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The effects of surface chemistry of mesoporous silica materials and solution pH on kinetics of molsidomine adsorption

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ABSTRACT

Adsorption kinetics of molsidomine on mesoporous silica material (UMS), the phenyl- (PhMS) and mercaptopropyl-functionalized (MMS) derivatives from solution with different pH and 298 K was studied. The adsorption kinetics was found to follow the pseudo-second-order kinetic model for all studied silica materials and pH. Effects of surface functional groups and pH on adsorption efficiency and kinetic adsorption parameters were investigated. At all studied pH, the highest molsidomine amount is adsorbed on PhMS due to π–π interactions and hydrogen bonding between surface groups of PhMS and molsidomine molecules. An increase of pH results in a decrease of the amounts of adsorbed molsidomine onto the silica materials. Furthermore, the highest adsorption rate kinetically evaluated using a pseudo-second-order model, is observed onto UMS and it strongly depends on pH. The mechanism of the adsorption process was determined from the intraparticle diffusion and Boyd kinetic film–diffusion models. The results showed that the molsidomine adsorption on the silica materials is controlled by film diffusion. Effect of pH on the diffusion parameters is discussed.

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1. Introduction

Studies on adsorption kinetics of drugs are of great interest not only for development of adsorption theory but for practical applications in various technologies, for example, drug separation and purification [1,2], removal of drugs from wastewater [3–7]. In the present time much attention has been paid to development of drug delivery systems for already known, clinically used drugs to improve their pharmacological and consumer properties. Application of various carriers for hosting and further delivering of such drugs allows to overcome some inconveniences and shortcomings of their clinical use and provides advantages over conventional drug therapies such as controlled drug release, concentration of drugs in the precise sites of the body within the optimum range, minimization of harmful side effects, etc. It has been shown that molecular drugs can be immobilized on carrier matrix by different ways. Adsorption has been proved to be a well-established and cheap route of drug immobilization. Therefore, the development of drug delivery systems often requires knowledge of kinetic characteristics of drug adsorption.

Molsidomine is well known drug possessing vasodilating and antiaggregatory effects [8,9]. However the duration of its action after single oral dosing is only 2–3 h [10]. Therefore, the drug must be taken 3–4 times a day. Available retarded forms of molsidomine contain higher doses of the drug which result in pronounced side effects [11]. This leads to necessity of development of efficient sustained release formulation of molsidomine. We suggested that mesoporous silica as the drug carrier may improve its pharmacokinetic and consumer properties. According to literature data, immobilization of aspirin [12], metoprolol and papaverine [13], nimodipine [14], ibuprofen [15] on mesoporous silica particles promotes delayed release of the drugs and the porous silica materials can be considered as potentially useful controlled drug release carriers.

In our previous works [16,17] we have synthesized mesoporous hybrid silica materials with various surface functional groups and studied their adsorption properties with respect to molsidomine at physiological pH. Effect of surface chemistry of the silica materials on amount of adsorbed molsidomine and thermodynamic characteristics of the adsorption has been investigated. Kinetic studies of the molsidomine adsorption on mesoporous silica materials can give information about time of reaching maximum drug loading, to elucidate mechanism of the process in order to create drug carrier with optimal properties. Therefore, the aim of the present work is to study kinetics of molsidomine adsorption on the mesoporous silica materials.

Kinetics of drug adsorption on porous materials can be affected by many factors: textural properties of adsorbent [3,5,7,18], chemical and structural properties of drugs [19,20], initial drug concentration in solution and adsorbent content [21], presence of surfactants in solution from which drug adsorption realizes [22],

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etc. Chemical surface properties of adsorbents strongly affect adsorption kinetics. As has been reported in [5], the initial adsorption rate of diclofenac and carbamazepine was highest in mercapto-functionalized hexagonal mesoporous silica, whereas it was by the far the slowest in amino-functionalized one. The nitroimidazole adsorption rate constant (k_1) is also related to surface chemical characteristics of the activated carbons. It was found that the constant increases reducing the oxygen percentage of the activated carbon and diminishing the content of carbonylic and phenolic groups. Such results were explained by the increase in carbon hydrophobicity [19].

Effect of pH on adsorption kinetics of drugs has been studied in numerous studies [4,6,7,21,23]. Strong influence of pH on adsorption kinetics of some drugs is caused by two reasons: pH affects state of drug molecules in solution and surface chemistry of adsorbents. Because drugs are often weak electrolytes, they have ionizable functional groups that depend on pH. Besides, depending on nature of surface functional groups, adsorbent may be neutral ($pH=pH_{pzc}$, at point of zero charge), positively ($pH < pH_{pzc}$) or negatively ($pH > pH_{pzc}$) charged due to protonation or dissociation of the functional groups. Therefore, pH is one of the most important factors controlling adsorption interactions and kinetics. For example, the studies of adsorption kinetics of sulfa drugs on high-silica zeolite have showed that the adsorption rate is higher under acidic conditions when the sulfa drugs exist mainly in the neutral form than that obtained at pH 8 when the proportion of the neutral form is less [4]. It was concluded that the adsorption mechanism was based on hydrophobic interactions.

