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Adsorptive removal of selected pharmaceuticals by mesoporous silica SBA-15

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ABSTRACT

The removal of five selected pharmaceuticals, viz., carbamazepine, clofibric acid, diclofenac, ibuprofen, and ketoprofen was examined by batch sorption experiments onto a synthesized mesoporous silica SBA-15. SBA-15 was synthesized and characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), N_2 adsorption–desorption measurement, and point of zero charge (PZC) measurement. Pharmaceutical adsorption kinetics was rapid and occurred on a scale of minutes, following a pseudo-second-order rate expression. Adsorption isotherms were best fitted by the Freundlich isotherm model. High removal rates of individual pharmaceuticals were achieved in acidic media (pH 3–5) and reached 85.2% for carbamazepine, 88.3% for diclofenac, 93.0% for ibuprofen, 94.3% for ketoprofen, and 49.0% for clofibric acid at pH 3 but decreased with increase in pH. SBA-15 also showed high efficiency for removal of a mixture of 5 pharmaceuticals. Except for clofibric acid (35.6%), the removal of pharmaceuticals in the mixture ranged from 75.2 to 89.3%. Based on adsorption and desorption results, the mechanism of the selected pharmaceuticals was found to be a hydrophilic interaction, providing valuable information for further studies to design materials for the purpose. The results of this study suggest that mesoporous-silica-based materials are promising adsorbents for removing pharmaceuticals from not only surface water but also wastewater of pharmaceutical industrial manufactures.

1. Introduction

It has been almost 10 years since scientists paid attention to pharmaceuticals as new emerging contaminants [1,2]. Numerous pharmaceuticals were found ubiquitously up to $\mu g\,L^{-1}$ level in aqueous environment [1–5], in soil [1,6] and as high as 100 $\mu g\,L^{-1}$ in effluent from drug manufactures [7]. The presence of pharmaceuticals in the environment originates from the fact that these contaminants cannot be removed completely in sewage treatment plants (STPs) [2,8] (removal efficiency of carbamazepine and clofibric acid was 7% [2] and 0–30% [8], respectively) and are persistent in the environment [9,10]. In general, total removal rates of pharmaceuticals in current STPs were 40–60% [2,8]. In drinking water treatment plants (DWTP), incomplete elimination of some pharmaceuticals such as clofibric acid was also observed [11,12]. Additionally, adverse effects of pharmaceuticals at $\mu g\,L^{-1}$ level on living organisms have been recently confirmed [5] and possibly there exist unknown chronic effects of pharmaceuticals, which have not been investigated yet. There is a need to optimize and improve current technologies used in STP and DWTP for elimination of pharmaceutical residues, especially for treatment of pharmaceutical industrial wastewater and purifying surface water in DWTP.

Removal of pharmaceuticals by adsorption is one of the most promising techniques, due to its convenience once applied into current water treatment processes. So far, the removal of pharmaceuticals can be achieved by adsorption using activated carbon [11–13]. Although, activated carbon displayed efficient removal for a number of pharmaceuticals, especially for hydrophobic compounds, inefficient removal for pharmaceuticals which are either electrically charged or hydrophilic has been observed [11–13]. The working capacity of activated carbon greatly decreases in the presence of natural organic matter. Furthermore, regeneration of adsorbents is questionable.

Mesoporous silica such as MCM-41, MCM-48 [14], SBA-15 [15] can be a promising adsorbent owing to its novel structure that comprises uniform ordered structure, high pore volume, and high surface area (up to 1000 m^2/g). Mesoporous materials have been investigated for adsorptive removal of various organics such as cyanuric acid and p-chlorophenol [16], phenols [17], and dyes [18–20] in aqueous solution. Recently, removal of naproxen on a MCM-41 incorporated with nickel(II) complexes has been reported [21]. However, only single component adsorption at mg L^{-1}-level concentration was investigated, while adsorption kinetic, isotherm, desorption results as well as effect of pH and chemical factors such as competing anions, humic acid on adsorption have been not considered.

In this study, SBA-15 was first attempted to apply for removal of five selected pharmaceuticals at $\mu g\,L^{-1}$ concentrations. SBA-15 was selected because of its benign synthesis pathway (due to employing

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Nomenclature

C_e	equilibrium pharmaceutical concentration (mg L^{-1})
q_e	amount of pharmaceuticals adsorbed at equilibrium (mg g^{-1})
q	amount of adsorbate sorbed at t (min)
q_m	maximum adsorption capacity (mg g^{-1})
$q_{e,m}$	equilibrium capacity obtained by calculated from the models (mg g^{-1})
k_2	equilibrium rate constant of pseudo-second-order chemical sorption (g mg^{-1} min^{-1})
K_F	Freundlich constants
K_L	Langmuir isotherm constant (L mg^{-1})
n	Freundlich isotherm exponent
t	reaction time (min)

Greek letters

χ^2	non-linear Chi-square value (mg g^{-1})

biodegradable non-ionic surfactant), easily reproducible method and large uniform pore structure [15]. The objective of the study is to (i) determine the removal efficiency of individual pharmaceuticals as well as their mixture on SBA-15, (ii) investigate the characteristics of pharmaceutical adsorption via kinetic, isotherm, desorption, dose effect, and pH effect results and (ii) understand the adsorption mechanism which is beneficial for further studies. As a part of this study, effect of anions (nitrate, phosphate, sulfate, silicate), cations (aluminum, ferric, calcium, magnesium), and humic acid on pharmaceutical adsorption have been also investigated and will be mentioned in another report.

