Chemosphere 235 (2019) 527–537

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Comprehensive evaluation of the removal mechanism of carbamazepine and ibuprofen by metal organic framework

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HIGHLIGHTS

- An MOF was employed for the removal of ibuprofen (IBP) and carbamazepine (CBM).
- Effects of various water quality conditions on removal were systematically evaluated.
- Adsorption mechanisms by MOF for selected pharmaceuticals were comprehensively investigated.
- Used MOF was easily regenerated by acetone as a cleaning solution.

ARTICLE INFO

Article history:
Received 10 May 2019
Received in revised form
21 June 2019
Accepted 26 June 2019
Available online 27 June 2019

Handling Editor: Klaus Kümmerer

Keywords:
Mechanism
Pharmaceuticals
Adsorption
Metal-organic framework
Water treatment

ABSTRACT

Pharmaceutical products (PhACs) in water sources are considered to be a severe environmental issue. To mitigate this issue, we used a metal-organic framework (MOF) as an adsorbent to remove selected PhACs (*i.e.*, carbamazepine (CBM) and ibuprofen (IBP)). This work was carried out to characterize the MOF, then confirm its feasibility for removing the selected PhACs. In particular, based on practical considerations, we investigated the effects of various water quality conditions, such as solution temperature, pH, ionic strength/background ions, and humic acid. MOF exhibited better removal rates than commercial powder activated carbon (PAC), considering pseudo-second order kinetic model. We clarified the competitive PhACs adsorption mechanisms based on the results obtained under various water quality conditions and found that hydrophobic interactions were the most important factors for both adsorbates. To confirm the practicality of MOF adsorption, we carried out regeneration tests with four adsorption and desorption cycles using acetone as a cleaning solution. Furthermore, to support the results of our regeneration tests, we characterized the MOF samples before and after adsorbate exposure using Fourier-transform infrared spectroscopy and X-ray photoelectron spectroscopy. Overall, MOF can be used in practical applications as efficient adsorbents to remove PhACs from water sources.

1. Introduction

Water source contamination by pharmaceutical compounds (PhACs), such as carbamazepine (CBM) and ibuprofen (IBP), is known to be a serious environmental issue (Im et al., 2014; Jun et al., 2019a; Jun et al., 2018b). PhACs have been detected in various water resources, including drinking water (Westerhoff et al., 2005). Therefore, efficient treatment of these water sources is an urgent environmental task. Increased levels of PhACs in water sources (*e.g.*, surface water and groundwater) is caused by irregular disposal of unused medicines, expired drugs, veterinary medications, *etc* (Al-Hamadani et al., 2017b). In particular, both CBM and IBP (which were selected as the PhACs in this study) have been widely used as antiepileptic medicines to control seizures (Li et al., 2011), and treat inflammatory disorders/muscular pain (Méndez-Arriaga et al., 2008), respectively. Thus, these PhACs are commonly detected in water bodies across widespread areas (Davarnejad et al., 2018; Zhang et al., 2008). For example, CBM and IBP have been detected at concentrations of up to 610 ng L^{-1} in the United States (Zhang et al., 2008), and 10 µg L^{-1} in Europe (Davarnejad et al., 2018).

Numerous studies have been carried out to develop efficient

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https://doi.org/10.1016/j.chemosphere.2019.06.208
0045-6535/

methods to treat water sources, including the removal of PhACs (*e.g.,* CBM, IBP, diclofenac, etc.) with or without natural organic matter (Bhadra et al., 2017; Boyd et al., 2003; Buser et al., 1998; Chen et al., 2016; Ciríaco et al., 2009; Esplugas et al., 2007; Farrington and Regan, 2007; Heo et al., 2012, 2013; Joss et al., 2006; Jun et al., 2017; Méndez-Arriaga et al., 2008; Salaeh et al., 2016; Zhang et al., 2014). Conventional and advanced water treatment processes for PhACs include: adsorption (Bhadra et al., 2017), biodegradation (Joss et al., 2006), membrane processes using ultrafiltration (Heo et al., 2012) and forward osmosis (Heo et al., 2013), coagulation/flocculation (Boyd et al., 2003), ozonation (Esplugas et al., 2007), photodegradation (Buser et al., 1998; Salaeh et al., 2016), electrochemical method (Ciríaco et al., 2009), and ultrasonication (Méndez-Arriaga et al., 2008). Above all, adsorption treatment of water containing PhACs is a good candidate due to its relative cost effectiveness, easy operation, high efficiency, and production of fewer toxic by-products (Bhadra et al., 2017; Gao et al., 2018).

