

Preparation of CSC-PPy-TiO₂ and application in photocatalytic for wastewater treatment

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Abstract. Polypyrrole modified TiO₂ (PPy-TiO₂) and coconut shell activated carbon (CSC) were used as raw materials, and Na₂SiO₃ was used to load PPy-TiO₂ on the surface of coconut shell activated carbon. Finally the CSC-PPy-TiO₂ photocatalyst was prepared. In this paper, the effects of the degradation effect of methyl orange on the factors such as the addition of PPy-TiO₂ and the amount of sodium silicate were discussed. The experimental results showed that CSC-PPy-TiO₂ had a good photocatalytic performance, and the decolorization rate of the methyl orange solution of 40mg /L was 88.52% in the light of metal halide lamp with 1.0g CSC-PPy-TiO₂.

1.Introduction

In the practical application process, nano TiO₂ often causes a large amount of catalyst waste because it is easy to reunite in aqueous solution.^[1,2] The effect of photocatalyst in the treatment of high concentration of organic pollutants and difficult degradation environmental pollutants is not ideal, and there is often a catalyst inactivation, at the same time in the practical application of separation recycling also there is a big difficulty, so nano catalyst need to find a suitable carrier for practical application.^[3,4]

The main content of this paper is to make the PPy-TiO₂ nano-catalyst load on the coconut shell activated carbon (CSC) to make the activated carbon load polypyrrole modified titanium dioxide composite(CSC-PPy-TiO₂). Activated carbon has developed pore structure, large specific surface area,^[5-7] in the absence of selective and thorough photocatalytic degradation of the reaction, the effective adsorption capacity and PPy-TiO₂ can form a good synergy, while maintaining the high catalytic activity of TiO₂, catalyst has better settling separation ability. The micropores of CSC account for about 90% of its volume, with a specific surface area between 1000-1600m²/g. CSC has the advantages of moderate pore size, uniform distribution, fast adsorption speed and few impurities, and has been widely used in water treatment in recent years. We pretreated the active carbon, compounded activated carbon and PPy-TiO₂ by sodium silicate,^[8,9] finally we made the CSC-PPy-TiO₂. We degraded methyl orange with CSC-PPy-TiO₂ in visible light. This paper provides theoretical basis for the actual treatment of organic wastewater.

2.Experimental

2.1 Instruments and Drugs

Instruments: BL-GHX-V Photochemical Reaction Instrument(Xi'an German Biological Technology Co., Ltd); 400W Metal Halide Lamp (Shanghai Seasonal Special Lighting Appliance Factory); Ultrasonic Cleaner(Ningbo Xinzhi Biotechnology Co., Ltd);TU1901 Spectrophotometer(with integrating sphere device, Beijing General Analysis Instrument Co., Ltd); Scanning Electron Microscope (German Carl Zeiss Company) - Spectrometer(British Oxford Instruments); XD-2 X-ray



diffractometer(Beijing General Analysis Instrument Co., Ltd)

Drugs: P25TiO₂(Degussa, Germany, 25nm); Pyrrole(AR, Cdu West Asia Chemical Industry Co., Ltd.); Anhydrous Ethanol(AR, Tianjin Fuyu Fine Chemical Co., Ltd); Ammonium Persulfate(AR,Tianjin Damao Chemical Reagent Factory); Hydrochloric Acid (GR, Zhuzhou City Xingkong Chemical Glass Co., Ltd.); Na₂SiO₃ (AR, Tianjin Hengxing Chemical Reagent Manufacturing Co., Ltd); Methyl Orange (AR, Guoyao Group Chemical Reagent Co., Ltd.); 30% H₂O₂ (AR, Sinopharm Chemical Reagent Co., Ltd); COD Oxidants and COD Catalysts (Jiangyan Yinhe Instrument Factory); HgSO₄(AR, Guizhou Tongren Chemical Reagent Factory); 20-40 mesh coconut shell activated carbon (CSC).

2.2 Preparation of CSC-PPy-TiO₂

2.2.1 Preparation of PPy-TiO₂

PPy-TiO₂ was prepared by in-situ polymerization. 2.0 g TiO₂ was added into a round-bottomed flask containing 200 mL of 1.0 mol/L hydrochloric acid; pyrrole monomer 0.04 mL was added, dispersed ultrasonically for 30 min; the flask was stirred in an ice-water bath at 0~3 °C. After 15 mL of 0.20 mol/L APS was added dropwise, the reaction was stirring for 5 h. The reaction product was suction filtered, washed with 1.0 mol/L hydrochloric acid, and washed with distilled water until the filtrate became neutral, and the filter was placed in the drying oven below 50 degrees centigrade. PPy-TiO₂ composites were finally used for grinding.

