results also indicated that the removal efficiency of SS in the papermaking wastewater by the ternary composite flocculation process was high enough to avoid the subsequent poisoning of the nano-TiO_2 colloid photocatalyst. Even after several recycles, the deactivated nano-TiO_2 colloid photocatalyst could still be used as a retention and drainage aid in the papermaking process (Chen *et al*. 2009).

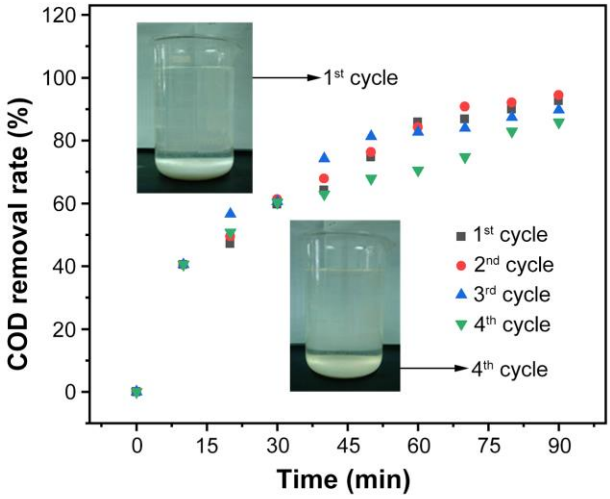

Fig. 6. Reusability of the nano-TiO_2 colloid photocatalyst in the PEPC treatment of papermaking wastewater. The embedded pictures were the wastewater samples after the 1st and 4th cycle.

As a supplementary issue, after the first round of the PEPC treatment of the papermaking wastewater, the residual amount of the nano-TiO_2 colloid photocatalyst in the PEPC effluent was measured with the diantipyryl methane spectrophotometric method (GB-T 6609.7-2004 2004). The measured Ti^{4+} concentration in the effluent was as low as 0.36 mg/L (TiO_2, 0.60 mg/L), and the non-toxicity of TiO_2 has been reported (Zhang *et al*. 2012; Garcia-Segura and Brillas 2017; Zhang *et al.* 2017). In addition, the COD value of the effluent after the PEPC treatment was as low as 10 mg/L. Therefore, the PEPC effluent with tiny amounts of residual TiO_2 and low COD value would be environmentally friendly.

Establishment of Pilot-scale PEPC System

According to the obtained optimal conditions of the developed PEPC treatment process, an automatic and continuous pilot-scale system was designed. As shown in Fig. 7, the pilot-scale system integrated the processes of the flocculation pre-treatment, PEPC treatment, and nano-TiO_2 colloid recycling. The process was designed as follows. First, in the flocculation process, the wastewater was pumped into Mixer 1 with centrifugal pump 1 (CP1), and peristaltic pump 1 (PP1), and both PP2 and PP3 were also started to pump the acid and the ternary flocculant into the system simultaneously.