Adsorption between adsorbents and adsorbates has been explained in terms of several mechanisms, as follows: electrostatic interactions, π - π stacking, hydrophobic interactions, acid-base interactions, and hydrogen bonding (Hasan and Jhung, 2015). Electrostatic interactions are mainly used to explain adsorption mechanisms for the removal of PhACs. For example, MIL-101-Cr grafted by ethylenediamine (with positive charge) has a better adsorption capacity than pristine adsorbent (with neutral charge), due to its electrostatic attraction with the negative charges of methyl orange (Haque et al., 2010). Furthermore, hydrophobic interactions (or π -complexation) have been widely utilized to explain the adsorption mechanism of hydrophobic adsorbates (*e.g.,* soybean oil (Lin et al., 2014) and some PhACs with high octanol-water partition coefficients (K_{ow})) (Scheytt et al., 2005), and of adsorbates containing benzene rings (*e.g.,* bisphenol A) (Bhadra et al., 2018) and hydrophobic adsorbents. Hydrogen bonding is also regarded as a significant adsorption mechanism, and some PhACs (*e.g.,* IBP and oxybenzone) were largely removed by MIL-101s via hydrogen bonding (Seo et al., 2016). Even though acid-base interactions are not commonly cited when explaining the removal of PhACs, the adsorption of naproxen and clofibric acid by functionalized MIL-101-Cr has mainly been explained in terms of acid-base interactions (Hasan et al., 2013). Furthermore, the surface area and porosity of the adsorbent are closely related to van der Waals interactions, and are thus commonly considered factors when seeking to increase the adsorption capacity, if there are no other strong interactions between the adsorbents and adsorbates as mentioned above (Bhadra et al., 2018). Therefore, it is important to understand several different mechanisms in detail to explain the relative effects of using different adsorbents and adsorbates.

To date, various adsorbents have been synthesized or developed to improve adsorption efficiency, as follows: activated carbon (Mestre et al., 2009; Nam et al., 2014), pillared clay (Ortiz-Martínez et al., 2016), biochar (Essandoh et al., 2015), ion-exchange resins (Jiang et al., 2015), graphene (Jauris et al., 2016), synthetic zeolites (Martucci et al., 2012), mesoporous silica (Bui and Choi, 2009; Bui et al., 2011), and metal-organic frameworks (MOFs) (Hasan and Jhung, 2015). MOFs are a recently developed, relatively new material with a 3D network structure having coordination bonds between metal ions and organic linkers (Li et al., 2019). Of the adsorbents mentioned, MOFs are highly attractive candidates as efficient adsorbents due to their unique characteristics, such as various functionalities, ready functionalizability, high specific surface area, uniform open cavities, tenable pore size, and simple synthesis (Gao et al., 2018; Lv et al., 2018). In other words, these outstanding characteristics of MOFs mean that they can be utilized as ideal adsorbents for the removal of PhACs.

Even though MOFs have been used to remove PhACs from several water sources (Gao et al., 2018; Hasan and Jhung, 2015), to the best of our knowledge, there have been no systematic investigations on the removal of both CBM and IBP (which we selected as PhACs in this study) by MOF (Basolite A100) under various water quality conditions, nor any comprehensive explanations of their adsorption mechanisms. Hence, in this research, we focused on a systematic approach to competitive adsorption between CBM and IBP under different doses, performed an isotherm/kinetic study, and assessed the effects of water qulaity parameters, such as the solution temperature, pH, ionic strength, background ions and humic acid (HA). Second, we investigated the practical feasibility of regeneration using acetone as a cleaning solution. Finally, we used Fourier-transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS) to explain our regeneration results.

2. Materials and methods

2.1. Chemicals

High-purity IBP ($C_{13}H_{18}O_2$, >98%), CBM ($C_{15}H_{12}N_2O$, > 99%), HA, sodium chloride (NaCl > 99%), hydrochloric acid (HCl, > 99%), calcium chloride ($CaCl_2$, >99%), sodium hydroxide (NaOH, > 98%), sodium sulfate (Na_2SO_4 > 99%), acetone, and Basolite A100 MOF ([Al(OH)($C_8H_4O_4$)]) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Aluminum-based A100 MOF was used as a main adsorbent in this study. Commercially available powder activated carbon (PAC; Evoqua Water Technologies, Pittsburgh, PA, USA) was used as a control group for the MOF. All chemicals were applied without any further purification, and Ultrapure deionized (DI) water was used in all of the experiments.

2.2. Procedure of adsorption experiments

We analyzed the CBM and IBP concentrations before and after adsorption using high-performance liquid chromatography (1200 series; Agilent Technologies, Santa Clara, CA, USA), as mentioned in previous studies (Al-Hamadani et al., 2017a, 2018). Adsorption experiments were conducted using 40 mL of 10 μM PhACs solution with 100 mg L^{-1} of adsorbent in a 50 mL amber vial. All of the experiments, except for the kinetic study, were carried out under (i) optimized adsorbent doses (25, 50, 75, or 100 mg L^{-1}), (ii) initial concentrations of adsorbates of 1, 2.5, 5, 7.5, 10, 15, or 20 μM for the isotherm study, (iii) solution temperatures of 298, 308, or 318 K, (iv) solution pH of 3.5, 5.5, 7.5, or 9.5, (v) NaCl ionic strength of 300, 600, or 1,200 μS cm^{-1}, and (vi) HA concentration of 2.5 or 10 mg L^{-1}, and 300 μS cm^{-1} each of $CaCl_2$, and Na_2SO_4 background ions. According to previously reported studies, we chose specific conditions for ionic strength, HA concentration, and background ions (Joseph et al., 2011; Jun et al., 2019b; Jung et al., 2013; Park et al., 2017). Furthermore, we carried out a kinetic study with a Phipps and Bird 7790–400 jar test apparatus (Richmond, VA, USA). Kinetic tests were performed using 100 mg L^{-1} of adsorbents (*i.e.,* PAC and MOF) and 1 L of 10 μM adsorbates (*i.e.,* IBP and CBM mixture) with stirring at 100 rpm. Solution samples from the 1 L cylinder beaker were confirmed at 10, 20, 30, 60, 120, 240, 480, and 1,440 min.