2.2.2 Activated carbon loading process

A 40 mesh screen was used to screen out a particle size CSC of 20-40 mesh for use. After CSC was ultrasonically boiling for 1 h, CSC was soaked with 1 mol/L nitric acid for 12 h. (The modification of CSC with nitric acid can increase the acidity of the surface of the CSC, and the surface oxygen content of the CSC is modified compared to H₂O₂ and O₃. With the increasing of oxygen-containing functional groups, in addition to its positive surface charge characteristics, but also to improve the adsorption of dispersion); Rinse with distilled water to neutral. Dry it with an oven.

1.2 g of sodium silicate was added to 100 mL of water and stirred for 30 min to fully dissolve. 1.2 g of Ppy-TiO₂ powder was ultrasonically mixed for 30 min and added to the sodium silicate suspension. Then adding 4 g CSC particles, and continue stirring for 30 min, stirring and mix well and drying at 70 °C.

3. Results and discussion

3.1 Catalyst Characterization Results and Discussion

3.1.1 X-Ray Diffraction (XRD) Analysis

XD-2 X-ray diffractometer was used to determine the phase and crystal structure of the sample, the measurement parameters: Cu Ka ($\lambda = 0.15406$ nm), Voltage 36 kV, Current 20 mA, scan range: 10° to 70°, speed: 4 ° / min. The XRD pattern of P25-type nano-TiO₂ and different Py-doped Ppy-TiO₂ samples is shown in Figure 1. Check JCPDS (Joint Powder Diffraction Standards Committee) No. 21-1276, No. 21-1272 and No. 76-1935 we knew that anatase phase, rutile phase and plate titanium ore phase characteristic peak of TiO₂ 2 θ values were (25.281, 48.049, 37.800 °), (27.492、54.434、36.149°) and (25.339、25.668、30.792°) respectively. As can be seen from figure 1, the P25 TiO₂ in the experiment is the mixed crystal type of anatase and rutile. In 25.4 °, 37.89 °, 25.4 °, 54.98 ° and 55.09 ° has its obvious characteristics of diffraction peaks. At the same time, it corresponded to TiO₂ (101), (004), (200), (105), and (211) crystal surface diffraction peak, we can know that different addition amount of PPy (0.04 mL) - TiO₂, PPy (0.12 mL) -TiO₂ is basically consistent with the X diffraction spectrum of pure TiO₂ from the graph b and c in figure 1, which illustrated that no new diffraction peaks appear, and it showed that the PPy-TiO₂ did not change the crystal structure of TiO₂, it only coated on the surface of nano TiO₂ particles in an amorphous form.

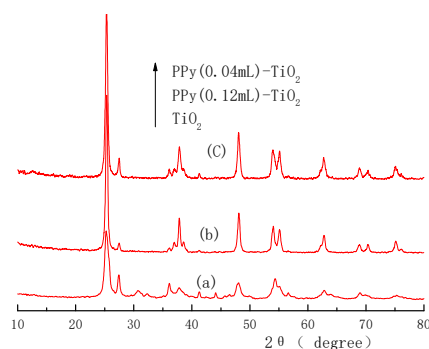


Fig.1 XRD patterns of TiO_2 and PPy- TiO_2

3.1.2 UV - visible diffuse reflectance spectra

Using UV-Vis spectrophotometer, the absorption spectra of TiO_2 and different pyrrole doped PPy- TiO_2 samples were measured.