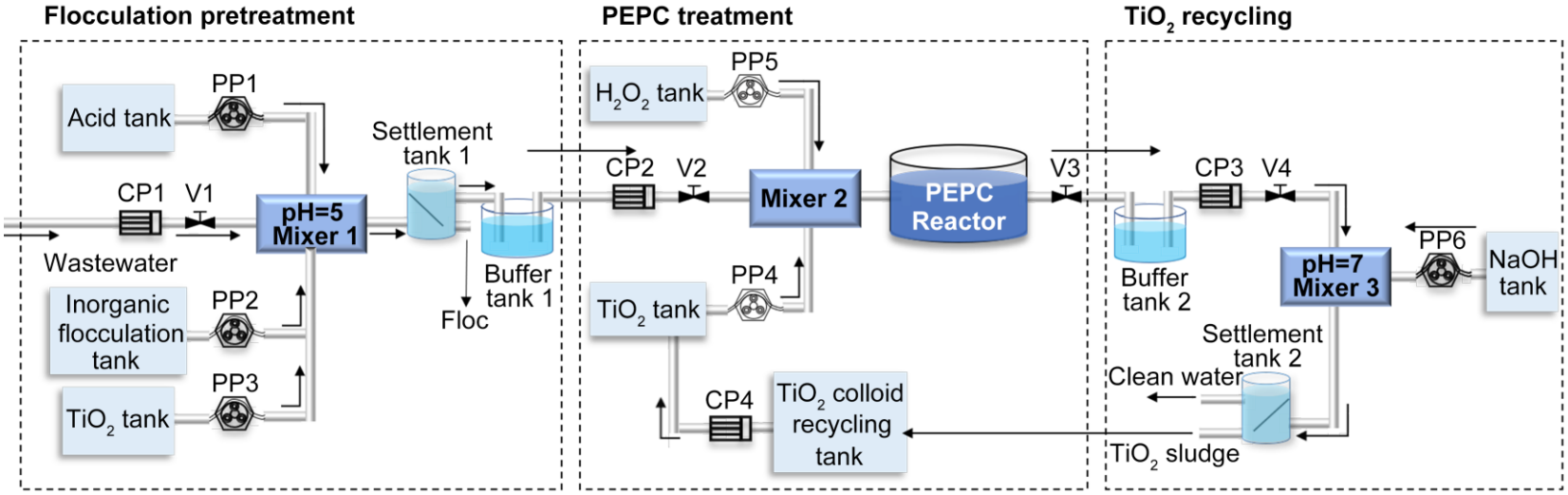

Fig. 7. Process diagram of the PEPC treatment of wastewater

After being mixed uniformly in Mixer 1, the wastewater entered settlement tank 1 with the occurrence of solid-liquid separation. The floc was discharged from the bottom of settlement tank 1, and the supernatant entered buffer tank 1 prepared for the subsequent PEPC treatment.

After being pumped into Mixer 2 by CP2, the flocculated wastewater was mixed with 0.05% nano-TiO_2 colloid photocatalyst (by PP4) and 2 mL/L H_2O_2 (by PP5), simultaneously. After being uniformly mixed in Mixer 2, the wastewater entered the PEPC reactor and the PEPC oxidation treatment process was performed.

Finally, after the PEPC treatment, the treated wastewater entered buffer tank 2, and then was pumped into Mixer 3 by CP3. Sodium hydroxide was pumped into Mixer 3 to adjust the pH value of wastewater to 7.0 by PP6. After being mixed uniformly, the treated wastewater entered into settlement tank 2, and the clean water was discharged from the top of settlement tank 2. The precipitated nano-TiO_2 sludge was recycled from the bottom of settlement tank 2 and transported to the nano-TiO_2 colloid recycling tank, and then pumped into TiO_2 tank by CP4 for recycling.

To achieve a continuous operating mode, the dosages of all the agents and the levels of wastewater were controlled by an automatic control system, and the human-machine interfaces (HMI) of the automatic control system were also developed, which were appended in Figs. S1-S8. Furthermore, to demonstrate its implementation in reality, an operating video of the pilot-scale system was shown in the section of the electronic supplementary information, which exhibited the industrialized potential of the developed PEPC technology.

CONCLUSIONS

1. The applied ternary composite flocculation process, using both the inorganic flocculant and the nano-TiO_2 colloid (1×10^{-3} wt%), had the best flocculation effect with an SS removal rate of 93.5% and a removal rate of 66.9% for chemical oxygen demand (COD).
2. The flocculated papermaking wastewater was treated by the photoelectocatalysis and heterogeneous photocatalysis (PEPC) process for 90 min, with the 0.05 wt% dosage of the nano-TiO_2 colloid photocatalyst, and the COD was removed by 93.6%.
3. After the PEPC advanced treatment, by adjusting the pH of the system to be neutral, the recycling of the nano-TiO_2 colloid photocatalyst was realized. After four cycles of the nano-TiO_2 colloid photocatalyst, the COD removal rate of the papermaking wastewater still attained 88.5%.
4. Based on the optimal lab-scale conditions of the PEPC treatment process, an automatic and continuous pilot-scale system was constructed.