3. Results and discussion

3.1. Kinetic study of adsorption by MOF and PAC

The contact time between the adsorbates and adsorbents is among the factors that must be taken into account when proper adsorption is required, and can be assessed by evaluating the equilibrium performance. We used commercially available PAC as a control for MOF to check the practical feasibility of MOF adsorption, because PAC is a widely used adsorbent for the removal of PhACs (Dhaka et al., 2019). Fig. 1 shows characterizations of MOF and detail explanation is described in the Supporting Information. Fig. 2 (a) and (b) shows the effects of contact time on the q_t and removal ratio of the PhACs using PAC and MOF. Both adsorbents reached equilibrium after approximately 2 h of contact time, and MOF performed better than PAC. This can be attributed to the higher surface area, as indicated by the Brunauer–Emmett–Teller (BET) results (Fig. 1 (a) and S1 (a)). The specific adsorption mechanism of MOF will be explained in Section 3.3. Based on these results, a 4 h contact time was selected for further experiments.

We investigated the relationship between contact time and adsorption in four different kinetic models (*i.e.*, pseudo-first order, pseudo-second order, Elovich, and intra-particle diffusion kinetic models). Fig. 2 (c) to (f) shows the results for the four different kinetic models, plotted based on kinetic data (Fig. 2 (a) and (b)). In these results, we also confirmed that MOF had better performance compared to PAC, considering four different kinetic parameters (Table S1). Both adsorbents were well adapted to the pseudo-second order model, based on the highest values of the correlation coefficients (R^2), as shown in Table S1. These outcomes are consistent with those of previous studies (Bhadra et al., 2017; Gao et al., 2018; Lv et al., 2018; Mirsoleimani-azizi et al., 2018). In the following Sections, we describe various experimental tests performed on the MOF, which were carried out to clarify their practical feasibility and adsorption mechanisms.

3.2. *Effect of water quality conditions on the adsorption of PhACs*

3.2.1. *Solution temperature*

The solution temperature is one of the key factors for determining adsorption performance (Lv et al., 2018; Mirsoleimani-azizi et al., 2018; Qu et al., 2009), and the effects of the solution temperature on tetracycline adsorption performance have been explained previously (Mirsoleimani-azizi et al., 2018). The removal