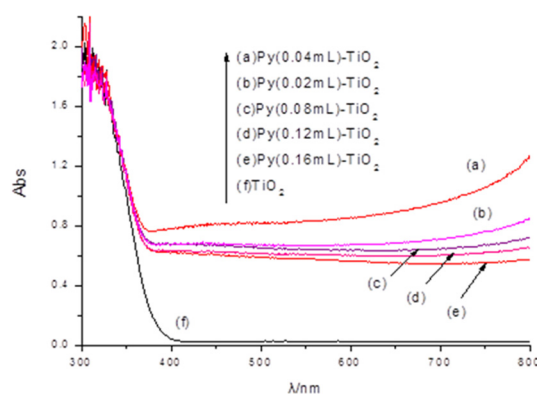
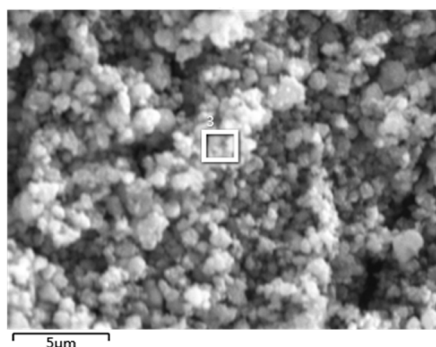
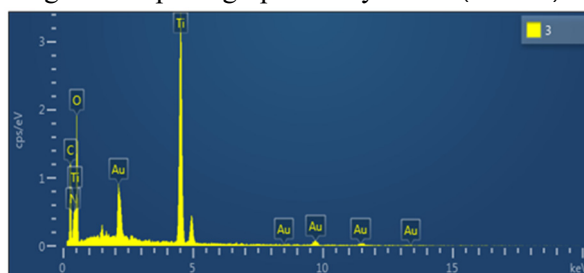


Fig. 2 UV Vis diffuse reflectance spectra of TiO_2 and PPy- TiO_2

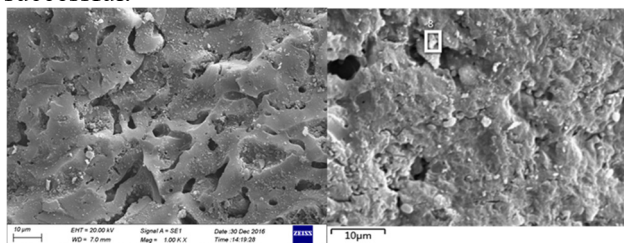
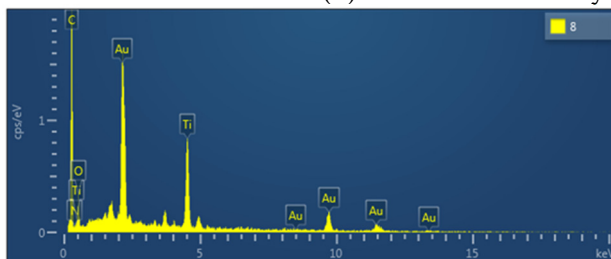
As shown in Figure 2, in the UV absorption region below 400nm, both pure TiO_2 and PPy- TiO_2 have strong absorption bands, which indicated that polypyrrole did not weaken the energy absorption of TiO_2 in the UV light region. In addition, pure TiO_2 can only absorb UV light below 400nm, but the PPy- TiO_2 absorption band between 400nm and 800nm is higher than pure TiO_2 , and PPy- TiO_2 broadened the spectral response range of TiO_2 . Due to the difference of the amount of pyrrole, the response of different PPy- TiO_2 to the visible region is different. The absorption intensity of the visible light region is Py (0.04 mL) TiO_2 > Py (0.02 mL) TiO_2 > Py (0.08 mL) TiO_2 > Py (0.12). Py (0.16 mL) TiO_2 > pure TiO_2 . The above results showed that compared with pure TiO_2 , the absorption band of PPy- TiO_2 is red shifted and visible light absorption is obvious, and the spectral response range of TiO_2 can be extended from the UV light region to the visible light region. This work provides the possibility for the application of PPy- TiO_2 to the photocatalytic degradation of organic pollutants by solar energy.

3.1.3 Scanning electron microscopy - energy spectrum (SEM-EDS) analysis

Fig.3 SEM photograph of PPy-TiO₂ (5000X)Fig.4 EDS picture of PPy-TiO₂Tab.1 Element content of EDS of PPy-TiO₂

Element	C	N	O	Ti	total
wt%	23.55	3.67	48.64	24.15	100.00
Atomic percent	35.13	2.83	54.47	7.57	100.00

Figure 3 is a scanning electron microscope (SEM) of Ppy-TiO₂ photocatalyst. From Fig. 3, it is known that pyrrole polymerization is coated on the surface of TiO₂, which is consistent with the 4 X ray diffraction pattern and does not change the structure of TiO₂. At the same time, from figure 4 and table 1, we can know that the C and N elements in the energy spectrum are pyrrole. It indicates that the modification of TiO₂ is successful.

