



Adsorptive Removal of a Pharmaceutical and Personal Care Product Oxybenzone from Water with Metal-Organic Frameworks

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Abstract

Oxybenzone, one of the most often detected pharmaceuticals and personal care products (PPCPs), from aqueous solutions and this PPCPs removal from water had been studied by using the highly porous metal-organic framework (MOF)) MIL-101(Cr) and a modified MIL-101(Cr) called MIL-101-OH. Adsorption results showed that MIL-101-OH which contains functional group such as – OH, which was very effective for oxybenzone adsorption. The adsorption performance of MIL-101-OH over MIL-101(OH) was found to be greater than that of MIL-101(Cr), which means the functionalization of primitive MOFs have a positive effect on adsorption. The kinetics of MIL-101-OH also showed higher result compare to MIL-101(Cr). So along with a high adsorption capacity and repaid adsorption which is important for commercial applications.

Keywords: Personal care product, Metal-organic frameworks, oxybenzone, adsorption, porous materials, aqueous solution

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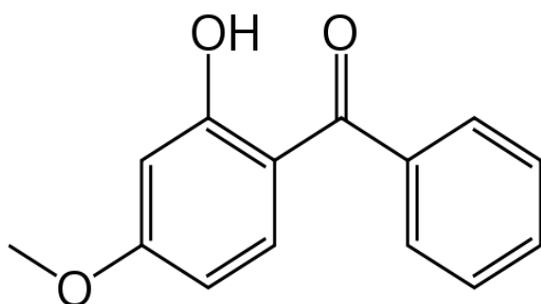
Ethical: This study follows all ethical practices during writing.

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1. Introduction

The use of pharmaceuticals and personal care products (PPCPs) is increasing day by day because of the increasing population all over the world, urbanization and living standards. For example the presence of PPCPs is already detectable in surface water, as in ground water [1-3] and bioaccumulation of these persistent PPCPs in the aquatic life will become a threat to the environment [4, 5]. PPCPs may often remain in the environment even after they have been consumed completely [3, 6-10] because PPCPs usually have long shelf lives to meet customer's demands, and some PPCPs are inadvertently dumped into environment; therefore, PPCPs are typical examples of so-called emerging contaminants [9, 10]. Oxybenzone (the structure of which is shown in scheme 1) is a component of many sunscreen lotions, is regarded as typical emerging contaminants with high environmental risk. The chemical structure of oxybenzone has various functional groups such as phenol, ketone groups that can interact effectively with adsorbents such as modified / functionalized MOFs.



(2-Hydroxy-4-methoxyphenyl)-phenylmethanone [C₁₅H₁₂O₂]
Scheme-1. Chemical structure of Oxybenzone

Over last few decades, significant advancements have been achieved in the field of porous materials because of the development of new functional materials, including metal-organic frameworks (MOFs) [11-19]. MOFs are receiving much attentions because of their high porosity, with their pore size/shape being controllable over both microporous and mesoporous regions. The physiochemical properties of MOF materials can be turned with easy modifications or functionalization, which ultimately increases their usability in various applications, such as adsorption [20-22] separation [23] and catalysis [24]. For example MOFs have recently been successfully used for fuel purification via adsorptive desulfurization [25-27] or denitrogenation [28-30]. MOFs have also been used for the aqueous-phase adsorption of different pollutants in water, such as heavy metals [31] phosphate [32] organics dyes [33-36] organic arsenic acids [37, 38] bisphenol-A [39, 40] and PPCPs (naproxen and clofibrac acid) [41-43] from water. In this study, we used MIL-101, MIL-101-OH and Oxybenzone as representatives MOF and PPCP, respectively.

2. Experimental

2.1 Chemicals and Synthesis and Modification of Adsorbent

Reagents and solvents were commercially available products and used without any further purification. Chromium (III) nitrate nanohydrate (Cr(NO₃)₃·9H₂O) (99%) and terephthalic acid (TPA,99%) were purchased from Daejung and Junsei Chemicals, respectively. Ethanolamine (ETA,98%) was obtained from Alfa Aesar. Toluene (99.5%) was procured from Daejung Chemicals. N,N-Dimethylformamide (99%) and ethanol (99.5%) for the purification of the MOFs were obtained from Daejung Chemicals. Methanol and acetone were obtained from Daejung Chemicals, and Oxybenzone was obtained from Alfa Aesar.

