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

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Abstract

The adsorptive removal of ibuprofen, one of the most frequently detected pharmaceuticals and personal care products (PPCPS), from aqueous solutions was studied by using the highly porous metal-organic framework (MOF) MIL-101 and a modified MIL-101 called MIL-101-OH. Adsorption results showed that MIL-101-OH which contains H-donor modified/functional group such as –OH, which was very effective for ibuprofen adsorption. On the contrary, the performance of MIL-101 was poor compare to the adsorption result of MIL-101-OH. The adsorbent with the highest adsorption capacity, MIL-101-OH, was very competitive when compared with pristine MIL-101. The effect of pH on the adsorption of ibuprofen also supports this interaction. Moreover, the MIL-101-OH could be recycled several times by simply washing with ethanol and reusable up to at least the third run with little change in the performance along with a high adsorption capacity and repaid adsorption.

Keywords: Personal care product, Water, Metal-organic frameworks

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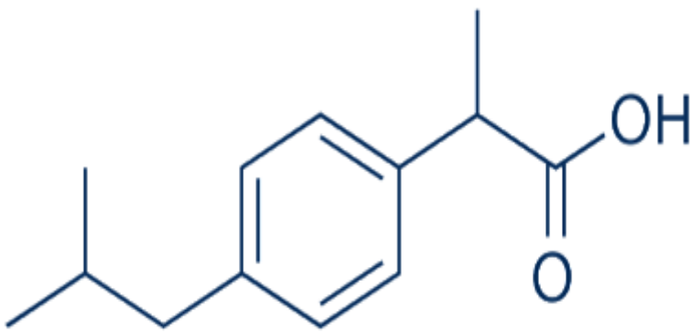
Contents

1. Introduction **2**
2. Experimental **2**
3. Results and Discussion **3**
4. Conclusion **5**
References **5**

1. Introduction

The use of pharmaceuticals and personal care products ($PPCP_S$) 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]. Ibuprofen (the structure of which is shown in Scheme 1) is nonsteroidal anti-inflammatory drug is widely used to reduce pain, inflammation, fever and stiffness, is regarded as typical emerging contaminants with high environmental risk. The chemical structure of ibuprofen has various functional groups such as phenol, ketone groups that can interact effectively with adsorbents such as modified / functionalized MOFs.



2-(4-Isobutylphenyl) propionic acid [$C_{13}H_{18}O_2$]
Scheme 1. Chemical structure of 'Ibuprofen'

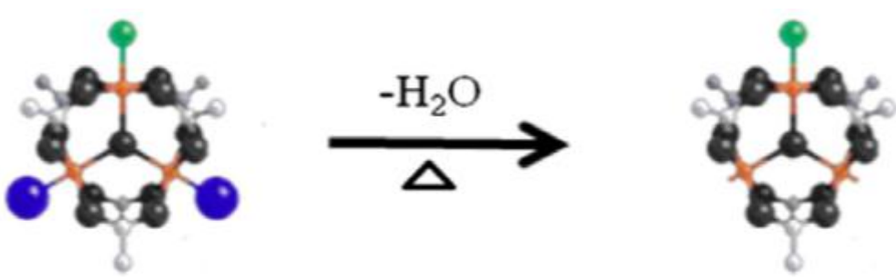
Over last few decades, significant advancements have been achieved in the field of porous materials because of the development of new functional materials, including metal-organic frameworks (MOFs) [11-19]. MOFs are receiving much attentions because of their high porosity, with their pore size/shape 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 clofibric acid)) [41-43] from water. In this study, we used MIL-101, MIL-101-OH and Ibuprofen 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 ($Cr(NO_3)_3.9H_2O$) (99%) and terephthalic acid (TPA,99%) were purchased from Daejung and Junsei Chemicals, repectively. 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 Ibuprofen was obtained from Alfa Aesar.

MIL-101 was synthesized from $Cr(NO_3)_3.9H_2O$, TPA, and deionized water similar to a previously described method [44-46]. $Cr(NO_3)_3.9H_2O$ (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 218 °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 (5,000xg, 10 min) 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 75 °C overnight, and then under vacuum (1×10^{-5} Torr) at ambient temperature for 2 days. 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 ^{0}C for 12 h in a vacuum oven to generate CUSs (coordinatively unsaturated sites).



Scheme-2. Generation of CUS or open metal sites through dehydration of water from MOFs.