In this work the effects of surface functional groups of mesoporous silica materials (hydroxyl, phenyl, mercaptopropyl) and solution pH on adsorption kinetics of molsidomine were studied. Chemically, molsidomine is sydnonimine, heterocyclic mesoionic compound [24]. Structural formula of molsidomine is presented in Fig. 1. On the one hand, its molecules contain heterocycle and exhibit aromatic properties but on the other hand, they are dipolar and should favor strong hydrophilic interactions (for example, electrostatic, ion–dipole, hydrogen bonding).

It is impossible to establish *a priori* what interactions will be responsible for molsidomine adsorption. Therefore, silica surface was modified by functional groups having different nature.

It has been found that molsidomine is stable in acid and neutral solutions. Titration of aqueous molsidomine with 1 N HCl allows estimation of pK_a that was found to be 3.34 at 298 K [25]. In extreme alkaline solutions, it decomposes to the carboxylate, ammonia, monoethyl carbonate, which further decomposes to ethanol and carbon dioxide [25].

2. Experimental

2.1. Materials

Molsidomine ((N-(ethoxycarbonyl)-3-(4-morpholino)sydnonimine)) (Aldrich), tetraethoxysilane (TEOS) (high purity grade, Russia), 3-mercaptopropyl triethoxysilane (MTEOS) (Aldrich, 95%), phenyltrimethoxysilane (PhTMOS) (Acros, 85%), D-glucose (ICN Biomedicals, >99% purity) were used without further purification. Sodium hydrogen phosphate and sodium dihydrogen phosphate (Russia, analytical grade) were used to prepare buffer solutions on the basis of doubly distilled deionized water (pH=4.8, 6.0, 7.4, 8.0; 50 mM).

2.2. Syntheses

The unmodified silica (UMS) was synthesized by sol–gel procedure using D-glucose as structure-forming agent and HCl as catalyst in the prehydrolysis followed by neutralization with NaOH for subsequent polycondensation in the presence of D-glucose as described in [26] Removal of the template was carried out by water extraction. The obtained unmodified silica serves as basic material for surface modification by grafting.

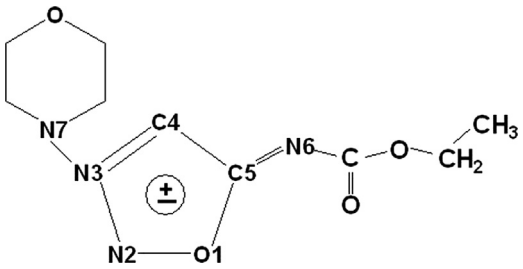

Fig. 1. Structural formula of molsidomine.

The phenyl modified (PhMS) and mercaptopropyl modified (MMS) silica materials were synthesized via grafting [16,17]. Appropriate modifier was added to suspension of UMS in ethanol and stirred at room temperature for 20 h. The sample was finally centrifuged and washed two times in ethanol.

2.3. Determination of zero charge (pH_{PZC}) of the synthesized silica materials

Determination of zero charge (pH_{PZC}) of the synthesized silica materials was carried out according to a method previously described in the literature [27]. In brief, a 0.01 M NaCl solution was placed in a series of test tubes. The initial pH of the NaCl solution was adjusted by adding either HCl (0.01 M) or KOH (0.01 M) and the weighed amount of silica was added to the solutions. The final pH was measured with an pH/ION analyzer (Radelkis, Budapest) after stirring of the suspensions for 48 h.

2.4. Determination of amount surface groups on the synthesized silica materials

Amounts of grafted mercaptopropyl and phenyl groups (mmol/g) were calculated according to Eq. (1) on the basis of the data obtained by the elemental analysis method:

$$C_{surf.gr.} = \frac{\%}{Ar \cdot n \cdot 100\%} \quad (1)$$

where Ar is the atom mass of element (equivalent to mole of functional groups containing the element), n is the number of atoms in the functional group.

Element contents of the samples were determined using a FlashEA 1112CHNS/O elemental analyzer. The contents of sulfur in MMS and carbon in PhMS are found to be 0.447% and 3.397%, respectively.

The hydroxyl group content of UMS was determined by thermogravimetric analysis. TG curve of UMS is presented in Fig. 2. Weight of the sample was 145 mg. The sample was thermally scanned from 20 to 1150 °C at 5°/min in air, then the total hydroxyl group content UNS was estimated from the weight loss [28] as:

$$C_{surf.gr.} = \frac{2(W(T_0) - W(T_{final})}{M_{H_2O}}, \quad (2)$$

where $W(T_0)$ and W (T_{final}) are the weighs of the sample at temperature T_0 corresponding to the beginning of dehydroxylation due to the condensation of the OH groups in UMS (196 °C) and at T_{final} (1150 °C), respectively; M_{H2O} is the molecular weight of the water.

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