Applied Catalysis B: Environmental 217 (2017) 603–614

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

journal homepage: www.elsevier.com/locate/apcatb

Research paper

Adsorption and photocatalytic degradation of sulfamethoxazole by a novel composite hydrogel with visible light irradiation

Jianhua Yang[a,b], Zhengkui Li[a,b,*], Hongjie Zhu[a,b]

[a] State Key Laboratory of Pollutant Control and Resource Reuse, Nanjing 210023, China
[b] School of the Environment, Nanjing University, Nanjing 210023, China

ARTICLE INFO

Article history:
Received 2 April 2017
Received in revised form 6 June 2017
Accepted 10 June 2017
Available online 12 June 2017

Keywords:
Composite hydrogel
Sulfamethoxazole
Adsorption
Photocatalytic degradation
Visible light

ABSTRACT

A novel hydrogel catalyst (p(HEA/NMMA)-CuS) with the function of adsorption and degradation of organic pollutants in water was successfully synthesized using irradiation polymerization and in situ precipitation methods The composite hydrogel catalyst was characterized by SEM-EDS, TEM, swelling kinetics, zeta potential, TGA, XPS, FTIR and XRD. Besides, the effects and mechanisms of adsorption and degradation of sulfamethoxazole(SMX) as the representative pollutant by p(HEA/NMMA)-CuS hydrogel were observed. The results presented that adsorption process of SMX on complex hydrogel fit well to Langmuir monolayer adsorption, and followed a pseudo-second-order rate equation. The decomposition of SMX by p(HEA/NMMA)-CuS hydrogel in aqueous solution under 500 w visible light achieved balance in 24 h, the removal ratio reached 95.91%, and the SMX was mineralized with 43.56%. Hydroxyl radicals was detected as the reactive species using EPR in the system, degradation intermediates of SMX were further analyzed by LC-TOF-MSMS, a possible pathway for SMX degradation was presented. The degradation mechanism of SMX was also illustrated by theoretical calculations of frontier electron densities. Furthermore, mineralization, stability and regeneration results indicated that the developed hydrogel catalyst, p(HEA/NMMA)-CuS hydrogel, was promising in practical application.

1. Introduction

Sulfonamide antibiotics(SAs) are well-known aqueous micro pollutants for the difficult degradation, making human and environmental organisms produce resistance to drugs, prompting the continuous emerging of super bacteria [1,2]. Sulfamethoxazole (SMX) as one of the most widely detected SAs in the water resources, has been used as a model SAs in many studies due to its universality, persistence, and toxicity [3]. SMX exists as a cation (SMX^+), neutral molecule (SMX^0) and as an anion (SMX^-) in water, owing to the protonation of the aromatic amine (-NH_3^+-, $pK_a \approx 1.7$) and the dissociation of sulfonamide group (-SO_2NH-, $pK_a \approx 5.7$) [4]. Because of the spatial structure of SMX molecule has a bond angle of 60°, it is vital to know the message of the structure-affinity relationship for adsorption, guide how to design adsorbents and their applications. Therefore, advanced treatment and remediation of wastewater containing sulfonamide antibiotics are urgently needed.

To date, many treatments have been studied in order to remove the antibiotic like SMX in the environmental water, mainly contains physical [5], chemical [6] and biological methods [7]. Adsorption is considered as the convenient operation and green treatment method. Sun et al. [8] studied the sorption of SMX on biochar micropores and found it was mainly via van der Waals and π–π interactions. A high silica zeolite Y was developed by Braschi et al. [9] to the adsorption of SMX through the heterocycle NH of sulfamethoxazole in amide. As an absorbent, hydrogels have excellent properties in the adsorptive of a wide range of aqueous pollutants like heavy metals [10], toxic organics and nutrients [11]. To achieve desired adsorption capacity and selectivity, it is critical to choose more specific interaction sites to remove SMX. In addition, the surface structure of the hydrogel influences its functionality and selectivity, thus the selection of synthetic monomers is also important. There are limited investigations reporting the polymerization hydrogel of *N*-methyl maleic acid(NMMA) and 2-hydroxyethyl acrylate(HEA) with effective functional groups.

