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Research Article

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Study on advanced treatment of pharmaceutical wastewater by fluidized bed laccase bioreactor

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ABSTRACT

This article designed laccase bioreactors base on characters of pharmaceutical wastewater. The experiment designed and made fluidized bed laccase bioreactor. The shape dimension was 260 mm × Φ 130 mm. The effective capacity of the laccase bioreactor was 1.5 L. The optimum conditions that fluidized bed laccase bioreactor treated pharmaceutical wastewater was reaction time 100min, mediator concentration 10mg/L, pH=5, laccase amount 35mg/L.In this condition, removal rate of chorma could reach 75% and removal rate of COD reach 67%.

Keywords: laccase, fluidized bioreactor, advanced treatment, pharmaceutical wastewater

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INTRODUCTION

Environment pollution is a focus problem in the world. And this problem is more serious in China. In recent years, the government drew up some new policies to control pollutant emission. Many pharmaceutical mills must use advanced treatment methods to suit new policies. Some methods, such as Fenton, flocculation method, maybe cause secondary pollution. Laccase can degrade phenolic and non-phenolic compounds, which mediators exist in reaction system. Pharmaceutical wastewater can not cause secondary pollution, if pharmaceutical mills adopt laccase to treat wastewater. Laccase is a green advanced treatment method for pharmaceutical wastewater. But lasscase will loss with drainage, if laccase is not fixed on some materials. This article designed laccase bioreactors base on characters of pharmaceutical wastewater. The article designed fluidized bed, and researched treatment effect with the bioreactor.

EXPERIMENTAL SECTION

Methods of definition laccase activity

Laccase solution, o-Tolidine solution (3.36mmmol/L) and acetic acid-sodium acetate buffer solution(pH=3.6) were mixed in proportion of 0.5:0.5:3.5. And then mixure solution was put in ultraviolet spectrophotometer that the wavelength was 600nm and was tested change of absorbance value in 5min. At the same time, it used distilled water as reference solution and tested change of absorbance value in 5min. One enzyme activity is enzyme amount that made absorbance value increase 0.001 per minute. [1] [2]

Specific activity of immobilized enzyme=total activity of immobilized enzyme/quality of immobilized enzyme

Activity retention of immobilized enzyme= activity of immobilized enzyme/activity of free enzyme

Methods of immobilized enzyme

15ml enzyme solution mixed with 150ml sodium alginate solution. And the mixed solution was decreased temperature to 5-10℃. The solution was injected in $CaCl_2$ solution with No.6 syringe needle and injecting height is 5cm. Mixed solution will form gel beads in $CaCl_2$ solution. Afterwards, gel beads were hardened in $CaCl_2$ solution

that maintained temperature at 4℃. Gel beads were used normal saline to wash three times after removed from $CaCl_2$ solution. At last, immobilized enzyme was stored in refrigerator with 0-5℃.3 -6

Methods of water quality analysis
Water quality analysis, such as COD, BOD and chroma base on national standard.

Materials
Concentrated sulfuric acid, $AgSO_4$, sodium alginate, $HgSO_4$, acetic acid, sodium acetate, NaOH, o-Tolidine.

