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Research on photocatalytic and degradation properties of SA hydrogel and advantages among photocatalytic materials

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Abstract:

Photocatalysts have attracted great research interest owing to their excellent properties and potential for simultaneously addressing challenges in wastewater treatment. For traditional photocatalytic materials, there are always some limitations. For example, their photocatalytic performance is limited due to their high band gap (UV range) and recombination time of photogenerated electron-hole pairs [1]. Additionally, photocatalytic materials face the challenges of secondary pollution to the environment and poor recycling performance. Hydrogel photocatalysts has been of high removal efficiency of water pollutants due to its adsorption capacities and good environmental compatibility. Hydrogels are macromolecular hydrophilic polymetric gels with cross-linked 3D structures that can easily entrap water molecules in their pores or interstitial spaces to swell up while remaining insoluble. Hydrogels exhibit high structural flexibility, chemical stability, elasticity and permeability, enhancing their water absorption capability. In this review, we will mainly focus on the photocatalytic degradation properties of sodium alginate (SA) hydrogel and explore its further application in wastewater treatment (dye degradation). Also, we compare the metal-ion-doped graphene hydrogel (MGH) with SA hydrogel in efficiency, conditions control and further prospects etc.

Keywords: wastewater treatment; photocatalysts; sodium alginate (SA) hydrogel; metal ion-doped graphene hydrogel (MGH); adsorption.

1. Introduction

Photocatalysis as well as adsorption have been most effective and indispensable processes which belong to tertiary treatment regarding wastewater treatment. Photocatalysis technology refers to the process that photocatalytic materials absorb photons and are excited to produce electron-hole pairs under light. Pho-

togenerated electron-hole pairs have strong reduction ability and oxidation ability. They will oxidize and degrade organic pollutants or heavy metal ions through chemical oxidation or reduction reactions.

With regard to semiconductor materials, Cu_2O has certain advantages. First of all, as a p-type semiconductor, its band gap is about 2.0-2.5 eV, so it can make full use of visible light [2]. However, cuprous oxide as a photocatalyst also has some problems. In order to solve the problem that photogenerated electrons and holes can not be separated effectively, the stability is poor and it is easy to be oxidized in water, it is mentioned earlier that it can be compounded with carbon and metal nanomaterials. In order to solve the problem that the powder is not easy to collect, it can be solved by loading on the carrier--foamed metals, plastics, hydrogels, and blending with polymers or adhesives [3].

Hydrogel is a kind of material which can absorb a large number of water molecules in aqueous solution, make itself swell and maintain a certain shape. The polymer segments are cross-linked with other segments by physical or chemical means, so that the hydrogel has a network-like cross-linking structure, contains a large number of functional groups, and has the effect of adsorption and degradation, which improves the catalytic performance of photocatalytic materials. Sodium alginate (SA) hydrogel is widely used as a natural hydrogel because of its wide range of sources, good biocompatibility, high adsorption performance, easy biodegradation and non-toxic degradation products [4]. This paper will focus on the adsorption and degradation properties of SA hydrogel and its advantages among photocatalytic materials.

2. Methods

The principle of photocatalytic reaction is mainly divided into three stages. In the first stage, the semiconductor photocatalyst absorbs energy under suitable light conditions, and the semiconductor material produces electron-hole pairs under the excitation of photon energy. In the second stage, electron-hole pairs migrate to the surface of the catalyst and react with water to form strongly oxidizing free radicals. In the third stage, the photocatalyst will adsorb and enrich the pollutants on the surface and react with free radicals to achieve degradation [5].

Currently methods for preparing hydrogel photocatalysts materials can be divided into three categories: embedding of photocatalysts in hydrogel networks, *in-situ* synthesis of photocatalysts in hydrogel networks and self-assembly of hydrogel photocatalysts [3]. Here in the experiment following, the second preparation method is used for the synthesis of SA hydrogel. Moreover, SA hydrogel is mainly based on the principal of cross-linking of divalent metal ions. The hydrogel pgotocatalysts promote synergistic effects of absorption of organic pollutants and *in-situ* photocatalytic degradation by Cu_2O [6].