Nevertheless, adsorption methods can't reach a completely "eliminate" or "destroyed" [3]. The photocatalysis in chemical measures, because of its simple operation, high efficiency and other advantages of gradually becomes a research focus [12]. So far various photocatalysis were studied, including composite catalysts

* Corresponding author.
E-mail addresses: zhkuili@nju.edu.cn, doctli@163.com (Z. Li).

http://dx.doi.org/10.1016/j.apcatb.2017.06.029
0926-3373/

with carbon nanotubes [13], dyed sensitizers [14], noble metals or metal ions incorporation [15], transition metals [16] and non-metals doping [17]. Among these catalysts, metal semiconductor (TiO_2, ZnO, Fe_2O_3, CdS, CuS, GaP and ZnS et al) catalysts have shown a great potential as an efficient, sustainable treatment technology in the wastewater industry. TiO_2 has been proved to be one of the best photocatalysts [18], but TiO_2 has a large band gap and can't effectively use solar energy [19]. More and more researches on catalysts of visible light responsive had made great efforts, to utilizing solar energy for visible-light degradation of contaminants [20,21]. Some studies have indicated that copper sulfide(CuS) nanoparticles are more responsive to visible light than TiO_2 on the oxidation of organic micro pollutants, and better mineralization rate could be obtained [22,23]. Additionally, considering the methods of preparation and effects of catalyst, copper sulfide nanocrystal material has become one of the hot research topics at domestic and abroad [24]. However, the main technical bottlenecks that hinder its engineering application remained on the recovery and reuse of the catalyst particles [25].

To solve this problem, many materials were studied for catalysis immobilized owing to their structural stability and possible adsorption capacity, including activated carbon [26], mesoporous clays [27], fibers [28], agar [29], nano-silica [30] and polymeric sorbents [31], etc. Herein, the hydrogel as one of high molecular polymer, attracted more and more attentions to the development and application of novel hydrogels in water treatment [11,32]. Additionally, the metal-organic frameworks (MOFs) like photocatalysis based on polymers is being actively investigated [33], as the potential technology in visible light utilizing processes, they could provide an platform for catalytic centers to achieve solar energy conversion [34]. However, the synthesis of three-dimensional (3D) hydrogel structures with photocatalyst copper sulfide nanoparticles for the adsorption and photodegradation organics have been rarely reported. It may be available to synthesis the composite hydrogels of adsorption and photocatalytic properties, to provide a new way for the removal of SMX in wastewater.

Therefore, a novel three-dimensional hydrogel(p(HEA/NMMA)-CuS) with adsorption property and high visible-light catalytic activity was synthesized by ^{60}Co-γ radiation-induced copolymerization and in situ precipitation of copper sulfide. To be a clean and environmental material for the removal of SMX in the water. Moreover, the p(HEA/NMMA)-CuS hydrogel was characterized by scanning electron microscope- Energy Disperse Spectroscopy (SEM-EDS), transmission electron microscopy (TEM), swelling kinetics, zeta potential, X-ray diffraction (XRD), Fourier transform infrared spectra (FTIR), thermo-gravimetric analysis (TGA) and X-ray photoelectron spectroscopy (XPS). Additionally, the study focused specifically on, (i) the adsorption capacity and mechanism of SMX on the p(HEA/NMMA)-CuS hydrogel in water; (ii) the identification of degradation products and possible transformation pathways of SMX in the p(HEA/NMMA)-CuS hydrogel system, (iii) the theoretical and experimental investigation of SMX degradation mechanism under visible light in aqueous solution.

2. Experiment and methods

2.1. Chemicals

SMX ($C_{10}H_{11}N_3O_3S$, CAS NO. 723-46-6, purity 98%) and 2-hydroxyethyl acrylate(HEA) were purchased from Aladdin, USA. *N*-Methyl maleic acid(NMMA) was obtained from Tokyo Chemical Industry (Shanghai, China). All the other reagents used such as $Cu(NO_3)_2{\cdot}3H_2O$ and Na_2S, were all of analytical grade and acquired from Sinopharm Chemical Reagent (Shanghai, China). Methanol and formic acid were of chromatography grade and obtained from Merck (Darmstadt, Germany). The spin-trapping agent 5,5-dimethyl-pyrroline-N-oxide(DMPO) was supplied from Aladdin (Shanghai, China). Ultrapurewater (>18.2 MU cm) was prepared with a Milli-Q Plus system (Millipore, Bedford, USA), and applied all over the paper.