MIL-101 was synthesized from Cr(NO₃)₃·9H₂O, TPA, and deionized water similar to a previously described method [44-46]. Cr(NO₃)₃·9H₂O (4.0 g) 10 mmol, terephthalic acid (TPA) (1.66 g) 10 mmol, and deionized water (40mL) were blended and briefly sonicated resulting in a dark blue-color suspension. The suspension was then placed in a Teflon-lined autoclave bomb and was kept in an oven at 220°C for 17 h without stirring. After the reaction, autoclave was cool to room temperature. After that the MOF solids with green-colored was separated from water using a centrifuge (3,134xg, 15min) and was washed with water, methanol and acetone. The suspension in acetone was centrifuged and separated, to remove the unreacted TPA, the solids was placed in N,N-dimethylformamide (40 mL) and the suspension was sonicated for 10 min and then keep at 70 °C overnight. The resulting solids were separated by centrifugation, repeatedly washed with methanol and acetone, was dried at 100°C overnight.

The -OH functionalized MIL-101s name MIL-101-OH was synthesized via grafting utilizing reported procedures [43, 47]. Before functionalization, MIL-101 was dehydrated at 150 °C for 12 h in a vacuum oven to generate CUSs (coordinatively unsaturated sites). The dehydrated MIL-101 (0.6 g) was suspended in anhydrous toluene (60 mL) in a round-bottom flask equipped with a reflux condenser and a magnetic stirrer, and each of 2 mmol of ETA (Ethanolamine) was added to this suspension. The mixture continuously was stirred and refluxed for 12 h. The obtained solid was cool to room temperature, was separated and was washed with ethanol/de-ionized water, and was dried at room temperature and then the MOFs solid was kept in desiccators for further use.

2.2 Characterization

X-ray powder diffraction patterns were obtained with a diffractometer (SWXD, CuKα radiation). FT-IR spectra were recorded on a Hyperion-2000 (ATR, maximum resolution). The nitrogen adsorptions of the adsorbents was obtained at -196 °C with a surface area and porosity analyzer (BRLSORP-max) after evacuation at 150 °C for 12 h. The surface area of adsorbents was calculated using the BET equation.

2.3 General Procedures for the Adsorption Experiments

Oxybenzone solutions with the desired concentrations were prepared using deionized water. An oxybenzone calibration curve was prepared by determining the absorbance at 230 nm with a series of standard oxybenzone solutions (1–10 mg/L), and the initial or equilibrium concentrations of oxybenzone was calculated with the calibration curve. Formerly to adsorption, the sample was dried for 12 h at 100 °C under vacuum conditions. For each adsorption experiment, approximately 5 mg of the sample was added to the oxybenzone solution (50mL, fixed concentration) and was stirred for 10 min to 12 h at 25 °C. After stirring the solution, the adsorbents was filtered with a syringe filter (PTFE, 0.45 μm) and the oxybenzone concentration was determined from the absorbance of the UV spectrum. In the case of a high oxybenzone concentration, the UV analysis was conducted after consecutive dilutions of the oxybenzone solutions.

The following mass-balance relation (Eq.1) was used to determine the amount of adsorbed oxybenzone

$$q_t = (C_0 - C_t) V/w \text{ ----- (1)}$$

where C_0 (mg/L) was the initial concentration, C_t (mg/L) was the concentration at time t , V (L) was the volume of the oxybenzone solution and w (g) was the weight of the adsorbents.

3. Results and Discussion

3.1 Characterization of the Adsorbents

The XRD patterns of the MIL-101s shown in Fig. 1a was accommodating with simulated one [43, 44] confirmed the MIL-101s were successfully prepared and that the crystal structure of pristine MIL-101 does not change with functionalization. However, the XRD intensities of the MIL-101s decreased slightly on modification, particularly those of MIL-101-(OH), probably because of some severe conditions which was required for these modifications. The nitrogen adsorption isotherms of the MIL-101s and the BET surface areas (Table 1) obtained from these isotherms show that the MIL-101s have considerable porosities, although functionalization (to introduce –OH group) reduced the porosities. This reduction could be due to the volumes of the functional groups and/or the decreased crystallinity with modifications (as shown by the XRD patterns). FTIR spectra of the modified MOFs shown in Fig. 2c confirmed the grafting was successful based on the presence of the band at 1216 cm^{-1} , which originate from the C-N stretching of the grafting agents [48].

