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Mini Review

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A Mini-Review of Catalytic Performance of Fe-Based Glass in Wastewater Treatment

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ABSTRACT

Metallic glass is another substance that exists relative to metallic crystals. Because of its unique disordered atomic structure, high density of low coordination, high surface residual stress and a large number of unsaturated sites, it is considered to be the most competitive new catalyst in the field of catalytic degradation in water environment. The catalyst has good catalytic degradation efficiency and stability for dye wastewater in both Fenton-like and persulfate systems. However, the development of traditional metallic glass catalysts has now reached a relatively difficult period. Therefore, it is a key problem to develop a new type of catalyst with better catalytic degradation efficiency and stability than traditional metallic glass.

Keywords: Metallic glass; Catalytic performance; Dye wastewater; Nanostructured

INTRODUCTION

Printing and dyeing wastewater is one of the main sources of industrial wastewater in the world. With the rapid development of global science and technology, and economic level, the use of automation technology to improve the efficiency of printing and dyeing industry at the same time, the increasing number of printing and dyeing wastewater has gradually attracted widespread attention [1]. The discharge of dye wastewater has caused serious pollution to the water environment on which human beings depend for survival, and has added troubles to the current situation of the shortage of fresh water resources. And dye wastewater has become the focus of attention in industrial wastewater because of its many kinds, high toxicity and difficult decomposition, etc. [2]. In the early years, the purification treatment methods for dye wastewater mainly include physical adsorption [3], biological treatment [4], membrane separation [5] and zero-valence metal method [6], etc. However, these methods are low in efficiency, complex in operation, time-consuming and laborious, which to a large extent limits the development of dye wastewater treatment. Therefore, finding new methods and exploring new materials is the key way to solve the problem of dye waste water.

LITERATURE REVIEW

Metallic glass is another substance that exists relative to metallic crystals. Due to the ultra-rapid cold solidification, the atoms have no time to carry out the ordered arrangement of crystallization, and the obtained solid metal atoms show a metastable structure of long-range disorder and short-range order called metallic glass [7]. In recent years, many scholars have found that metallic glass is considered as the most competitive new catalyst in the field of catalytic degradation in water environment because of its unique disordered atomic structure, high density of low coordination sites, high surface residual stress and a large number of unsaturated sites [8]. At present, the metallic glass systems reported for catalytic degradation of dye wastewater are mainly Mg- [9], Al- [10], Co- [11] and Fe-based [12]. It was found that the metallic glass of the above four systems had good catalytic degradation ability of dye wastewater. Among them, Fe-based metallic glass is superior to other systems in terms of degradation rate, application range, fabricate process, cost and so on. Therefore, Fe-based metallic glass is considered by many scholars to be the most promising new environmental catalyst [13]. Theoretical calculations confirmed that the unique nanoscale heterogeneous disordered structure in the hierarchical gradient metallic glass catalyst has strong charge transferability, and has high adsorption energy, low energy barrier and low generation energy in the process of facilitating $S_2O_8^{2-}$ to $SO_4^{-\bullet}$ conversion. However, recent studies have found that the catalytic efficiency and stability of traditional metallic glass in catalytic degradation of dye wastewater have reached a bottleneck period. Meanwhile, some researchers believe that the efficiency and stability of traditional metallic glass catalysts are affected by their atomic configuration. Therefore, designing and regulating the atomic structure of metallic glasses to improve their catalytic efficiency and stability remains a challenge.

DISCUSSION

In recent years, many scholars have made clever use of the principle of Fenton reaction [14]. It was found that Fe-based metallic glass would undergo an Advanced Oxidation Process (AOP) in a dye solution with a certain amount of Hydrogen Peroxide (H_2O_2) and a low pH value, which is called Fenton-like reaction [15]. The Fenton-like reaction is to decompose the organic wastewater discharged from industrial production into non-toxic and harmless small molecule substances by generating active groups with a high redox potential [16]. The process of Fe-based metallic glass catalytic degradation of dye wastewater through Fenton-like reaction is generally divided into three steps [17]:

$$Fe^0+H_2O_2 \rightarrow Fe^{2+}+2OH^- \quad (Eq…1)$$

$$Fe^{2+}+H_2O_2 \rightarrow Fe^{3+}+{}^\bullet OH+OH^- \quad (Eq…2)$$

$$OH\ Organics \rightarrow Products \quad (Eq…3)$$

The rapid occurrence of the Fenton-like reaction must be induced by H_2O_2 and low pH value. In the study, it was found that the lower the concentration of H_2O_2, the catalytic reaction rate will also decrease. Surprisingly, as the concentration of H_2O_2 increased, the catalytic reaction rate first increased and then gradually decreased. In view of this phenomenon, most scholars believe that appropriate addition of H_2O_2 can effectively accelerate the degradation. However, excessive H_2O_2 causes the original $^{\bullet}OH$ to be removed, thus slowing down the rate, the reaction formula is as follows [18]:

$$H_2O_2 + {}^{\bullet}OH \rightarrow H_2O + {}^{\bullet}O_2H \qquad (Eq\ldots4)$$

