Design of a continuous fixed film photocatalytic reactor based on Bi₂WO₆/ZnFe₂O₄ magnetic photocatalyst and application in tetracycline degradation

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Abstract. A kind of continuous magnetic fixed-film reactor was designed and applied in tetracycline degradation based on the Bi₂WO₆/ZnFe₂O₄ magnetic photocatalyst. The effects of light intensity, initial TC concentration and HRT on the photocatalytic effect were investigated. At the pollutant concentration of 51.58 mg/L, light intensity of 3.20×10⁵ lux and HRT of 94 min, the TC removal rate in the reactor was enhanced to above 90% and maximized to 94.05%. From the different pollutant concentrations, the specific outflow criterion could be achieved by regulating the HRT within a certain range, so as to maximize the reactor use efficiency. Compared with conventional fixed-film reactors, the new reactor had larger reaction contact area and avoided the defect of catalyst shedding.

1. Introduction
Water pollution, especially from pharmaceutical enterprises and livestock production, has become a serious environmental issue to be treated [1, 2]. To date, among various technologies in treatment of antibiotic pollutants, the photocatalysis technology is recognized as one of the most promising approaches [3] because of its use of clean energy, high efficiency, and complete degradation of pollutants [4, 5]. Thus, many kinds of photocatalysts have been synthesized to degrade antibiotics [6], but the research focuses on the synthesis of new materials rather than application. Still, the gap between high-performance catalysts and application in photocatalytic reactors is not resolved [7].

Among the wastewater processing processes based on photocatalysis, the photocatalytic reactors can be divided by the existing form of the catalyst into suspended reactors and fixed film reactors [8]. Due to the sufficient mixing between the catalyst grains and the reaction liquid, the suspended reactors reserve the large specific surface areas and have high photon absorptive ability and mass transfer efficiency [9]. Thus, these reactors allow for high pollutant degradation efficiency and can be designed and machined very simply. However, their practical application is limited by the difficulty in powder catalyst separation & recovery and the loss of catalysts. On the contrary, the problem of catalyst loss can be solved by the fixed film reactors [10]. Moreover, the significantly reduced mass transfer resistance between the reactants and products in such reactors contributes to improving the photocatalyst activity. However, in these reactors, films are needed to fix the powder catalyst, further complicating the catalyst preparation, but the too long reaction time would lead to film shedding [11].
Given these problems, here starting from the fixed photocatalytic reactors and with magnetic Bi$_2$WO$_6$/ZnFe$_2$O$_4$ [12] (achievements from our preliminary research) as the catalyst material, we designed a continuous-flow magnetic fixed film photocatalytic reactor by using large-surface-area magnetic beads as the fixation carriers. Compared with conventional fixed-film reactors, the new reactor had larger reaction contact area and avoided the defect of catalyst shedding. Then the operation parameters of this reactor were validated by using tetracycline (TC) as the wastewater pollutant, and the findings would offer some technical guidance for the practical application of magnetic catalysts.

2. Experimental

2.1 Batch preparation of Bi$_2$WO$_6$/ZnFe$_2$O$_4$ magnetic photocatalyst

Bi$_2$WO$_6$/ZnFe$_2$O$_4$ magnetic photocatalysts were obtained by a reported method [12], but we used 200 ml Teflon-lined autoclaves instead of 100 ml in order to obtain more photocatalysts at one time. Then the samples were characterized by an X-ray diffractometer (XRD), a transmission electron microscope (TEM, FECNAI F20), an energy-dispersive X-ray spectroscop (EDS, Bruker) and a vibrating sample magnetometer (Lakeshore 7410) to certify the quality was the same as in our previous work.

2.2 Design of the fixed film photocatalytic reactor

The continuous-flow magnetic fixed-film photocatalytic reactor was illustrated in Fig. 1. This reactor consisted of 3 segments of quartz tubes connected in horizontal series. The quartz tubes were in internal diameter of 10 mm and length of 100 mm. The LED light sources were placed above the tube reactor and their heights could be adjusted spontaneously. Also reflectors, which ensured the light received areas of the reactor, were installed below the reactor. Each segment of tubes was filled with 25 sequentially-connected magnetic beads (in diameter of 5 mm). The two ends of each magnetic bead chain were fixed onto the tube mouth plugs that were located at two sides of each tube, so that the bead chain was located in the middle of each quartz tube. The Bi$_2$WO$_6$/ZnFe$_2$O$_4$ photocatalyst was evenly coated onto the surfaces of the magnetic beads. The amount of surface catalysts in each segment of tubes was 0.600 g. The available capacity of the reactor was calculated to be 47.02 cm$^3$.