Fig.5. The SEM of activated carbon before and after the load
(a) Surface of activated carbon (b) Surface of CSC-PPy-TiO₂Fig.6 EDS picture of CSC-PPy-TiO₂

Tab.2 Element content of EDS of CSC-PPy-TiO₂

Element	C	N	O	Ti	total
wt%	63.15	2.15	21.50	15.36	100.00
Atomic percent	75.96	1.46	19.41	3.17	100.00

The (a) and (b) in Figure 5 are the electron microscopic scanning (SEM) of the surface of activated carbon and CSC-PPy-TiO₂. From the diagram we can see that there were lots of pores on the surface of the activated carbon before the load was unloaded. After the PPy-TiO₂ photocatalyst was loaded, most of the pores of the activated carbon were covered, and the effect of the load was very good. At the same time, it was known from figure C and table 2 that the N element in the energy spectrum was the pyrrole and Ti element was TiO₂, which showed that the experiment was successful for the load of PPy-TiO₂.

3.2 Analysis of experimental results.

3.2.1 Determination of CSC adsorption capacity.

In order to verify the photocatalytic effect of CSC-PPy-TiO₂, which was due to the synergistic effect of the adsorption efficiency of activated carbon and the photocatalytic efficiency of TiO₂, so the methyl orange decolorization rate of CSC dark adsorption was investigated. 2 g CSC was mixed with 200 mL methyl orange solution (40 mg/L) for dark adsorption experiment. Take the sample every 5 minutes and measure the absorbance.

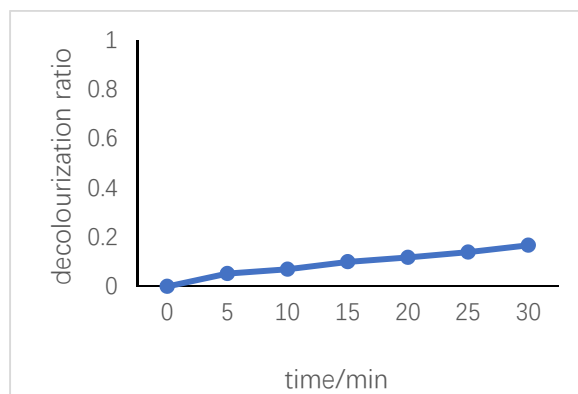


Fig.7 Activated carbon adsorption effect after pretreatment

3.2.2 Determination of the load ratio of activated carbon to PPy-TiO₂

1.2 g sodium silicate was added and dissolved in water of 100 mL, a magnetic stirrer was used to stir for 30 min for making solution fully dissolved. The PPy-TiO₂ (0.2 g, 0.4 g, 0.6 g, 0.8 g, 1 g, 1.2 g, 1.4 g) was added in ultrasonic cleaner ultrasonic for 30 min and added it into the sodium silicate suspension mixing. 4 g CSC was added in it and continue stirring for 30 min, then the solid filtered from the mixture is placed in the oven, constant temperature of 100 °C drying after filtering. The CSC-PPy-TiO₂ for various load ratios were made, 1g CSC-PPy-TiO₂ was added separately. and them were added into 200 mL methyl orange (40 mg/L) in a mixed system of 30 min in a photocatalytic reactor, the 400W metal halide lamp was turned on, every 5 min sampling once. The absorbance of reaction liquid was measured and the decolorization rate was calculated.