RESULTS AND DISCUSSION

Fluidized bed design and running

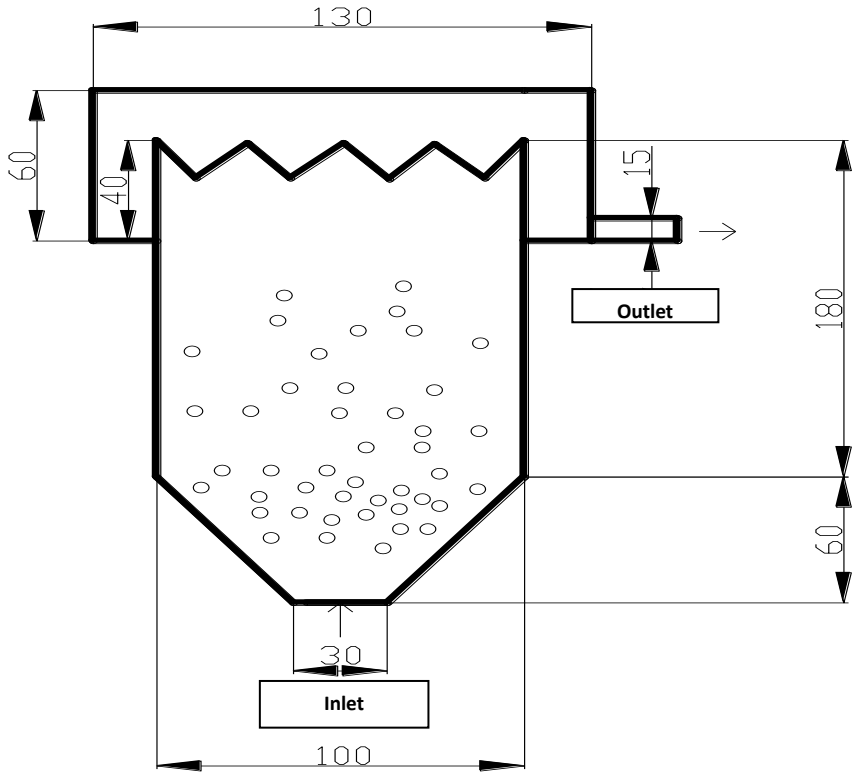

Fig.1- The shape and size of the fluidized bed laccase reactor（unit：mm）

The experiment design and made fluidized bed laccase bioreactor, such as fig 1. The shape dimension is 260 mm × Φ 130 mm. The effective capacity of the laccase bioreactor was 1.5 L, with sodium alginate embedding method to immobilized laccase. Bioreactor bottom was like a bucket. The bucket shape was 60cm high, 100mm top width and 30mm bottom width. This design was good for free movement of immobilized laccase.

The fig 2 was closed cycle system of fluidized bed and fig 3 was the picture of fluidized bed laccase bioreactor system.

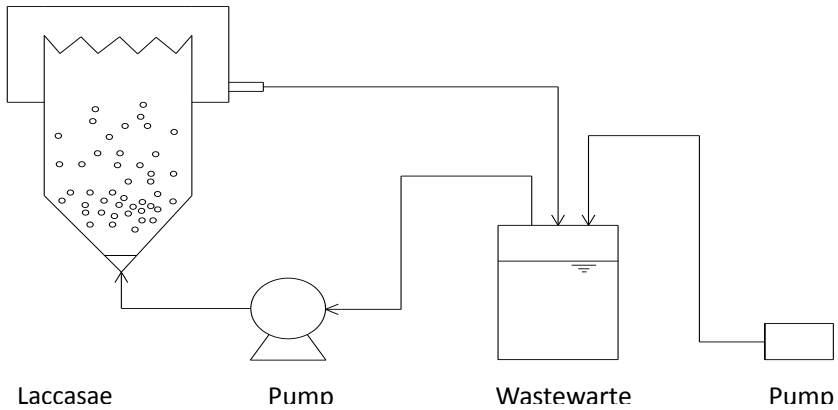

Fig.2-Flow chart of the fluidized bed laccase bioreactor system

Fig.3-Physical map of the fluidized bed laccase reactor system

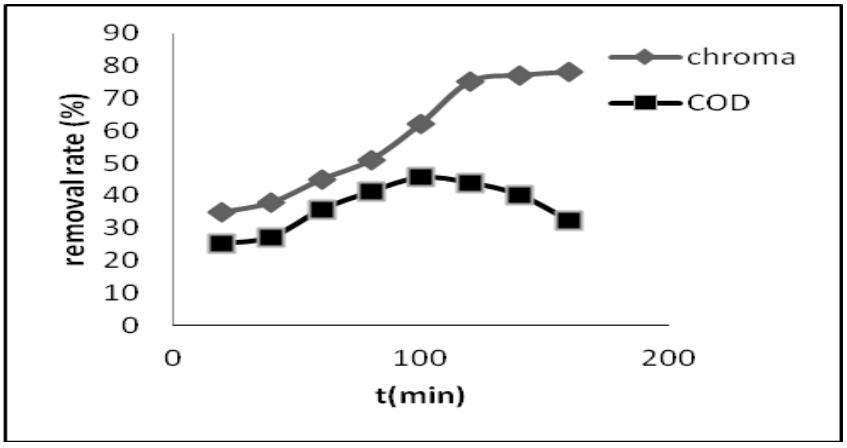

Fig.4-Reaction time effected on the result of wastewater treatment by the fluidized bed laccase reactor

3.2 Fluidized bed bioreactor advanced treated pharmaceutical waste water

3.2.1 Reaction time effected on the result of wastewater treatment

Treatment conditions: mediator concentration 10mg/L, pH=5, activity of immobilized enzyme 1000U/g, laccase

amount 40mg/L .As Fig4 shown, chroma removal rate was increase with prolong of reaction time. The trend of increased was slowdown after 120min. But COD removal rate had the optimum value at 100min. Lignin degradation and benzene ring cracking could COD value increase in the system. Comprehensive consideration, the optimum reaction time was 100min.