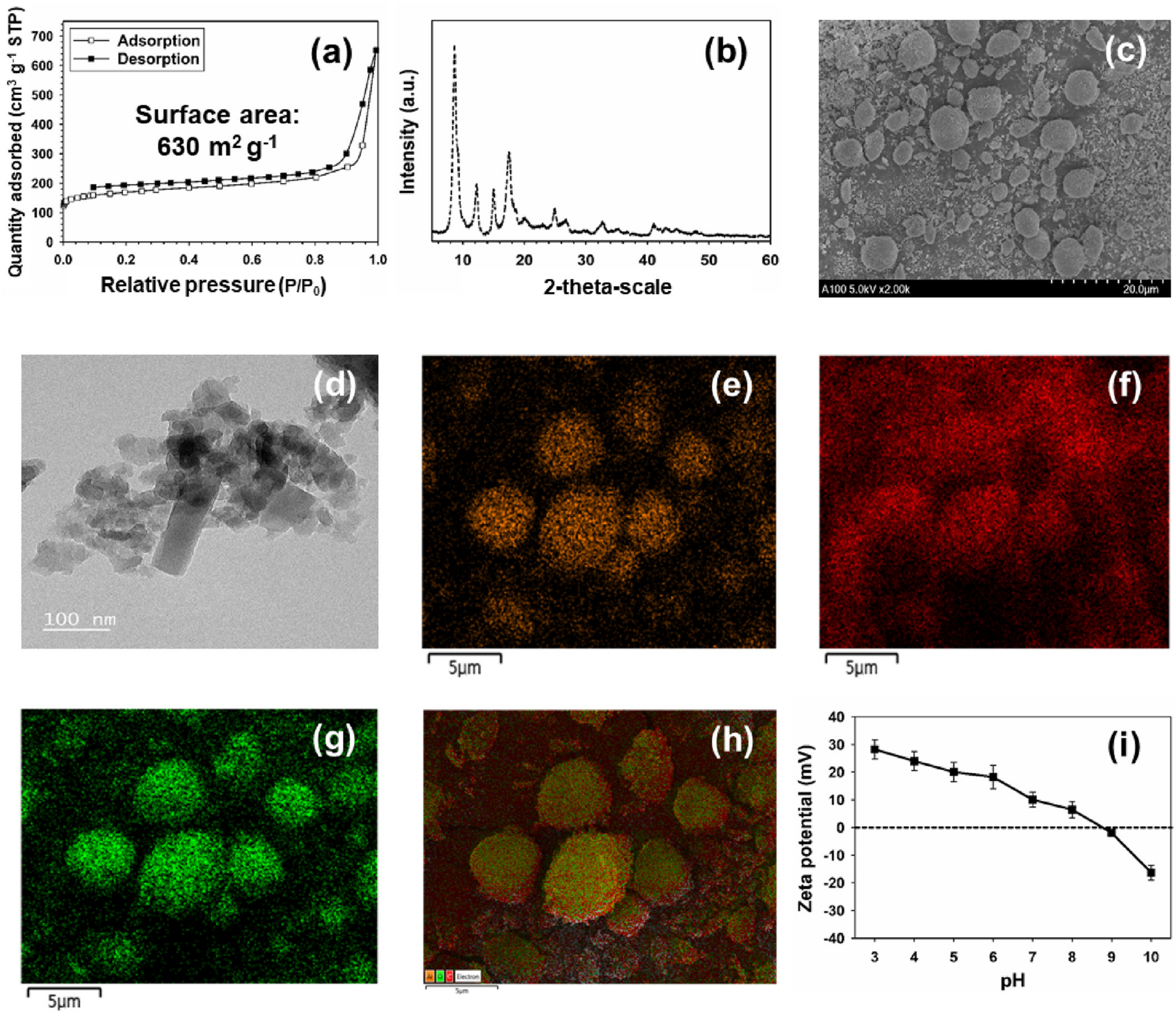


Fig. 1. Characterizations of MOF using (a) BET, (b) PXRD, (c) SEM, (d) TEM, (e-h) SEM-EDS for elemental mapping of Al, C, O, and total, respectively, and (i) zeta potential.

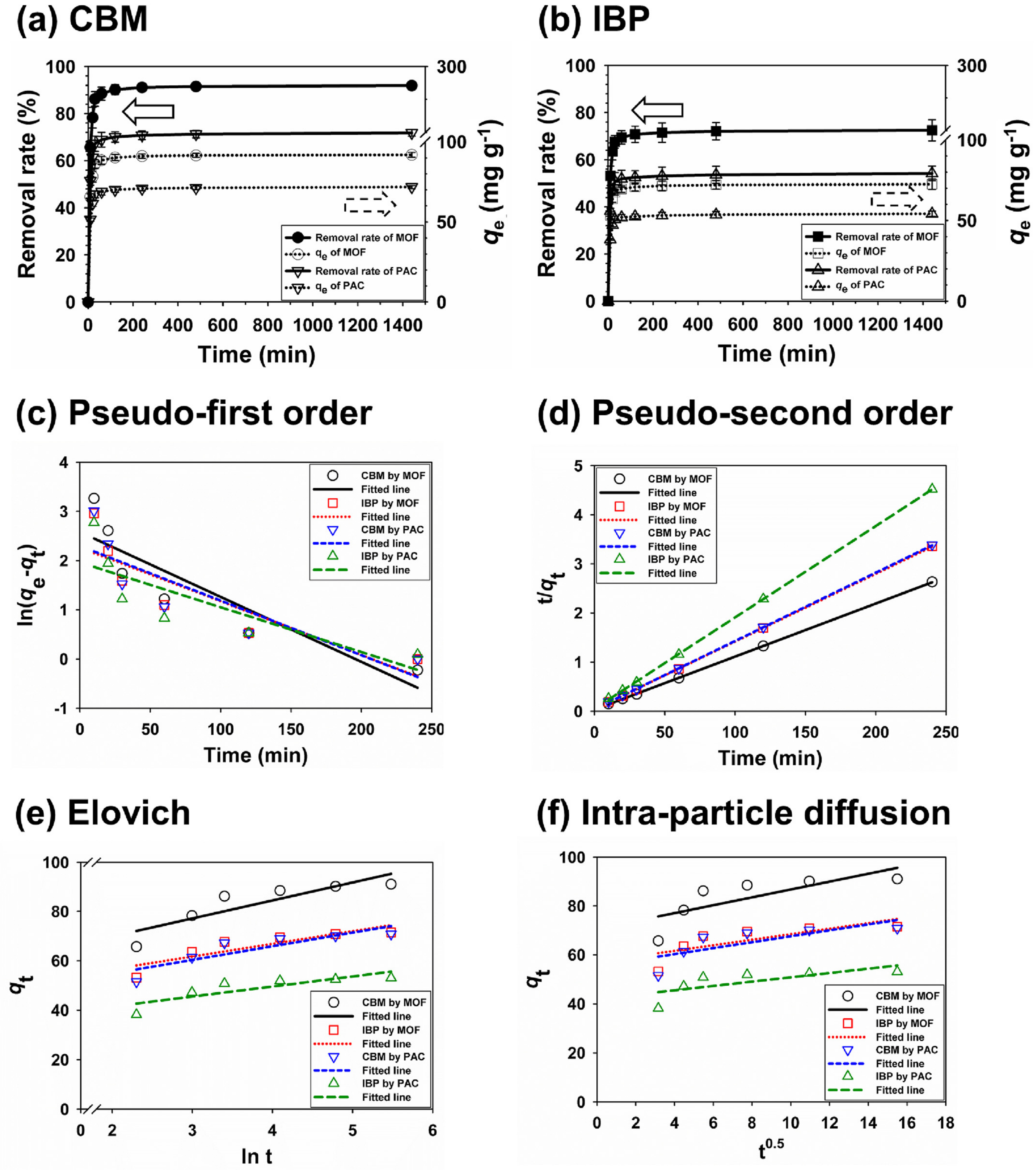


Fig. 2. Effect of contact time on the adsorption of (a) CBM and (b) IBP using 100 mg L^{-1} MOF and PAC for kinetic study. (c - f) Linear fitting form of adsorption of PhACs by adsorbents to the pseudo-first order, pseudo-second order, Elovich, and intra-particle diffusion kinetic model, respectively.