2. Materials and methods

2.1. Chemicals

The reagent grade chemicals used in the study (KCl, NaCl, HCl, NaOH) were purchased from Aldrich and Junsei chemical companies. Tetraethyl orthosilicate (TEOS) and Pluronic P123 ($EO_{20}PO_{70}EO_{20}$, M_{av} = 5800) were obtained from Junsei, BASF, respectively.

2.2. Adsorbent and target compounds

SBA-15 was synthesized by the method described elsewhere [15]. Briefly, a mixture solution of Pluronic P123 and TEOS was prepared in acidic media. Subsequently, the mixture was kept at 35 °C for 20 h and aged at 100 °C for 1 day. Finally, the sample was washed with de-ionized (DI) water and calcined in air at 550 °C for 6 h. The synthesized material was characterized by X-ray powder diffraction (XRD) using a Rigaku D/MAX Uitima III diffractometer with Cu Kα radiation. Transmission electron microscopy (TEM) images of the materials were acquired on a JEOL 2010 electron microscope operating at 200 kV. Nitrogen adsorption–desorption measurement were carried out using a Micromeritics ASAP 2020 analyzer at 77 K. The point of zero charge (PZC) of SBA-15 was estimated by the titration method as described elsewhere [22].

Five pharmaceuticals were selected in this research as target compounds: carbamazepine (an antiepileptic), clofibric acid (a lipid regulator), diclofenac, ibuprofen, and ketoprofen (nonsteroidal anti-inflammatory drugs) and two compounds were utilized as surrogate standards: cloprop (2-(3-chlorophenoxy) propionic acid) and 10,11-dihydrocarbamazepine (DHC); all were purchased from Aldrich. These pharmaceuticals were selected because they are either widely used and detected [1–5], resilient during treatment processes [2,8,11,12], or persistent [9,10] in the aqueous environment. Moreover, they have been evaluated to possess high environmental risk (risk quotient > 1) [23]. The molecular structure and physicochemical properties of these pharmaceuticals are summarized in Table 1.

Stock solutions of pharmaceuticals were prepared as 10 mg L^{-1} by first dissolved in methanol and then added with DI water. The amount of methanol was less than 0.1% in the final samples and thus had negligible impact on sorption. Stock solutions were stored at 4 °C, and used within 1 month after preparation.

2.3. Batch adsorption and desorption experiments

Batch adsorption of individual pharmaceuticals was studied in 40-mL amber vials containing 10 mg of SBA-15 in 10 mL of pharmaceuticals solution in 0.01 M KCl. Reactions proceeded for 2 h at 25 °C in an incubator (200 rpm). The 2 h reaction time was shown to be adequate by preliminary experiments for equilibrium to be attained (Fig. 1). After 2 h, the supernatant solution was filtered through a 0.45-μm cellulose acetate membrane filter (MFS), subsequently extracted by a solid-phase extraction (SPE) procedure and analyzed by a LC–MS/MS system. All experiments were performed in duplicate, and the solutions were analyzed triplicate for pharmaceuticals by LC–MS/MS.

Adsorption kinetics was resulted by taking the samples after different intervals (1–120 min) with a fixed pharmaceutical starting concentration (100 μg L^{-1}). Adsorption isotherms were produced by varying the pharmaceutical starting concentration from 10 to 300 μg L^{-1} and the pH-dependent adsorption were generated with a fixed pharmaceuticals concentration (100 μg L^{-1}) and varying pH from 3 to 9. The solution pH was adjusted using 0.1 M NaOH or HCl to the desired pH value, measured by Orion (model 3 Star) pH meter. Except for the experiment to estimate the effect of pH, the solution pH was kept at pH 3 for clofibric acid and pH 5 for the other ones (unless otherwise specified). Regarding effect of dosage, mass of SBA-15 was varied from 1 mg to 20 mg in 10 mL of pharmaceutical solution at a fixed pharmaceutical concentration (100 μg L^{-1}).

Desorption of pharmaceuticals from SBA-15 was investigated to study the interaction between pharmaceuticals and silica surface. First, adsorption of individual pharmaceuticals (100 μg L^{-1}) on SBA-15 (1 g L^{-1}) in 0.01 M KCl was conducted. After 2 h, the pharmaceutical-adsorbed SBA-15 was centrifuged, separated and gently washed with water to remove aqueous pharmaceuticals. The pharmaceutical-adsorbed SBA-15 was agitated for 12 h with 10 mL of 1 mM phosphate buffer (pH 7 and 9). Aliquots of supernatant

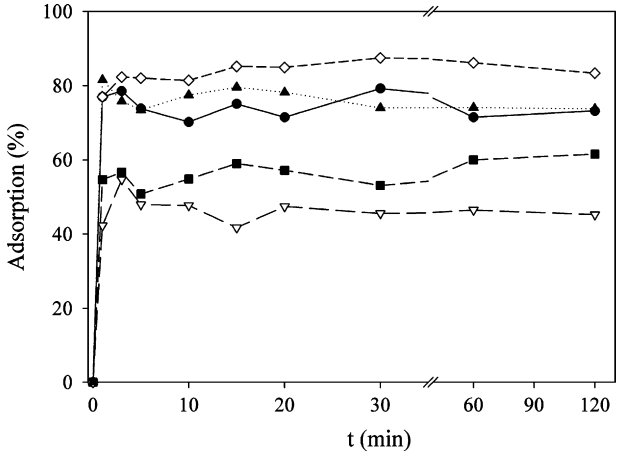
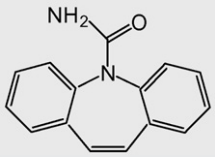
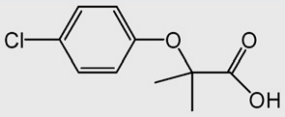
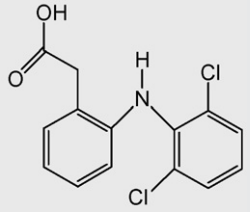
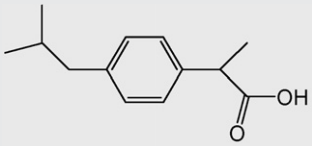
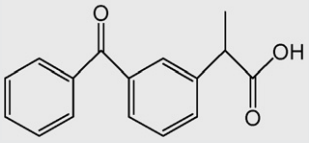
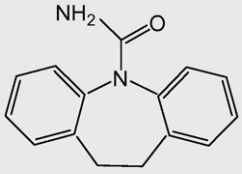
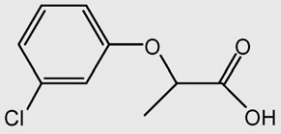


