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Adsorption of BSA onto hexagonal mesoporous silicate loaded by APTES and tannin: Isotherm, thermodynamic and kinetic studies

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ABSTRACT

In the present study, hexagonal mesoporous silica (HMS) was synthesized and modified by tannic acid as a natural poly-phenol and amine (TA-A-HMS) and was applied for the adsorption of bovine serum albumin (BSA) from aqueous media. To investigate the structure of HMS and TA-A-HMS, SEM, TEM, XRD, BET and FTIR analysis were applied. The effects of pH, adsorbent dosage, contact time and temperature on the BSA adsorption were studied. After modification, BET surface area of HMS was reduced from 885 m²/g to 51 m²/g which confirms the presence of tannin and amine groups that inhibit the adsorption of nitrogen molecules. According to the results of equilibrium data, it is shown that Langmuir isotherm with maximum adsorption capacity of 1000 mg/g is the predominant model and adsorption is mono-layer. Kinetic and thermodynamic studies also reveal that adsorption kinetic followed by pseudo-second order model and the adsorption process is exothermic.

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1. Introduction

With the growth of biotechnology and propagation of its applications in various fields such as food processing, biosensors, pharmaceutical and drug delivery, artificial organs and tissues and purification of proteins, protein adsorption have been emerged as an influenced knowledge and very important field of research. Development of a facile and easy technique for fabrication of various types of adsorbent with potential of application in the adsorption of highly abundant proteins (HAP) from a biological sample is so crucial [1]. The protein adsorption interferes in many related sciences like biotechnology, biomedical and environmental engineering and so on [2]. BSA plays an important role in the physiological operations, for example preserving the osmotic pressure and pH of blood and transfer of some compounds containing fatty acids, metal, amino acids, steroids and drugs [3,4].

Mesoporous silicate such as hexagonal mesoporous silicate (HMS) can be synthesized by sol-gel or hydrothermal methods. Ease of the synthesize and surface modification, high specific surface area, well ordered pore sizes, nontoxic effects and chemical stability of these nanomaterials are the reason for the world wide applications of mesoporous silicates in biological field such as drug

delivery systems, transfect ion devices, adsorbents and carriers of drugs and regenerative medicines [5]. Protein covers the surface of nano-materials by a dense layer when are injected in blood flow. So, nano-materials like mesoporous silicates seem to be the promising adsorbents for the adsorption of proteins [6]. For protein adsorption process, mesoporous silicates should have large mesopore sizes for easy access of proteins to the internal surface areas [7–9] or the surface of mesoporous silicate should be modified by some functional groups to interact with bioactive species such as proteins [10,11]. Small sized SBA-15 rods with pore size of 8.3 nm was synthesized by Yang et al. [12] and its adsorption capacity for the adsorption of large protein molecules such as bovine serum albumin and lysozyme was compared with traditional SBA-15 having relatively larger particle sizes and MCM-41 with smaller pore sizes of 2 nm. The findings show that the large pore size is very important for effective adsorption of large protein molecules.

Surface modification of mesoporous silicate SBA-15 with different functional groups such as amino, thiol, chloride and carboxylic acid also has been applied for improvement the adsorption capacity [13]. Sulfonic acid-functionalized SBA-15 (SBA-15-SO₃H) was synthesized by Xiaoyan Liu et al. [14] for the adsorption of proteins (BSA and cytochrome) and polypeptides (insulin and glucagon). Under optimum state, the maximum adsorption capacity of SBA-15-SO₃H for insulin and glucagon was 430 and 1303 mg/g, respectively. So, functionalized SBA-15 can be applied as an efficient

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adsorbent for immobilization of biomolecules. Today, natural and waste materials are considered as useful sources of low-cost adsorbents for the adsorption of different adsorbates. Waste sugar beet pulp [15], degreased coffee bean [16], garlic peel [17], pumpkin seed hull [18], beech wood sawdust [19], biomass fly ash [20], olive pomace [21], orange peel activated carbon [22], potato plant wastes [23], and cotton plant wastes [24] are some natural adsorbents which have been applied by researchers for different aims. Tannin is a natural growing plant contains high content of multiple phenolic hydroxyls. Tannin is a non-toxic and biodegradable material, so its application in biological medium is considerable. In the research was investigated by Meral Yurtsever and Ayhan Sengil [25] adsorption of Pb (II) on modified quebracho tannin resin (QTR) was studied. Whereas tannin is water-soluble, so water-insoluble supports like agarose, cellulose, silicates and collagen fiber are used for immobilization of tannin [26,27]. Preparation of tannin-immobilized mesoporous silica (BT-SiO₂) was also investigated by Xin Huang and co-workers to remove chromium cations from aqueous media [28]. Up to now, no studies have been reported in the literature about the application of HMS and tannin for the adsorption of BSA from aqueous media. To the best of our knowledge and surveying of the literatures, tannin has not been used for the adsorption of proteins from biological media. In the present study, HMS based adsorbent functionalized by tannic acid and APTES (TA-A-HMS) was synthesized. Characteristics of the synthesized adsorbent were analyzed by SEM, TEM, FTIR, XRD and BET techniques. The performance of TA-A-HMS for the adsorption of BSA from aqueous media was studied. The effect of pH, adsorbent dosage, BSA concentration, contact time and temperature were investigated. To understand the mechanism of BSA adsorption onto the tannin modified HMS, equilibrium isotherms, kinetics and thermodynamics data were evaluated.