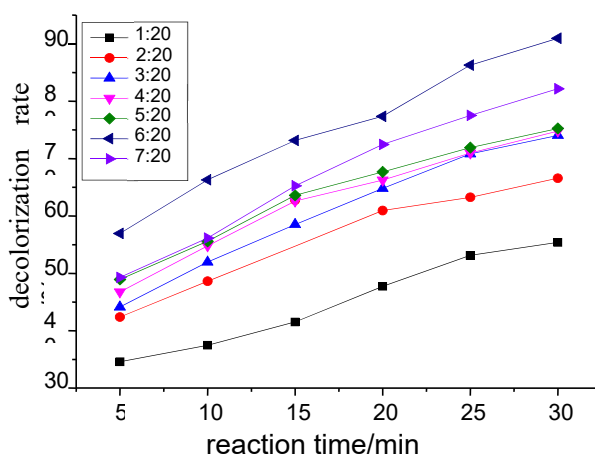


Fig.8 Effect of load ratio of catalyst and activated carbon on degradation rate

As shown in Figure 8, when the load ratio of activated carbon and PPy-TiO₂ was from 1:20 to 6:20, the degradation rate of methyl orange was increased, and the photocatalytic efficiency of CSC-PPy-TiO₂ increased synchronously. When the load ratio was more than 6:20, the degradation rate of methyl orange was no longer increased with the increase of the load ratio. The main reason is that the amount of catalyst is more, the adhesive is limited and can't fully adhere to the surface of activated carbon. The overmuch photocatalyst is easily reunited and forms secondary nanoparticles. When the load ratio is less than 6:20, the active carbon particles can adsorb more methyl orange to the surface, but when the amount of catalyst is too little, which causes the surface methyl orange not to degrade in time. When the load ratio is greater than 6:20, although the amount of catalyst is much more, the overmuch catalyst blocked the pore of the surface of the activated carbon, so that the adsorption property of activated carbon was declined. When the load ratio is 3:10, the methyl orange adsorbed on the surface can fully react with the PPy-TiO₂, and the methyl orange can be decolorated on the surface of activated carbon in time and form the effect of desorption equilibrium. The CSC-PPy-TiO₂ photocatalytic efficiency is the highest at this moment, so the decolorization rate of methyl orange is the best.

3.2.3 Sodium silicate dosage

After determining the addition of PPy-TiO₂, the amount of sodium silicate was to change to make CSC-PPy-TiO₂, and then conducted the visible light screening experiment.

Sodium silicate was dissolved respectively in 100 mL of distilled water, a magnetic stirrer was used to mix 30 min, 1.2 g PPy - TiO₂ powder was mixed by ultrasound for 30 min after sodium silicate suspension was added, 4 g CSC was added, continue to stir for 30 min, then the solid obtained mixture filter was placed in the oven, under the constant temperature of 100 °C for drying. The 1.00g various load CSC - PPy - TiO₂ was added respectively into 40 mg/L, 200 mL of methyl orange in the mixed system after adsorption for 30 min, open the 400W metal halide light source, once every 5 min interval sampling, calculated the decolorization rate.

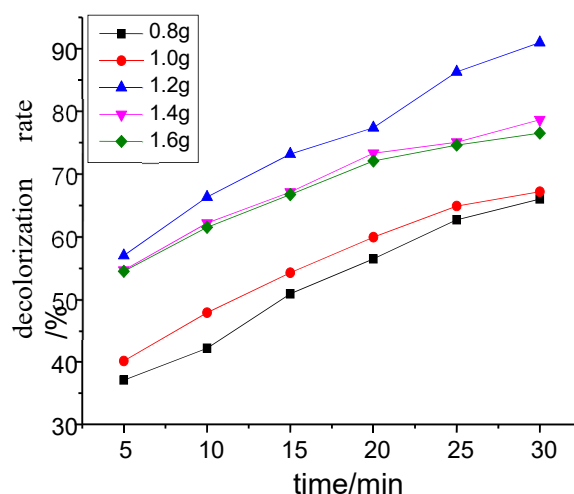


Fig.9 Effect of sodium silicate addition on decolorization rate

The figure 9 showed that when the amount of the addition of sodium silicate range from 0.8 g to 1.2 g, with the increasing of the amount of sodium silicate, CSC-PPy-TiO₂ activity was also gradually increasing, its decoloring capacity for methyl orange also gradually enhanced. When sodium silicate was added from 1.2 g to 1.6 g, the decolorization rate of methyl orange no longer increased with the increase of sodium silicate, but gradually decreased: the main reason is that the less amount of sodium silicate, the PPy-TiO₂ can glue stick on the activated carbon particles, although activated carbon particles can absorb much methyl orange to the surface, there is not enough of PPy-TiO₂ on the surface to degrade the methyl orange. The adsorption position in activated carbon is gradually filled, and the in-situ regeneration of activated carbon cannot be realized. Therefore, the photocatalytic activity of CSC-PPy-TiO₂ is relatively low; when too much sodium silicate was added, a large amount of sodium silicate glued on the activated carbon and sealed the porosity of the activated carbon, which makes the activated carbon adsorption ability can't promote the effect on PPy-TiO₂ and the photocatalytic efficiency was reduced; When the load ratio was 1:1, photocatalyst had the best photocatalytic effect.

4. Conclusion

Under the condition of 400W gold halide lighting, the CSC-PPy-TiO₂ was used to degrade methyl orange, and when other conditions were not changed, the optimal sodium silicate addition was 1.2g, and the optimal load ratio of activated carbon and catalyst was 3:10.

By means of characterization analysis, we found that most of CSC pores were coated with PPy-TiO₂, and the coating effect was good. CSC-PPy-TiO₂ showed good synergistic effect on methyl orange solution under simulated sunlight. The nano-catalyst was fixed on the CSC to make it difficult to reunite and easy to recycle. This paper has the role of guiding wastewater treatment.

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