The dehydrated MIL-101 (0.6 g) was suspended in anhydrous toluene (60 mL) in a round-bottom flask equippe 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 obtaind 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 diffract meter D2 Phaser (Bruker, with CuKα radiation). FT–IR spectra was recorded on a FTIR-4100 (ATR, maximum resolution: 0.9 cm^{-1}), and elemental analyses of the adsorbents was done using an elemental analyzer (Thermo Fisher, Flash-2000) with a TCD detector. The nitrogen adsorptions of the adsorbents was obtain at -196 ^{0}C with a surface area and porosity analyzer (Micromeritics, Tristar II 3020) after evacuation at 150 ^{0}C for 12 h. The surface area of adsorbents was calculated using the BET equation.

2.3. General Procedures for the Adsorption Experiments

Ibuprofen solutions with the desire concentrations were prepared using deionized water. An ibuprofen calibration curve was prepared by determining the absorbance at 230 nm with a series of standard ibuprofen solutions (1–50 mg/L) at pH 5.4, and the initial or equilibrium concentrations of ibuprofen was calculated with the calibration curve. Prior to adsorption, the sample was dried for 12 h at 100 ^{0}C under vacuum conditions. For each batch, approximately 5 mg of the sample was added to the ibuprofen solution (50 mL, fixed concentration, pH 5.4) and was stirred for 10 min to 12 h at 25 ^{0}C. After stirring the solution, the adsorbents was filtered with a syringe filter (PTFE, hydrophobic,0.5 lm) and the ibuprofen concentration was determined from the absorbance of the UV spectrum. In the case of a high ibuprofen concentration, the UV analysis was conducted after successive dilutions of the ibuprofen solution.

To determine the amount of adsorb ibuprofen, the following mass-balance relation (Eq.1) was used:

$$Q_t = (C_0 - C_t)\frac{V}{W} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

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 ibuprofen solution and w (g) was the weight of the adsorbents. To determine the adsorption capacity at various condition of acidity, the pH of the ibuprofen solution (30 mg/L) was adjust with 0.1 M aqueous solutions of HCl or NaOH.

Regeneration of used adsorbent was carried out at room temperature by mixing the used adsorbent and ethanol for 4 h under magnetic stirring, was followed by sonication for 1 h, filtration, was washed with ethanol, and finally dried in a vacuum oven for further use. A similar regeneration process was repeated up to the third run.

3. Results and Discussion

3.1. Characterization of the Adsorbents

The XRD patterns of the MIL-101s shown in Fig. 1a was agreeable 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 harsh conditions required for these modifications. The nitrogen adsorption isotherms (Fig. 1b) 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].

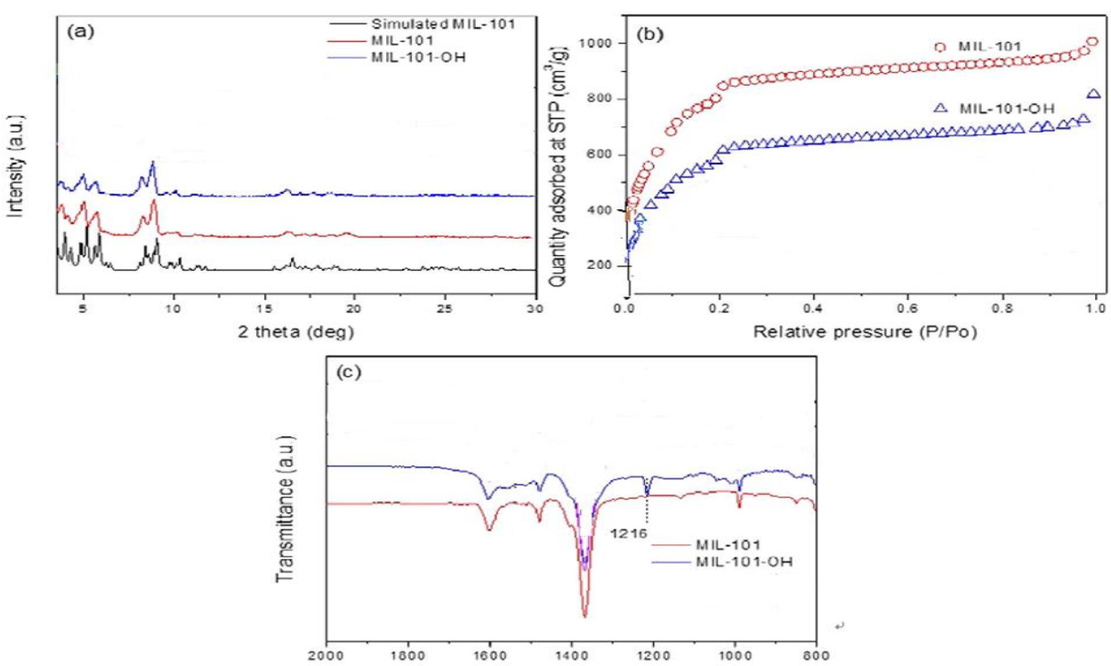


Figure-1. (a) XRD patterns, (b) nitrogen adsorption isotherms and (c) FTIR spectra of MIL-101s

Table-1. BET surface areas and maximum adsorption capacities (based on weight and surface area of adsorbent) of MIL-101s for ibuprofen.