Fig. 1. Pharmaceutical adsorption onto SBA-15 as a function of contact time, ●: carbamazepine, ▽: clofibric acid, ■: diclofenac, ◊: ibuprofen, ▲: ketoprofen.

Table 1
Molecular structure, physicochemical properties, relative recovery (%) (with the corresponding surrogate standard) of pharmaceuticals.

Pharmaceuticals	CAS number	Structure	pK_a[a]	log K_{ow}[a]	Water Solubility (mg L^{-1})[b]	Relative recovery (%) $n = 5$
Carbamazepine	298-46-4		13.90	2.45	17.7	99 ± 1[c]
Clofibric acid	882-09-7		2.84[d]	2.57[e]	583	94 ± 2
Diclofenac	15307-86-5		4.15	4.51	2.37[f]	87 ± 5
Ibuprofen	15687-27-1		4.91	3.97	21	99 ± 4
Ketoprofen	22071-15-4		4.45	3.12	51	76 ± 4
10,11-Dihydrocarbamazepine	3564-73-6		–	2.46[b]	16.8	–
Cloprop	101-10-0		–	2.39[b]	1200	–

[a] Reference [13].
[b] http://www.syrres.com/esc/physdemo.htm (accessed on 20 May 2008).
[c] Relative standard deviation (%).
[d] Reference [9].
[e] Reference [10].
[f] This is water solubility of diclofenac; however, in this study sodium salt of diclofenac (CAS: 15307-79-6) was used, its solubility in water is 2430 mg L^{-1} (http://www.syrres.com/esc/physdemo.htm).

solution were filtered (0.45 μm), extracted and analyzed by the LC–MS/MS system.

Adsorption of a mixture of five selected pharmaceuticals was conducted by introducing 10 mg SBA-15 into 10 mL solution of five pharmaceuticals at the same concentration (25 μg L^{-1}) at pH 5. The samples were taken after 5, 15, 30, 60, 120, 480, and 1440 min. Aliquots of supernatant solution were filtered (0.45 μm), extracted and analyzed by the LC–MS/MS system.

2.4. Sample preparation and analytical methods

Before analysis, the samples obtained after filtration were extracted further by a SPE procedure using 60 mg Oasis HLB cartridges. Then, pharmaceuticals were analyzed on a LC–MS/MS system equipped with a HPLC Waters 2695 Separations Module accompanied with Waters 2996 PAD, a mass spectrometer (Waters (Micromass) Quattro micro API), and a XTerra MS C18 5 μm col-

umn (Waters, 2.1 × 50 mm). (The experimental details of sample preparation and analytical methods are present in Supplementary Information.)

3. Results and discussions

3.1. Characterization of SBA-15

The XRD pattern of SBA-15 sample is shown in Fig. S1 (Supplementary Information), which exhibits three well-resolved peaks at 2θ between 0.5° and 3°, characterizing a well-ordered mesoporous structure with *P6* mm hexagonal symmetry [15]. The well-ordered hexagonal arrays of mesopores are also confirmed by the TEM image (Fig. S2, Supplementary Information) with high uniformity and the pore size evaluated at ~ 8 nm. Based on N_2 adsorption–desorption measurement, the Brunauer–Emmett–Teller (BET) specific surface area, pore volume, and pore size of SBA-15 was estimated at 737 m^2/g, 1.03 cm^3/g, and ~8 nm, respectively, which is consistent with the TEM image and the reported data [15]. PZC of SBA-15 was estimated from the intersection point of three titration curves obtained at different concentrations of the inert electrolyte NaCl. PZC of SBA-15 was determined as 4.0 ± 0.1, which is similar to the isoelectric point of a mesoporous silica MCM-41 (3.6 ± 0.18) [24].

3.2. Kinetics of pharmaceutical adsorption

Adsorption of all pharmaceuticals reaches equilibrium in very short time (<15 min), even in 1 min (Fig. 1). The contact time needed for mesoporous silica is significantly shorter than the adequate time (4 h) for adsorption of pharmaceuticals on activated carbon [12,25], which can be resulted from the well-ordered mesoporous structure of SBA-15 rather than a disordered microporous structure of activated carbons. As mentioned above, SBA-15 possesses a system of uniform and large pores that may allow pharmaceutical molecules to diffuse easily into the pores and adsorb on the surface in a short time.

The adsorption kinetic data were examined using a pseudo-second-order reaction kinetics expression [26]:

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (1)$$

where k_2 (g mg^{-1} min^{-1}) is the equilibrium rate constant of pseudo-second-order chemical sorption; q_e is the amount of adsorbate sorbed at equilibrium (mg g^{-1}); q is the amount of adsorbate sorbed at t (min). The straight-line plots of (t/q) versus t have been tested to obtain rate parameters. Fig. S3 (Supplementary Information) shows good compliance with the pseudo-second-order equation for all pharmaceuticals, which is reflected by the extremely high determination coefficients (R^2 > 0.997) of the linear plots. Interestingly, adsorption of ibuprofen on activated carbon from aqueous phase also obeyed the pseudo-second-order equation [25].

