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Organically functionalized mesoporous SBA-15 as sorbents for removal of selected pharmaceuticals from water

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ABSTRACT

Mesoporous silica SBA-15 and its postfunctionalized counterparts with hydroxymethyl (HM-SBA-15), aminopropyl (AP-SBA-15), and trimethylsilyl (TMS-SBA-15) were prepared and characterized by powder X-ray diffraction, N_2 adsorption–desorption measurement, Fourier-transform infrared spectroscopy, and elemental analysis. The removal of a mixture of 12 selected pharmaceuticals was investigated by batch adsorption experiments onto SBA-15 and the grafted materials. SBA-15 showed to have moderate adsorption affinity with amino-containing (atenolol, trimethoprim) and hydrophobic pharmaceuticals, but it displayed minimal adsorption affinity toward hydrophilic compounds. HM-SBA-15 was analogous with SBA-15 in terms of the adsorption efficiency toward all pharmaceuticals. AP-SBA-15 exhibited an increase in the adsorption of two acidic compounds (clofibric acid, diclofenac) but a decrease in the adsorption of estrone and the two amino-containing compounds. Among the grafted materials, TMS-SBA-15 had the highest adsorption affinity toward most pharmaceuticals. Moreover, the adsorption of nine pharmaceuticals to TMS-SBA-15 was significantly higher than that to SBA-15; seven of which showed the removal percentages from 70.6% to 98.9% onto TMS-SBA-15. The number of pharmaceuticals showing high adsorption efficiency onto TMS-SBA-15 did not alter significantly as the pH changed in the range of 5.5–7.6. The results suggest that TMS-SBA-15 is a promising material for the removal of pharmaceuticals from aqueous phase, especially for the treatment of wastewater from drug manufacturers.

1. Introduction

Recently, pollution of pharmaceuticals in water is an environmental concern [1–3]. Numerous pharmaceuticals are ubiquitously detected in aqueous environment [2,4]. Unknown chronic ecotoxicities effects [4] together with antibiotic resistance issue [5] are making increasingly anxieties due to wide spreads of pharmaceuticals. The current technologies used in water treatment systems are not effective enough to eliminate many pharmaceuticals [6,7]. Therefore, treatment technologies that achieve effective pharmaceutical removal need to be developed. The treatment of wastewater from drug manufacturers and households, where pharmaceuticals are often present at $\mu g\,L^{-1}$ level [4,8] and even up to $100\,\mu g\,L^{-1}$ [9], should be considered with a priority.

Among several considered methods, adsorption has been receiving a lot of attention, due to its convenience once applied into current water treatment processes. Various types of sorbents have been proposed for the removal of pharmaceuticals, for example, activated carbon [10], zeolites [11], montmorillonite [12], and mesoporous silica [13]. Among them, mesoporous silica, first synthesized in 1992 [14], are good candidates for the adsorptive removal of pharmaceuticals since these materials have high surface area, large and uniform pore size, and tunable pore structure. Mesoporous silica SBA-15 was effective for the adsorption of neutral and acidic pharmaceuticals in acidic media [13], though its effectiveness was significantly reduced at a neutral pH because of its low point of zero charge. This shortcoming, fortunately, may be overcome by altering the surface chemistry of mesoporous silica by means of grafting with suitable functional groups. Recently, mesoporous silica SBA-15 was grafted with cobalt(II), nickel(II), and copper(II) amine complexes and then applied for the adsorption of naproxen [15]. Copper(II) amine supported SBA-15 showed high adsorption efficiency toward naproxen though alkaline conditions (pH 13) were needed.

Pharmaceutical compounds are known to have distinct physicochemical properties, particularly hydrophobicity ($\log K_{ow}$) and acidity (pK_a), which are often important characteristics of a sorbate in aqueous media. Pharmaceuticals are categorized from hydrophilic to hydrophobic and basic to acidic compounds [16]. A material used for the removal of pharmaceuticals, therefore,

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must have an adequate hydrophobicity and acidity, which can be achieved by grafting with a proper organic functional group on the surface. Organically functionalized mesoporous silica have demonstrated their potential in application for removal of various organic contaminants, such as aromatic compounds, dyes, and pesticides [17]. To the best of our knowledge, the use of mesoporous silica functionalized with different organic moieties for adsorption of pharmaceuticals in aqueous phase has yet to be reported elsewhere.

In the present study, SBA-15 was grafted with three different organic moieties such as aminopropyl, hydroxymethyl, and trimethylsilyl groups, which possess different hydrophobicity and acidity. SBA-15 and the grafted SBA-15 materials were then examined as sorbents for the adsorption of a mixture of pharmaceuticals in water. For this task, 12 pharmaceuticals were selected based on their frequent detection in aqueous environments [4,8], diverse properties in terms of hydrophobicity (K_{ow}) and acidity (pK_a), and different medication categories. A mixture of pharmaceuticals was used in all experiments, in accordance with real situations [2,18].