2.1 Preparation of SA hydrogel

At the beginning, several solutions were prepared. 0.8g sodium alginate in the form of white powder was dissolved in 30mL pure water in a measuring cup and stirred by the magnetic agitator for about 1 hour. Next, 1.7g CuO is poured into the 15mL water in a small beaker and poured into the SA solution after stirring by the magnetic agitator for 10 minutes. As CuO is insoluble in water, a large amount of black mixture remained in the beaker. PVA and PVP-K30 were dissolved respectively. 1.7g PVP-K30 white powder was dissolved in 20mL pure water. Polyvinylpyrrolidone (PVP) is a water-soluble polymer that has positive effects on protection, viscosity, absorbency and solubilization. PVP added here would help CuO disperse to a larger extent and become more stable in polymerization thanks to the viscosity and colloid protection of PVP. As for polyvinyl alcohol (PVA), the polymer will form hydrogen bonding with SA and also been synthesized into hydrogel because of the physical cross-linking method of freezing and thawing which made PVA molecules more organized in the following steps. Thus, efficiency of adsorption and photocatalytic degradation was improved. Then, 15mL of 20g/L PVA solution and PVP solution were added to the beaker used in the previous step respectively, stirred and poured into the measuring cup. Take 10mL of ultra-pure water to wash the beaker and pour into the measuring cup. Lastly, the dissolved glucono-1,5-lactone (GDL) (3.8g GDL powder was dissolved in 20mL water) was added and stirred using a glass rod. GDL as a weak acid could release H^+ in order to get Cu^{2+}. Then, gelation occurred and the mixture was poured into the mold which formed the rudiment of the SA composite hydrogel. The hydrogel in liquid state was next experienced freezing (20 hours) and thawing (4 hours) for three times.

2.2 Organic waste liquid preparation

0.01g Cationic red 6B was weighed and dissolved. Followed, it was poured into a volumetric bottle to fix the volume. We removed of 500mL of the dye with the pipette gun and dilute to 5mL. Lastly, the diluted dye was transferred to a 48-well plate followed by absorbance measurement.

2.3 Photocatalysis experiment

10mL of the cationic res 6B dye solution was measured and mixed with 40mL of water to form a 20mg/L solution.

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Then, we weigh 0.2g unheated hydrogel materials and put it into the dye solution. Stirred by the magnetic agitator. During the photocatalytic degradation period, 500mL dye solution were transferred to the 48-well plate each time at 0, 10, 20, 30, 40, 50, 60, 90 and 120 minutes.

Same steps repeated with heat-treated SA composite hydrogel (at approximately 180℃). Except for the difference for hydrogel material, 500mL dye solution were transferred to the 48-well plate each time at 0, 10, 20, 30, 40, 50, 60, 80, 100, and 120 minutes.

Degradation rate was measured by enzyme-labeled instrument. Furthermore, catalytic degradation curves of two different SA composite hydrogels were plotted.

3. Results

Catalytic degradation rate plotting against time could be seen in fig. 1. Two degradation curves with untreated hydrogel material and heat-treated hydrogel material were shown respectively. As for the curve in red, a catalytic degradation rate of approximately 74% was achieved from my experiment. Additionally, the degradation rate experienced a sharp increase to about 40% and marked rise to reach the peak for the rest of the time while a moderate rise could be seen with the use of untreated hydrogel material over the whole period.

Except for the SA composite hydrogel itself, heat treatment did play an important role in increasing the catalytic effect. To explain, during the heat treatment, CuO as a semiconductor photocatalytic material added in SA hydrogel photocatalyst is reduced to Cu and Cu_2O with some amount of CuO remained. Furthermore, some of the OH groups are removed due to high temperature and heterojuction is also involved in this process. In the process from low temperature to high temperature, Cu_2O is formed through the loss of bound water, skeleton fracture, partial carbonization of the product and final oxidative decomposition of carbides. As a result, the biomass (SA) becomes easily broken as its $Cu/Cu_2O/CuO$ heterojunction net is less stable [6].