![Figure 1 Schematic diagram of the magnetic fixed film photocatalytic reactor](image-url)
2.3 Commissioning of operating parameters of the reactor
With TC as the target pollutant of wastewater, we investigated the effects of hydraulic retention time (HRT) (13, 24, 51, 94 min), light source intensity (0.82×10^5, 2.30×10^5, 3.20×10^5 lux), and initial pollutant concentration (C₀) (19.45, 29.48, 40.44, 51.58 mg/L) on the photocatalytic efficiency of the reactor in a continuous inflow and outflow mode. During the experiments, the reactor was firstly injected full with the initial TC solution and after 1 h of stabilization (time recorded as 0), the solution were sampled every 15 min, followed by TC detection on a UV-vis spectrophotometer (UV-2550).

3. Results and discussion
Characterization results of the Bi₂WO₆/ZnFe₂O₄ photocatalyst were shown in Fig.2. Compared to our previous work, the Bi₂WO₆/ZnFe₂O₄ that synthesized by a 200 ml autoclave in this study also exhibited similar results. Particles with polycrystalline structures were disperse and homogeneous, with particle sizes 10-20 nm (Fig.2a). The diffraction peaks of BWZn were mainly consistent with that of BW, the peaks of ZnFe₂O₄ in the composites were very weak due to the low combined dosage (Fig.2b), but the saturation magnetization of the BWZn was obviously (Fig.2c). Results in Fig.2d confirmed the catalyst was mainly composed of Bi, W, O, Fe and Zn, without showing the peak of any impurity.

Fig. 2 Characterization results of BWZn (a) TEM; (b) XRD; (c) magnetism; (d) EDX
Clearly, with the gradual prolonging of HRT, the outflow TC concentration gradually declined (Fig. 3a). At HRT=13 min, the TC removal rate of 47.06%-51.73% relative to the inflow TC concentration of 51.58 mg/L. Then the HRT was extended to 24 min, the outflow TC concentration first rapidly declined and then stabilized at 12 mg/L, at which the TC removal ratio was enhanced to 74.26%-78.47%. When HRT was prolonged to 51 min, the outflow TC removal rate slowly decreased to 81.15%. At the HRT of 94 min, the outflow TC concentration gradually decreased and stabilized at 4.52 mg/L, corresponding to the TC removal rate of 91.24%. Clearly, in the magnetic fixed-film photocatalytic reactor, regulating the HRT critically contributed to enhancing the photocatalytic efficiency of the reactor.
The light intensity affected the overall photocatalytic effect to some extent, and especially the weak light intensity led to decreased photocatalytic efficiency (Fig. 3b). When the light intensity was $3.20 \times 10^5$ lux, the outlet TC removal rate stabilized around 91.11%-93.78% relative to the inflow TC concentration of 51.58 mg/L and indicated high removal efficiency. At the light intensity of $2.30 \times 10^5$ lux, the outflow TC removal rates was 85.17%-89.84%. When the light intensity declined to $0.82 \times 10^5$ lux, the outflow TC concentration gradually rose and the removal rates finally stabilized at 70.78%-72.79%. The light intensity of $3.20 \times 10^5$ lux was sufficient for the reactor and ensured the TC removal rate would be above 90%.

When the initial TC concentration in the inflow differed, the outflow TC concentration was closely associated with the HRT in the reactor (Fig. 3c). Generally, from the reaction time of 0-60 min (HRT = 94 min), the outflow TC concentration gradually declined, especially when $C_0$ was very high, which was because the quantity of the catalyst was constant in the reactor and its adsorbed amount was finite[12]. Moreover, the catalyst affected the adsorption performance at the beginning of the reaction, and the outflow TC concentration was larger at higher $C_0$. After the reaction stabilized, the photocatalytic action became dominant, and the outflow TC concentration gradually decreased and stabilized. When the reaction time was 60-120 min, the outflow TC concentrations all were below 5.00 mg/L. As the HRT was shorter, the outflow TC concentrations along with the increasing initial concentration first rose and then stabilized; the outflow effect was gradually recovered when the HRT returned to the initial level, indicating the catalyst was very stable. Moreover, at different inflow concentrations, the specific outflow criterion could be achieved by regulating the HRT within a certain range, so as to maximize the reactor use efficiency.
4. Conclusion

A continuous magnetic fixed-film reactor was designed and the magnetic Bi$_2$WO$_6$/ZnFe$_2$O$_4$ catalysts were fixed onto the magnetic bead carrier. The effects of light intensity, initial TC concentration and HRT on the photocatalytic effect were investigated. It was found the reactor efficiency was most severely affected by HRT, followed by the initial pollutant concentration and the light source intensity. At the pollutant concentration of 51.58 mg/L, light intensity of $3.20 \times 10^5$ lux and HRT of 94 min, the TC removal rate in the reactor was enhanced to 94.05%. From the different pollutant concentrations, the specific outflow criterion could be achieved by regulating the HRT within a certain range, so as to maximize the reactor use efficiency. Compared with conventional fixed-film reactors, the new reactor had larger reaction contact area and avoided the defect of catalyst shedding.

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