Adsorptive removal of naproxen and clofibric acid from water using metal-organic frameworks

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ABSTRACT

Adsorptive removal of naproxen and clofibric acid, two typical PPCPs (pharmaceuticals and personal care products), has been studied using metal-organic frameworks (MOFs) for the first time. The removal efficiency decreases in the order of MIL-101 > MIL-100-Fe > activated carbon both in adsorption rate and adsorption capacity. The adsorption kinetics and capacity of PPCPs generally depend on the average pore size and surface area (or pore volume), respectively, of the adsorbents. The adsorption mechanism may be explained with a simple electrostatic interaction between PPCPs and the adsorbent. Finally, it can be suggested that MOFs having high porosity and large pore size can be potential adsorbents to remove harmful PPCPs in contaminated water.

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1. Introduction

Pharmaceuticals and personal care products (PPCPs) have become an essential and indispensible element for life. PPCPs as pollutants generally include a class of chemical contaminants that can arise from the use of prescription medicines, cosmetics, fragrances, veterinary drugs, fungicides, disinfectants and agricultural practices [1,2]. In 1980s, the existence of PPCPs in the environment was confirmed for the first time [3,4]. Several research works have demonstrated the presence of these kinds of pharmaceuticals in the effluent of wastewater treatment plants, rivers, lakes and occasionally, in groundwater [5]. The demand of PPCPs is increasing day by day due to the rapid increase of population in the world. Moreover, PPCPs are produced with long shelf-life to meet the customers' demand which makes PPCPs to be persistent in the environment even after these products have been used up [4,6,7]. Although the adverse impact of PPCPs on human health or environment is still not fully understood, it is reported that these contaminants may cause endocrine disruptions that may change hormonal actions [8,9]. Still now, PPCPs in the environment or drinking water are not regulated [9]. However, the removal of these so called emerging contaminants from our potable water and aquatic systems is an important issue for worldwide researchers [4,7,10].

Up to now, various methods have been adopted to remove PPCPs from the drinking or wastewater. Coagulation–flocculation [11], biodegradation [12,13], photodegradation [14], biofiltration [15], ozonation [16], chlorination [17] and adsorption [2,4,10] are some of the methods studied so far. However, it is reported that conventional treatments such as coagulation, sedimentation and filtration cannot remove more than 25% of PPCPs [18]. The removal of PPCPs by adsorption is gaining much interest as this process is simple and cost effective. So far, activated carbon is the widely used adsorbent for the removal of PPCPs. Some other adsorbents such as MCM-41 [4], SBA-15 [10], amberlite XAD-7 [19] and bentonite [20] have also been investigated. Moreover, with the invention of several novel adsorbents such as mesoporous carbon and mesoporous aluminosilicates, the applicability of adsorption is exploring to various field [21–24].

Metal organic frameworks (MOFs) are crystalline porous materials which are well known for their various potential applications [25–31]. The particular interest in the MOF materials is due to the easy tunability of their pore size and shape from a microporous to a mesoporous scale by changing the connectivity of the inorganic moiety and the nature of organic linkers [25–27]. MOFs are especially interesting in the field of adsorption, separation and storage of gases and vapors. Removal of hazardous materials such as sulfur-containing compounds [32–34], dyes [35,36] and benzene [37] has also been studied.

Among the numerous MOFs reported so far, two of the most topical solids are the porous chromium-benzenedicarboxylate

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(Cr-BDC called MIL-101) [38,39] (MIL stands for Material of Institute Lavoisier) and the iron-benzenetricarboxylate (Fe-BTC named MIL-100-Fe) [40,41], which are largely studied for their potential applications. MIL-101 with a chemical formula of $Cr_3O(F/OH)(H_2O)_2[C_6H_4(CO_2)_2]$, has a cubic structure and huge pore volume of $1.9\,cm^3/g$[38,39]. MIL-101 has been studied for adsorptive removal of dyes [35] and benzene [37]. MIL-100-Fe, with a chemical formula $Fe_3^{(III)}O(H_2O)_2(F)\{C_6H_3(CO_2)_3\}_2 \cdot nH_2O$ ($n \sim 14.5$), is a reusable oxidative catalyst for the aerobic oxidation of thiols to disulfides [41]. MIL-100-Fe is also used for the adsorption of hydrocarbons such as propane, propene and propyne [42].

