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Effective adsorption and concentration of carnosine by nickel species within mesoporous silica

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ABSTRACT

Carnosine (Car) abundantly exists in meat-derived wastes and has various functions with attractive application as food supplement. Therefore, it is of vital importance to recover Car from the low-value food stuff. Herein, carboxyl group functionalized mesoporous silica of SBA-15 was synthesized to facilely incorporating NiO, ZnO and CoO for Car extraction. Among these, Ni/SBA-15 has the highest adsorption capability. The correlation between the most significant parameters was optimized, and the effects of these parameters on the adsorption efficiency of Car were investigated. Due to the adequate pore size and high Ni loading, the adsorption capacity of Car approached as high as 0.839 mmol/g. The excellent adsorption characteristics of the current adsorbents toward Car were preserved in a commonly used pH window and could be hardly infected by the background salts. The pseudo-second-order rate equation effectively described the uptake kinetics. The Langmuir model exhibited a better fit to adsorption isotherm than the Freundlich model. Therefore, nickel species within functionalized SBA-15 is a kind of efficient materials for recovering histidine-containing peptides from egg-laying hens and makes it a favorable candidate as chromatographic column materials for histidine-containing dipeptides analysis.

1. Introduction

Carnosine (Car, β-alanyl-L-histidine), a naturally occurring histidine-containing dipeptide (HCDPs), is an attractive material for food supplement and medicinal product. It acts as cytosolic buffering agents, antioxidants, free radical scavengers, as well as neurotransmitter (Bellia, Vecchio, Cuzzocrea, Calabrese, & Rizzarelli, 2011; Boldyrev, Aldini, & Derave, 2013; Guiotto, Calderan, Ruzza, & Borin, 2005; Sale et al., 2013). In addition, it demonstrates treatment of Alzheimer's disease (Herculano et al., 2013), acute spinal cord injury (Di Paola et al., 2011), metabolic syndrome (Song, Joo, Aldini, & Yeum, 2014) and cancer (Gaunitz & Hipkiss, 2012). Car exists in meat products (Lukton & Olcott, 1958), and meat-derived extracts and wastes (James, Gutzke, & Feruguson, 1995) which could be used for cheap recovery of Car. Beyond that, non-histidine peptides in theses food resource could seriously impact on extraction of Car. Thus, it is of vital importance to recover Car from the low-value food stuff.

To date, many strategies have been reported on the efficient separation of Car from a mixture of amino acids and salts such as membrane (Centenaro et al., 2014; Maikhunthod & Intarapichet, 2005), ion exchange techniques (Nabetani et al., 2012) and immobilized metal affinity chromatography (IMAC) (Oshima, Kanemaru, Tachiyama, Ohe, & Baba, 2008; Oshima, Tachiyama, Kanemaru, Ohe, & Baba, 2009). Among these, IMAC is a selective separation tool for biomolecules, due to differences in the affinities between immobilized metal ions and functional groups of biomolecules. Histidine residue shows the strongest affinity for the transition metal on the basis of the principles of hard and soft acids and bases (HSAB) (Pearson & Songstad, 1967). Hence, Ni, Co and Zn are useful

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for the selective recovery of His-tagged proteins over native proteins (Clemmitt & Chase, 2000; Feczkó et al., 2008; Lee et al., 2006). In particular, Ni exhibits its unique physical and chemical properties for a wide range of applications, including biomolecule immobilization or separation, biosensors, targeted drug delivery, biocatalysis and so on (Ling et al., 2014; Wahab & Darain, 2014). While, on account of high cost, the application of IMAC in food industry is restricted. Therefore, it is of significance to solve these problems by developing new adsorbents immobilized metal which have high adsorption capacities and low cost.

Since Zhao et al. (Zhao et al., 1998) extended the family of highly ordered mesoporous silicates by synthesizing Santa Barbara Amorphous (SBA) type materials, SBA-15 has received substantial attention. Owing to its large surface area, narrow pore size distribution, and superior pore structure (Ling et al., 2014), SBA-15 has proved to be excellent solid supports for catalysts (Karimi & Vafaeezadeh, 2012), chemosensor (Prathap, Kaur, & Srivastava, 2012), adsorption (Katiyar, Ji, Smirniotis, & Pinto, 2005) and protein and peptides separation (Yiu, Botting, Botting, & Wright, 2001).

Toward this direction, mesoporous silica SBA-15 spheres partially functionalized with transfer metals, have been used for separation of protein molecules from a mixture solution, especially Ni. For example, Wahab & Darain, 2014 reported a pure mesoporous NiO materials to immobilized streptavidin protein (with hexa-histidine tag). Besides, Ling et al., 2014 designed a NiO nanoparticle decorated mesoporous silica to immobilized site-directed enzyme. However, a pure SBA-15 material without modification cannot effectively bind Ni(II) ions in the pore structure. In this study, in order to improving the Ni loading, we report a simple wet impregnation method to obtain Ni and other transition metal ions nanoparticles in mesoporous silica SBA-15 functionalized with carboxylic acid groups (Chen et al., 2013). The structural characteristics, adsorption properties of the Ni/SBA-15 including kinetic, isotherm, and elution selection towards Car, as the typical example of HCPs, were described and discussed in detail.

