International Journal of Biological Macromolecules 80 (2015) 520–528

Contents lists available at ScienceDirect

International Journal of Biological Macromolecules

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

Adsorptive removal of patulin from aqueous solution using thiourea modified chitosan resin

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ARTICLE INFO

Article history:
Received 1 June 2015
Received in revised form 29 June 2015
Accepted 12 July 2015
Available online 16 July 2015

Keywords:
Thiourea
Chitosan resin
Patulin
Adsorption
Kinetics
Isotherm

ABSTRACT

In the present paper, thiourea modified chitosan resin (TMCR) was firstly prepared through converting hydroxyl groups of chitosan resin into thiol groups, using glutaraldehyde as cross-linking agent and thiourea as modification agent. TMCR was characterized by FTIR, EDXS, SEM, XRD and AFM technologies. Batch adsorption experiments were performed to study the adsorption capacity of TMCR for patulin at different pH, temperature, contact time and patulin concentration. The result showed that TMCR was effective in removal of patulin from aqueous solution. The adsorption capacity of TMCR for patulin was 1.0 mg/g at pH 4.0, 25 °C for 24 h. Adsorption process could be well described by pseudo-first order model, Freundlich isotherm model and intraparticle diffusion model. It indicated that TMCR is expected to be a new material for patulin adsorption from aqueous solutions.

1. Introduction

Chitosan is a kind of linear biomacromolecules, which is produced commercially by deacetylation of chitin and composed of randomly distributed β-(1, 4) linked D-glucosamine and N-acetyl-D-glucosamine [1]. Owing to its biocompatibility and biodegradability, chitosan has been extensively used for a wide range of applications, such as agriculture [2], food [3], water filtration [4], cosmetics [5], biomedical [6], and manufacture [7]. The advantages of chitin are remained in chitosan and many activity amino groups are obtained by deacetylation [8]. The existence of amino and hydroxyl groups of chitosan can make it be chemically modified easily, meanwhile, greatly extends application areas of chitosan and its derivative [9]. In water processing, chitosan can also be used as a part of filtration process in order to remove suspended particles, phosphorus, heavy minerals, oils and other harmful ingredients [10]. Furthermore, chitosan can be prepared into chitosan resin, which have better mechanical performance and retrievability than that of chitosan powders [10]. Therefore, as a kind of good adsorption material, chitosan resin is often applied in the removal of harmful materials [11].

Nowadays, development of materials based on biopolymers especially chitosan in sorption process for removal of pollutants from wastewater has been considered by many researchers. The nanocomposite of thiacalix[4]arene functionalized chitosan (CS-g-TC4A nanogel and CS-g-TC4A super-paramagnetic nanocomposite) was synthesized to adsorb heavy metal [12]. Superparamagnetic nanocomposite and nanogel as effective nanosorbents based on SA were synthesized [13]. The nanocomposite demonstrated higher affinity for the selected metal ions. Pandi et al. [14] synthesized carboxylated alginic acid (CAA) and metal ions coordinated CAA (M-CAA) for defluoridation studies. The developed M-CAA materials are low cost, eco-friendly, biodegradable and biocompatible sorbents for selective fluoride removal. The chitosan resin was usually chemically modified by chemical reagents such as tetraethylenepentamine (TEPA), thiourea and sulphur compounds to produce amine, sulphonic bearing chitosan [15–17]. Ionic composites based on cross-linked chitosan (CS) as matrix and poly(amidoxime) grafted on potato starch (AOX) as entrapped chelating resin and facile fabrication of magnetic chitosan beads were prepared to adsorb copper, which exhibits considerable potential in environmental remediation [18,19]. In our previous work, chitosan resin was synthesized to remove patulin from aqueous solution, however, the adsorption capacity was low, therefore, it should be modified by chemical method [20].

Patulin (see Fig. 1) is a water-soluble secondary fungal metabolite, produced by a variety of molds mainly by *aspergillus* and

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http://dx.doi.org/10.1016/j.ijbiomac.2015.07.015
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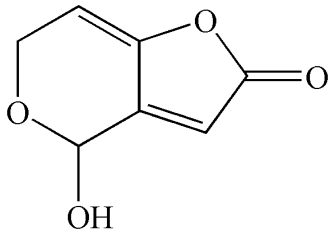
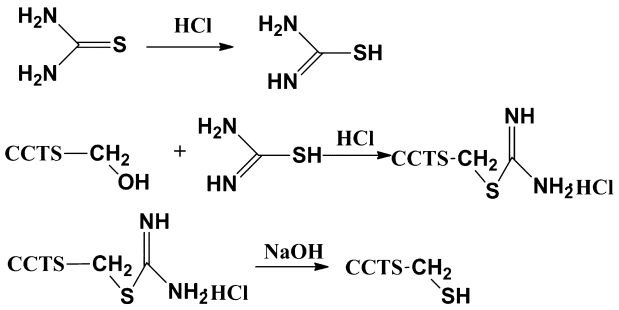


Fig. 1. Chemical structure of patulin.