efficiency of tetracycline increased from approximately 20%–85% as we increased the solution temperature from 293 to 328 K, due to the following factors (Mirsoleimani-azizi et al., 2018): (i) decreased thickness of the boundary layer near the adsorbent, (ii) increased number of active sites of the adsorbent, and (iii) increased diffusion rate and mobility of the absorbent owing to decreased viscosity of solution. Another study investigated the adsorption performance of perfluorooctanoic acid by PAC at different temperatures, and found that the removal efficiency decreased slightly as the temperature increased from 313 to 323 K (Qu et al., 2009). This was attributed to the decreased hydrophobic characteristics of adsorbates due to the increased solubility and vibrational energy for desorption of adsorbates from adsorbents (Qu et al., 2009). The negative effect of solution temperature on the adsorption capacity was also confirmed in another study on the removal of p-arsanilic acid by MOF (Lv et al., 2018). The adsorption quantities (q_e) of the PhACs in this study increased continuously from 298 to 318 K, as shown in Fig. 3 (a). These results are due to the dominantly positive effect of the solution temperature on adsorption capacity. Furthermore, the thermodynamic parameters for the adsorption of CBM and IBP on MOF were the positive value of ΔH^0 (16.5 and 5.23 kJ mol^{-1}, respectively) and positive value of ΔS^0 (0.11 and 0.06 kJ K^{-1} mol^{-1}, respectively), as summarized in Table S2. In other words, these result showed endothermic process and increased randomness in this study. In addition, ΔG^0 results was negative value, indicating a spontaneous process for the adsorption of PhACs on MOF.

3.2.2. Solution pH

The solution pH affects the surface characteristics (*e.g.*, surface charge and hydrophobicity) of both the adsorbate and adsorbent (Bhadra et al., 2017), and is hence known to be a critical factor determining removal rate of the adsorbate. For example, the zeta potential of MOF indicated that the pH_{pzc} was approximately 9, as shown in Fig. 1 (i), therefore, negative or positive surface charges, respectively, are predominant when the pH is above or below pH_{pzc}. The pH range measured in this study varied from 3.5 to 9.5, which we selected after considering the practical applications and pH_{pzc} of MOF. Fig. 3 (b) shows the q_e and removal rate of CBM and IBP with respect to the solution pH. We observed that the effects of the solution pH on the adsorption performance were smaller in the case of CBM. In other words, the q_e of IBP decreased markedly more than that of CBM as we increased the solution pH. This phenomenon can be attributed to multiple effects related to the adsorption mechanism, in turn resulting from changes in the surface characteristics with increasing solution pH (Bhadra et al., 2017; Kim et al., 2014).

3.2.3. Effect of ionic strength and background ions

We investigated the effects of varying the ionic strength and background ions on the adsorption performance, to assess the suitability of MOF for practical applications with various water sources (Zhao et al., 2016). Fig. 3 (c) shows the effects of different ionic strengths and background ions on q_e and the removal rate of CBM and IBP. According to previous studies, these results may be due to synergistic effects (Wong et al., 2016; Zhao et al., 2016). First of all, an increase in ionic strength affects the electrical double layer, so plentiful ions screen the surfaces of both the adsorbates and adsorbents, thus weakening electrostatic interactions (Wong et al., 2016). Second, the salting-out effect reduces the solubility of the adsorbates, increasing hydrophobicity (Wong et al., 2016). Third, adsorbents aggregate with increasing ionic strength (Seo et al., 2016). Finally, background ions could interrupt the adsorption between adsorbates and adsorbents due to competition (Wong et al., 2016). The removal of CBM was not significantly affected by