2. Material and methods

2.1. Synthesis of metal nanoparticles in mesoporous silica SBA-15 functionalized with carboxylic acid groups

The SBA-15 with tunable particle sizes and carboxylic functionalized SBA-15, were prepared according to the literature with slight modification (Chen, Chen, Chen, & Kao, 2011; Tsai et al., 2009). Briefly, the triblock copolymer Pluronic P123 (Sigma-Aldrich, USA) was dissolved in 1.9 mol/L HCl. Premixed tetraethoxysilane (TEOS, Sinopharm Chemical Reagent, China) and carboxyethylsilanetriol (CES, 25 wt%, Molebase, China) in water were added dropwise to the solution with vigorous stirring for 20 h at 40 °C. The composition of the reaction mixture was 0.2 CES: 0.8 TEOS: 0.0168 P123: 5.85 HCl: 162.68 H_2O. The milky reaction mixture was subsequently hydrothermally treated at 80 °C for 24 h. The resultant precipitate was filtered, washed and dried. Template removal was accomplished by suspending 1 g synthesized material in 300 mL HCl-ethanol mixture at 78 °C for 24 h. The product was washed, and finally dried at 80 °C.

The Ni/SBA-15 was prepared by impregnating SBA-15 that contained carboxylic acid groups with 20 mL of an aqueous solution of $Ni(NO_3)_2 \cdot 6H_2O$ (20, 50, and 100 mmol/L, respectively) at pH 8. After 20 h, the mixture was filtered and dried 80 °C for 12 h. Then the materials were calcined at 300 °C for 5 h. Zn/SBA-15 and Co/SBA-15 were prepared in similar manner using $Zn(NO_3)_2 \cdot 6H_2O$, and $Co(NO_3)_2 \cdot 6H_2O$, respectively.

2.2. Characterization of Ni/SBA-15

N_2 adsorption-desorption isotherms were collected with a Quantachrome NOVA 4200E porosimeter at −196 °C. All the samples were degassed under vacuum for 12 h before measurements. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface areas using adsorption data in a relative pressure range from 0.2 to 0.4. The pore volumes and average pore size were derived from the adsorption branches of isotherms by using the Barrett-Joyner-Halenda (BJH) model, and the total pore volumes were estimated from the adsorbed amount at a relative pressure P/P_0 of 0.99. The Ni loading was determined by the ICP-OES analysis (Vanan 710).

2.3. Adsorption experiments

An aqueous solution of Car with different concentration (0.2–4 mmol/L) was prepared in deionized water. The Car concentrations were determined on High-pressure liquid chromatography (Series 1200, Agilent, USA). The measurement of carnosine concentration was conducted as described by Dunnett & Harris, 1997) with slight modifications. The OPA-derivatized carnosine was separated using a binary gradient formed solvent A [12.5 mmol/L sodium acetate, pH 7.2-tetrahydrofuran (995:5, v/v)] and solvent B [methanol-acetonitrile (700:300, v/v)]. The gradient composition was: 0 min, 40% solvent B; 15 min, 60% solvent B; 20 min, 100% solvent B; 30 min 100% solvent B. The flow-rate was 1.0 ml/min and analysis time was 40 min per sample. The ultraviolet detector wavelengths was 338 nm. Before adsorption, the functionalized SBA-15 was dried at 80 °C for 12 h and kept in a desiccator.

To study the adsorption capacities at different pH, we adjusted the pH of the Car solutions by adding negligible volumes of 0.1 mol/L HCl or 0.1 mol/L NaOH aqueous solutions. To study the interference effect of the salt on the adsorption of Car, different kinds of salt (NaCl, KCl, Na_2SO_4, $CaCl_2$ and $MgSO_4$) with different concentrations were added into the adsorption solutions under the same condition as the above adsorption experiments.

The adsorption kinetic studies were conducted at pH 7 in 50 mL of aqueous Car solutions with an initial concentration of 2 mmol/L at 20 °C, and the contents of adsorbents was 0.5, 1.0 and 2.0 g/L, respectively. The mixture of Car and the adsorbents was shaken in a thermostated shaker (200 rpm) and measured at the time range from 0 min to 400 min. After adsorption for a predetermined time, the mixture was centrifuged and the Car concentrations in the supernatants were determined by HPLC. Batch adsorption experiments of Car onto functioned SBA-15 were performed at different temperatures (20, 30 and 40 °C) at pH 7 for 300 min. The amounts of adsorbed Car was measured from the difference between the initial (C_0) and equilibrium (C_e) concentrations in the supernatant after centrifugation. The equilibrium uptake was calculated by eq. 1

$$q_e = (C_0 - C_e)\frac{V}{W} \quad (1)$$

Where q_e (mmol/g) is equilibrium adsorption capacity of Car on Ni/SBA-15. V presents the volume of the used Car solution (L), and W is the weight of the used adsorbents (g).

2.4. Elution experiments

Elution experiments of Car from Ni/SBA-15 materials as eluents (imidazole, citric acid, sodium citrate and acetic acid) were tested as follows: Adsorption of Car on Ni/SBA-15 was examined in a same way that described in the above section. After shaking at 20 °C for