However, so far, there has been no report to use the MOFs including MIL-101 and MIL-100-Fe in the removal of PPCPs. In this work, we report, for the first time, the results of the adsorption of the typical PPCPs over the MOFs, especially well-studied MIL-101 and MIL-100-Fe, to understand the characteristics of adsorption and possibility of using MOFs as adsorbents for the removal of PPCPs from contaminated water.

As representative PPCPs, a common drug named naproxen was selected for this study. Naproxen is a nonsteroidal anti-inflammatory drug (NSAID) that is widely used for the reduction of pain, fever, inflammation and stiffness. The adsorption of other common PPCPs named clofibric acid was also investigated. Clofibric acid is bioactive metabolite of various lipid regulating pro-drugs. The chemical structures of the two PPCPs are shown below.

2. Experimental

2.1. Materials and reagents

All solvents and reactants are commercially available and were used without further purification. For synthesis of MIL-101, chromium nitrate nonahydrate ($Cr(NO_3)_3 \cdot 9H_2O$, 99%) and terephthalic acid (TPA, 99%) were purchased from Samchun and Junsei chemicals, respectively. Again, 1,3,5-benzenetricarboxylic acid (H_3BTC, 99%), nitric acid (HNO_3, 60%) were obtained from Aldrich and OCI chemicals, respectively. Metallic iron and hydrofluoric acid (HF, 40%) were purchased from DC Chemical. N,N-dimethylformamide (99%) and ethanol (99.5%) was obtained from OCI chemical which was used for purification of MOFs. Activated carbon (granule, size: 2–3 mm) was purchased from the Duksan pure chemical. Naproxen and clofibric acid (97%) were received from Aldrich.

MIL-101 was synthesized from $Cr(NO_3)_3 \cdot 9H_2O$, TPA and deionized water similar to a reported method [43]. The reactants composition was 1.0 $Cr(NO_3)_3 \cdot 9H_2O$:1.0 TPA:300 H_2O. The precursor of 30 g was loaded in a Teflon-lined autoclave and put in a preheated electric oven at 210 °C for 8 h. After the reaction, the autoclave was cooled to room temperature and solid green-colored products were recovered by filtration. To remove the unreacted TPA, the as-synthesized MIL-101 was further purified by treatment with N,N-dimethylformamide following a reported method [44]. The purified MIL-101 was dried overnight at 100 °C and stored in a desiccator after cooling to room temperature.

MIL-100-Fe was synthesized from metallic iron, H_3BTC, HF, HNO_3 and deionized water similar to a reported method [40] under autogenous pressure at 180 °C. The reactant composition for the syntheses was 1.0 Fe^0:0.66 H_3BTC:2.0 HF:1.2 HNO_3:280 H_2O. A reaction mixture of 30 g was loaded into a 100 mL Teflon autoclave, which was sealed and placed in a microwave oven (MARS-5, CEM, maximum power of 1200 W) in order to take advantage of rapid synthesis under microwave irradiation [45,46]. The autoclave in the microwave oven was heated to the reaction temperature in

2 min and maintained for 2 h. The microwave power was 400 W throughout all the synthesis steps including the heating-up stage. After the crystallization for 2 h, the autoclave was cooled to room temperature and light orange solid product was recovered by filtration. The purification of the as-synthesized MIL-100-Fe was performed in two steps using hot water (stirring 1 g of MIL-100-Fe in 350 mL of water at 80 °C for 5 h) and hot ethanol (stirring 1 g of MIL-100-Fe in 200 mL of ethanol at 60 °C for 3 h). The purified MIL-100-Fe, after filtration, was dried overnight in air and stored in a desiccator.

2.2. Adsorption experiments

Naproxen (Aldrich) and clofibric acid (Aldrich) solutions with desired concentrations were prepared using deionized water. The naproxen and clofibric acid concentrations were determined using the absorbance (at 230 nm and 227 nm, respectively) of the solutions after getting the UV spectra of the solution with a spectrophotometer (Shimadzu UV spectrophotometer, UV-1800). A calibration curve for naproxen was obtained from the spectra of the standard solutions (1–10 ppm, due to low solubility of naproxen in water) at a specific pH 4.5. A calibration curve was also obtained for clofibric acid from the spectra of the standard solutions (10–50 ppm) at a specific pH 4.0. The pH of 4.0 or 4.5 was selected based on the fact that the PPCPs aqueous solution is weak acidic (due to −COOH group of naproxen and clofibric acid and dissolved carbon dioxide).

