Section 1. Biotechnologies

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POROUS TITANIUM DIOXIDE/CALCIUM ALGINATE COMPOSITE HYDROGEL FOR PHOTOCATALYTIC DEGRADATION OF WASTEWATER

Abstract. Nano-titanium dioxide (TiO_2) is one of the most promising photocatalysts. It has the advantages of low cost, non-toxicity, high photocatalytic activity, etc. However, the nano-titanium dioxide has a problem in difficult to recycle and reuse. If it cannot be recycled, nano-titanium dioxide dispersed in water will cause secondary pollution. Since the material that used for current approach for recycling TiO_2 – steel wire, glass beads, ceramic, cotton fabric and other materials- would absorb or block light, the photocatalytic efficiency of titanium dioxide nanoparticles is drastically reduced. In order to improve the photocatalytic efficiency of titanium dioxide nanoparticles, we decided to prepare a titanium dioxide/sodium alginate mixed solution and prepared titanium dioxide/calcium alginate composite hydrogel spheres by calcium chloride cross-linking. The size of a single particle is about 20 nm. By using the spectrometer, under the irradiation of ultraviolet lamp, the photocatalytic efficiency of titanium dioxide nanoparticles can be determined by the rate of the degradation of methyl orange which is the simulation of pollutant. The result of experiment showed that the porous titanium dioxide/calcium alginate composite hydrogel beads have a higher photocatalytic activity, approximately about an increase of 20% in the degradation of methyl orange after 120 minutes. This experiment has a good reference value for the preparation of high activity and easy recovery photocatalysts in large quantities.

Keywords: *Photocatalysis,* TiO_2.

1. Introduction

According to the World Health Organization (WHO), at least 2 billion people use a drinking water source contaminated, 80% of human diseases are related to water pollution, and more than 800000 people die of diarrhea caused by unsafe water every year [1]. Due to the relatively backward industrial technology and weak awareness of environmental protection, many countries are facing serious water pollution. In recent years, with the continuous development of industry, environmental pollution is increasing. Industrial sewage, agricultural sewage and domestic sewage contain a large number of organic pollutants [2]. Among these pollutants, the proportion of organic pollutants with high toxicity, complex components and difficult biodegradation is high. At present, the commonly methods for treating organic wastewater include biochemical method, physicochemical method (adsorption, filtration, flocculation and sedimentation) and chemical oxidation technology (ozone oxidation and chlorination). However, these methods can not completely remove some highly toxic organics. At the same time, there are still some problems, such as high energy consumption, expensive equipment and so on [3].

Figure 1. Photos of sewage

The development of solar energy utilization technology is expected to solve the current environmental pollution problem. Therefore, finding photocatalysts that can absorb solar energy has become an urgent task [4]. Nano titanium dioxide (TiO_2) is one of the most promising photocatalysts. When TiO_2 is exposed to sunlight, especially ultraviolet rays, the electrons in the valence band will be triggered and move to the conduction band, to generate free electrons-hole pairs. Free electron-hole pairs have strong redox ability, which can activate oxygen and water in the air to generate active oxygen and hydroxyl radicals. When benzene, toluene, formaldehyde, bacteria, viruses and other pollutants are adsorbed on the surface of TiO_2, they will combine with free electrons or holes to cause redox reactions and be decomposed into carbon dioxide and water. At present, nano TiO_2 has been widely used in the fields of air purification, sewage treatment, water splitting to produce hydrogen, CO_2 reduction [5].

