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Experimental study on treating cellulose acetate wastewater based on electro-Fenton

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Abstract: The anaerobic effluent from cellulose acetate wastewater was used as experimental object, removal rates of organic phosphorus and COD_{Cr} are used as index, the influence of reaction time, Fe/C particles, original pH value and current density on removal rate were investigated by electro-Fenton. The results of study show that the removal rate of organic phosphorus reaches 87.5 % and the removal rate of COD_{Cr} reaches 74.3% by adding Fe/C particles between the electrode plates, which meets "Sewage discharge into the city sewer water quality standards Wastewater quality standards for sewage discharge to municipal sewers" (GB/T 31962-2015) Class B standard (TP<8mg/L, COD_{Cr}<500mg/L). The optimal reaction conditions are as follows: The reaction time is 40 minutes, pH = 3.5, current density is 4 mA/cm^2, voltage is 10.6V. Compared with the single electrolysis method, the introduction of Fe/C particulates in the electrolysis system can improve the removal rates of organic phosphorus and COD_{Cr} by 10% ~ 15%. It provides a new idea to remove organic phosphorus in wastewater of cellulose acetate.

Introduction

Cellulose acetate production wastewater has the characteristics of complex composition, large pollutant concentration and high COD_{Cr}. The phosphorus content of its production wastewater is high due to the introduction of $(NH_4)_2HPO_4$ catalyst in the production of acetic anhydride, and partially converted to organic phosphorus. Currently, Adsorption, chemical precipitation and crystallization [1-3] are common phosphorus removal process. The above methods of removing organic phosphorus in wastewater has little effect according to preliminary experimental results, the removal rate of organic phosphorus is less than 30%. The organic phosphorus content in the wastewater is still very high after biological anaerobic treatment, which is difficult to meet the "Wastewater quality standards for sewage discharge to municipal sewers" (GB/T 31962-2015) Class B standard. The advanced oxidation has become a hot research topic because of the advantages of quick reaction, no selectivity and no secondary pollution [4]. The advanced oxidation method can produce hydroxyl radical (•OH) with extremely high oxidation-reduction potential and strong oxidation property.

Common advanced oxidation processes include wet air oxidation, photo catalytic oxidation, supercritical water oxidation, electro-catalytic oxidation and ozone oxidation process [5-8], etc. The electro-catalytic oxidation method has the characteristics of cheap, easy to obtain experimental materials and wide application range. Its basic principle is to produce H_2O_2 on the surface of a suitable cathode materials by the oxidation-reduction reaction (ORR) of two electrons [9-10], as shown in formula (1), (2). The anaerobic effluent from cellulose acetate production wastewater was used as experimental object. The influence of reaction time, Fe/C particles, original pH value and current density on removal rate were investigated by electrolysis method of advanced oxidation processes. The treatment method of introducing Fe/C particulates filler into the electrolysis reaction system was proposed, which improve the removal efficiency of organic phosphorus and COD_{Cr} effectively. It provides a new idea to remove organic phosphorus in wastewater from cellulose acetate production.

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \quad (1)$$

$$Fe^{2+} + H_2O_2 \rightarrow [Fe(OH)_2]^{2+} \rightarrow Fe^{3+} + OH^- + \cdot OH \quad (2)$$

Experimental

Experimental devices, materials and apparatus

Experimental devices：(1)UASB anaerobic reactor was purchased from Shanghai Tongguang Science and Education Instrument Co., Model: TG – 271, inlet flow rate: 2 ~ 5L/h, cylinder diameter: Φ 150mm×2000mm, (2) Electro - Fenton reaction device is self - made square reactor. The size of reactor: 150mm×200mm×150 mm. The steel electrode plates coated Titanium were placed on both sides of the reactor, the aeration device is placed at the bottom of the reactor between the two plates, The electrode plates are connected with a regulated DC power. The effective electrolytic area is 140 cm^2.