3.3. Adsorption isotherms

From the various isotherm equations that may be used to analyze adsorption data in aqueous phase, the Langmuir [27]—the theoretical equilibrium isotherm and the Freundlich [28]—the empirical equilibrium isotherm are the most common models. The linear forms of these equations are displayed as equation (2) (Langmuir) and (3) (Freundlich):

$$\frac{1}{q_e} = \frac{1}{q_m K_L C_e} + \frac{1}{q_m} \quad (2)$$

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (3)$$

where q_m (mg g^{-1}) is the maximum adsorption capacity, q_e (mg g^{-1}) is the amount of adsorbed pharmaceuticals, C_e (mg L^{-1}) is the equilibrium pharmaceutical concentration, K_F and n are the Freundlich constants, and K_L (L mg^{-1}) is the Langmuir constant. The linear Langmuir and Freundlich isotherms were fitted to the experimental data. The Langmuir and Freundlich parameters, along with the coefficients of determination (R^2) of the linear plots, are presented in Table 2. Adsorption of pharmaceuticals on SBA-15 can be fitted by both Langmuir and Freundlich model with R^2 > 0.91; however, only Freundlich curves are shown in Fig. 2. In a recent study, Ho [29] discussed the advantages of using non-linear Chi-square analysis (χ^2) to compare the fitting of experimental data to isotherm models. χ^2 (mg g^{-1}) determined using the following equation:

$$\chi^2 = \sum \frac{(q_e - q_{e,m})^2}{q_{e,m}} \quad (4)$$

where q_e (mg g^{-1}) is the experimental equilibrium capacity and $q_{e,m}$ (mg g^{-1}) is the equilibrium capacity obtained by calculated from the models. As Ho suggested, the smaller χ^2 values display the better match of the model [29]. In Table 2, the results of χ^2 are also presented. χ^2 values of the Freundlich isotherm for all pharmaceuticals were lower than those of the Langmuir isotherm, indicating that the Freundlich isotherm is the better fitting isotherm for adsorption of pharmaceuticals on SBA-15. As reported earlier, adsorption of antibiotic ofloxacin and tetracycline onto mesoporous silica followed Langmuir–Freundlich model [30] and a dual site adsorption model [31], respectively.

In general, as the K_F value increases, the adsorption capacity of the adsorbent for a given pharmaceuticals increases, reflecting partially the affinity of pharmaceuticals toward the adsorbent. From that viewpoint, affinity of pharmaceuticals with SBA-15 follows the order: ibuprofen > carbamazepine ~ ketoprofen > diclofenac > clofibric acid. For acidic pharmaceuticals, this affinity order obeys well their pK_a values: ibuprofen (pK_a = 4.91) > ketoprofen (pK_a = 4.45) > diclofenac (pK_a = 4.15) > clofibric acid (pK_a = 2.84). More explanation about adsorption mechanism will be discussed in detail later.

3.4. Effect of dosage

The removal efficiency of pharmaceuticals increases significantly as the adsorbent concentration was increased from 0.1

Table 2
Isotherm parameters obtained by fitting equilibrium data with the Freundlich and Langmuir isotherms for the adsorption of pharmaceuticals on SBA-15.

	Freundlich equation				Langmuir equation			
Pharmaceuticals	K_F ($mg^{1-1/n}$ $L^{1/n}$ g^{-1})	n	R^2	χ^2 (mg g^{-1})	K_L (L mg^{-1})	q_m (mg g^{-1})	R^2	χ^2 (mg g^{-1})
Carbamazepine	1.10	1.34	0.99	0.008	33.81	0.16	0.99	0.065
Clofibric acid	0.56	1.15	0.92	0.054	22.15	0.07	0.92	0.244
Diclofenac	0.72	1.04	0.96	0.027	2.61	0.34	0.99	0.037
Ibuprofen	1.50	1.29	0.97	0.027	13.33	0.41	0.97	0.035
Ketoprofen	1.09	1.31	0.96	0.011	14.69	0.28	0.91	0.019

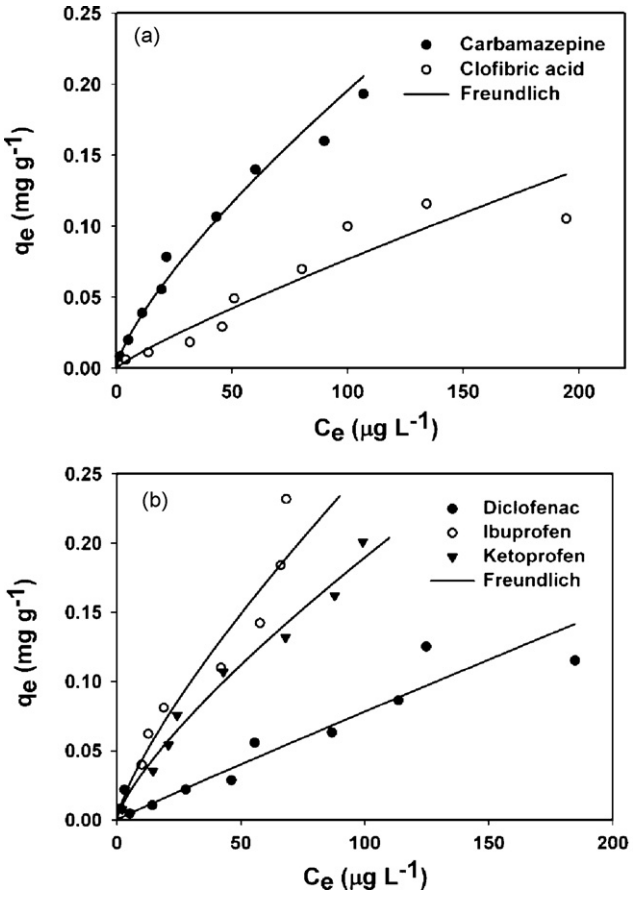


Fig. 2. Adsorption isotherms of (a) carbamazepine and clofibric acid and (b) diclofenac, ibuprofen, and ketoprofen on SBA-15 at 25 °C, pH 3 for clofibric acid, pH 5 for the other ones.