Before adsorption, the adsorbents were dried overnight under vacuum at 100 °C and were kept in a desiccator. An exact amount of the adsorbents ($\sim$5.0 mg) was put in the aqueous naproxen solution (50 mL) having a fixed concentration. The naproxen solution (pH: $\sim$4.5) containing the adsorbents were mixed well with magnetic stirring and maintained for a fixed time (10 min to 12 h) at 25 °C. After adsorption for a pre-determined time, the solution was separated from the adsorbents with a syringe filter (PTFE, hydrophobic, 0.5 μm), and the naproxen concentration was calculated by using the absorbance of the UV spectra. If necessary, the PPCP solutions were diluted for UV measurement.

The amount of naproxen adsorbed onto different adsorbents was calculated by mass-balance relationship Eq. (1):

$$q_t = (C_0 - C_t)\frac{V}{W} \tag{1}$$

where C_0 and C_t (mg/L) are the liquid-phase concentrations of the naproxen at time = 0 and t, respectively. V (L) and W (g) are the volume of the solution and the weight (g) of the adsorbents, respectively. To determine the adsorption capacity at various conditions of acidity, the pH of the naproxen solution was adjusted with 0.1 M HCl or 0.1–0.2 M NaOH aqueous solution (volume < 0.2 mL). The very similar procedure was applied to study the adsorption of clofibric acid. However, the initial concentrations of clofibric acid were 50–150 ppm due to high solubility in water.

3. Results and discussion

3.1. Characterization and properties of adsorbents

The crystal structure of the synthesized materials was confirmed to be MIL-101 and MIL-100-Fe as determined by the XRD patterns in Supporting Fig. 1(a) and (b) [38,40]. The nitrogen adsorption isotherms of activated carbon, MIL-100-Fe and MIL-101 are shown in Supporting Fig. 2. The summarized textural properties are shown in Supporting Table 1 which shows that the BET or Langmuir surface area and total pore volume of the three adsorbents are in the order of activated carbon < MIL-100-Fe < MIL-101. Similarly, as shown in
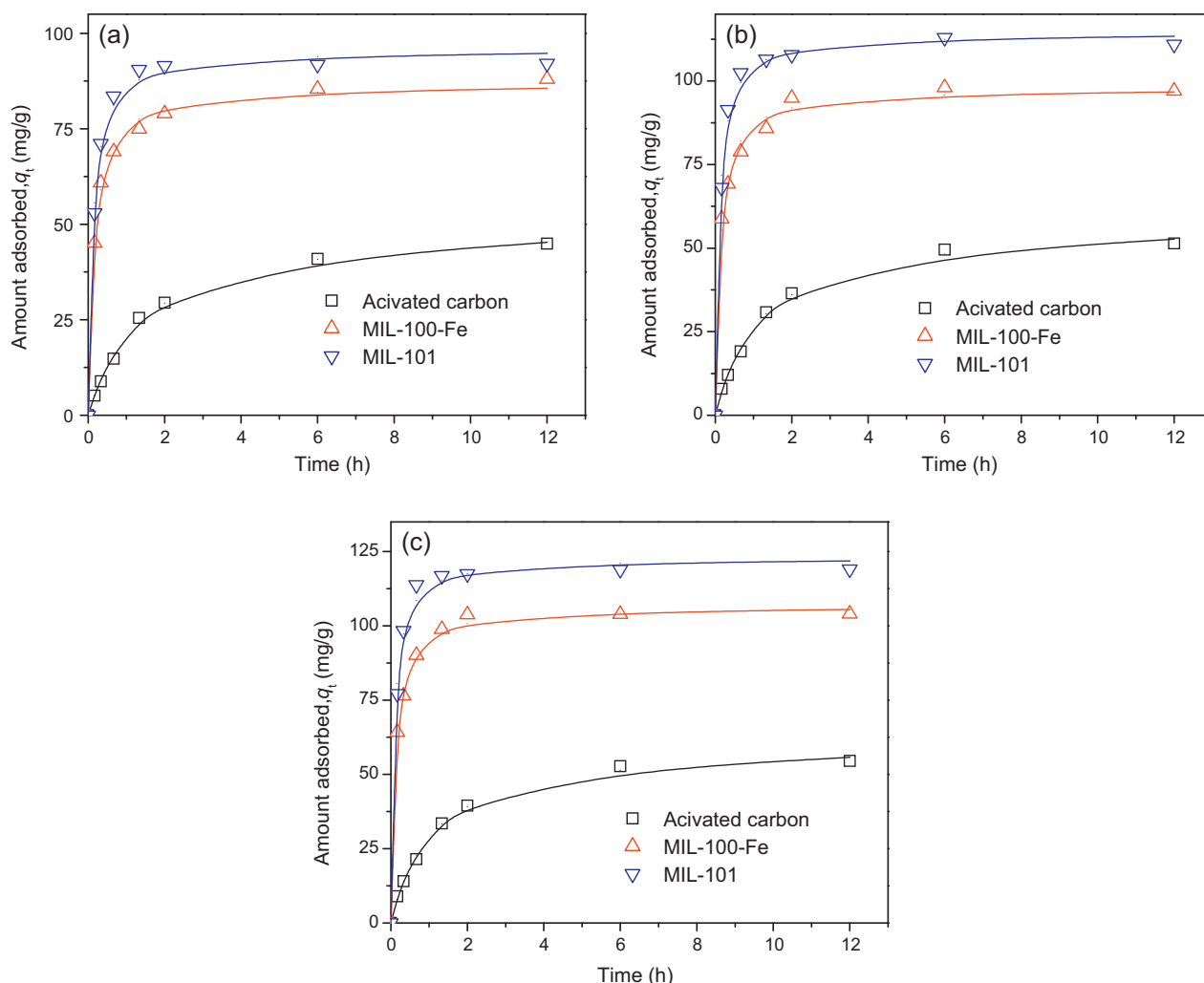
Fig. 1. Effect of contact time on the adsorption of naproxen over the three adsorbents at different initial naproxen concentrations of (a) $C_i = 10$ ppm; (b) $C_i = 13$ ppm; (c) $C_i = 15$ ppm. The solid lines show the calculated results derived from pseudo-second order non-linear method.