Experimental materials：(1)Wastewater was from a chemical industry company in Ningbo, the COD_{Cr} of anaerobic effluent is about 1000mg/L, The concentration of organic phosphorus is about 60 mg/L, pH≈7.5 ; (2) Iron filings, activated carbon, sodium silicate and calcium carbonate are burned into Fe/C particles by 6:2:1.5:0.5; (3) All other reagents used in the experiment were analytical reagents.

Experimental apparatus: (1) UV-visible spectrophotometer was purchased from Shanghai Analytical Instrument Co., Model: UV-5500(PC); (2) PHS-3C pH meter; (3) Chemical oxygen demand analyzer, Model: COD-572.

Experimental process and method

Experimental process: the pH of original wastewater adjusted to 7.5-8 moved to the sewage tank with capacity of 40L, start peristaltic pump, wastewater was transferred to the UASB anaerobic reactor for 24 hour in the condition of 30℃, and the anaerobic effluent of cellulose acetate production wastewater is transferred to a pH adjustment tank, the pH of anaerobic effluent was adjusted to 3~4,and then wastewater was transferred to electro - Fenton reactor; Wastewater electrolyzed was subside with $CaCO_3$ at last. The experimental apparatus is shown as Fig.1.

Experimental method: The influence of reaction time, original pH value and current density on the removal rates of organic phosphorus and COD_{Cr} were studied by controlling variables, and compare the results whether Fe/C particles are added or not.

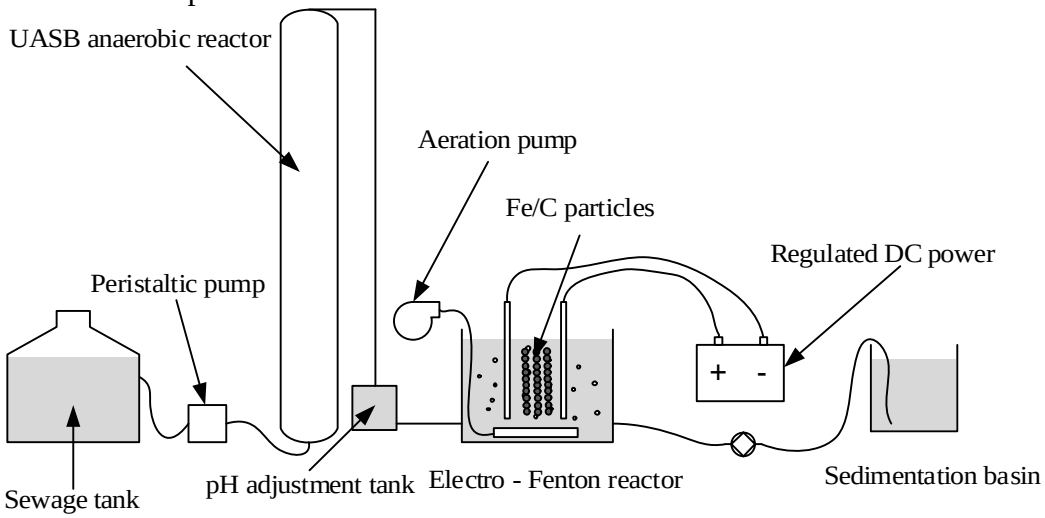

Fig.1 Experimental devices

Analytical method and Data processing

The organic phosphorus was measured using chloroform extraction combined with “Water quality-Determination of total phosphorus-Ammonium molybdate spectrophotometric method” (GB11893-89). Take 250mL wastewater sample placed in 500mL separating funnel and add 8g of

sodium chloride, the organic phosphorus was extracted for three times with 30ml of chloroform. 25mL of water, 5mL of 10% $K_2S_2O_4$ and 1mL of 5 mol/L H_2SO_4 were added to the extraction. The extraction was heated to evaporate chloroform at low temperature and micro-boiled 30min, and wait for cooling to indoor temperature. Then total phosphorus of the sample is detected by GB-11893-89. So TP hereinafter measured is organic phosphorus content of the sample. The COD in wastewater is determined by "Water quality-Determination of chemical oxygen demand-Dichromate method" (GB11914-1989). The removal rates were calculated according to equation (3), (4):

$$h_{COD} = \frac{COD_0 - COD_i}{COD_0} \times 100\% \quad (3)$$

$$h_{TP} = \frac{TP_0 - TP_i}{TP_0} \times 100\% \quad (4)$$

η represents the removal rate. (%)
COD_0 represents COD_{Cr} before treatment. (mg/L)
COD_i represents COD_{Cr} after treatment. (mg/L)
TP_0 represents the organic phosphorus content before treatment. (mg/L)
TP_i represents the organic phosphorus content after treatment. (mg/L)