Adsorbent	BET surface area SA^{BET}(m^2/g)	Langmuir surface area Q_0(mg/g)	Q_0(100*mg/m^2)	r^2
MIL-101	3022	113	3.73	0.981
MIL-101-OH	2170	184	8.47	0.991

3.2. Adsorption Isotherms and Effect of Functional Groups on Adsorption

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.

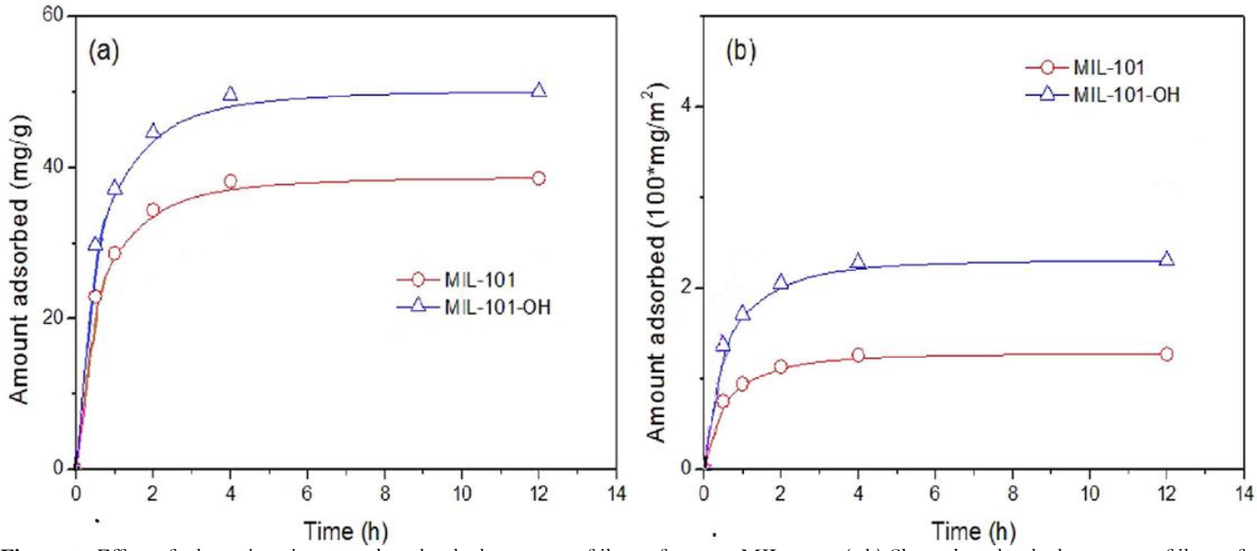


Figure-2. Effect of adsorption times on the adsorbed amounts of ibuprofen over MIL-101s. (a,b) Show the adsorbed amounts of ibuprofen based on the unit weight and surface area, respectively, of adsorbents. The initial concentration of ibuprofen was 50 ppm. The legends in (b) are the very same as those in (a).