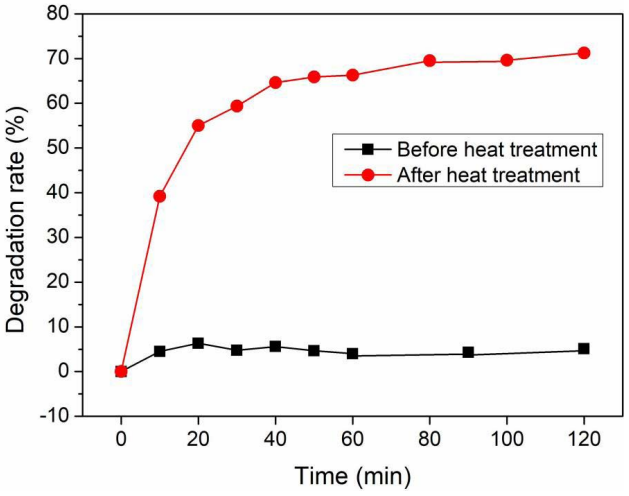

Fig. 1 Catalytic degradation curve

4. Outlook for Technological Development

In this paper, we choose the doped graphene hydrogel, which is also based on metal ions and mainly used in dye adsorption and photodegradation in wastewater. it is compared with our object cuprous oxide sodium alginate hydrogel in many aspects in order to explore the advantages of cuprous oxide sodium alginate hydrogel.

Metal ion-doped graphene hydrogel (MGH) was prepared by hydrothermal method and *in-situ* addition method, while our SA hydrogel was prepared by *in-situ* release method and divalent metal ion cross-linking principle. In contrast, the hydrothermal method has certain limitations under similar temperature conditions. As a wet chemical method under high pressure (0.3~4MPa), it is highly dependent on production equipment, so large-scale production is easy to produce large errors. The latter combines physical cross-linking with ionic cross-linking (including the physical cross-linking of PVA in the preparation process), which not only has low mechanical strength, but also has reversible cross-linking.

In the process of low temperature drying, there is no cross-linked three-dimensional porous aerogel structure in MGH, which is mainly caused by the hydrothermal reaction of doped metal ions to form nanoparticles deposited on the surface, while the lamellar structure of graphene in the hydrogel is not obvious and there are a large number of pores [8]. There are no similar problems in the heat treatment of similar sodium alginate hydrogel.

Aiming at the photocatalytic degradation rate of dyes, taking Cu^{2+}-doped graphene hydrogel CuGH as an example, the degradation rate of rhodamine is slow and the degradation efficiency is low. One of the reasons is that in

the hydrothermal reaction of graphene, the hydrolyzability of Cu^{2+} is poor, so it is difficult to form metal oxides and hydroxides. The above experimental results show that the photocatalytic degradation efficiency of SA hydrogel to cationic red 6B organic dye can reach 70% to 80%.

In addition, the effect of graphene hydrogel doped with metal ions on the degradation of rhodamine was affected by many factors, such as the concentration of metal ions, graphene oxide was not completely reduced [9], and the effect of quenchants such as oxalate amine reduced the degradation rate to less than 40% [10].

In a word, as a natural hydrogel, sodium alginate hydrogel has the advantages of biodegradable, renewable, green, pollution-free and cheap. Specifically, this material has a flexible structure, which solves the disadvantage that the photocatalyst powder is not easy to be recovered. Make full use of the three-dimensional porous structure of the carrier to fix the catalyst powder, so that it is not easy to agglomerate. Based on the three-dimensional porous structure and the adsorption characteristics of the polar groups on the macromolecular chain, the adsorption and photocatalytic degradation were combined to improve the catalytic effect.

5. Conclusion

As a natural polymer, sodium alginate is a promising material with the characteristics of green, non-pollution, renewable, cheap and so on. The sodium alginate hydrogel has shown excellent swelling and adsorption capacity in wastewater treatment. It exhibits excellent performance in the photocatalytic activity toward degradation of dyes in wastewater. It is known from the experiment that the photocatalytic material of SA hydrogel after heat treatment has higher catalytic degradation efficiency in dyes. Compared with other photocatalytic materials, the preparation method is simple and degradable, and the catalytic effect is greatly improved by using the three-dimensional porous structure and the adsorption characteristics of polar groups to dyes. It is a relatively mature and environmentally friendly recyclable water treatment technology material with broad prospects.

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