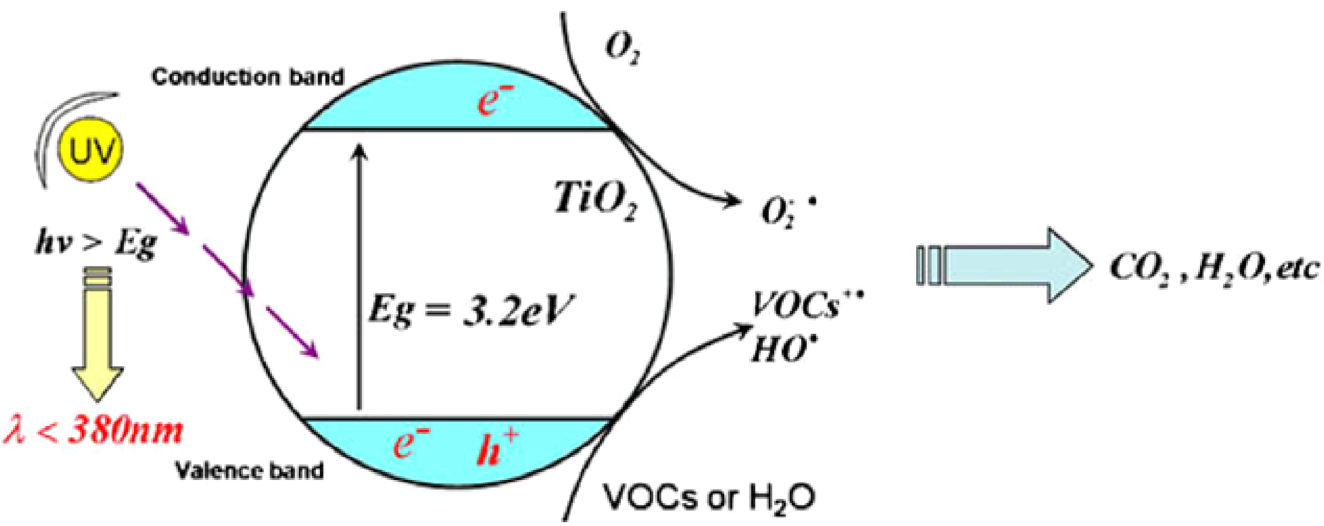

Figure 2. Schematic diagram of TiO_2 catalytic degradation of pollutants under UV irradiation [5]

Nano titanium dioxide can degrade organic pollutants with low concentration and high toxicity by sunlight, but it is difficult to recycle [6]. If it cannot be recycled, nano titanium dioxide dispersed in water will form secondary pollution. Therefore, scientists think of many ways to immobilize nano titanium dioxide, such as fixing nano titanium dioxide on steel wire, glass beads, ceramics, cotton fabric and other materials [7]. However, the above materials will absorb or block sunlight, the photocatalytic efficiency of nano titanium dioxide is greatly reduced.

Hydrogel is a gel with water as the dispersion medium, which has a three-dimensional network cross-linking structure. In particular, many hydrogels have excellent light transmittance and small molecular pollutants can enter and exit hydrogels. Some researchers tried to embed nano titanium dioxide in hydrogels to prepare nano titanium dioxide composite hydrogels that are easy to recover [8]. However, due to the slow permeation of pollutants in the hydrogel, the photocatalytic efficiency of titanium dioxide decreased significantly.

Sodium alginate (Na-Alg) is a natural polysaccharide polymer material extracted from kelp, Sargasso and other marine plants. It is non-toxic, non irritating and has good biocompatibility. Calcium alginate gel can be used as an immobilized carrier for enzymes and catalysts, so it has important applications in medicine, agriculture, industrial production and other fields [9]. Sodium alginate can be complexed and crosslinked with calcium ions [10]. Calcium ions displace sodium ions and interact with two molecular chains to form an insoluble, nontoxic and strong calcium alginate gel (Ca-Alg). Calcium alginate has a three-dimensional reticular gel structure, which is usually called an "egg box" structure, and its schematic diagram is as follows [11].