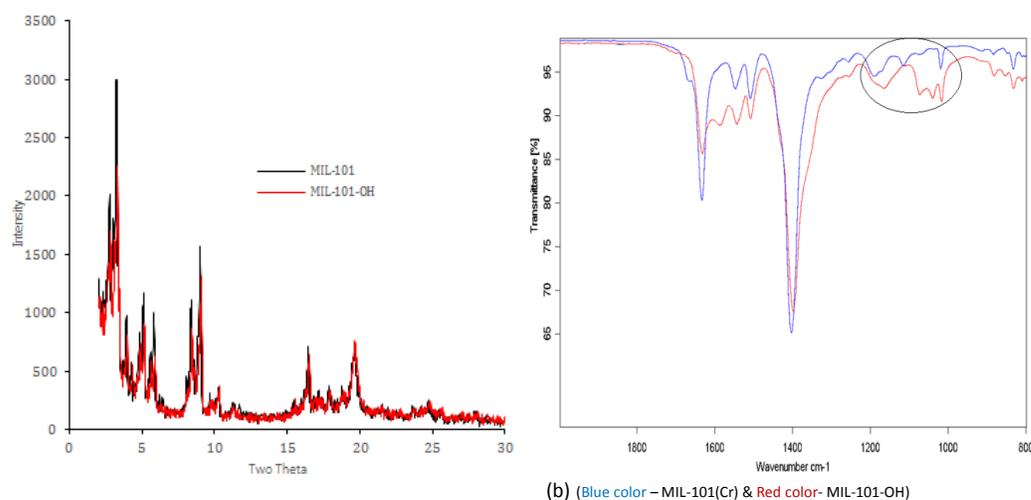


Figure-1. (a) XRD patterns, and (b) FTIR spectra of MIL-101s

Table-1. BET surface areas and total pore volume of MIL-101s

Adsorbent	BET surface area SA^{BET} (m^2/g)	Total pore volume [$\text{cm}^3 \text{g}^{-1}$]
MIL-101(Cr)	2,534.4	1.847
MIL-101-OH	1,951.5	0.9615

3.2 Adsorption Isotherms and Kinetics Results

Isotherms for oxybenzone adsorption by MIL-101s were obtained at 20–25 °C after 12 h of adsorption, which is sufficient for equilibrium, and the results are shown in Fig. 3. The adsorbed amounts (based on weight of MIL-101s) at equilibrium decreased in the order MIL-101-OH > MIL-101, which was the same order as observed for quantity adsorbed after various times with different concentration (Fig.2). The maximum adsorbed quantities (Q_0) obtained from Langmuir plots are summarized in Table 2, and the results again show that MIL-101s functionalized with –OH groups were highly effective at adsorbing oxybenzone from water.

Table-2. Relative adsorbed amounts of PPCPs over the two MOFs (MIL-101, MIL-101-OH) after 12 h of Adsorption

MOFs	PPCPs	Maximum adsorption (Q_0 mg/g)	r^2
MIL-101(Cr)	Oxybenzone	73.50	0.9999
MIL-101-OH	Oxybenzone	121	0.9998

Isotherms for ibuprofen adsorption by MIL-101s were obtained at 25 °C after 12 h of adsorption, which is sufficient for equilibrium, and the results are shown in Fig. 3. The adsorbed amounts (based on weight of MIL-

101s) at equilibrium decreased in the order MIL-101-OH > MIL-101, which was the same order as observed for quantity adsorbed after various times (Fig.2). The maximum adsorbed quantities (Q₀) obtained from Langmuir plots are summarized in Table 1, and the results again show that MIL-101s functionalized with -OH groups were highly effective at adsorbing ibuprofen from water.