Supporting Fig. 3, the pore sizes increases in the order of activated carbon < MIL-100-Fe < MIL-101.

3.2. Adsorption kinetics

The effect of contact time on the naproxen adsorption over different adsorbents at different initial concentrations (10–15 ppm) is depicted in Fig. 1. The naproxen adsorption over activated carbon, MIL-100-Fe and MIL-100 was rapid at the initial stages of the contact period, and thereafter it approached to equilibrium. This may be due to the presence of huge number of available vacant surface sites for adsorption during the initial stages of the adsorption [47]. As time passes, number of available vacant sites decreases and the adsorption sites become saturated. As shown in Fig. 1, the adsorbed quantity of naproxen is in the order of activated carbon < MIL-100-Fe < MIL-101 for the whole adsorption time from any initial naproxen concentration. The adsorption time needed for saturation is in the order of activated carbon > MIL-100-Fe > MIL-101. The adsorption over MIL-101 and MIL-100-Fe is practically completed in 2 h; however, the adsorbed naproxen increases steadily with time (up to 12 h) over the activated carbon.

To design a proper adsorption technology, it is important to have profound knowledge and clear idea about the kinetics of the particular process. Dynamics of naproxen adsorption can be interpreted by the pseudo-second-order model [48,49], which is expressed by the following equation.

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \tag{2}$$

where, q_e (mg/g) is amount adsorbed at equilibrium; q_t (mg/g) is amount adsorbed at time t; t (min) is adsorption time; k_2 (g mg^{-1} min^{-1}) is the pseudo-second-order rate constant.

A trial-and-error procedure [48] was adapted to calculate the pseudo-second order kinetic parameters in the case of non-linear method by using the solver add-in with Microsoft's spreadsheet, Microsoft Excel. The coefficient of determination, r^2 was calculated by following Eq. (3)

$$r^2 = \frac{\sum (q_m - \bar{q}_t)^2}{\sum (q_m - \bar{q}_t)^2 + \sum (q_m - q_t)^2} \tag{3}$$

where, q_m (mg/g) is amount of naproxen on the surface of adsorbents at any time t, obtained from the second order kinetic model; q_t (mg/g) is amount of naproxen on the surface of adsorbents at any time t, obtained from experiments; and $\bar{q}_t$ (mg/g) is average of q_t.