2. Experimental

2.1. Chemicals

All chemicals were used in this research containing tetraethylorthosilicate (TEOS), dodecylamine, ethanol (99.8%), hydrochloric acid, dodecylamine (C₁₂H₂₅NH₂), 3-Aminopropyltriethoxysilane, tannic acid, glutaraldehyde, acetone, NaOH for the adjustment of pH, deionized water, Bradford reagent (Coomassie Brilliant Blue G-250 dye, ortho-phosphoric acid (85%)), filter paper Whatman and bovine serum albumin (BSA) were purchased from Merck, Germany.

2.2. Synthesis of hexagonal mesoporous silicate (HMS)

Hexagonal mesoporous silica (HMS) was prepared briefly as follows: 30 g of tetraethylorthosilicate and 42 g of ethanol were mixed in room temperature for 30 min. Then, 2.8 mL of HCl (1M), 7 g of 2-decylamine as a surfactant and 92 mL distilled water were mixed for 6 h to obtain a gel-like solution. After that, the gel mixture was kept in room condition for 18 h [29]. The resulting gel was filtered and washed several times with distilled water and dried in an oven at 100 °C for 6 h. Finally, the prepared silicate powder was calcinated at 500 °C for 6 h.

2.3. Preparation of amine functionalized HMS

To synthesize the aminated HMS, 2.50 g of HMS and 10 mL of 3-aminopropyltriethoxysilane (APTES) were stirred with 50 mL of normal hexane under the reflux for 6 h. Then, the prepared nanoparticles were filtered, washed with acetone and deionized water, and finally dried for 24 h under vacuum at 323 K [30].

2.4. Preparation of TA-A-HMS

Phenolic rings have nucleophilic tendency. So, electrophilic agents such as glutaraldehyde could form covalent bond with the existing rings. Glutaraldehyde can also react with the amino groups of aminated HMS. Therefore, immobilization of tannin on the surface of amine functionalized HMS nano-powder takes place which glutaraldehyde acts as the cross-linking agent and forms the covalent bond [31].

After preparation of 0.6% tannic acid solution, 2.00 g of the prepared aminated HMS nano-powder was mixed with tannin solution. The mixtures were then stirred for 2 h at room temperature. Then, 4 mL of glutaraldehyde (50%, w/w) was added to the mixtures. Then, the mixtures were stirred for 24 h at 298 K. Subsequently, the mixtures were filtered, washed with deionized water and dried in a vacuum oven at 323 K. So, brown TA-A-HMS nano-powder was obtained. Tannin grafting extent of HMS can be calculated based on the concentration difference of tannin solution before and after the loading where it was measured using ultraviolet-visible spectrophotometer (6310, JENWAY, UK). The result showed that the loading of HMS by 0.6% tannin solution was 38.5%. Fig. 1 shows the trend of the synthesis of TA-A-HMS.

2.5. Characterization

X-ray diffraction (XRD) patterns of samples were carried out in the range of $2\theta = 0-80^\circ$ using refractometer (XRD, Philips instruments, Australia). The operating conditions were 35 kV, 28.5 mA, and 25 °C where copper anode was used as a radioactive source. The BET surface area was evaluated from the linear part of BET plot. Pore size and pore volume distributions were also estimated from the adsorption curve of N₂ adsorption-desorption isotherm by BJH (Barrett-Joyner-Halenda) method (Quantachrome NovaWin2, USA). The presence of tannin and amine groups on the surface of HMS was proved by Fourier transform infrared spectrometry (FTIR, 8400S, Shimadzu, Japan) in the wave numbers range of 400–4000 cm⁻¹. Surface morphologies were analyzed by scanning electron microscopy (SEM) equipped with an energy dispersive X-ray spectroscopy (HITACHI S-4160) and transmission electron microscopy (TEM) images (CM120, PHILIPS, Holland, 150 kV).

2.6. Batch adsorption experiments/determination of the protein concentration

Optimum condition of some important parameters such as, pH, contact time, BSA concentration, adsorbent dosage and temperature were determined. pH of BSA solution in the range of 3–11 were investigated. At optimum pH, adsorbent dosage (0.01–0.06 g), adsorption kinetic parameters and contact time (15–120 min) were studied. Then, adsorption isotherm models were determined. Finally, to study the thermodynamic of process, effects of temperature in the range of 25–45 °C on adsorption process in various concentrations of protein solution (200–350 ppm) at optimum values of pH, contact time and dosage were evaluated. For measurement of protein concentration during the adsorption process, after determination of calibration curve of BSA solution by using the Bradford method [32], 100 μ L of unknown protein sample and 900 μ L of distilled water was mixed well. Then, 5 mL of Bradford reagent was added to the solution and after 5 min, the VIS absorption value of the unknown protein sample was measured at the wavelength of 595 nm, using an UV/VIS spectrophotometer (6310, JENWAY, UK). Then, BSA concentration was read from calibration standard curve. Batch equilibrium experiments were carried out to determine the adsorption capacity of BSA onto TA-A-HMS at equilibrium and as obtained through the following relationship:

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