to 2.0 g/L (Fig. 3). At 2.0 g/L SBA-15 dosage, removal of clofibric acid, diclofenac, carbamazepine, ibuprofen, and ketoprofen can be achieved 62.5, 66.7, 84.4, 95.1, and 91.2%, respectively. In the range of 0.1–1.0 g/L SBA-15 dosage, pharmaceutical adsorption increased almost linearly with adsorbent concentration, but the increase of adsorbent dosage from 1.0 to 2.0 g/L does not make a significant effect. By increasing the dosage of SBA-15 from 1.0 to 2.0 g/L, the removal of pharmaceuticals was increased only from 6 to 16%.

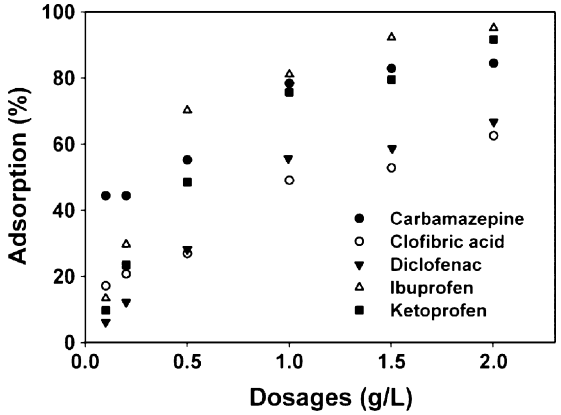


Fig. 3. Effect of mass of adsorbent (SBA-15) on pharmaceutical adsorption.

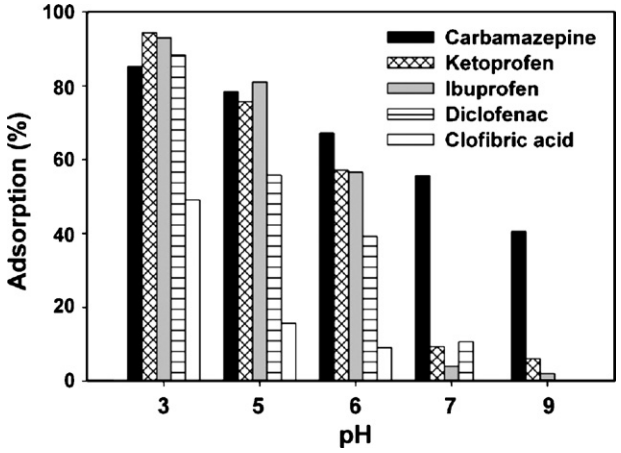


Fig. 4. Adsorption of pharmaceuticals on SBA-15 as a function of pH.

3.5. Effect of pH on pharmaceutical adsorption

The removal efficiencies of pharmaceuticals on SBA-15 presented in Fig. 4 shows that, as expected, adsorption of pharmaceuticals is strongly dependent on pH. Adsorption of pharmaceuticals onto SBA-15 can be formed and controlled by both non-electrostatic and electrostatic interaction. In the case of carbamazepine (pK_a = 13.90, Table 1), a neutral compound in the tested pH range, its binding onto SBA-15 is solely responsible by a non-electrostatic interaction involving hydrogen bonding [31]. This hydrogen bonding is preferred at pH lower than 4.0 (PZC of SBA-15), at which silica surface has a net positive charge; however, it becomes less favorable on negative silica surface as pH higher than 4.0, resulting a decrease in adsorption of carbamazepine. Meanwhile, uptake of acidic pharmaceuticals (clofibric acid, diclofenac, ibuprofen, and ketoprofen) on silica surface is attributed to both kinds of interaction, dependent on solution pH. At pH below the pK_a, acidic pharmaceuticals are neutral molecules, interacting with silica surface via non-electrostatic interaction and its behavior is similar to carbamazepine. When the pH is above the pK_a (pH >3 with clofibric acid and 5 with the others), acidic pharmaceuticals have negative charge while surface of silica gradually becomes more negatively charged, leading to an electrostatic repulsion between them. Consequently, adsorption of acidic pharmaceuticals dropped sharply. Furthermore, when pH is above 7, acidic pharmaceutical molecules and surface groups on SBA-15 completely become negatively charged, leading to no significant adsorption.

The experimental results also displayed that, for carbamazepine, diclofenac, ibuprofen, and ketoprofen, the removal efficiency is as high as 90% at pH 3 and about 75.6–81.0% (except for diclofenac) at pH 5. The removal of clofibric acid is only 49.0% at pH 3, however it is still higher than that in case of using high ozone doses (2.5–3.0 mg L^{-1}) (<40%) [11]. When pH was increased from 3 to 9, the removal of carbamazepine reduced gradually from 85.2% to 40.5%, while removal of acidic pharmaceuticals declined significantly and was almost negligible at pH 9.