Fig. 1 also shows the non-linear plot of the pseudo-second-order rate equation, and Table 1 describes the pseudo-second-order kinetic parameters for different initial concentrations of naproxen obtained utilizing the non-linear curve fitting analysis method. From Table 1, it can be said that the pseudo-second-order model

Table 1
The pseudo-second-order kinetic parameters with coefficient of determination (r^2) for the adsorption of naproxen over the three adsorbents at various initial concentrations obtained from non-linear regression method.

Initial Conc. C_i (ppm)	MIL-101				MIL-100-Fe				Activated carbon			
	$q_{e,exp}$ (mg/g)	$q_{e,cal}$ (mg/g)	k_2 (g mg^{-1} min^{-1})	r^2	$q_{e,exp}$ (mg/g)	$q_{e,cal}$ (mg/g)	k_2 (g mg^{-1} min^{-1})	r^2	$q_{e,exp}$ (mg/g)	$q_{e,cal}$ (mg/g)	k_2 (g mg^{-1} min^{-1})	r^2
10	92.1	94.7	1.45×10^{-3}	0.984	88.0	85.6	1.31×10^{-3}	0.967	44.9	45.3	2.30×10^{-4}	0.997
13	111.0	113.3	1.47×10^{-3}	0.985	96.9	96.7	1.33×10^{-3}	0.976	51.4	52.6	2.40×10^{-4}	0.996
15	119.1	121.8	1.55×10^{-3}	0.996	104.	105.6	1.34×10^{-3}	0.997	54.5	55.7	2.50×10^{-4}	0.997

fits the experimental results to a high degree of accuracy for all naproxen concentrations similar to a previous report [50]. It also confirms a good agreement between the experimental and the calculated q_e values (see Table 1). This indicates that the adsorption of naproxen over the three adsorbents can be interpreted with the pseudo-second order kinetic model.

Moreover, as shown in Table 1, for all three adsorbents, amount adsorbed at equilibrium (q_e) increase steadily with increasing initial naproxen concentrations. This may be attributed to the fact that higher initial concentration provides a higher driving force to overcome all mass transfer resistances of solutes between the aqueous and solid phases [51]. Again, the rate constant, k_2 for naproxen adsorption is in the order of activated carbon < MIL-Fe-100 < MIL-101 (see Table 1). This tendency agrees with the pore size distributions of the adsorbents (see Supporting Fig. 3). It has also been reported that a kinetic constant of adsorption generally increases with increasing the pore size of a porous material for both liquid-phase and gas-phase adsorptions [37,52–54]. Therefore, this result shows the importance of pore size and suggests potential applications of MOFs with large pore size (like MIL-101) in PPCPs removal.

3.3. The adsorption isotherms

The adsorption isotherms were obtained after adsorption for sufficient time of 12 h, and the results are compared in Fig. 2(a). The amount of adsorbed naproxen over MOF-101 is higher than that of MIL-100-Fe and activated carbon for the experimental conditions, suggesting the efficiency of the MIL-101 in the adsorption.

Langmuir isotherm is used in this study to describe the adsorption isotherms. Langmuir model assumes monolayer adsorption onto a surface which consists of finite number of active sites having a uniform energy [51,55]. The linear form of Langmuir isotherm equation is given as:

$$\frac{C_e}{q_e} = \frac{C_e}{Q_0} + \frac{1}{Q_0 b} \tag{4}$$

where, C_e (mg/L) is equilibrium concentration of adsorbate; q_e (mg/g) is the amount of adsorbate adsorbed; Q_0 (mg/g) is Langmuir constant (maximum adsorption capacity); b (L/mg or L/mol) is Langmuir constant. Therefore, the Q_0 can be obtained from the reciprocal of the slope of a plot of C_e/q_e against C_e. Fig. 2(b) shows the linear Langmuir plots for the adsorption of naproxen over the three adsorbents, and the Q_0 values that are determined from Fig. 2(b) are summarized in Table 2. The result shows that the Q_0 values of naproxen over MIL-101 are 132 mg/g, which is 1.15 times and 1.63 times higher than that of MIL-100-Fe and activated carbon, respectively, confirming the potential application of MIL-101 in the adsorptive removal. It is reported that Q_0 has a noteworthy relation to the surface area or pore volume of adsorbents [54,56]. In other words, adsorbents having larger pore volume or surface area can accumulate more solute which results in the increase of Q_0. In this study, we have also found that the Q_0 values of naproxen adsorption increase with increase of surface area or pore volume
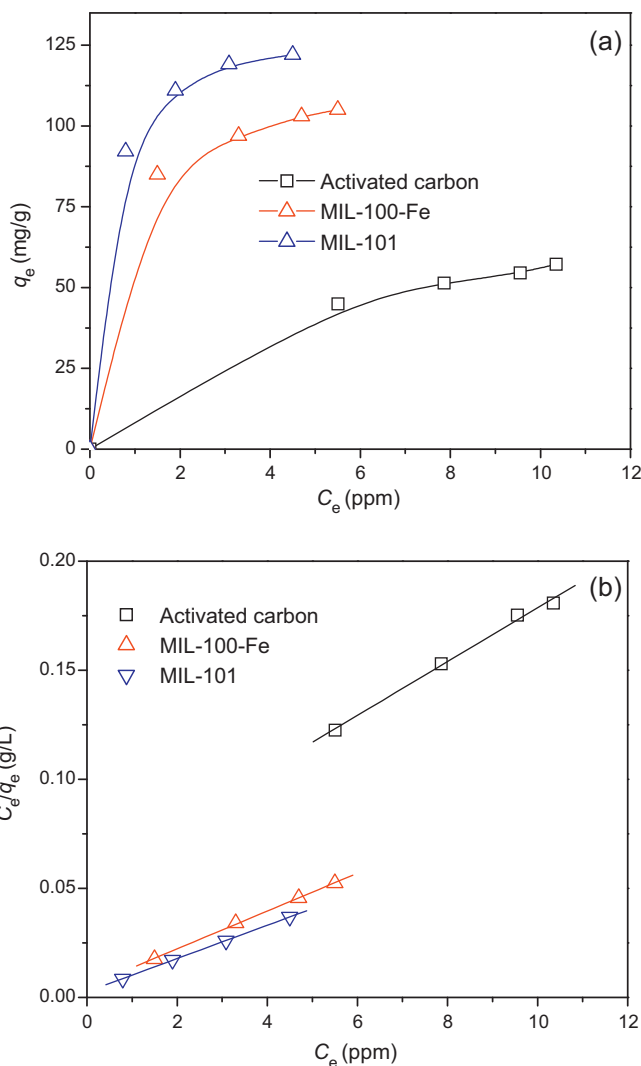

Fig. 2. (a) Adsorption isotherms for naproxen over the three adsorbents; and (b) Langmuir plots of the isotherms.

Table 2
Langmuir isotherm parameters for the naproxen adsorption over activated carbon, MIL-100-Fe and MIL-101.

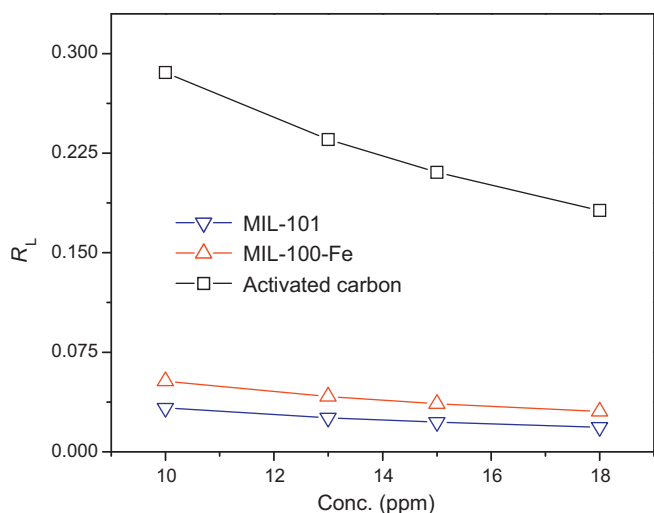| Adsorbents	Langmuir parameters		
	b (L/mg)	Q_0 (mg/g)	R^2
Activated carbon	0.22	81	0.999
MIL-100-Fe	1.78	115	0.999
MIL-101	2.92	132	0.999

Fig. 3. Effect of initial naproxen concentrations on the separation factor R_L for the three adsorbents.