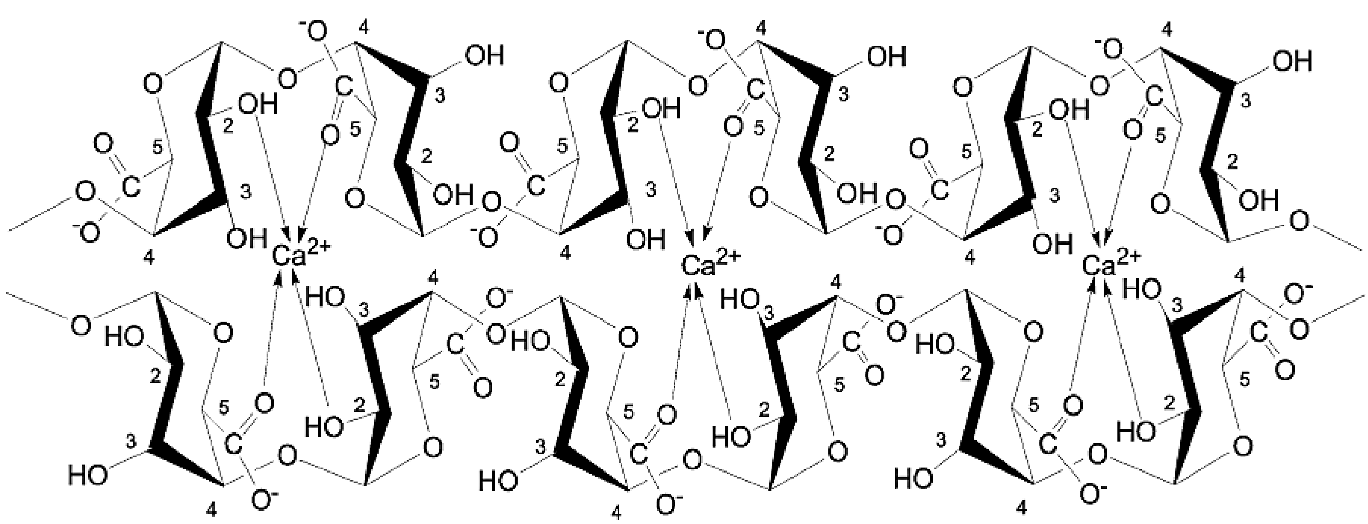

Figure 3. Schematic diagram of calcium alginate gel [10]

Therefore, we tried to prepare TiO_2/sodium alginate mixed solution (TiO_2/Na-Alg), and prepared TiO_2/calcium alginate composite hydrogel beads (TiO_2/Ca-Alg) by calcium chloride crosslinking. In order to improve the inlet and outlet speed of pollutants, we added magnesium hydroxide to the composite hydrogel beads, and then dissolved the magnesium hydroxide with hydrochloric acid to prepare porous TiO_2/calcium alginate composite hydrogel beads (TiO_2/Ca-Alg), which significantly improved the photocatalysis efficiency of the composite hydrogel.

2. Experiment

2.1 Material

Nano titanium dioxide, white powder, average particle size of 21 nm, about 20% rutile and 80% anatase, specific surface area of about 50 m^2/g, Degussa Evonik, Germany.

Sodium alginate, light brown powder, 100 g, Sinopharm Reagent Co., Ltd.

Anhydrous calcium chloride, white powder, 500 g, analytical pure, Sinopharm Reagent Co., Ltd.

Methyl orange, orange powder, 25 g, analytical pure, Tianjin Fuchen Chemical Reagent Co., Ltd.

Precipitation magnesium hydroxide, white powder, 500 g, Jinan Taixing Fine Chemical Co., Ltd.

2.2 Preparation of porous composite hydrogel beads

4g sodium alginate was added into a beaker containing 100g deionized water and mechanically stirred for 1h to obtain a transparent sodium alginate aqueous solution with a concentration of 4%.

Add 0.4 g nano titanium dioxide into a beaker containing 100 g deionized water, ultrasonic for 10 minutes, then add 20 g magnesium hydroxide powder, magnetic stirring for 1 hour and ultrasonic dispersion for 10 minutes to obtain a white uniform nano titanium dioxide/magnesium hydroxide aqueous dispersion solution.

The sodium alginate aqueous solution and the nano titanium dioxide/magnesium hydroxide aqueous dispersion solution were mixed together and stirred for 1 hour to obtain the nano titanium dioxide/sodium alginate mixed solution.

4 g anhydrous calcium chloride was added to a beaker containing 100 g deionized water and stirred magnetically for 10 minutes to obtain a transparent calcium chloride solution.

Use a 5 ml syringe to add the nano titanium dioxide/sodium alginate mixed solution drop by drop to the 4% calcium chloride solution (magnetic stirring continuously), and the height of the syringe from the liquid level of calcium chloride solution is about 15 cm. The calcium ions in the solution will immediately crosslink the droplets to obtain a spherical nano titanium dioxide/calcium alginate composite hydrogel. After crosslinking for 30 minutes, the composite hydrogel beads were fished out.

Figure 4. Dropping and crosslinking process of nano titania/calcium alginate composite hydrogel

Add 20 g hydrochloric acid into 180g deionized water and stir to obtain dilute hydrochloric acid solution. 50 g hydrogel beads are added to dilute hydrochloric acid solution. Hydrochloric acid will dissolve magnesium hydroxide, magnetic stirring for 2 hours, wash with dilute hydrochloric acid solution again, and finally soak and wash with deionized water for 3 times to obtain porous nano titanium dioxide/calcium alginate composite hydrogel beads.

Non porous nano TiO_2/calcium alginate composite hydrogel beads, porous calcium alginate gel beads and composite hydrogel beads with different concentrations were prepared by the same method.

