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Patulin removal from apple juice using a novel cysteine-functionalized metal-organic framework adsorbent

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Folin-Ciocalteu reagent (PubChem CID: 6342)
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ABSTRACT

Patulin (PAT) is one of the most common toxic contaminants of apple juice, which causes severe food safety issues throughout the apple industry. In order to remove PAT efficiently, a metal-organic framework-based adsorbent (UiO-66(NH_2)@Au-Cys) was successfully synthesized and used for PAT removal from juice-pH simulation solution and real apple juice. Batch adsorption experiments were systematically performed to study the adsorption behavior for PAT. The results showed that adsorption process could be well described by the Pseudo-second order model and Freundlich isotherm model. The maximum adsorption capacity (4.38 μg/mg) was 10 times higher than the microbe-based biosorbents. Thermodynamic investigation demonstrated that adsorption process was spontaneous and endothermic. Furthermore, no marked cytotoxicity on NIH 3T3 cell lines was observed when the concentration of the adsorbent was lower than 10 μg/mL. Therefore, UiO-66(NH_2)@Au-Cys is a potential adsorbent for PAT removal from apple juice with little quality changes.

1. Introduction

Patulin (PAT, $C_7H_6O_4$) is a type of water soluble mycotoxin that has been frequently found in numerous fruits and vegetables. Apples are susceptible to be infected by fungus and always serve as a suitable medium for PAT production during the harvest, storage and even processing. Moreover, PAT also existed in apple derivative products ranging from non-fermented apple juice to apple purees, which was ascribed to the wake effect of the most types of food processing on the overall stability of PAT (Beltrán, Ibáñez, Sancho, & Hernández, 2014; Sanzani, Reverberi, Punelli, Ippolito, & Fanelli, 2012; Tannous et al., 2017). Due to the detrimental effects on humans, such as edema, diarrhea and intestinal inflammation (Boussabbeh et al., 2015; Puel, Galtier, & Oswald, 2010), the concentration of PAT was considered as a crucial quality standard of apple juice productions, for which the majority of regulatory agencies had placed caps on PAT concentration at the level of 50 μg/kg in apple juice (U.S. Food and Drug Administration, 2013). Additionally, with the remarkable increasing of the apple juice consumption throughout the world, PAT contamination in apple juice not only caused widespread worries about food safety but also resulted in enormous financial losses (Peng et al., 2016). Therefore, it is necessary to remove PAT from apple juice to meet the increasingly

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stringent food quality standards and food safety requirements.

There were various physical and chemical approaches developed to solve the problem of PAT contamination in apple juice, such as radio-degradation, sulfur dioxide treatment and oxidation with ammonia or potassium permanganate (Moake, Padilla-Zakour, & Worobo, 2005; Yun et al., 2008). Among the reported methods, adsorption was considered as one of the most effective processes to remove PAT (Qiu, et al., 2018). On this account, developing an efficient and reliable adsorbent has been considered as an active demand. To date, various adsorbents, such as activated carbon, alginate gel (Yue et al., 2013), cyclodetrin-based polymer (Appell & Jackson, 2010), propylthiol functionalized SBA-15 silica (Appell, Jackson, & Dombrink-Kurtzman, 2011), chitosan-based materials (Li, Wang, Meng, & Liu, 2015; Liu et al., 2015; Luo, Zhou, & Yue, 2017; Peng et al., 2016) and some microorganisms including yeast and lactic acid bacteria (Luo, Wang, Yuan, Zhou, & Yue, 2016; Wang et al., 2015), had been reported to considerably decrease PAT levels in contaminated apple juice and other liquids. However, these adsorbents did not satisfy the requirements for apple juice industry since their negative effects on juice quality such as clarity, brix and pH. Moreover, a tedious and complex adsorption process was needed for the application of the reported adsorbents, such as multi-step preparation of adsorbent and requirement of long adsorption time (at least 10 h). Therefore, it is urgent to exploit a new adsorbent with enhanced absorption capacity and high efficiency for PAT removal without deteriorating the quality of the products.

Metal-organic frameworks (MOFs) as a kind of novel adsorbent had attracted tremendous research interests because of their fascinating properties, such as high internal surface area and wide turnable composition (Wang et al., 2017; Yang, Wang, Chen et al., 2018). Zirconium-based MOFs gained additional attention due to the stability toward moisture and acids (Cavka et al., 2008; Peterson, Mahle, DeCoste, Gordon, & Rossin, 2016; Yang, Wang, Wang et al., 2018). Given the attractive features of the zirconium-based MOF materials, UiO-66(NH_2) was chosen as the adsorbent for PAT removal. However, the lack of binding sites for the target toxin was the great obstacle for the utilization of UiO-66(NH_2). Thus we hypothesized that the chemical modification for UiO-66(NH_2) could improve the adsorption efficiency for PAT removal.