(see Supporting Table 1) which is in good agreement with previous reports [54,56,57]. As shown in Table 2, the Langmuir constant b decreases in the order of MIL-101 > MIL-100-Fe > activated carbon, showing the more favorable adsorption [58] over MIL-101 than the adsorption over MIL-100-Fe or activated carbon. This is in accordance with the adsorption capacities Q_0 of the adsorbents.

A dimensionless constant called separation factor or equilibrium parameter, R_L was suggested to describe an adsorption process [55].

$$R_L = \frac{1}{1 + bC_0} \tag{5}$$

Fig. 3 describes the calculated R_L values versus the initial concentration of naproxen at the adsorption condition. All the R_L values were from 0 to 1, indicating the favorable adsorption of naproxen over the three adsorbents [50] at the conditions being studied. Moreover, it is observed that the R_L values decreases as the initial concentration increases from 10 to 18 ppm, showing the adsorption is more favorable at higher initial concentrations in accordance with the adsorption kinetics (see above). Moreover, it can be understood that the adsorption is most favorable over MIL-101 among three catalysts at the same initial concentration as the separation
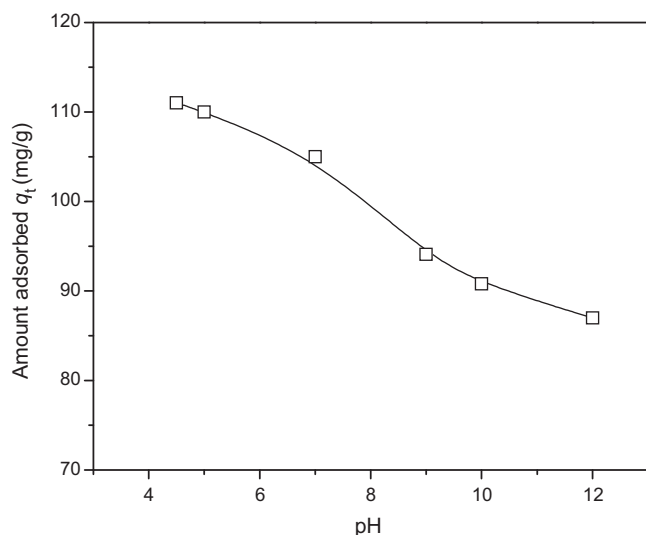

Fig. 4. Effect of solution pH on the adsorption of naproxen over MIL-101. The initial naproxen concentration C_i is 13 ppm and adsorption time is 12 h.
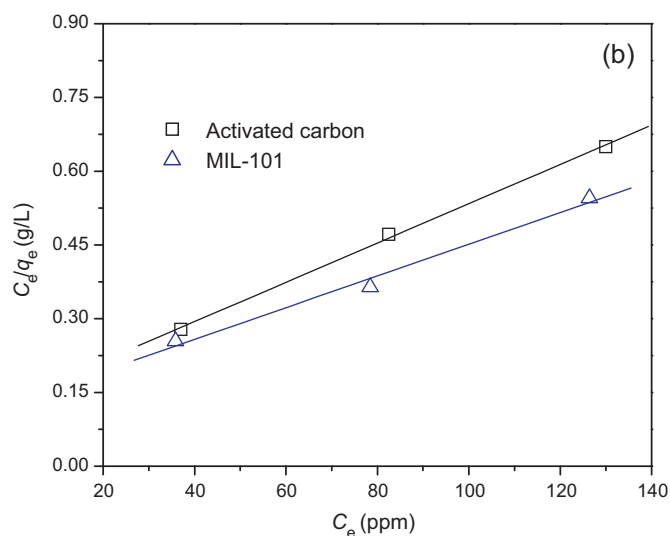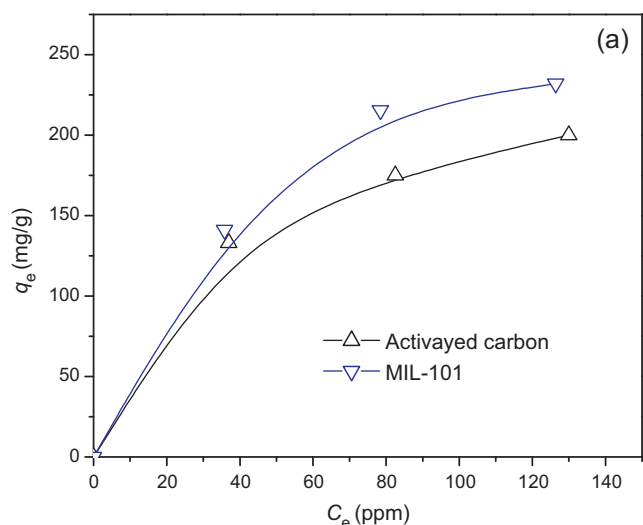