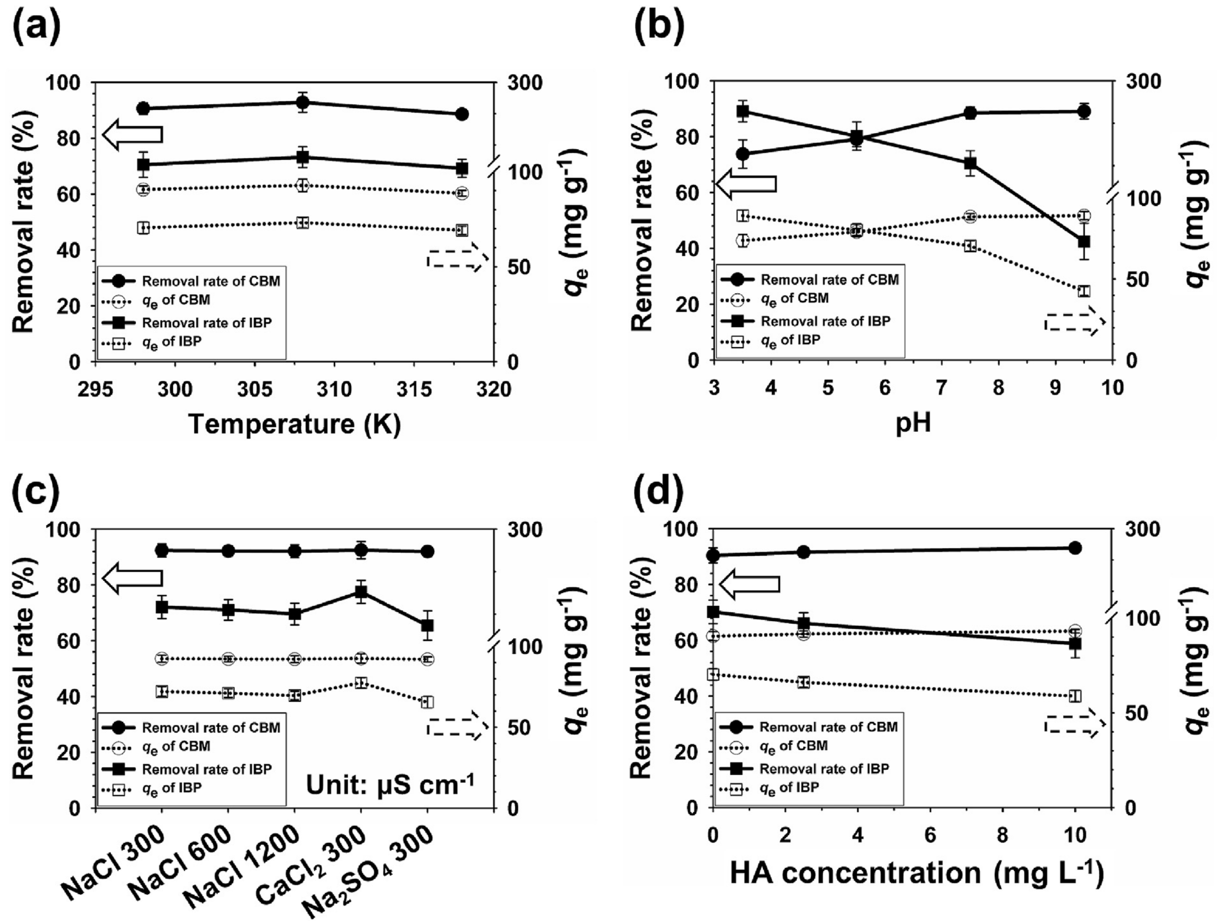


Fig. 3. Adsorption capacity and removal rate at different water quality conditions as follows: (a) Solution temperature, (b) solution pH, (c) various ionic strength and ions, and (d) HA for MOF.

environmental ion conditions. However, the removal of IBP varied significantly with the ionic strength and background ions (*i.e.*, divalent cations and anions). According to previous reports, the different adsorption trends of CBM and IBP are due to differences in their intrinsic physico-chemical properties (Kim et al., 2014; Scheytt et al., 2005; Wong et al., 2016; Zhao et al., 2016).

3.2.4. Effect of HA

Humic substances, which consist of phenolic and carboxylic acids (Bhatnagar and Sillanpää, 2017), are widely distributed in natural water, soil, and sediment. In this study, HA was selected as a model humic substance, based on previous studies (Bhadra and Jhung, 2017; Bhatnagar and Sillanpää, 2017). Hence, the removal of adsorbates when HA is present is required to confirm the feasibility of the MOF. HA has a negative surface charge at neutral pH values due to the deprotonation of carboxylic acids. Fig. 3 (d) shows the q_e and removal rate of CBM and IBP with increasing HA concentration. The results show that HA promotes and interrupts adsorption in the cases of CBM and IBP, respectively. The specific adsorption mechanisms of both adsorbates, judging from the effects of various water chemistry parameters on adsorption performance, will be clarified in Section 3.3.

3.3. Plausible PhACs adsorption mechanism

It is essential to investigate the adsorption mechanism when selecting proper adsorbents for removal of specific adsorbates from wastewater. For example, the surface area and porosity of adsorbents are known to affect the fundamental adsorption mechanism (Bhadra et al., 2018; Lv et al., 2018; Zhao et al., 2016), and are highly correlated with adsorption capacity if there are no strong interactions. For this reason, high removal rates of CBM and IBP were achieved by using MOF rather than PAC as the adsorbents in this study (Fig. 2 (a) and (b)). However, the differences between CBM and IBP are not only explained by the physical properties of the adsorbents (*i.e.*, surface area (Fig. 1 (a) and S1 (a)); other adsorption mechanisms, in addition to the surface area, should be considered to clarify the adsorption phenomena observed in this study. According to previous research (Bhadra and Jhung, 2017; Wong et al., 2016; Zhao et al., 2016), five main mechanisms have been used to clarify the adsorption of CBM and IBP by MOF, as follows: (i) Lewis acid-base interactions, (ii) coordination by framework metals, (iii) hydrogen bonding, (iv) electrostatic interactions, and (v) hydrophobic interactions, including π - π stacking.

3.3.1. Lewis acid-base interactions

Acid-base interactions are generally cited when explaining adsorption mechanisms (Hasan and Jhung, 2015; Zhao et al., 2016). For example, MOF functionalized with $-SO_3H$ and $-NH_2$ groups had much better capacity for adsorption of naproxen and clofibric acid than pristine MOF due to acid-base interactions (Hasan et al., 2012). Thus, we investigated the effects of acid-base interactions on the adsorption of CBM and IBP. A possible acid-base interaction in this study is between the amine of CBM and carboxylic acid of unreacted MOF under highly acidic conditions (*i.e.*, pH 3.5 in this study), which is a neutral state for both amines and carboxylic acid (Table 1). That is, we expected the CBM adsorption capacity to be higher than that of IBP at pH 3.5 if the Lewis acid-base was the main adsorption mechanism. However, our experimental results (3 (b)) did not indicate this to be the case. Therefore, acid-base interactions were not the main adsorption mechanism of CBM and IBP.