Experimental results and discussion

Influence of time

The influence of time on the removal rates of organic phosphorus and COD_{Cr} was studied in the condition of the temperature of 25 ℃, original pH = 3.5, current density = 4mA/cm^2 and voltage = 10.6V. The experimental results were shown in Fig.2

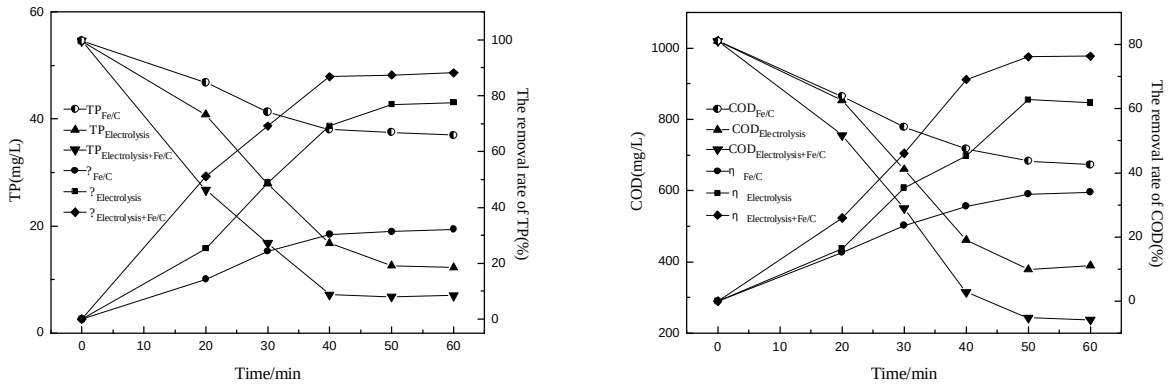

Fig.2 Influence of time on removal rates of organic phosphorus and COD_{Cr}

The experimental results show that the concentration of organic matter continues to decrease and the removal rates of organic phosphorus and COD_{Cr} increase more and more slowly with extension of time. The removal rate can reach its peak faster by using electrolysis + Fe/C. In the conditions of single Fe/C micro-electrolysis, the removal rate of organic phosphorus stabilized at 32% after 50 minutes (TP≈37 mg/L), and the removal rate of COD_{Cr} stabilized at 31% (COD_{Cr}≈680 mg/L). In the conditions of single electrolysis, the removal rate of organic phosphorus stabilized at 76% after 40 min (TP≈12mg/L), and the removal rate of COD_{Cr} stabilized at 60% (COD_{Cr}≈385mg/L). In the conditions of electrolysis+ Fe/C particles：If the above two methods are irrelevant and the reduction of organic matter concentration resulting in reduced removal rate wasn't took into account, the removal rate of COD_{Cr} should be calculated as follow: η_{COD}≤ 1-(1-60%)×(1-31%)=72%; the removal rate of TP should be calculated as follow: η_{TP}≤ 1-(1-76%)×(1-32%)=83%. But experiment result shows that the

removal of COD_{Cr} reach a peak of 76 %(> 73%) at 50 min (COD_{Cr}≈240mg/L) and the removal of TP reach a peak of 87.6 %(> 83%) at 40 minutes (TP≈7mg/L). The experimental results show that Fe/C combined with electrolysis have weak synergistic effect.