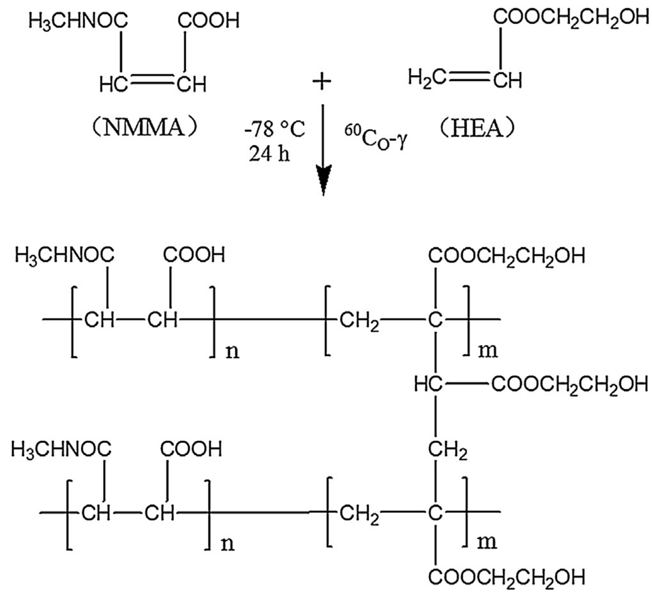

Fig. 1. Scheme for synthesis of p(HEA/NMMA) hydrogel.

2.2. Preparation of hydrogels

2.2.1. Preparation of p(HEA/NMMA) hydrogel

The p(HEA/NMMA) hydrogel was synthetized by the irradiation polymerization method. Fig. 1 presents a possible radiation reaction path of p(HEA/NMMA) hydrogel, in this process, primarily, the mixture of 2 −hydroxyethyl acrylate(HEA) and *N*-methyl maleic acid(NMMA) monomers was prepared with deionized water (v./v. = 3:7), and the molar ratio of monomers was fixed value of 9:1. After that the solution was put in shaker for mixed fully, a nitrogen atmosphere was kept in the process. ^{60}Co-γ radiation-induced copolymerization was employed for 24 h to reach a total dose of 20 kGy, the reaction was operated at −78 °C in dry ice-alcohol system. Finally, the obtained solid hydrogel was washed with deionized water until clean and cut into 5 × 5 × 5 mm dimension of small cubes, then were dried and ready to used.

2.2.2. Preparation of p(HEA/NMMA)-CuS hydrogel

The p(HEA/NMMA)-CuS hydrogel was prepared via loading copper sulfide catalyst on p(HEA/NMMA) hydrogel with in-situ precipitation method, and this in-situ precipitation method was conducted according to Sahiner [35]. Briefly, the dried p(HEA/NMMA) hydrogel cubes was mixed with 40 mM $Cu(NO_3)_2$ solution for 24 h to make sure the Cu(II) ions adsorbed onto p(HEA/NMMA) hydrogel, afterwards, p(HEA/NMMA)-Cu was transferred into 40 mM Na_2S solution for 12 h then washed and dried. The above procedures were carried out at the shaking bath speed of 150 r/min, and temperature of 25 ± 0.5 °C.

2.3. Characterization

SEM (Quanta 250 FEG, FEI, USA) and EDS (Aztec X-MAX^N 80, Oxford, UK) were used to observe the surface feature of p(HEA/NMMA) and p(HEA/NMMA)-CuS hydrogels. FTIR was performed on Bruker Vertex 70 v (Karlsruhe, Germany) in the range of 400–4000 cm^{-1}. TGA was carried out on Pyris 1 DSC (PerkinElmer,