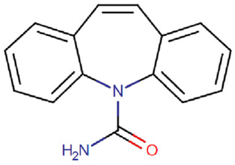
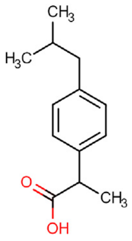
3.3.2. Coordination by framework metal

MOFs consist of coordination bonds between metal ions and organic linkers (Li et al., 2019), so coordinatively unsaturated sites or open metal sites are possible active sites for adsorbates (Hasan and Jhung, 2015). There have been reports showing that coordination by framework metals is the main adsorption mechanism (*e.g.*, benzotriazole (Wang et al., 2017) and ethion insecticide (Abdelhameed et al., 2016)). Aluminum, which is the main metal of the MOF used in this study, would likely be coordinated with anionic IBP due to a lack of electrons. If this hypothesis is true, the q_e of IBP should be higher than that of CBM at both pH 5.5 and 7.5, considering the pK_a of IBP (Table 1) and the positive surface charge of the MOF (Fig. 1 (i)). However, our results did not fit this hypothesis either, so the coordination effect due to the framework metal was not the main adsorption mechanism.

3.3.3. Hydrogen bonding

The effect of hydrogen bonding between adsorbates and adsorbents is a good candidate for explaining the main adsorption mechanism. For example, hydrogen bonding was a major factor contributing to the adsorption of nitroimidazole antibiotics by

Table 1
Physicochemical properties of the used PhACs.

Pharmaceuticals	Carbamazepine ($C_{15}H_{12}N_2O$) [CBM]	Ibuprofen ($C_{13}H_{18}O_2$) [IBP]
Molecular weight[a] (g mol^{-1})	236.3	206.3
pK_a[a]	15.96	4.85
Log K_{OW}[a]	2.77	3.84
Log D_{OW}[a] (at pH 3.5, 5.5, 7.5, 9.5)	2.77, 2.77, 2.77, 2.77	3.83, 3.11, 1.25, 0.35
Number of H-bond acceptor (at pH 3.5, 5.5, 7.5, 9.5)	3, 3, 3, 3	2, 2, 2, 2
Number of H-bond donor (at pH 3.5, 5.5, 7.5, 9.5)	1, 1, 1, 1	1, 0, 0, 0
Water solubility[b] (S_W) (mg L^{-1} at 25 °C)	17.7	21
Chemical structure[a]		

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[a] Chemicalize.org by ChemAxon (http://www.chemicalize.org).
[b] Drugbank.ca by DrugBank (http://www.drugbank.ca).

pristine MOF and MOF modified by urea or melamine (Seo et al., 2017). Furthermore, other researchers also exploited hydrogen bonding as the main adsorption mechanism (Bhadra et al., 2017; Lv et al., 2018; Zhao et al., 2016). Therefore, we investigated the effects of hydrogen bonding on the adsorption of CBM and IBP by MOF. Hydrogen bonding interactions arise due to interactions between hydrogen acceptors and hydrogen donors. In other words, it is important that the number of active sites is related to the numbers of hydrogen acceptors and donors, as summarized in Table 1. First, adsorbents can be assumed to be hydrogen acceptors, considering that there are numerous oxygenated functional groups in MOF (Liang et al., 2015). The number of hydrogen donors in each adsorbate is critical for determining hydrogen bonding effects in this case. The higher q_e of CBM than IBP at pH values of 7.5 and 9.5 can be attributed to the larger number of hydrogen donors (Table 1). However, the same logic cannot be applied in the cases of pH values of 3.5 and 5.5 (Fig. 3 (b)). If this case was reversed (*i.e.*, adsorbent and adsorbates were used as hydrogen donors and acceptors, respectively), we would predict that q_e would be higher for CBM than IBP under all pH conditions. However, this is not what we observed, as shown in Fig. 3 (b). Thus, the effects of hydrogen bonding on adsorption were not the main factors affecting the adsorption mechanism in this study.

3.3.4. *Electrostatic interactions*

Confirmation of electrostatic interactions may explain the competitive adsorption mechanism between CBM and IBP, because it has been used as a general method for clarifying the adsorption of organic pollutants from wastewater (Bhadra et al., 2017; Gao et al., 2018; Lv et al., 2018). In particular, the adsorbates used in this study evidently have different pK_a values, as shown in Table 1, leading to different electrostatic characteristics as the pH varies from 3.5 to 9.5. In other words, surface charges of CBM and IBP are present in neutral and neutral/anionic states, depending on the solution pH. Electrostatic interactions between adsorbates and adsorbents are deeply related to the solution pH and environmental solution conditions (Seo et al., 2017; Wong et al., 2016). Therefore, we need to explain electrostatic interactions in terms of three water chemistry factors, as follows: pH, ionic strength/background ions, and HA.