The main reasons for the experimental results are as follow after analysis: (1) the concentration of organic matter continues to decrease with the process of reaction, the probability of collision of hydroxyl radicals and organic matter reduce significantly. The probability of effective collision approaches 0 when the concentration of organic matter is extremely low; (2) when Fe/C particles were added into the electrolysis reaction system, on the one hand, Fe/C micro-electrolysis can not only promote the degradation of organic matter but also many new tiny electrodes formed under the action of electrodes;(3) Fe/C particles can provide Fe^{2+} for Fenton reaction under acidic conditions and improve the efficiency of the electrolysis method.

Influence of original pH

The influence of original pH on the removal rates of organic phosphorus and COD_{Cr} was studied in the condition of the temperature of 25 ℃, time = 40 minutes, current density = 4mA/cm^2 and voltage =10.6V. The experimental results were shown in Fig.3.

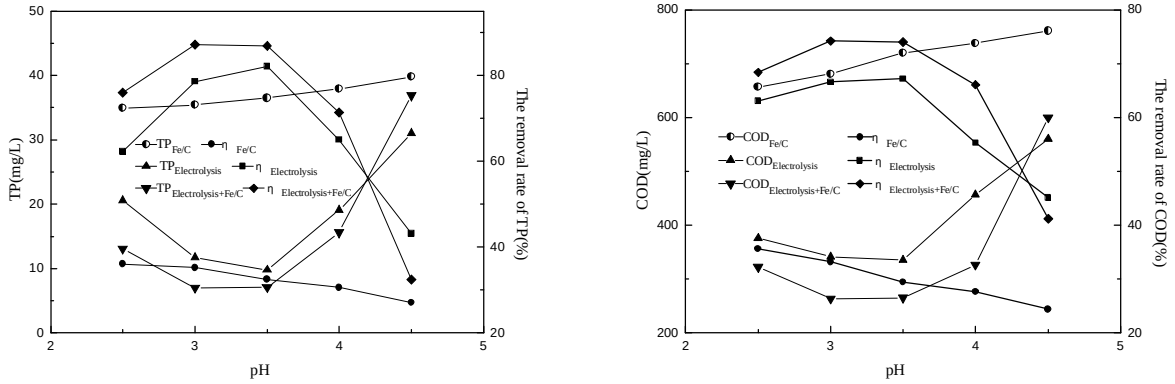

Fig.3 Influence of original pH on removal rates of organic phosphorus and COD_{Cr}

The experimental results was shown as Fig.3: In the conditions of single Fe/C micro-electrolysis, the removal rates of organic phosphorus and COD_{Cr} decrease faster and faster with the increase of pH value. The removal rate of organic reach 33% (TP=35mg/L) when original pH is 2.5, and the removal rate of COD_{Cr} reach 32 % (COD_{Cr}=655mg/L). In the conditions of single electrolysis, the removal rates of organic phosphorus and COD_{Cr} slowly increase at pH=2.5~3.5, the effect of treatment decrease significantly when original pH continue to be increased. The removal rate of organic phosphorus stabilized at 80% (TP≈11mg/L) when pH=3~3.5, and the removal rate of COD_{Cr} stabilized at 67% (COD_{Cr}≈335mg/L). In the conditions of electrolysis+ Fe/C particles, the removal rates of organic phosphorus and COD_{Cr} slowly increase at pH=2.5~3.5, the effect of treatment decrease quickly when original pH continues to be increased. The removal rates of organic phosphorus stabilized at 87% (TP≈7mg/L) when pH=3~3.5, and the removal rate of COD_{Cr} stabilized at 74.3% (COD_{Cr}≈260mg/L). The pH = 3.5 is the optimal value because acid is needed to adjust pH before electrolysis.

The main reasons are as follows according to the reaction (1), (2) after analysis: the concentration of H^+ is sufficient to maintain the progress of the reaction at pH=2.5~3.5. The secondary reaction $2H^+ + 2e^- = H_2$ was exacerbated and hinder the formation of H_2O_2 when the pH is low. The concentration of H^+ becomes the main factor that restricts the reaction and the generation of hydroxyl radical is limited at pH > 3.5. Fe were oxidized by H^+ under acidic conditions, which exacerbate consumption of H^+ and retard the degradation of pollutants.

