



Preparation and characterization of organo-functionalized silicas for bilirubin removal



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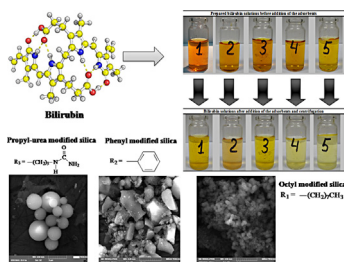
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HIGHLIGHTS

- Organo-functionalized silicas were synthesized via sol–gel method.
- Functional groups have influence on morphological properties of the final products.
- The adsorption efficiency mostly depends on the type of surface functional groups.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 9 June 2014

Received in revised form

26 September 2014

Accepted 6 October 2014

Available online 17 October 2014

Keywords:

Sol–gel

Functionalized silicas

Surface modification

Bilirubin adsorption

Surface properties

ABSTRACT

Hybrid-silica materials containing octyl, phenyl and urea-propyl functional groups were reported. These functionalized silicas were prepared by a via one-pot synthesis method through co-condensation of tetraethyl ortosilicate with organosilanes co-precursors. The obtained materials were analyzed by a number of techniques including scanning electron microscopy, Fourier transform infrared spectroscopy, X-ray diffraction pattern and nitrogen sorption measurement. The main elements: morphology and surface properties of the final products that are basically dependent on the type and the quantity of functional-containing groups were fully discussed. The adsorption properties of the modified silicas were investigated against bilirubin in aqueous solution at pH 7.4, the effect of time was studied as well. The modified silicas showed a greatly increasing of adsorption capacity for bilirubin compared to pure amorphous silica. The results indicate that the type of functional-containing groups and surface properties affect the adsorption behavior. These materials show a potential application as effective adsorbents for bilirubin removal.

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1. Introduction

Silica gel is an amorphous inorganic polymer composed of internal siloxane groups (Si–O–Si) with silanol groups (Si–OH) distributed on the surface. Nowadays, silica gel is widely used in many chemical processes to provide new technical application due to

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its valuable physical and structural characteristics such as a high chemical and thermal stability, a large surface area and a pore size, chemical inertness, and it is a great potential for fabricating nanostructures [1–4].

Moreover, modified silica gels have increased their potential application in many scientific and technological branches such as a high performance liquid chromatography (HPLC) bonded phases for specific separations, supports for catalysts in specific organic reactions, supports for microorganism and pesticides [5], and the extractions of metallic cations from aqueous and nonaqueous solvents by forming immobilized metallic complexes [6]. Modification of silica surface can be achieved via several methods: (1) functionalization with organic functional groups [7]; (2) via a physical adsorption of active species leading to a variety of useful supported reagents [8]; (3) modification via incorporation of natural or synthetic polymers [9–11]. Functionalization of mesoporous silicas with silane-coupling agents via two-steps methods has attracted considerable attention [12,13]. This is mostly due to its a large surface area and pore size in comparison to non porous silica [14]. Several mesoporous silicas have been functionalized with different ligands and intensively investigated over the last decade [14–17]. Moreover, at present time the preparation of organo-functionalized mesoporous silicas using one-pot synthesis method have been received much attention [18,19]. According to the grafting two-step method of synthesis, the population of the organic groups is limited to the original number of surface silanols on the mesoporous silica, and thus, a low surface coverage is obtained [20]. The most promising method is based on one-pot synthesis [22]. In recently published article [21] the one-pot grafting method of polystyrene on polydopamine coated silica particles was investigated. The obtained results showed that one-pot grafting approach exhibited higher grafting density when compared to two-steps grafting strategy. What is more, the nature of functional groups grafted on silica surface plays an important role in the surface properties of modified materials such as a hydrophobicity and a chemical reactivity [2,22] what makes its great potential to use these materials in drug delivery systems or a treatment of different toxicological diseases.