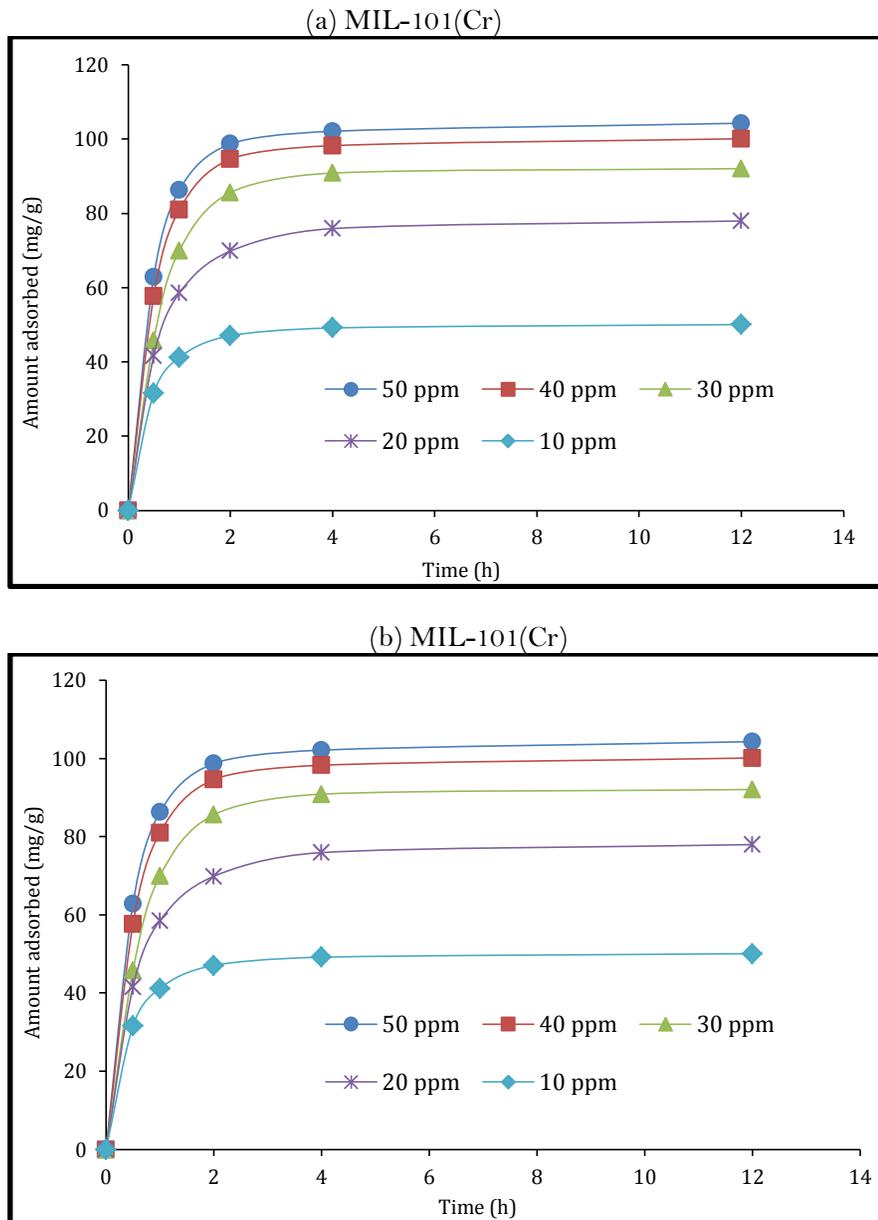


Figure-2. Effect of adsorption times on the adsorbed amounts of oxybenzone over (a) MIL-101(Cr) and (b) MIL-101-OH. Show the adsorbed amounts of oxybenzone based on the unit weight of adsorbents. The initial concentration of oxybenzone was (10-50 ppm.)

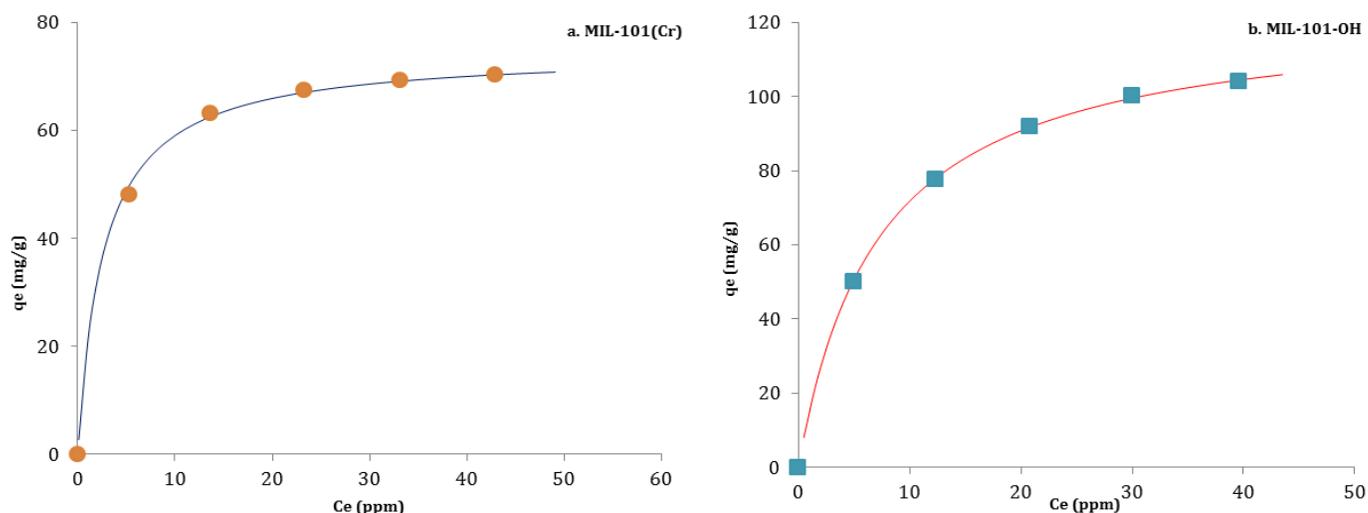
The kinetics of oxybenzone adsorption of different concentration over MIL-101(Cr) and MIL-101-OH had been calculated. Oxybenzone adsorption kinetics followed previously described method [49] the pseudo-second-order equation can exactly illustrated. The Equation (2) for pseudo-second-order model which can explain the kinetics has given below

