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Nanoporous silica-based materials for sorption of pharmaceuticals and biomolecules

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Our concern in this paper is to review four kinds of mesoporous silica materials which can be used as potential sorbents for pharmaceuticals. It is known that a continuous development of science, medicine and food industry has an effect on contamination of the natural environment. Moreover, many impurities, such as drugs, vitamins or proteins etc., which get into environment from urban and hospital wastes, can also influence on human organisms. Thus, there is a need to control an amount of those compounds, especially in the natural waters and wastewaters [1-4]. In this work, we present four types of silica materials which can be helpful in water purification by using adsorption process.

Keywords: nanoporous silica-based materials, adsorption, pharmaceuticals, biomolecules, environmental protection

1. INTRODUCTION

Nowadays, an increased interest of the adsorption process of pharmaceuticals and biomolecules, such as drugs, enzymes or proteins, from solutions onto solid surfaces is observed [5,6]. It is due to their increasing amount in the natural environment and human bodies. The

adsorption process is taking into account due to its promising results in water purification. Above-mentioned biocompounds have a huge influence on living organisms. Beyond the positive effects they can also (in high concentrations) cause damage in some organs or tissues, e.g. some proteins can facilitate adsorption of fibrous proteins causing adverse biological consequences [7-9], such as increased blood clotting or heart disease [10]. Therefore, it is necessary to control the amount of those biocompounds and other pharmaceuticals in the surrounding hydro- and biosphere. Thus, the new methods and new materials as potential sorbents have been searched. This is due to the fact that efficient adsorption techniques have huge commercial importance and find applications in different fields, such as biotechnology, biocatalysis, medicine, and controlled drug delivery systems.

Nanoporous Silica-based Materials (NSM) are attractive as adsorbents due to their simplicity of synthesis, facility of surface functionalization and biocompatibility. Each group have a different particle morphology, porous structure and surface composition. These above-mentioned groups of nanoporous silica materials are:

- OMS – Ordered Mesoporous Silicas,
- MCF – Meso-Cellular Silica Foams,
- ASX – Amorphous Silica Xerogels,
- PSN – Porous Silica Nanotubes.

The ordered mesoporous silica materials were synthesized in early 90s by Mobil researches [11, 12]. This group of silicas was named as M41S and it was the first group belonging to the other, bigger group – OMS. This discovery initiated the beginning of interest of mesoporous silicas, which has led to further studies on MCF, ASX and PSN.

In the next paragraph, the structural properties and surface chemistry of four of the above-mentioned materials, in related to their sorption properties, will be described.

2. GENERAL CONSIDERATIONS

The organosilicas are considered as good materials for adsorption, immobilization, separation and encapsulation of pharmaceuticals for many reasons. Silica is safe and non-toxic relative to the living organisms and resistant to microbial attack, and not swell in water like many organic polymers. It is also chemically and mechanically stable compound. Moreover, excellent properties of nanoporous silica materials, such as

high specific surface area, high total pore volume and well defined pores with narrow pore size distribution, are very attractive for the adsorption of pharmaceuticals and other biocompounds. Due to ordered porous structure physical adsorption onto nanoporous silica surface is possible. However, to make adsorption process more efficient the surfaces of sorbents have to be modified with basic (amine or aminopropyl [13-15]) or acid (thiol [14-17]) functional groups by co-condensation [18, 19] or post-grafting [20] processes. In this paragraph, four of the above-mentioned groups of NMS in regard to their use as efficient sorbents for pharmaceuticals and biomolecules, will be described.

Consideration on OMS will be introduced only in description of MCM-41 and SBA-15. MCM-41 was synthesized in 1992 by a group of scientists employed by the Mobile Corporation [11, 12]. This was the first synthesized silica-based material characterized by hexagonally ordered structure with cylindrical mesopores without any connections between them. Its specific surface are reaches 1200 m^2/g, while average pore size and total pore volume reach 10 nm and 1.2 cm^3/g, respectively [11]. SBA-15 material was synthesized in 1998 [21,22] by American's researches at Santa Barbara's University. SBA-15 is characterized by ordered structure, with high specific surface area range 690-1040 m^2/g, pore size and total pore volume reach 30 nm and 2.5 cm^3/g, respectively [22]. SBA-15 shows hexagonal arrays of cylindrical mesopores connected by micropores. Both, MCM-41 and SBA-15, are the most popular silica materials used in many fields of industry, such as biotechnology, biocatalysis, medicine, biosensors and bioreactors and controlled drug delivery systems [23, 24].