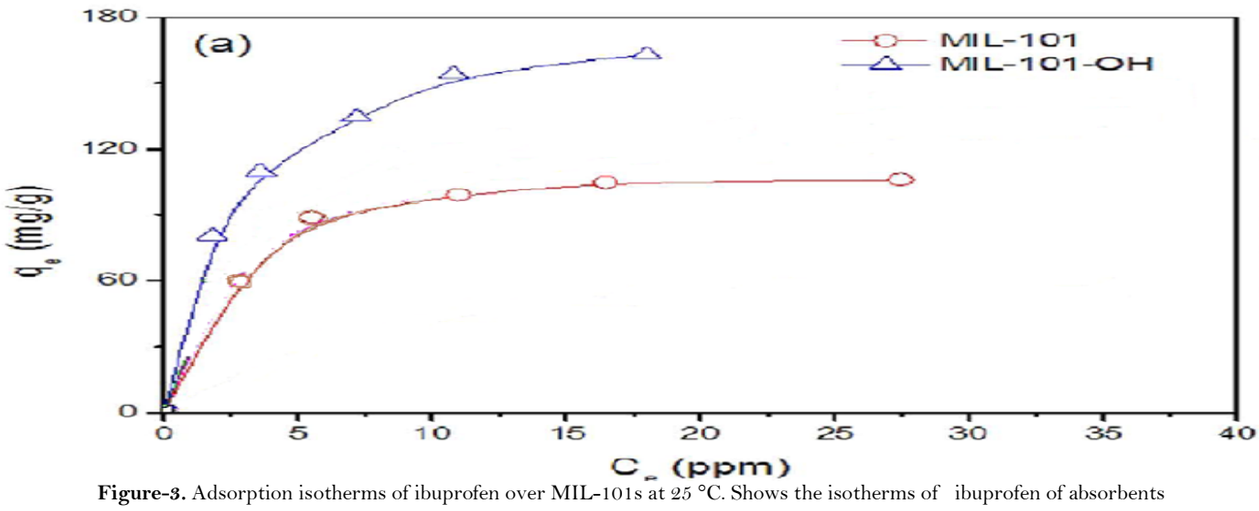


Figure-3. Adsorption isotherms of ibuprofen over MIL-101s at 25 °C. Shows the isotherms of ibuprofen of absorbents

3.3. Discussion

In order to confirm the mechanism of H-bonding, similar PPCPs such as ibuprofen was adsorbed over MIL-101 with or without free hydroxyl groups (MIL-101, MIL-101-OH). The MIL-101-OH showed the highest adsorption capacities (Fig 2a) for the ibuprofen (per unit weight) even though the surface area of the MOF was not the highest. Figure 2b showed that the amounts of adsorbed ibuprofen (per unit surface area) decrease on the order MIL-101-OH > MIL-101. Table 2. Showed relative adsorbed amounts of PPCPs over the two MOFs (MIL-101, MIL-101-OH) after 12 h of adsorption. At the condition of adsorption (pH: 5.4). The q12 h values were based on unit surface area and the q12 h of MIL-101 was set 100 to check easily the effect of –OH of MOFs on the adsorbed amounts.

Table-2. Relative adsorbed amounts of PPCPs over the two MOFs (MIL-101, MIL-101-OH) after 12 h of adsorption (q12 h). *At the condition of adsorption (pH: 5.4). The q12 h values were based on unit surface area and the q12 h of MIL-101 was set 100 to check easily the effect of –OH of MOFs on the adsorbed amounts.

PPCP (number/status of O species)	Functional group of PPCP*	MIL-101	MIL-101-OH
Ibuprofen (1O, 1O^-)	-COO-	100	180

3.4. Effect of pH

The pH of a solution is very important [49] in the adsorption of organics from water considering the protonation/deprotonation of adasorbates and/or changes in the surface of adsorbents with different pH values. In

this work, MOFs such as MIL-101-OH and pristine MIL-101 were studied at various pH values. As shown in Fig.4, the amounts of ibuprofen adsorbed by MIL-101 and MIL-101-OH decreased as solution pH increased, which is similar to previous results for pristine MIL-101 [43, 50] In other words, repulsive interactions between MIL-101s and ibuprofen were expected at high pH. Very curiously, the amount adsorbed by MIL-101-OH per unit surface area at a pH 10 was very similar to that of pristine MIL-101.