2.3 Photocatalytic process of composite hydrogel beads

Preparation of methyl orange solution: methyl orange is a common dye. We used methyl orange as a simulated pollutant to evaluate the photocatalytic performance of the composite hydrogel. Add 0.2 g methyl orange powder to the beaker, add 100 g water, stir and dissolve to obtain dark red methyl orange solution. Add 10 g dark red methyl orange solution to a 1L beaker, and then add 990 g water for dilution to obtain 20 mg/L orange red methyl orange solution.

Figure 5. Photocatalytic process of nano TiO_2/calcium alginate composite hydrogel

Photocatalysis process: add 20 g composite hydrogel beads (including 40 mg nano TiO_2) into a beaker containing 150 ml methyl orange solution, then place the beaker under the UV lamp (7W, 365 nm, light intensity 500 mw/cm^2), the UV lamp is about 10 cm away from the liquid surface, start stirring, 200 r/min, take samples every 20 minutes, and test the concentration of methyl orange solution.

2.4 Performance testing

Transmission electron microscope (TEM) and scanning electron microscope (SEM) were used to observe the morphology of the sample. The acceleration voltage of the scanning electron microscope (SU8020, Hitachi) was 15 KV. In order to prepare of the sample of scanning electron microscope, nano titanium dioxide was diluted with alcohol and dropped on the sample stage. After the diluted nano titanium dioxide was dry, gold was sprayed on the surface. Then the sample was ready for observation. In order to prepare the sample of the projection electron microscope sample, nanometer titanium dioxide was diluted with alcohol and dropped on the supporting carbon net. The sample was ready for observation after drying. The absorbance of the methyl orange solution (MO) solution at the maximum absorption wavelength of 465 nm was measured with an ultraviolet-visible absorption spectrometer (Lovibond, ET99731). The measurement was repeated for three times, and the average value was calculated. The degree of degradation of MO was described by $C_t/C_0(= A_t/A_0)$. The $C_t/C_0 - t$ curve was plotted.

3. Results and Discussion

It can be seen from the figure that the magnesium hydroxide used is flaky and uneven in size, with an average size of about 1 micron. Many small magnesium hydroxide tablets are adsorbed on the surface of large magnesium hydroxide particles. The size of these small magnesium hydroxide nano tablets is about 50 nm, and no impurities are found in magnesium hydroxide. It is feasible to use this kind of magnesium hydroxide as a porogen.

It can be seen from the figure that the nano titanium dioxide used has a small amount of agglomeration, but also monodisperse particles, which may be related to the sample preparation process.