penicillium [21]. It has been most commonly found in rotting grains, fruits, and vegetables, especially in apples and apple products such as juices, jams, and ciders [22]. Frequently, patulin has been found in many fruits such as cherries, blueberries, plums, kiwifruit, pears, bananas, apricots, peaches, strawberries, and grapes etc [23,24]. Although the harm of patulin to human health has remained inconclusive, a number of animals and cells studies have suggested that patulin could cause teratogenic effects [25], carcinogenic effects [26], reproductive toxicity [27] and genotoxicity [28]. In general, the amount of patulin in apple products is viewed as a measure of quality standard. Patulin contaminations within foods have been a worldwide problem, many survey reports on the presence of mycotoxin, patulin, were conducted all over the world [29–32]. The World Health Organization has recommended that the maximum concentration of patulin in apple juice is 50 μg/L [33]. In the European Union, the limit is set to 50 μg/kg in both apple juice and cider, and to half of that concentration, 25 μg/kg, in solid apple products and 10 μg/kg in products for infants and young children [34].

Control methods of patulin including mainly two phases: preproduction phase and postproduction phase [35–38]. In the first phase, patulin contaminations occur largely during the preharvest, harvest, processing, and storage process. The most effective measures were to prevent decay and remove rot part, but it was infeasible in practical production. Hence, mainly methods for preventing mycotoxin contamination of foods including good manufacturing practices and quality assurance efforts were made [39–41], but the problem remained unsolved. In the second phase, it mostly includes four sections as follows: filtering and adsorption, chemical decontamination, biological control and electromagnetic irradiation. Chemical decontamination has also been shown to be effective and is likely to be the most easily suitable way in industry. Numerous chemical treatments such as ammonia, sulfur dioxide, glutathione, cysteine, thioglycolate, organic acids and vitamins, and ozone, have been utilized to detoxify patulin [42]. The basic theories of detoxify are designed to oxidize patulin into less toxic compounds and bind up patulin into less toxic thiol-based adducts. The method of biological control with yeast is limited to products that can be fermented [43]. Furthermore, yeasts are sensitive to patulin, and it has been shown to be completely inhibited, preventing fermentive detoxification at the concentrations of 200 g/mL [44]. The studies of reducing the content of patulin by electromagnetic radiation are just starting [45]. The most simple and feasible method is filtration and adsorption, a number of studies have been devoted to remove patulin from juice using adsorption materials [46]. The removal of natural toxins from aqueous solutions has always been a complex problem. Many studies have shown that patulin reacts readily with —SH groups and more slowly with —NH_2 groups [47–49].

The aim of this work was to synthesize a new sulfur material for removal of patulin from aqueous solution. Chitosan resin was modified by grafting thiourea onto TMCR. It was characterized by Fourier Transform Infrared Spectroscopy (FTIR) and Energy Dispersive X-ray Spectroscopy (EDXS). Various effecting parameters including pH, temperature, contact time and initial concentration on the adsorption capacity of TMCR were evaluated. The experimental data were fitted with adsorption isotherms and kinetics models.



Scheme 1. Proposed reaction mechanism for preparing thiourea modified chitosan resin.

2. Materials and methods

2.1. Materials

Chitosan (CS) was supplied by Shandong Hecreat Marine Biotech Co. Ltd., (Qingdao, China) with a degree of deacetylation of 94.5% and average molecular weight of 550 kDa. Absolute ethyl alcohol, thiourea, hydrochloric acid, sodium hydroxide, ethylacetate, acetone were of analytical grade or better and used as received without further purification. The patulin standard solution was purchased from Sigma–Aldrich Co. Ltd. Chitosan resin was prepared by method of inverse suspension crosslinking. Ultrapure water (Millipore, Billeriac, MA) was used to prepare all of aqueous solutions.

2.2. Preparation of TMCR

The chitosan resin was prepared using the inverse phase emulsion dispersion method [50], and then modified with thiourea. TMCR was prepared as follows: 10 g thiourea was dissolved into 200 mL hydrochloric acid solution (1:3) and mixed until thiourea agent dissolved completely, and 10 g chitosan resin was added into this solution, shaking at room temperature for 24 h. After that, the resin was collected by leaching and washed with ultrapure water, and then added into NaOH aqueous solution at pH 10–12, shaking at room temperature for 6 h (Scheme 1). Finally, it was collected by leaching and washed with acetone, absolute ethyl alcohol and ultrapure water in sequence to remove excess agents. The product was dried and stored at room temperature.

2.3. Characterization of TMCR

The FTIR spectra of chitosan resin and TMCR were recorded using Nexus 470 FTIR Spectrometer. Chitosan resin and TMCR were ground into powder separately. For each type of samples, 1 mg of the powder was mixed with 100 mg of spectroscopy grade KBr in an agate mortar and pressed into a tablet under high pressure. The spectra of the tablets were scanned within the spectral range of 400–4000 cm^{-1} at the resolution of 4 cm^{-1}. The results were used to confirm the functional groups present [51].

The EDXS spectra of chitosan resin and TMCR were recorded using EMAX energy dispersive X-ray spectrometer. The energy dispersive X-ray spectrometer was used to quantitative analysis of the elements. The results were used to confirm the elemental composition of TMCR. Microscopic observation of dried TMCR was carried out by using a scanning electron microscope (S-4800, Hitachi Ins).

The crystalline phase of chitosan, chitosan resin and TMCR was examined by XRD analysis. Powdered XRD patterns were