It is known that the sorption capacities strongly depend on number of sorption sites and pores size. Thus, such porous structure makes MCM-41 and SBA-15 very attractive materials for capturing (or immobilizing) pharmaceuticals and biomolecules. Diaz et al. [25] showed that the sorption capacities of various enzymes, cytochrome c, papain and trypsin onto MCM-41 depend on the molecule size. Anderson co-workers [26] proved that the degree of ibuprofen loading was strongly dependent on the specific surface area and the pore diameter of the host matrix. The bigger surface area is the most effective is adsorption process [27]. Qu et al. tested the dependence between average pore size and efficiency of captopril adsorption onto SBA-15 and MCM-41 [28]. The obtained results showed that the bigger pores are the higher is amount of adsorbed biomolecule onto silicas.

A lot of pharmaceuticals have been tried to capture by pristine MCM-41 and SBA-15 materials. For example, Wang et al. [29] used above-mentioned materials as suitable sorbents for immobilizing catalase, while Doadrio co-workers tested the mesoporous silica SBA-15 for adsorption of gentamicin [30] and erythromycin [31]. Vallet-Regi et al. [32] adsorbed antibiotic amoxicillin onto pristine SBA-15 and discovered that the sorption capacities depend on pH and amoxicillin concentration.

It is worth to mention, that for pure SBA-15 only silanol groups exist on its surface. To make it more effective for capturing biocompounds, the surface modification with various functional groups should be done [33]. Recently, there is observed a huge interest of use functionalized SBA-15 as efficient sorbents for biomolecules from liquid phase. Nanoporous silicas have been tested as adsorbents for amino acids and proteins. For example, Gao and co-workers [34] examined SBA-15 and modified SBA-15 as potential sorbents for arginine, glutamic acid, phenylalanine, leucyne and demonstrated that the sorption capacities strongly depend on pH and nature of particular amino acids. O'Connor et al. [35] proved that adsorption of amino acid onto MCM-41 also depends on ionic strength. MCM-41 materials were used for the immobilizing glutamic acid, phenylalanine and lysine by Ernst et al. [36,37]. Zhao et al. [38] used functionalized SBA-15 materials for separation of proteins by using chromatography technique. Deere et al. [39,40]. Washmon-Kriel et al. [41] and Humphrey et al. [42] examined different mesoporous sorbents as potential materials for capture cytochrome c. Vinu and co-workers investigated the influence of the solution pH on the adsorption of cytochrome c [43,44]. Other biocompounds, such as conalbumin, bovine serum albumin, trypsin, ovalbumin, myoglobin and β-lactoglubulin were also successfully adsorbed onto SBA-15 and thiol-functionalized SBA-15 [42]. Song et al. used pristine SBA-15 and amine-functionalized [45] SBA-15 as efficient sorbents for ibuprofen and bovine serum albumin. There was observed a huge difference on sorption capacities between pristine and modified adsorbents. The better sorption capacities are obtained for modified silica materials. Ibuprofen was also adsorbed onto MCM-41 [26,45-47] and Al-modified MCM-41 [48]. The adsorption of riboflavin (vitamin B2) was studied by Kisler et al. [49] and the obtained adsorption capacities were satisfied. Bilirubin adsorption process was tested, both onto pristine and amine-modified SBA-15 [13,50]. The obtained results showed that the better adsorption capacities were observed onto SBA-15 with amine groups.

The OMS is the best known and the most often used (in a broad range) group of silica sorbents. Their practical applications in many fields are still being extended.

MCFs were synthesized by Schmidt-Winkel et al. in 2000 [51]. The route of the synthesis is very similar to synthesis of SBA-15, but in this case pore-expander is involved. The most popular used expanders are 1,3,5-trimethylbenzene (TMB) and 1,3,5-triethylbenzene (TEB). Thus, MCFs have larger pore volumes than SBA-15. MCFs consist of spherical voids (22-42 nm in diameter) interconnected by "windows" of 10 nm with tunable sizes [51-53]. Such structure of pores can be described as "ink-bottled" [54]. Their surfaces areas reach 800 m^2/g and strongly depend on aging time and concentration of HCl [51, 54].