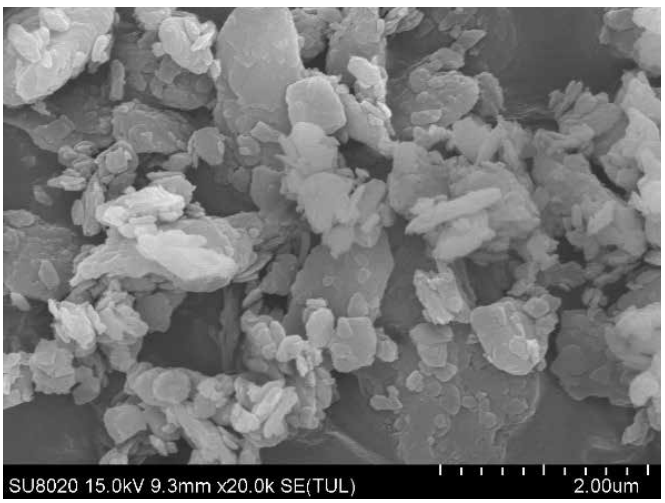

Figure 6. SEM of $Mg(OH)_2$

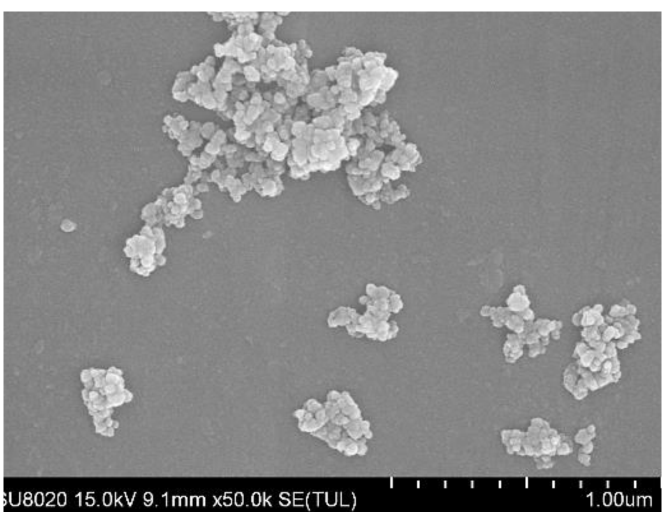

Figure 7. SEM of nano TiO_2

Nano titanium dioxide is a kind of spherical particles, and the size of a single particle is less than 50 nm. For further analysis, we observed the nano titanium dioxide by transmission electron microscope. It can be seen from the photo that the nano titanium dioxide is agglomerated, but does not grow together. The size of a single particle is about 20 nm. Most of the nano titanium dioxide are spherical like particles.

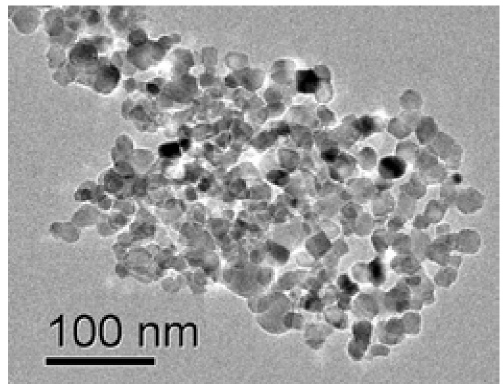

Figure 8. TEM of nano TiO_2

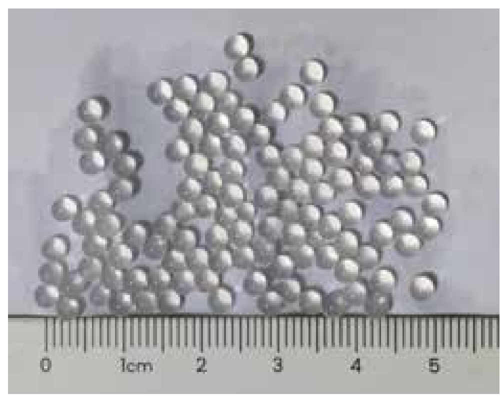

Figure 9. Photo of Calcium alginate hydrogel beads

Figure 10. Photo of $Mg(OH)_2$/ Calcium alginate hydrogel beads

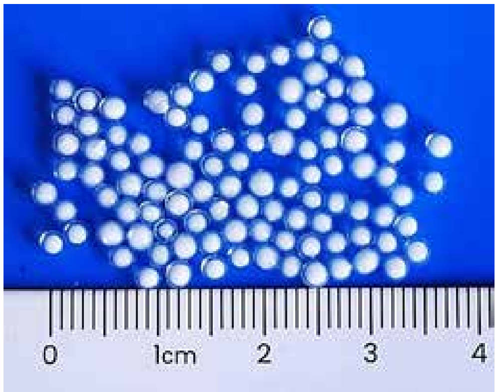

Figure 11. Photo of calcium alginate hydrogel beads after hydrochloric acid dissolves part of $Mg(OH)_2$

When sodium alginate solution is dropped into calcium chloride solution, the surface of the drop will solidify immediately, and after a few minutes, the whole ball will become an elastic and insoluble hydrogel.

It can be seen from the figure that the pure calcium alginate hydrogel is transparent, with a particle size of about 2.5mm and uniform size. The addition of magnesium hydroxide does not affect the formation of small spheres. The small spheres of magnesium hydroxide/calcium alginate hydrogel are white and opaque, with a particle size of about 2.5mm and uniform size. After the magnesium hydroxide/calcium alginate hydrogel beads are put into dilute hydrochloric acid, the surface of the beads will slowly become transparent, and the inside is still white, indicating that hydrochloric acid can dissolve the magnesium hydroxide in the hydrogel, forming a large number of cavities. About 10 minutes later, the whole beads will become transparent, indicating that the route we designed is feasible.