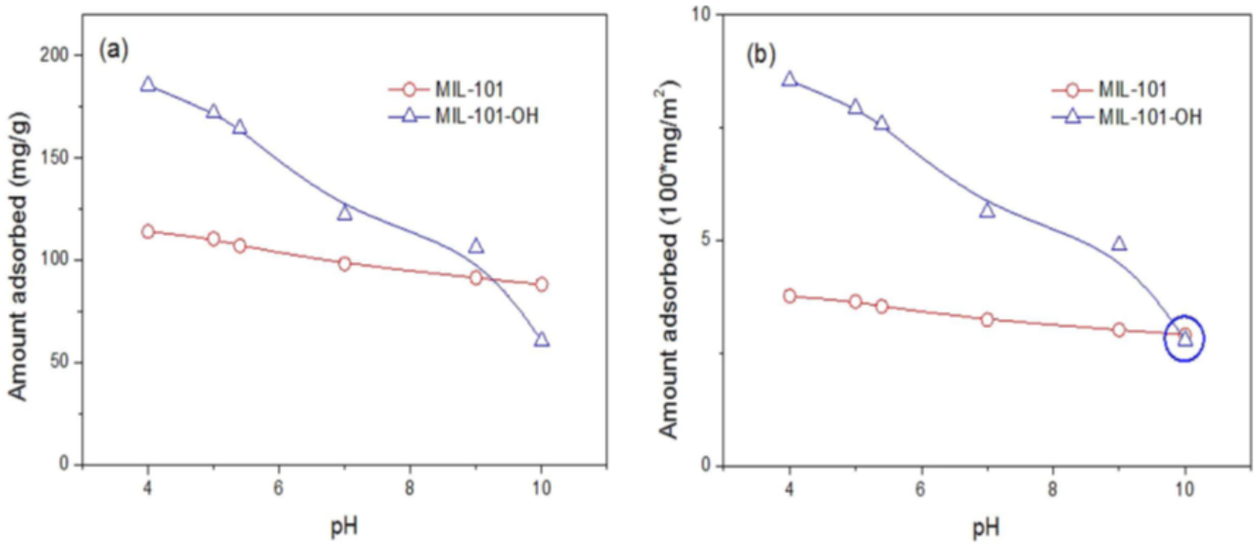


Figure-4. Effect of pH of solution on the adsorbed amounts of ibuprofen over MIL-101 and MIL-101-OH. (a,b)

Show adsorbed amounts based on the unit weight and surface area, respectively, of adsorbents.

3.5. Reusability of the Adsorbents

Reusability of adsorbents is an important parameter to be considered for commercial applications. In this study, the reusability of MIL-101-OH was evaluated after washing the used MOFs with two different solvents, water and ethanol. From Fig 5a, it can be understood that regeneration using ethanol showed better reusability compared to water, and this may be due to the high solubility of ibuprofen in ethanol rather than in water. After regeneration with solvent washing, the crystal structure of MIL-101-OH was retained, which was confirmed by XRD and FTIR (data not shown). Even though the adsorbed amounts decreased steadily with number of recycles, the adsorbed amounts did not change remarkably after regeneration, Fig 5b.

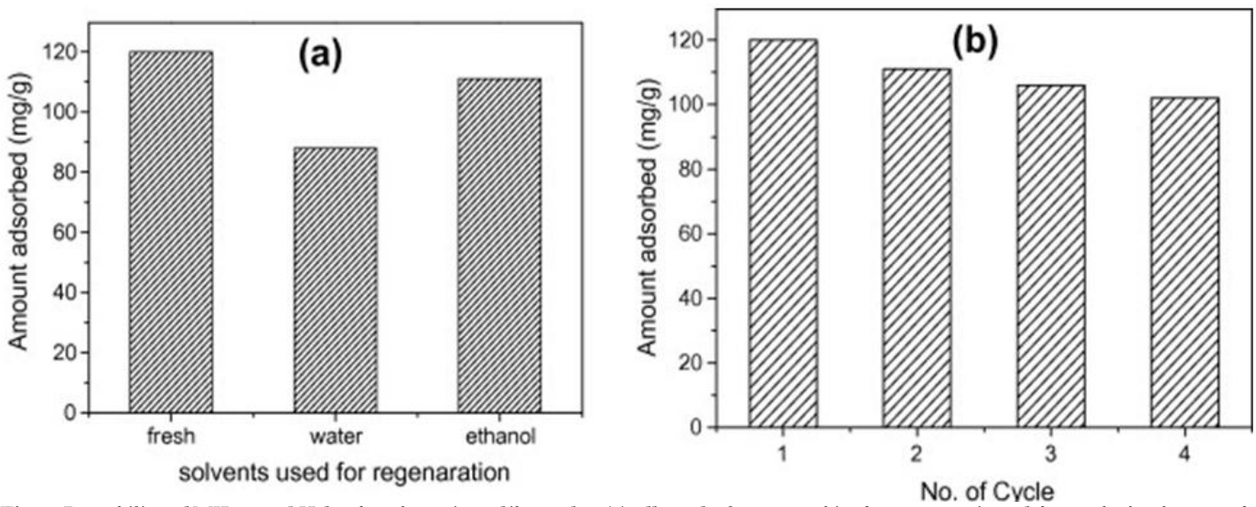


Fig-5. Reusability of MIL-101-OH for the adsorption of ibuprofen: (a) effect of solvents used in the regeneration of the used adsorbent on the adsorption of ibuprofen and (b) effect of the number of recycles on the adsorption of ibuprofen.

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 ibuprofen 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 its reusability and competitive adsorption when compared with carbonaceous materials, mesoporous materials [51, 52] and pristine MIL-101.

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