3.2.2 Laccase amount affected on the result of wastewater treatment

Treatment conditions: reaction time 100min, mediator concentration 10mg/L, pH=5, activity of immobilized enzyme 1000U/g. As Fig5 shown, removal rates of chroma and COD both increase with increasing of laccase amount. Their trends of increased was slowdown after 35mg/L. So the optimum of laccase amount was 35mg/L.

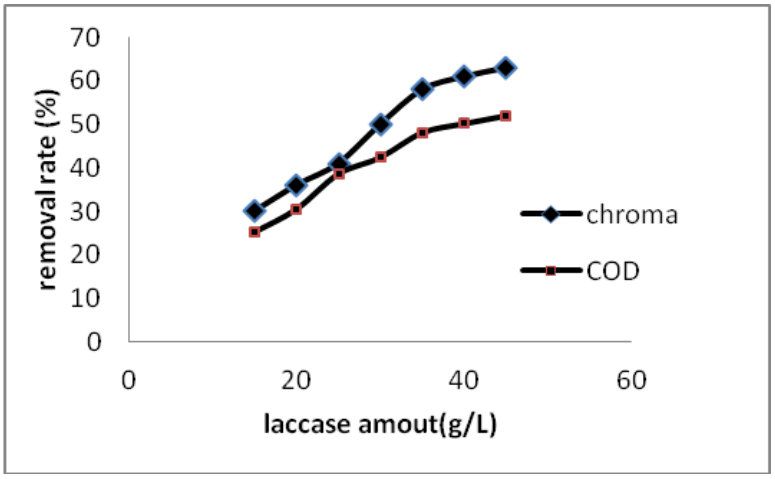

Fig.5- Laccase amount effected on the result of wastewater treatment by the fluidized bed laccase reactor

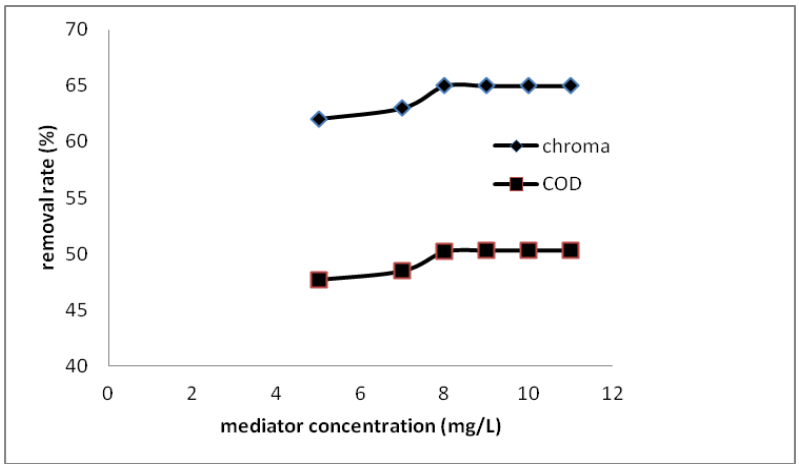

Fig.6- HBT amount affected on the result of wastewater treatment by the fluidized bed laccase reactor

3.2.3 Mediator amount affected on the result of wastewater treatment

Treatment conditions: reaction time 100min, laccase amount 35mg/L, pH=4. As Fig6 shown, removal rates of chroma and COD both were unchanged, after that mediator concentration was more than 8mg/L. Due to economic factors, the optimum mediator concentration was 8mg/L.

3.3 Blank comparison experiment of laccase bioreactor

The article designed a comparison experiment for removing absorption disturbance of gel beads. Blank experiment use gel beads that had not laccase to treat pharmaceutical wastewater. Treatment conditions: reaction time 100min, mediator concentration 10mg/L, pH=5, laccase amount 35mg/L. The Tab1 showed results. The removal rate COD of Non-laccase bioreactor was low, but removal rate chroma was 30%. This phenomenon could prove adsorption of gel beads. This experiment proved that catalytic oxidation of laccase was main reaction in fluidized bed bioreactor.

Table1-Results of comparison experimental

Reactors	Removal rate of COD(%)	Removal rate of chroma(%)
Non-laccase	7	30
laccase	67	75

CONCLUSION

4.1 The experiment design and made fluidized bed laccase bioreactor. The shape dimension is 260 mm × Φ 130 mm. The effective capacity of the laccase bioreactor is 1.5 L. This design is good for free movement of immobilized laccase.

4.2 The optimum conditions that fluidized bed laccase bioreactor treated pharmaceutical wastewater was reaction time 100min, mediator concentration 10mg/L, pH=5, laccase amount 35mg/L.

4.3 Comparison experiment proved that catalytic oxidation of laccase was main reaction in fluidized bed bioreactor. Fluidized bed laccase bioreactor was good for advanced treatment of pharmaceutical wastewater.

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