Influence of current density

The influence of current density on the removal rates of organic phosphorus and COD_{Cr} was studied in the condition of the temperature of 25 ℃, time = 40 minutes, pH = 3.5 and voltage =10.6V. The experimental results were shown in Fig.4.

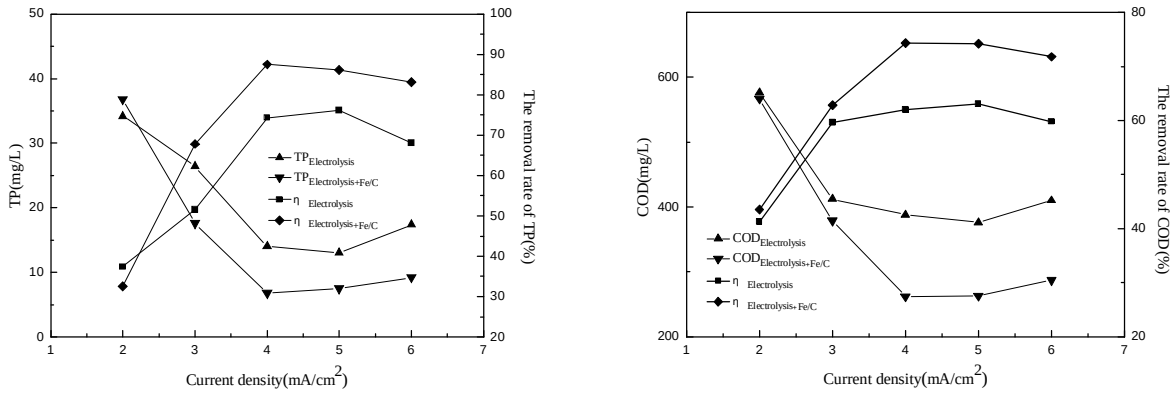

Fig.4 Influence of current density on removal rates of organic phosphorus and COD_{Cr}

The experimental results show that the removal rates of organic phosphorus and COD_{Cr} increase rapidly with the increase of current density when current density is between 2mA/cm^2 and 4mA/cm^2. In the conditions of single electrolysis, the removal rate of organic phosphorus and COD_{Cr} reach 76.2% (TP=13mg/L) and 63.1% (376mg/L) respectively when the current density was 5mA/cm^2; In the conditions of electrolysis+ Fe/C particles, the removal rate of organic phosphorus and COD_{Cr} reach 87.5% (TP=6.8mg/L) and 74.3% (COD_{Cr}=262mg/L) respectively when the current density was 4mA/cm^2. The removal rates of organic phosphorus and COD_{Cr} decrease slightly when the current density continues to be increased. The addition of Fe/C particles increase the peak of current density and the removal rates of organic phosphorus and COD_{Cr}.

The main reasons are as follows: The secondary reaction $H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$ was exacerbated rapidly with the increase of voltage when voltage is too high, the consumption of effective substances increases, and the removal rate of organic phosphorus and COD_{Cr} decrease. On the other hand, addition of Fe/C particulates filler increases the cathode area and improves utilization of electron and achieve higher peak of current density.

Conclusions

(1) The anaerobic effluent of cellulose acetate wastewater was treated by electrolysis + Fe/C, the removal rate of organic phosphorus reached 87.5%, TP=6.8mg/L<8mg/L, COD_{Cr} removal rate reached 74.3%, COD_{Cr}=262mg/L<300mg/L, which meet the “Wastewater quality standards for sewage discharge to municipal sewers” (GB/T 31962-2015) Class B standard. The optimal reaction conditions are as follows: The reaction time is 40 minutes, pH = 3.5, current density is 4 mA/cm^2, voltage is 10.5V.

(2) Compared with the single electrolysis method, the introduction of Fe/C particulates in the electrolysis system can improve the removal rates of organic phosphorus and COD_{Cr} by 10% ~15%.

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