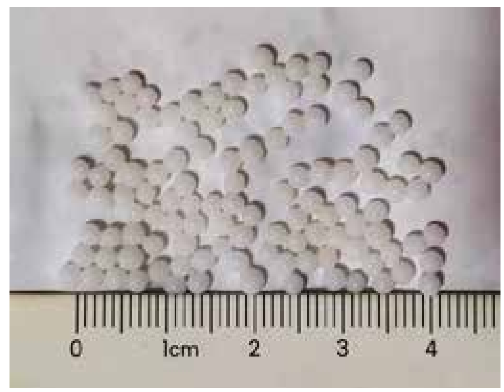

Figure 12. Photo of porous TiO_2/calcium alginate composite hydrogel beads

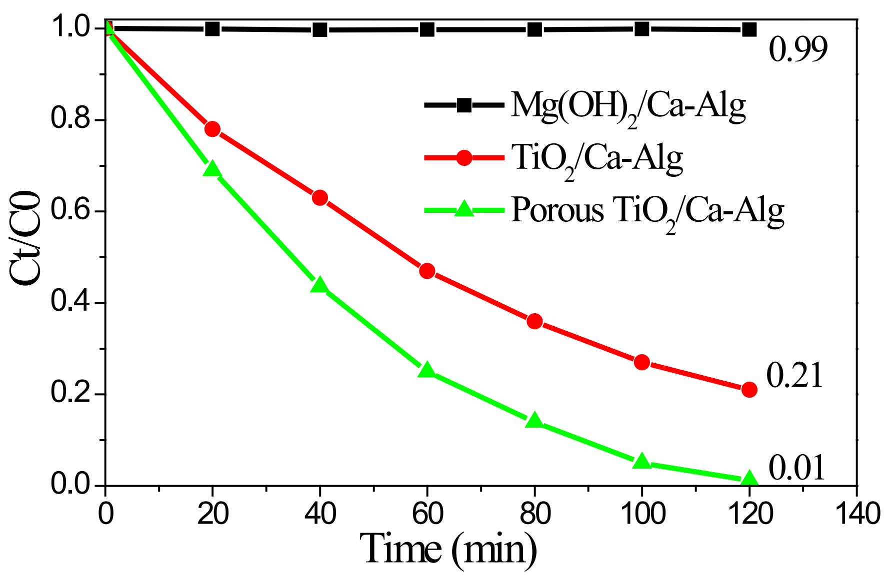

Figure 13. Concentration change curve of methyl orange photocatalyzed by composite hydrogel beads under UV light irradiation

It can be seen from the figure that the prepared porous titanium dioxide/calcium alginate composite hydrogel beads are white and translucent. It can be seen that during the dissolution of magnesium hydroxide by hydrochloric acid, the nano titanium dioxide cannot be dissolved and will not be cleaned out. Porous titanium dioxide/calcium alginate composite hydrogel spheres are uniform in size, about 2.5mm in size.

After the nano magnesium hydroxide is dissolved in hydrochloric acid, the whole sphere is relatively complete and elastic.

Under the irradiation of ultraviolet lamp, pure methyl orange solution does not degrade, and the concentration is almost unchanged. Magnesium hydroxide/hydrogel beads have no photocatalytic function, and the concentration of methyl orange solution is almost unchanged after 120 min ultraviolet irradiation. Titanium dioxide/calcium alginate composite hydrogel beads have photocatalytic function and can significantly catalyze the degradation of methyl orange. With the extension of irradiation time, the concentration of methyl orange solution continues to decline, but the decline rate of methyl orange solution is slower, indicating that the photocatalytic reaction is affected by the concentration of pollutants. The lower the concentration of pollutants, the slower the speed of pollutants entering and leaving the hydrogel, less pollutants are adsorbed on the surface of nano titanium dioxide per unit time, and less pollutants are photocatalytic degraded per unit time.

Shown from the Figure 13, the TiO_2/calcium alginate composite hydrogel beads degraded 79% of methyl orange after 120 min UV irradiation. The porous TiO_2/calcium alginate composite hydrogel beads, however, degraded 99% of methyl orange after the same time period, which showed higher photocatalytic activity and the rate of concentration of methyl orange solution decreased is faster. During the catalytic process, the color of methyl orange solution gradually became lighter until colorless. The results show that the porous structure is conducive to the entry and exit of pollutants into the composite hydrogel and improves the photocatalytic efficiency.

Figure 14. Color change of methyl orange catalyzed by porous composite hydrogel beads under UV irradiation

To sum up, through ingenious experimental design, we prepared titanium dioxide/calcium alginate composite hydrogel beads, which solved the problem of difficult recovery of nano titanium dioxide. Titanium dioxide/calcium alginate composite hydrogel beads with porous structure were prepared by dissolving magnesium hydroxide in hydrochloric acid, which further improved the photocatalytic performance of the composite hydrogel.

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