In this work, a cysteine-functionalized UiO-66(NH_2)-based adsorbent (UiO-66(NH_2)@Au-Cys) was successfully synthesized and used to efficiently remove PAT from apple juice via its abundant active sites including amine, hydroxyl and carboxyl that were obtained from Cys. Parameters (such as pH, temperature and adsorption time) influencing the adsorption capacity of UiO-66(NH_2)@Au-Cys were optimized. Moreover, kinetic, isotherm and thermodynamic study were also performed to illustrate the characteristics of UiO-66(NH_2)@Au-Cys during the PAT adsorption process. Furthermore, the cytotoxicity and PAT removal capacity of the proposed adsorbent in apple juice were also evaluated. Variation of brix, titratable acidity, clarity, total phenol and vitamin C content were measured to evaluate the influence of UiO-66(NH_2)@Au-Cys on the quality of apple juice during PAT adsorption process.

2. Materials and methods

2.1. Chemicals

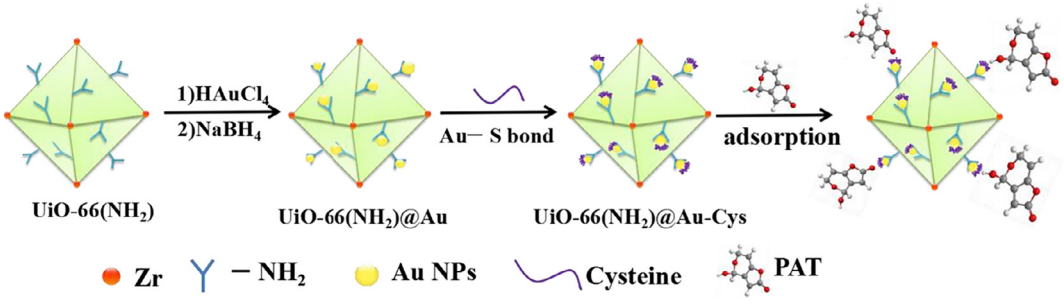
Zirconium chloride ($ZrCl_4$), 2-amino terephthalic acid (H_2BDC-NH_2), sodium borohydride ($NaBH_4$), N,N′-dimethylformamide (DMF), standard patulin, vitamin C powder, 2,6-dichloroindophenol sodium salt, methyl thiazol tetrazolium bromide (MTT) and dimethylsulfoxide (DMSO) were purchased from Aladdin Chemical Reagent Co., Ltd, China. In addition, Dulbecco's Modified Eagle Medium (DMEM) and chloroauric acid ($HAuCl_4{\cdot}3H_2O$) were purchased from Sigma-Aldrich. All other chemicals used in the experiment were obtained from the local chemical reagent company. All of the above chemicals were at least analytical grade. The mobile phase (acetonitrile) of chromatographic analysis was HPLC-grade. Ultrapure water produced by Milli-Q element (18.2 X, Millipore, Massachusetts) was used to prepare all of the solutions.

2.2. Synthesis of UiO-66(NH_2)@Au-Cys adsorbent

UiO-66(NH_2) was synthesized according to Wang's method (Wang et al., 2017). In brief, 10.49 mg $ZrCl_4$, 8.15 mg H_2BDC-NH_2 and 1.2 mL acetic acid were mixed in 10 mL DMF solution to form a homogeneous solution by bath sonication. Afterwards, the mixture was sealed in a Teflon-lined autoclave and heated at 120 °C for 24 h in an oven. Before vacuum drying at 90 °C, the white products of UiO-66(NH_2) nanoparticles were collected by centrifuging (10,000 rpm, 5 min) and washed with methanol/DMF solution (v/v = 1:4) for three times. Highly dispersed Au nanoparticles were immobilized on UiO-66(NH_2) via reduction method described as follows: (1) 200 mg UiO-66(NH_2) was dispersed in 40 mL 0.025 M $HAuCl_4{\cdot}3H_2O$ solution containing water/methanol (1:1, v/v); (2) the mixture was continuously stirred in an ice bath for 1 h to accelerate the electrostatic interaction between NH_4^+ of UiO-66(NH_2) and $[AuCl_4]^-$; (3) $NaBH_4$ solution (10 mL, 0.05 M) was added and kept in an ice bath for 0.5 h to reduce the $[AuCl_4]^-$ into Au nanoparticle (Scheme 1); (4) the red products of UiO-66(NH_2)@Au were washed with methanol (10,000 rpm, 5 min) for three times. Finally, the UiO-66(NH_2)@Au was resuspended in 0.2 M Cys solution and stirred at room temperature for 24 h to obtain the UiO-66(NH_2)@Au-Cys nanocomposites (Ma et al., 2017).

2.3. Characterization

The morphologies of the obtained nanoparticles were characterized with S-4800 scanning electron microscopes (SEM, Hitachi, Tokyo, Japan). The X-ray diffraction (XRD) patterns of nanoparticles were obtained by a Bruker D8 Advanced Diffractometer System (Bruker AXS, Germany), which equipped with Cu Ka radiation source at an operating voltage of 40 kV. Fourier-transform infrared (FT-IR) spectra were collected by a Vetex70 (BRUKER Corp., Germany) equipped with a KBr beam splitter.



Scheme 1. Schematic representation of the UiO-66(NH_2)@Au-Cys and the PAT adsorption.