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LINK TO RELATED VIDEO

An operating video of the entire pilot-scale system processing (avi) can be viewed on YouTube by using the following URL link: https://youtu.be/ESvUrebpy4U

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APPENDIX

Supplementary Information

An operating video of the entire pilot-scale system processing (avi) can be viewed on YouTube by using the following URL link: https://youtu.be/ESvUrebpy4U

Fig. S1. Human-machine interface of monitoring center

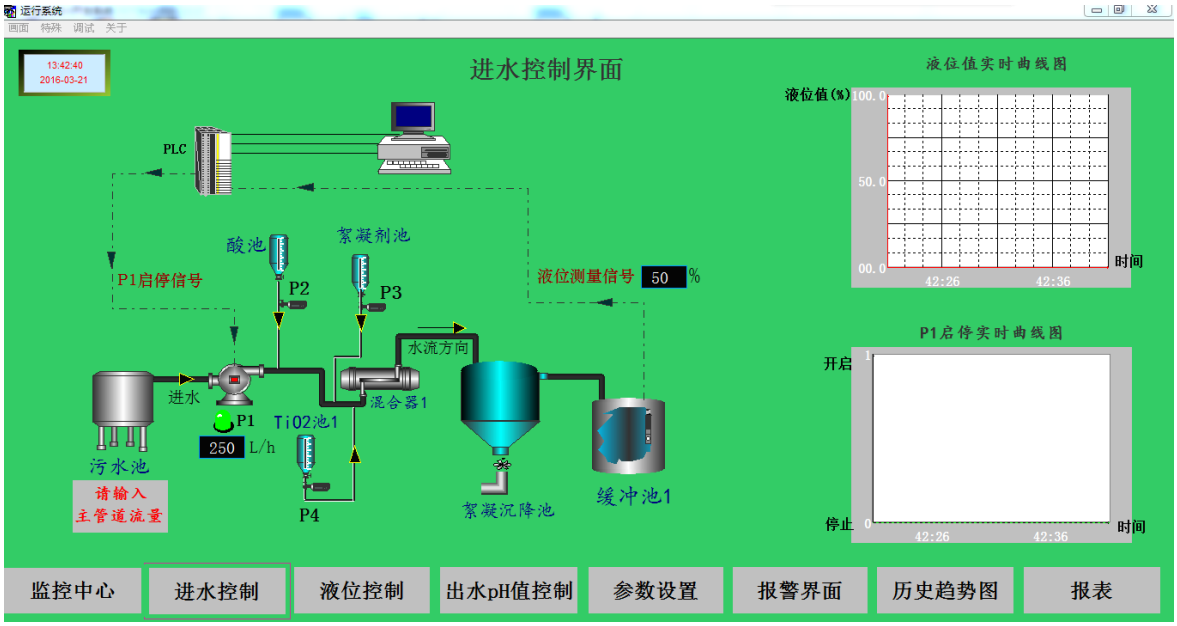

Fig. S2. Human-machine interface for the inlet control

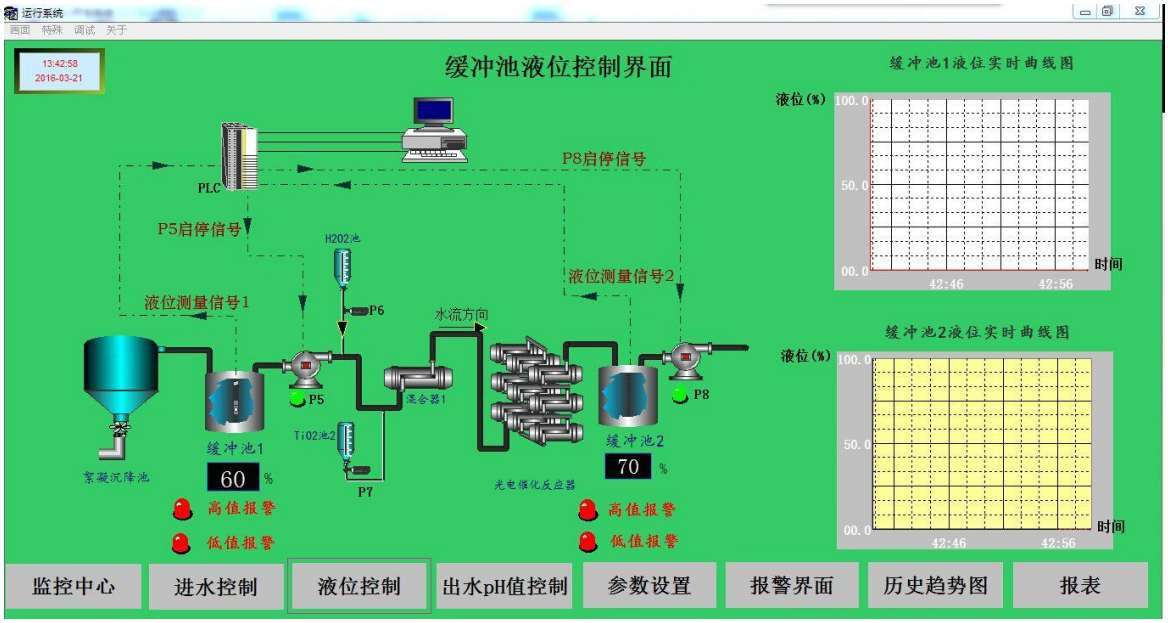

Fig. S3. Human-machine interface for the level control of the buffer

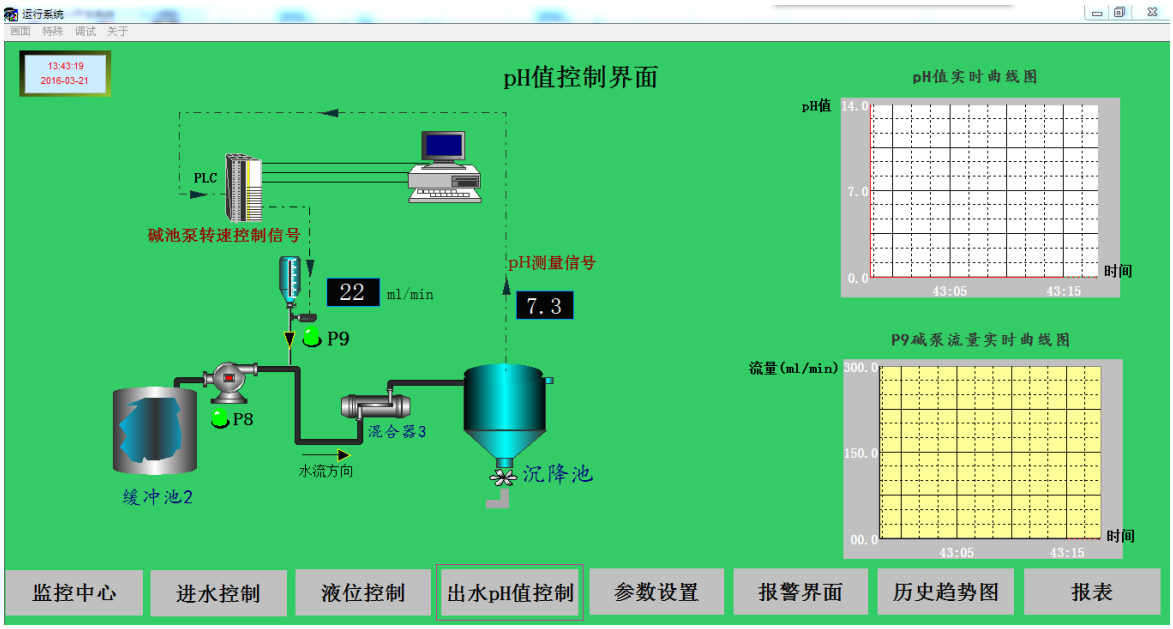

Fig. S4. Human-machine interface for the pH control of the effluent

Fig. S5. Human-machine interface for the parameters setting

Fig. S6. Human-machine interface for the alarm

Fig. S7. Human-machine interface for the historical trend graph

Fig. S8. Human-machine interface for the exporting report