In comparison among acidic pharmaceuticals, clofibric acid (pK_a = 2.84) showed the lowest removal rates, followed by diclofenac (pK_a = 4.15) (Fig. 4), because of their lower pK_a values, compared to that of ibuprofen (pK_a = 4.91) and ketoprofen (pK_a = 4.45). The lower-pK_a compounds are more readily deprotonated to become negatively charged. Therefore, more molecules exist in anion forms at the same pH, leading less favorable adsorption on silica surface.

At pH 3, carbamazepine, diclofenac, ibuprofen, and ketoprofen are all neutral molecules and showed quite similar adsorption (see

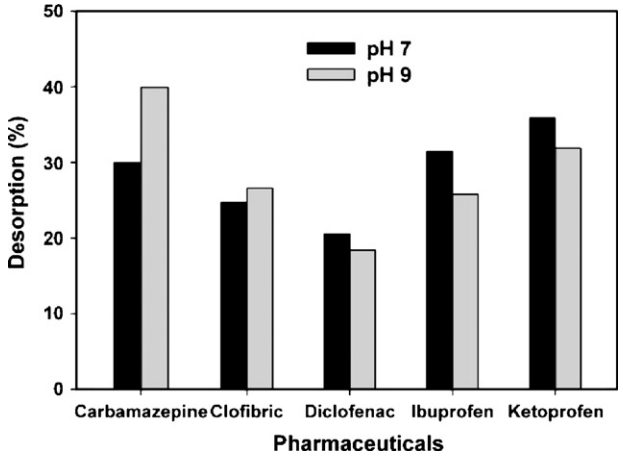


Fig. 5. Desorption of pharmaceuticals after 2 h sorption step on SBA-15 (in 1 mM phosphate buffer, pH 7 and 9, ionic strength 0.01 M KCl, 25 °C, reaction time 12 h).

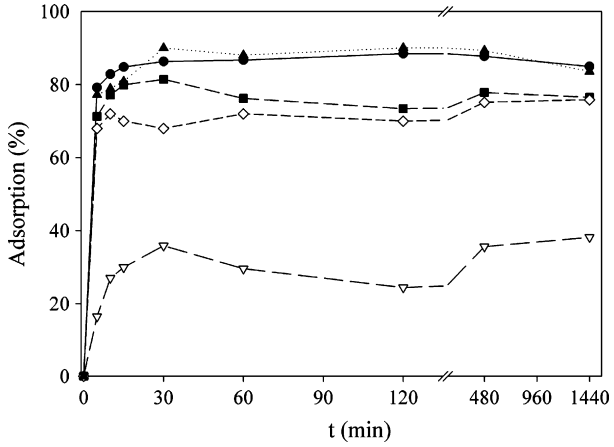


Fig. 6. Adsorption of a mixture of five pharmaceuticals onto SBA-15 (starting concentration of each pharmaceuticals of 25 $\mu g\,L^{-1}$, at 25 °C, pH 5) as a function of contact time, ●: carbamazepine, ▽: clofibric acid, ■: diclofenac, ◇: ibuprofen, ▲: ketoprofen.

Fig. 4), in spite of their differences in hydrophobicity (see Table 1). This result suggests that adsorption of the studied pharmaceuticals on mesoporous silica is mainly controlled by hydrophilic interactions between functional groups in pharmaceutical molecules and silanol groups on silica surface, rather than a hydrophobic sorption [32].

3.6. Desorption studies

Desorption of pharmaceuticals adsorbed on SBA-15 was performed in neutral (phosphate buffer at pH 7) and alkaline media (phosphate buffer at pH 9). Aforementioned, adsorption percentage of acidic pharmaceuticals on SBA-15 is almost negligible at pH 9 and less than 10% at pH 7, as such desorption of pharmaceuticals under these conditions expected to be almost complete. However, as shown in Fig. 5, desorption percentage of five pharmaceuticals varied from 20 to 40%. The results suggest that the adsorption is not completely reversible. In the other words, pharmaceuticals can be both reversibly and irreversibly adsorbed on the silica surface [31], which can be the result of heterogeneity of the silica surface (several types of silanol groups) and multifunctional nature of the adsorbates. As a result, there might be strong interactions between pharmaceuticals and silica surface, corresponding to irreversible adsorbed pharmaceuticals.

3.7. Mechanism of pharmaceutical adsorption onto SBA-15

The strongly pH-dependent adsorption of pharmaceuticals proposes that the interaction between pharmaceuticals and surface of the mesoporous silica is a hydrophilic case. Moreover, the low desorption percentages of pharmaceuticals from silica surface in alkaline media suggest that a fraction of pharmaceuticals are strongly adsorbed on SBA-15. One should remember that there are several types of functional groups on the silica surface, for example: ≡SiOH, ≡Si—O···H···O—Si≡, $\equiv SiOH_2^+$, $\equiv SiO^-$, etc. The strength of interaction between pharmaceuticals and silica surface is always variable and dependent on adsorption active sites (silanol groups). There exist adsorbed pharmaceuticals which bind tightly on silica surface and are difficult to desorb. Such strong bindings between pharmaceuticals and silica surface can be explained by hydrogen bonding or chemical bonding. In cases of acidic pharmaceuticals which possess carboxylic groups (—COOH), the interaction between pharmaceuticals and silanol groups can be postulated as follows:

$$\equiv Si{-}OH + HOOC{-}B \rightarrow \equiv Si{-}OOC{-}B + H_2O \quad (5)$$

$$\text{Or} \equiv Si{-}OH + HOOC{-}B \rightarrow \equiv Si{-}O\cdots H\cdots OOC{-}B + H^+ \quad (6)$$

where B is the remaining part of acidic pharmaceuticals. Generally, a hydrogen bonding reaction (Eq. (6)) is easier to occur, compared to a ligand-exchange reaction (Eq. (5)), due to its lower demand of activation energy. Sorption of the antibiotic ofloxacin to Al_2O_3 solids through the ketone and carboxylate functional groups via a ligand-exchange mechanism was reported [30]. In the case of carbamazepine—a neutral compound, the hydrogen bonding between the amide groups of carbamazepine and the silanol groups of silica is mainly responsible for its adsorption [31].