One of the well-known endogenous toxins is bilirubin [23]. Bilirubin is a pathogenic substance and one of the products of hemoglobin's metabolism. Normally, bilirubin is transported to the liver as a complex with albumin where it is conjugated with glucuronic acid and excreted into bile [24,25]. However, when the bilirubin concentration in plasma is higher than the normal level (>15 mg/dL), it is usually caused by pathogenic liver disease. Moreover, the extra free bilirubin binds and deposits onto carious tissues, including the brain tissues [26]. Many techniques have been employed for the removal of a high concentration of bilirubin from plasma in order to prevent the liver disease and brain damage such as plasma apheresis, hemodialysis, photocatalytic or affinity membrane chromatography [26]. However, hemoperfusion treatment is one of the most effective techniques at the moment [27,28]. This technique is based on the circulation of blood through a special unit containing an adsorbent for bilirubin removal. So, bilirubin interaction with various compounds which then might be used for surface modification of the adsorbent is interesting subject of many publications [29–32]. Due to the fact that bilirubin has several hydrophobic and hydrophilic reaction sites in its structure and also contains carboxyl and imine groups, the interactions of matrices with tetrapyrrole may be carried out by various ways [23,29]. Conformational state of bilirubin also plays a significant role during the interaction processes. The “ridge-tile” conformation of the pigment is one of the most stable conformations in majority of solutions and solids (Fig. 1) when binding processes are investigated. It was reported by McDonagh group the additional interactions between bilirubin molecule and

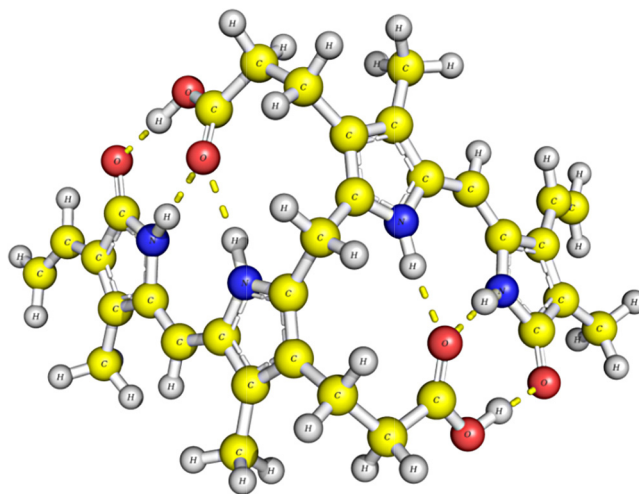


Fig. 1. Structure formula of bilirubin in “ridge-tile” 5Z, 15Z conformation stabilized by six intramolecular hydrogen bonds.

protein occur via hydrogen-bonding of the carbonyl oxygen in the protein and two nitrogen atoms of bilirubin [23]. It was shown when considering the bilirubin and β -cyclodextrin binding, that the hydrophobic interactions can play a critical role for inclusion ability for bilirubin [33]. It was shown that extra free bilirubin can be attached to cyclodextrine (CD) family via electrostatic forces [34]. Another work [35] describes a complex formation of poly(zincprotoporphyrin-methacrylic acid-ethyl glycol dimethylacrylate) matrix (ZnPP) with bilirubin. It is established that the four pyrrole-rings of ZnPP could form π - π stacking interaction with the four-pyrrole rings of bilirubin. The zinc in the ZnPP structure could further coordinate with bilirubin to form much rigid recognition sites in the matrix. To sum up, we can conclude that the different mechanisms of bilirubin interaction with various substances can be successfully applied to develop a new approaches of bilirubin utilization from the human organism [36]. Up to now, several adsorbents with different physical and chemical characteristics were used for bilirubin removal. In recent article [37], bilirubin adsorption capacities on single-wall carbon nanohorns (SWNHs) were investigated. Authors showed that bilirubin is selectively adsorbed to the SWNHs, especially to the SWNHs with high oxidation levels against albumin simultaneously mixed in solution. In another paper [38], the analysis of the bilirubin adsorption confirmed the possibility of electrostatic interactions between bilirubin molecules and guanidine polymers incorporated inside silica matrix.

Although a lot of publications concerning the preparation of surface-modified silica particles have been written but the effect of functional groups on the surface properties, morphological structure and, therefore, their influence on the bilirubin adsorption are not clearly understood. Here, a comparative study of the influence of organosilane co-precursors on the morphological structure of the final products and bilirubin adsorption from aqueous solution at pH 7.4 has been performed. The adsorbents for bilirubin removal were prepared using tetraethyl ortosilicate and organosilane co-precursors as starting materials for surface modification. Octyltriethoxysilane and phenyltriethoxysilane were chosen as the agents for modification due to the presence of octyl and phenyl functional groups exhibiting hydrophobic properties. The 1-[3-(trimethoxysilyl)-propyl]urea was chosen because of the presence of amine and carboxyl functional groups. For all hybrid materials ratios of tetraethyl ortosilicate and organosilane co-precursors were employed, to explore the effect of this parameter on their properties.

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