Fig. 5. (a) Adsorption isotherms for clofibric acid over MIL-101 and activated carbon; and (b) Langmuir plots of the isotherms.

factor R_L [59,60] is in the order of MIL-101 < MIL-100-Fe < activated carbon. This is also in accordance with the adsorption capacities Q_0 of the adsorbents (MIL-101 > MIL-100-Fe > activated carbon).

3.4. Effect of pH

The adsorption of PPCPs usually highly depends on the pH of the solution [5,10,61]. Naproxen adsorption over MIL-101 was studied for a fixed time of 12 h at various pH values. As shown in Fig. 4, the amounts of adsorbed naproxen decrease with increasing the pH of the naproxen solution, which is quite similar to previous reports [5,10,61]. Generally, at pH value higher than pKa, a polar compound is mostly in ionic form in a solution due to deprotonation. As the pKa of naproxen is ∼4, it exists in ionic form in the whole range of the experimental condition [10]. On the other hand, it is reported that the density of positive charge on MIL-101 is decreased with increasing pH [35]. Hence, adsorption at higher pH leads to a comparatively weaker interaction between naproxen anion and the adsorbent MIL-101 (less positive) which resulted in the decrease of naproxen adsorption. Therefore, the mechanism of naproxen adsorption on MIL-101 may be explained with a simple electrostatic interaction between naproxen and the adsorbent. The

Table 3
Langmuir isotherm parameters for the adsorption of clofibric acid over activated carbon and MIL-101.

Adsorbents	Langmuir parameters		
	b (L/mg)	Q_0 (mg/g)	R^2
Activated carbon	0.029	244	0.995
MIL-101	0.025	312	0.992

adsorption of naproxen at lower pH was not studied because of the low solubility of the naproxen in lower pH [5].

3.5. Adsorption of clofibric acid

From the above discussion, it is clear that MIL-101 is very efficient in removing naproxen from contaminated water *via* adsorption. To check the usability of MIL-101 for adsorptive removal of other PPCPs, we extended our works for the adsorption of clofibric acid where activated carbon was taken as a reference adsorbent. Here, MIL-101 also shows better performance than activated carbon not only in kinetics but also in adsorption capacity. The non-linear plot of the pseudo-second-order rate equation and the obtained pseudo-second-order kinetic parameters (for different initial concentrations of clofibric acid) are summarized in Supporting Fig. 4 and Table 2, respectively. Fig. 5(a) and (b) show adsorption isotherms and corresponding linear Langmuir plots for the adsorption of clofibric acid, respectively. It should also be noted that the MIL-101 shows the highest adsorption capacity for clofibric acid (312 mg/g, see Table 3) among any other adsorbents reported so far in open literatures [61,62]. Similar to the adsorption of naproxen, adsorption of clofibric acid is also preferred at low pH which is described in Supporting Fig. 5. This may be due to the very similar functional group (—COOH) of the two PPCPs. Once again, the MIL-101 shows the potential applications in removing PPCPs in the viewpoint of kinetics and adsorption capacity.

4. Conclusion

The liquid-phase adsorption of naproxen and clofibric acid (two representative PPCPs) has been studied for the first time using MOFs such as MIL-100-Fe and MIL-101. The adsorption kinetics follows the pseudo-second-order kinetic model (with a non-linear regression method) with high coefficient of determination (r^2). MIL-101, compared with activated carbon, shows fast adsorption rates for both naproxen and clofibric acid probably due to the large pore size of MIL-101. The equilibrium data can be interpreted with Langmuir isotherm and the high adsorption capacity of MIL-101 for the PPCPs shows the importance of the porosity of an adsorbent. Lower solution pH is proved to be more favorable for the adsorption of the PPCPs over MIL-101 which shows the importance of simple electrostatic interaction between the PPCPs and MIL-101 for the adsorption. From this study, it can be suggested that MOF-type materials can be applied in the adsorptive removal of PPCPs in contaminated water.

Acknowledgement

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2012.01.005.

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