3.8. Adsorption of a mixture of pharmaceuticals

As mentioned earlier, SBA-15 showed efficient removal for individual pharmaceuticals in acidic media. However, one should remember that pharmaceuticals usually occur in the environment as a mixture and though individual pharmaceuticals were generally detected at low-levels, total concentrations commonly exceed 1 $\mu g\,L^{-1}$ [3]. The behavior of pharmaceuticals in a mixture is definitely different and complicated, not as individual cases. Therefore, investigation of adsorption of a mixture of pharmaceuticals is required as a succeeding step for further application.

Fig. 6 presents interesting results for adsorption of a five-pharmaceutical mixture onto SBA-15 as a function of contact time. Adsorption of the mixture can reach steady state in 30 min which is close to the equilibrium time needed for the cases of individual pharmaceuticals (see Fig. 1). Except for clofibric acid, removal of four remaining pharmaceuticals is very effective. Removal efficiency is 88.4% for carbamazepine, 77.8% for diclofenac, 75.2% for ibuprofen, 89.3% for ketoprofen, and 35.6% for clofibric acid. In comparison with single component case at the same initial concentration (25 $\mu g\,L^{-1}$) where the removal is 79.6, 42.4, and 86.5% for carbamazepine, diclofenac, ketoprofen, respectively, the removal of these compounds in the mixture is surprisingly higher, especially for diclofenac. Considering two remaining pharmaceuticals, removal of ibuprofen (75.2%) and clofibric acid (35.6%) in the mixture is somewhat smaller than that for the individual cases (87.6% for ibuprofen and 44.8% for clofibric acid). However, it should be mentioned that in the individual case the removal of clofibric acid was estimated at pH 3, instead of pH 5 in the mixture.

It was expected that the removal of every pharmaceuticals in the mixture would be much lower than that in the individual case, due to competitive adsorption among pharmaceuticals. In contrast, the adsorption of diclofenac, carbamazepine, and ketoprofen displayed higher values in the mixture compared to the single case. This

synergistic effect can be explained by uncompetitive co-adsorption or succeeding adsorption to form a multilayer of these pharmaceuticals. It can be visualized that there exist some kinds of binding, interaction or even reaction among diclofenac, carbamazepine, and ketoprofen, which induce the adsorption of the three compounds at the same time on surface of mesoporous silica. As reported earlier [33], in aqueous medium of pH 5.33, penicillin interacts with berberine, forming ion associates through electrostatic attraction of the polar head groups of penicillin and berberine. Whereas, ibuprofen and clofibric acid compete with the remaining compounds for the adsorption, leading to a decrease in their removal efficiency.

4. Conclusions

This study showed that mesoporous silica SBA-15 is a promising adsorbent for removal of pharmaceuticals not only for surface water but also for wastewater from pharmaceutical industrial manufactures where high-level concentrations of pharmaceuticals have been observed. SBA-15 presented very effective removals for tested pharmaceuticals in acidic media as individual and mixture forms in a short time. The low desorption percentages were confirmed, which implies that pharmaceuticals are not easily detached from adsorbents to get back into the treated water. The kinetics and equilibrium of pharmaceutical adsorption were best described using pseudo-second-order equation and Freundlich isotherm model, respectively. Moreover, information about adsorption mechanisms is valuable for further development of adsorbent materials. One should remember that pharmaceutical-adsorbed SBA-15 and mesoporous silica-based materials can be regenerated by combustion without loss, due to stability of mesoporous silica structure up to 850 °C [15]. Further results about effect of anions, humic acid, and cations on pharmaceutical adsorption will be provided for evaluating feasibility of application of SBA-15 in real situations.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2009.02.072.