2. Experimental

2.1. Chemicals

Tetraethylorthosilicate (TEOS 98%, Aldrich), Pluronic P123 (BASF), hydrochloric acid (HCl, 37%, Sigma–Aldrich) (3-aminopropyl)triethoxysilane (APTES, 99%, Aldrich), hydroxymethyl triethoxysilane (HMTES, 50%, Gelest Inc.), hexamethyldisilazane (HMDS, 99%, Aldrich), anhydrous toluene (99.8%, Sigma–Aldrich), absolute ethanol (HPLC grade, Fisher scientific), and acetone (HPLC grade, Fisher scientific) were used for the synthesis and surface modification of SBA-15. Acetaminophen, atenolol, carbamazepine, clofibric acid, diclofenac sodium, estrone, gemfibrozil, ibuprofen, ketoprofen, sulfamethoxazole, and trimethoprim were purchased from Sigma–Aldrich; iopromide was obtained from United States Pharmacopeia. Nine surrogate standards include non-deuterated compounds (dihydrocarbamazepine, cloprop) obtained from Sigma–Aldrich and deuterated compounds (acetaminophen-d_4, atenolol-d_7, estrone-d_4, ibuprofen-d_3, iopromide-d_3, sulfamethoxazole-d_4, and trimethoprim-d_9) received from Toronto Research Chemicals. The purity of all chemicals used in this study is ≥97%. In addition, stock mixed solutions of all pharmaceuticals (100 mg L^{-1}) and surrogate standards (10 mg L^{-1}) were separately prepared in methanol and stored at −20 °C prior to use. The physicochemical properties of the studied compounds are presented in Table 1.

2.2. Preparation of sorbent materials

SBA-15 was synthesized using a method described elsewhere [13,19]. Monomeric organically functionalized SBA-15 materials were prepared using a post-grafting method. Firstly, calcined SBA-15 (1.0 g) was pretreated at 190 °C *in vacuo* for 6 h. The pretreated SBA-15 was then slurried in anhydrous toluene (100 mL) for 1 h under a dry N_2 flow. Next, an organosilane precursor (APTES, HMTES, and HMDS) in anhydrous toluene (50 mL) was added. An adequate amount of APTES (0.66 mL) and HMTES (1.26 mL) to make a monolayer of organic groups was used, whereas an excess amount of HMDS (5.90 mL) was employed. The reaction system was refluxed in the cases of alkoxysilanes (APTES, HMTES) but was kept at room temperature in the case of HMDS [20]; all reaction systems were stirred for 24 h under a dry N_2 flow. After reaction, the products were filtered and washed with toluene, ethanol, and acetone consecutively. Finally, the samples were dried *in vacuo* at 150 °C for 4 h and stored in a desiccator. The three functionalized

Table 1
Sorbate characteristics.

Compound	CAS No.	Use	MW	C_s (mg L^{-1})[a]	pK_a	δ[e]	$\alpha_{+/-}$ (%)[f]			$\log K_{ow}^{pHg}$		
							pH 5.5	pH 6.6	pH 7.6	pH 5.5	pH 6.6	pH 7.6
Acetaminophen	103-90-2	Analgesic	151.2	1.4×10^4	9.86[b], 9.38[c] [0/−][d]	−	0.0	0.1	0.6	0.48	0.47	0.47
Atenolol	29122-68-7	Beta blockers	266.3	1.33×10^4	9.43[b], 9.6[c] [+/0][d]	+	100.0	99.9	98.5	−3.70	−2.60	−1.60
Carbamazepine	298-46-4	Anti-epileptic	236.3	112	13.94[b] [0/−]	−	0.0	0.0	0.0	1.89	1.89	1.89
Clofibric acid	882-09-7	Lipid regulator	214.7	583	3.18[b] [0/−]	−	99.5	100.0	100.0	0.11	−0.99	−1.99
Diclofenac	15307-86-5	Arthritis	296.2	2.37	4.18[b], 4.15[c] [0/−]	−	95.4	99.6	100.0	3.20	2.12	1.12
Estrone	53-16-7	Steroid	270.4	30	10.25[b] [0/−]	−	0.0	0.0	0.2	3.62	3.62	3.62
Gemfibrozil	25812-30-0	Anti-chloresterol	250.3	10.9	4.75[b] [0/−]	−	84.9	98.6	99.9	3.49	2.45	1.46
Ibuprofen	15687-27-1	Pain reliever	206.3	21	4.41[b], 4.91[c] [0/−]	−	92.5	99.4	99.9	2.38	1.31	0.31
Iopromide	73334-07-3	X-ray contrast media	791.1	23.8	10.62[b] [0/−]; 12.36[b] [−/−−]	−	0.0	0.0	0.1	-2.66	−2.66	−2.66
Ketoprofen	22071-15-4	Pain reliever	254.3	51	4.23[b], 4.45[c] [0/−]	−	94.9	99.6	100.0	1.62	0.54	−0.46
Sulfamethoxazole	723-46-6	Antibiotic	253.3	610	1.39[b] [+/0], 5.81[b] [0/−]	−	32.9	86.1	98.4	0.57	0.078	−0.81
Trimethoprim	738-70-5	Antibiotic	290.3	400	7.04[b], 7.12[c] [+/0]	+	97.2	73.4	21.6	−0.97	0.012	0.49

[a] C_s denote water solubility; values come from SRC PhysProp (accessed on October 03, 2010).
[b] Values calculated with ACD/Labs pK_a dB v. 12 program.
[c] Values come from SRC PhysProp (accessed on October 03, 2010).
[d] [0/−], transitions from neutral to anionic form; [+/0], transitions from cationic to neutral form.
[e] The dominant ionized species at the tested pH range (5.5–7.6): anionic (−) and cationic (+).
[f] $\alpha_{+/-}$: Fraction of the dominant ionized species (%), calculated based on the pK_a values from ACD/Labs pK_a dB v. 12 program.
[g] K_{ow}^{pH}: pH-dependent octanol–water coefficient; values calculated with ACD/Labs LogD v. 12 program at zero ionic strength.