The oxidation potential of the generated free radical $^{\bullet}O_2H$ is much smaller than that of the $^{\bullet}OH$, so the oxidation rate of the dye wastewater is reduced. The effect of pH value on catalytic degradation rate is higher than that of H_2O_2 concentration. Wang et al., showed that the degradation rate at pH=2 is lower than that at pH=3, which may be because when the concentration of H^+ in the dye solution is too high, the Fe element in the metallic glass will be dissolved and hydrogen will be generated, the formula is as follows [18]:

$$H^+ + Fe^0 \rightarrow Fe^{2+} + H_2 \uparrow \qquad (Eq\ldots5)$$

When pH >3, the catalytic degradation rate of the dye solution decreases with the increase of pH, because only enough H^+ in the solution can carry out the Fenton-like reaction. And in neutral and alkaline dye solutions, almost no catalytic degradation effect was observed. Through the above summary, it can be found that although Fenton-like reaction can achieve catalytic degradation of dye wastewater, its scope of application is greatly limited. And hydrochloric acid and sulfuric acid must be introduced to adjust the pH of the dye solution, objectively introducing other ions into the solution. Therefore, looking for other inducers that can be applied to a wider range is a good research point.

In 2016, Jia et al., used $Fe_{78}Si_9B_{13}$ metallic glass for the first time to activate sulfate radicals ($SO_4^{-\bullet}$) with high oxidation potential from persulfates. In addition, persulfate and metallic glass can also be activated to produce $^{\bullet}OH$, the formula is as follows [19]:

$$Fe^{2+} + S_2O8^{2-} \rightarrow Fe^{3+} + SO4^{-\bullet} + SO_4^{2-} \qquad (Eq\ldots6)$$

$$Fe^{2+} + S_2O_8^{2-} + H_2O \rightarrow Fe^{3} + {}^{\bullet}OH + SO_4^{2-} \qquad (Eq\ldots7)$$

It was found that the $Fe_{78}Si_9B_{13}$ metallic glass activated persulfate can be used for catalytic degradation of methylene blue dye solution for 30 times. Compared with Fenton-like reaction, it is significantly improved. Later, Jia et al., developed a non-noble and multi-component $Fe_{83}Si_2B_{11}P_3C_1$ metallic glass catalyst, which has excellent catalytic efficiency while maintaining the catalytic degradation stability of dye wastewater. Theoretical calculations show that the excellent efficiency of the catalyst is due to a unique atomic coordination that causes electron delocalization and enhances electron transfer. The discovery of this catalyst was one of the best environmental catalysts available at the time for both catalytic efficiency and stability [20].

Regarding this challenge, recently, Chen et al., found that a hierarchical gradient metallic glass catalyst with a nanoscale heterogeneous disordered structure can be fabricated using non-noble $Fe_{75}P_{15}C_{10}$ metallic glass as a precursor by annealing and acid leaching at a specific temperature [21]. The catalyst showed excellent performance in catalytic degradation of dye wastewater, such as high rate, strong TOC removal and low activation energy. Compared with traditional metallic glass, the catalytic capacity ($k_{SA} \cdot C_0$) of hierarchical gradient metallic glass catalyst was increased from 1144 $mg \cdot m^{-2} \cdot min^{-1}$ to 3101 $mg \cdot m^{-2} \cdot min^{-1}$, and the stability test showed that the catalyst could be reused for 39 consecutive times without significant efficiency decay, which is one of the environmental catalysts with the best catalytic degradation ability and stability reported so far.

CONCLUSION

The above research indicates that it is possible to fabricate new metallic glass with higher catalytic activity than traditional metallic glass by using non-noble materials, and reveals that its nanoscale heterogeneous disordered structure is a new strategy to obtain excellent catalytic degradation performance.

In the future, the purification and treatment of dye wastewater should be started from two aspects. 1) Search for more efficient and widely applicable inducers in order to achieve effective decomposition of dye molecules in different water environmental systems. 2) The development of nanostructured metallic glass with better performance than traditional metallic glass. Firstly, the problem of nanoscale metallic glass fabricate cannot be ignored. Secondly, when exploring the new system of nanoscale metal glass, it is necessary to start with non-noble metals. Finally, the structure of nanoscale metallic glass should realize the common development of biphase and polyphase.

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