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

q_t (mg/g) at time t, the amount of adsorbed, q_e (mg/g) at equilibrium stage the amount of adsorbed, t(hour) time (adsorption time) and k_2 (g/mg, hour) pseudo-second-order rate constant. The kinetics results of oxybenzone adsorption over MIL-101s have been given in Table 3. The kinetics of oxybenzon adsorption over MIL-101s showed that the q_e value and k_2 value of oxybenzone adsorption over MIL-101(Cr) and MIL-101-OH were decreased in the order of MIL-101-OH > MIL-101(Cr) respectively. The kinetics of oxybenzon adsorption over MIL-101s showed that the q_e value and k_2 value of oxybenzone adsorption over MIL-101(Cr) and MIL-101-OH were decreased in the order of MIL-101-OH > MIL-101(Cr) respectively.

Table-3. The kinetics of oxybenzone adsorption over MIL-101(Cr) and MIL-101-OH. [when the Concentrations of oxybenzone solutions were 40 & 50ppm]

MOF(adsorbent)	Initial concentration	q_e (mg/g)	k_2 (g/mg.hour)
MIL-101(Cr)	10ppm	47.26	0.0291
	20ppm	63.59	0.0305
	30ppm	67.90	0.0312
	40ppm	69.92	0.0372
	50ppm	70.94	0.0475
MIL-101-OH	10ppm	60.25	0.0385
	20ppm	81.05	0.0403
	30ppm	92.34	0.0422
	40ppm	102.12	0.0528
	50ppm	104.16	0.0561

**Figure-3.** Adsorption isotherms of oxybenzone over (a) MIL-101 and (b) MIL-101-OH (at 20- 25 °C)

3.3 Discussion

From the above tables (Table 2 and Table 3), Q_0 means the highest oxybenzone adsorption capacity of MOFs and q_e means the adsorbed amount during equilibrium. So in this research the highest oxybenzone adsorption capacity of MIL-101(Cr) was **73.50 mg/g** (based on unit weight of MIL-101) and highest oxybenzone adsorption capacity of MIL-101-OH was **120 mg/g** (based on unit weight of MIL-101-OH) and the kinetics of oxybenzone adsorption over MIL-101s showed that the q_e value and k_2 value of oxybenzone adsorption over MIL-101(Cr) and MIL-101-OH were decreased in the order of MIL-101-OH > MIL-101(Cr) respectively. So on the basis of comparison the adsorption capacity of MIL-101-OH was higher than the adsorption capacity of MIL-101(Cr), and oxybenzone's adsorption capacity of both MOFs were decreased on the order MIL-101-OH > MIL-101(Cr) (based on unit weight). The reason for which, MIL-101-OH oxybenzone's adsorption capacity was higher compared to MIL-101(Cr) because it contain H-bonding and that H-bonding was maybe responsible for making MIL-101-OH more capable for oxybenzone's higher adsorption. Again from the kinetics the q_e value and k_2 value of oxybenzone adsorption over MIL-101(Cr) and MIL-101-OH at different initial concentrations were gradually decrease on the discipline of MIL-101-OH > MIL-101(Cr) (based on unit weight).

4. Conclusion

In conclusion, a typical MOF with high porosity (MIL-101) was modified to introduce functional group such as -OH in order to use it for the adsorptive removal of PPCPs such as oxybenzone from an aqueous solution. Even though the surface area of the virgin MOF decreased noticeably, the modified MIL-101 was very effective at the PPCPs adsorption. MIL-101-OH showed the highest PPCPs uptakes based on weight and surface area, respectively. Finally, MIL-101-OH is suggested to be a potential adsorbent for PPCPs removal based on competitive adsorption when compared with carbonaceous materials, mesoporous materials [50, 51] and pristine MIL-101.

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