References

[1] B. Halling-Sorensen, S. Nors Nielsen, P.F. Lanzky, F. Ingerslev, H.C. Holten Lutzhoft, S.E. Jorgensen, Occurrence, fate and effects of pharmaceutical substances in the environment—a review, Chemosphere 36 (1998) 357–393.
[2] T.A. Ternes, Occurrence of drugs in German sewage treatment plants and rivers, Water Res. 32 (1998) 3245–3260.
[3] D.W. Kolpin, E.T. Furlong, M.T. Meyer, E.M. Thurman, S.D. Zaugg, L.B. Barber, H.T. Buxton, Pharmaceuticals, hormones, and other organic wastewater contaminants in U.S. streams, 1999–2000: a national reconnaissance, Environ. Sci. Technol. 36 (2002) 1202–1211.
[4] A. Nikolaou, S. Meric, D. Fatta, Occurrence patterns of pharmaceuticals in water and wastewater environments, Anal. Bioanal. Chem. 387 (2007) 1225–1234.
[5] K. Fent, A.A. Weston, D. Caminada, Ecotoxicology of human pharmaceuticals, Aquat. Toxicol. 76 (2006) 122–159.
[6] S. Thiele-Bruhn, Pharmaceutical antibiotic compounds in soils–a review, J. Plant Nutr. Soil Sci. 166 (2003) 145–167.
[7] D.G.J. Larsson, C. de Pedro, N. Paxeus, Effluent from drug manufactures contains extremely high levels of pharmaceuticals, J. Hazard. Mater. 148 (2007) 751–755.
[8] S. Castiglioni, R. Bagnati, R. Fanelli, F. Pomati, D. Calamari, E. Zuccato, Removal of pharmaceuticals in sewage treatment plants in Italy, Environ. Sci. Technol. 40 (2006) 357–363.
[9] D. Loffler, J. Rombke, M. Meller, T.A. Ternes, Environmental fate of pharmaceuticals in water/sediment systems, Environ. Sci. Technol. 39 (2005) 5209–5218.
[10] C. Tixier, H.P. Singer, S. Oellers, S.R. Muller, Occurrence and fate of carbamazepine, clofibric acid, diclofenac, ibuprofen, ketoprofen, and naproxen in surface waters, Environ. Sci. Technol. 37 (2003) 1061–1068.
[11] T.A. Ternes, M. Meisenheimer, D. McDowell, F. Sacher, H.J. Brauch, B. Haist-Gulde, G. Preuss, U. Wilme, N. Zulei-Seibert, Removal of pharmaceuticals during drinking water treatment, Environ. Sci. Technol. 36 (2002) 3855–3863.
[12] P. Westerhoff, Y. Yoon, S. Snyder, E. Wert, Fate of endocrine-disruptor, pharmaceutical, and personal care product chemicals during simulated drinking water treatment processes, Environ. Sci. Technol. 39 (2005) 6649–6663.
[13] N.M. Vieno, H. Harkki, T. Tuhkanen, L. Kronberg, Occurrence of pharmaceuticals in river water and their elimination in a pilot-scale drinking water treatment plant, Environ. Sci. Technol. 41 (2007) 5077–5084.
[14] C.T. Kresge, M.E. Leonowicz, W.J. Roth, J.C. Vartuli, J.S. Beck, Ordered mesoporous molecular sieves synthesized by a liquid-crystal template mechanism, Nature 359 (1992) 710–712.
[15] D. Zhao, J. Feng, Q. Huo, N. Melosh, G.H. Fredrickson, B.F. Chmelka, G.D. Stucky, Triblock copolymer syntheses of mesoporous silica with periodic 50 to 300 angstrom pores, Science 279 (1998) 548–552.
[16] C. Cooper, R. Burch, Mesoporous materials for water treatment processes, Water Res. 33 (1999) 3689–3694.
[17] M.C. Burleigh, M.A. Markowitz, M.S. Spector, B.P. Gaber, Porous polysilsesquioxanes for the adsorption of phenols, Environ. Sci. Technol. 36 (2002) 2515–2518.
[18] K.Y. Ho, G. McKay, K.L. Yeung, Selective adsorbents from ordered mesoporous silica, Langmuir 19 (2003) 3019–3024.
[19] L.-C. Juang, C.-C. Wang, C.-K. Lee, Adsorption of basic dyes onto MCM-41, Chemosphere 64 (2006) 1920–1928.
[20] S. Wang, H. Li, Structure directed reversible adsorption of organic dye on mesoporous silica in aqueous solution, Microporous Mesoporous Mater. 97 (2006) 21–26.
[21] S.M. Rivera-Jiménez, A.J. Hernández-Maldonado, Nickel(II) grafted MCM-41: a novel sorbent for the removal of Naproxen from water, Microporous Mesoporous Mater. 116 (2008) 246–252.
[22] Y. Wang, C. Bryan, H. Xu, P. Pohl, Y. Yang, C.J. Brinker, Interface chemistry of nanostructured materials: ion adsorption on mesoporous alumina, J. Coll. Interf. Sci. 254 (2002) 23–30.
[23] M.D. Hernando, M. Mezcua, A.R. Fernandez-Alba, D. Barcelo, Environmental risk assessment of pharmaceutical residues in wastewater effluents, surface waters and sediments, Talanta 69 (2006) 334–342.
[24] J. Deere, E. Magner, J.G. Wall, B.K. Hodnett, Mechanistic and structural features of protein adsorption onto mesoporous silicates, J. Phys. Chem. B 106 (2002) 7340–7347.
[25] A.S. Mestre, J. Pires, J.M.F. Nogueira, A.P. Carvalho, Activated carbons for the adsorption of ibuprofen, Carbon 45 (2007) 1979–1988.
[26] Y.S. Ho, G. McKay, Sorption of dye from aqueous solution by peat, Chem. Eng. J. 70 (1998) 115–124.
[27] I. Langmuir, The constitution and fundamental properties of solids and liquids. Part I. Solids, J. Am. Chem. Soc. 38 (1916) 2221–2295.
[28] H. Freundlich, Über die adsorption in Lösungen, Z. Physik. Chem. 57 (1907) 385–470.
[29] Y.-S. Ho, Selection of optimum sorption isotherm, Carbon 42 (2004) 2115–2116.
[30] K.W. Goyne, J. Chorover, J.D. Kubicki, A.R. Zimmerman, S.L. Brantley, Sorption of the antibiotic ofloxacin to mesoporous and nonporous alumina and silica, J. Coll. Interf. Sci. 283 (2005) 160–170.
[31] I. Turku, T. Sainio, E. Paatero, Thermodynamics of tetracycline adsorption on silica, Environ. Chem. Lett. 5 (2007) 225–228.
[32] O. Lorphensri, J. Intravijit, D.A. Sabatini, T.C.G. Kibbey, K. Osathaphan, C. Saiwan, Sorption of acetaminophen, 17α-ethynyl estradiol, nalidixic acid, and norfloxacin to silica, alumina, and a hydrophobic medium, Water Res. 40 (2006) 1481–1491.
[33] C.Z. Huang, P. Feng, Y.F. Li, K.J. Tan, H.Y. Wang, Adsorption of penicillin–berberine ion associates at a water/tetrachloromethane interface and determination of penicillin based on total internal-reflected resonance light scattering measurements, Anal. Chim. Acta 538 (2005) 337–343.