Specialist literature reports that Meso-Cellular Silica Foams can be successfully used as efficient sorbents for L-tryptophan, lysozyme from chicken egg and bovine serum albumin (BSA) [54-56]. Russo et al. [57] investigated the influence of surface functionalization on adsorption capacities of BSA and lysozyme onto MCFs. Pandaya et al. [58] carried out immobilization of α-amylase onto MCM-41, SBA-15 and MCF. The obtained results showed that adsorption onto SBA and MCM takes place on external, while onto MCF on internal, pores. Modified Fe_3O_4-MCF was used as potential sorbents for cytochrome c, BSA and aspirin by Huang and co-workers and Yang et al. [59, 60]. The obtained adsorption capacities were bigger for BSA than aspirin. BSA was also adsorbed by Sezoes et al. [61]. Zhao et al. [62] used amine-modified MCF for the immobilization of penicillin G acylase (PGA). Ibuprofen was also adsorbed onto pristine and polyizoprene (PI) modified MCF by Zhu et al. [63]. The obtained results clearly showed that better sorption capacities have been received for PI-MCF. Laccase [64, 65], lactase and papain [66] were also immobilized on MCF.

ASXs in contrast to OMSs are characterized by well-developed but disordered porous structure. To synthesis Amorphous Silica Xerogels the sol-gel method connected with slowly evaporation of solvent is employed. Their specific surface areas range from 50 to 1000 m^2/g obtained by Kumara et al. [67]. The pore size and total pore volume obtained by Kumara et al. ranged from 1 to 50 nm and 0.2-0.4. cm^3/g, respectively. L. A. de Miranda et al. investigated the influence of extraction processes amount on porous structure of obtained xerogels [68]. They demonstrated that with increasing number of extraction total pore volume and pore size also increase. C.A. Aerts and co-workers [69] examined how silica source and type of solvent influence on porous

structure of final material. They tested as-obtained materials as potential sorbents for ibuprofen. Tortajada et al. [70] successfully adsorbed lysozyme and α-L-arabinofuranosidase onto ASXs.

The Porous Silica Nanotubes (PSNs) have structure similar to carbon nanotubes [71] and pore diameter ranging 10-20 nm. The first Porous Silica Nanotubes were synthesized by Nakamura and co-workers in 1995 [72]. Like other silica materials, PSNs are also characterized by high hydrothermal resistance and biocompatibility. Their specific surface area can reach 800 m^2/g [73] and obtained pore size reach 20 nm [74]. The porous structure of PSN was precisely described by Wang et al. [75]. They obtained PSN with specific surface area reach to 1000 m^2/g, with total pore volume and average pore size 0.92 cm^3/g and 3.5 nm, respectively.

PSN is a relatively new group of silica materials and their potential applications as sorbents are not sufficient. There are only a few papers regard to adsorption biomolecules onto PSN. For example, Yang and co-workers [76] tested PSN in control doxorubicin release, while Ding et al. [77] immobilized lysozyme onto PSN. Xiao and co-workers [73] used PSNs in immobilization of glucose oxidase.

There is still a large gap in professional literature about MCFs, ASXs and PSNs as efficient sorbents for pharmaceuticals and other biocompounds. Thus, a lot of scientific groups have focused on those materials due to their attractive properties which could be used in sorption processes.

Parameters of porous structure of obtained materials depend on synthesis conditions, e.g. temperature, time of aging, pore expander addition etc. The better morphology, chemistry composition and porous structure of sorbents are the more effective is adsorption process. Therefore, there is a need to control above-mentioned parameters to obtain efficient materials which can be successfully used in adsorption process from the liquid phase. The capture properties with regards to pharmaceuticals will differ, because each of these groups can have different particles morphology, porosity and chemistry of the surface. The last one is the most important factor influence on the efficiency of the adsorption process of various pharmaceuticals and biomolecules onto NSMs structure.

3. CONCLUSIONS

An overview of organosilica materials with emphasis of their use as efficient sorbents for environmental pollutants, such as pharmaceuticals and biomolecules has been provided. Recent advances make possible to create selective sorbents by controlling pore size and tailoring surface chemistry by modifying the surface with the appropriate functional group. Thus, it is possible to design the desired properties of the final materials for a targeted application.

Adsorption of bioactive compounds becomes necessary due to their increasing amounts in the natural environment. Moreover, the biocompounds and pharmaceuticals are considered as new impurities which have to be removed from waters and wastewaters. Therefore, it is necessary to control their concentration in hydrosphere, biosphere, and so on. It is also very important to develop new methods which will be helpful in purification of the above-mentioned fields.

Summing up, porous structure, chemistry surface and other properties makes NSM good sorbents of biomolecules and pharmaceuticals.

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