First, considering the isoelectric point of MOF (approximately pH 9, as shown in Fig. 1 (i)) and the pK_a values of the adsorbates (the pK_a values of CBM and IBP are 15.96 and 4.85, respectively, as shown in Table 1), the surface charges of MOF, CBM, and IBP under different solution pHs are as follows:

(i) $3.5 < pH < 4.9$: MOF (+), CBM (neutral), and IBP (neutral)
(ii) $4.9 < pH < {\sim}9.0$: MOF (+), CBM (neutral), and IBP (−)
(iii) ${\sim}9.0 < pH < 10.5$: MOF (−), CBM (neutral), and IBP (−)

That is, the change in solution pH has little impact on the adsorption of CBM; however, electrostatic interactions and repulsion between MOF and IBP should be dominant at pH values below and above approximately 9, respectively. According to Fig. 3 (b), electrostatic interactions are insignificant and important with respect to the adsorption of CBM and IBP, respectively. Furthermore, the higher q_e value of IBP than CBM at pH values of 3.5 and 5.5 can be attributed to the electrostatic attraction between MOF and IBP. However, it is difficult to explain why the q_e of CBM was higher than that of IBP at pH 7.5 if electrostatic interactions have the strongest effect on the adsorption.

Fig. 3 (c) shows that IBP was much more affected than CBM as the ionic strength and background ions were varied. As mentioned above, the increase in ionic strength weakened the electrostatic interactions by screening the adsorbates and adsorbents (Wong et al., 2016). Therefore, the decrease in the q_e value of IBP with increasing ionic strength at neutral pH values can be explained by the decrease in electrostatic interactions. Furthermore, divalent cations and anions will increase and decrease the q_e of IBP, respectively. That is, divalent cations, as counter-ions for IBPs, may promote electrostatic interactions between MOF and IBPs due to the bridge effect, as explained previously (Liu et al., 2018). However, divalent anions as co-ions of IBP may interrupt the electrostatic interactions between MOF and IBP due to competitive adsorption.

We observed a similar pattern to the divalent anion case for HA, which is a multivalent anion material due to the deprotonation of carboxylic acids at neutral pHs (Jordão et al., 2009). These phenomena can also be explained in terms of the competitive adsorption between HA and IBP on MOF. Meanwhile, we obtained unpredictable results in the case of CBM (Fig. 3 (d)). The q_e of CBM increased with the HA concentration and was not correlated with the divalent CBM anions in the same way. Some experimental results can be clarified by considering electrostatic interactions. However, another adsorption mechanism is still required for us to completely understand the results of this study. Therefore, we concluded that electrostatic interactions have supplementary adsorption effects, based on the results of our analysis of the three water chemistry factors mentioned above.

3.3.5. *Hydrophobic interactions including π -π stacking*

Hydrophobic interactions between adsorbates and adsorbents can be considered as critical factors when highly hydrophobic adsorbates are treated and other adsorption mechanisms are not dominant (Bhadra et al., 2017; Gao et al., 2018; Hasan and Jhung, 2015; Zhao et al., 2016). For example, the maximum adsorption capacity of bisphenol A, which has a high K_{ow} value, was determined based on the hydrophobic characteristics of MOF (*i.e.*, π -π stacking) regardless of surface area (Hasan and Jhung, 2015). Therefore, the effects of hydrophobic interactions were confirmed to support the incomplete explanation of competitive adsorption, as mentioned above, in terms of: pH, ionic strength, and existence of HA.

First of all, a high quantity of surface charges on the adsorbent can decrease the hydrophobicity (Wong et al., 2016), so the pH of the solution is not negligible in terms of its effect on hydrophobic interactions. According to Fig. 1 (i), the amount of the surface positive charge of the MOF monotonically decreased as the pH increased from 3.5 to 9.5, resulting in strong hydrophobic interactions. This phenomenon was correlated with the trend in the q_e of CBM with increasing solution pH, as shown in Fig. 3 (b). The distribution coefficient (log D_{ow} value) represents the hydrophobic characteristics at different solution pH values (Wong et al., 2016). Compared to CBM, which has the same log D_{ow} value in the pH range from 3.5 to 9.5, the carboxylic acid group of IBP became deprotonated, resulting in a decrease in the log D_{ow} value (Table 1). These results are in good agreement with the reversal between the q_e values of CBM and IBP at pH 7.5.

The ionic strength also affects the hydrophobicity of adsorbates due to the salting-out effect and aggregation of adsorbents (Seo et al., 2016; Wong et al., 2016). In other words, increased ionic strength is positive for hydrophobic interactions, due to the increased hydrophobicity, but negative for q_e because the number of active sites decreases due to the aggregation of adsorbents. The effect of the ionic strength on the q_e of CBM was negligible; however, the q_e value of IBP decreased monotonically, as shown in Fig. 3 (c). If these two factors affecting hydrophobic interactions cancel each other out, like in the case of CBM, the IBP results could be attributed to the synergistic effects of both hydrophobic interactions and electrostatic interactions, as explained above

(Section 3.3.4).

Finally, increasing the HA concentration increased and decreased the q_e value in the cases of CBM and IBP, respectively (Fig. 3 (d)). The decreased q_e value of IBP can be explained by the competitive adsorption at neutral pHs between anionic HA and IBP on the positively charged MOF surface, as described in Section 3.3.4. However, the q_e value of CBM increased in the neutral state. This phenomenon can be explained by the fact that the hydrophobic interactions between MOF and CBM would be promoted by the nonphenolic and aromatic hydrophobic functional groups of HA (Chu et al., 2017).

To sum up the adsorption mechanisms observed in this study, considering the pH, ionic strength, and existence of HA factors, the adsorption of CBM was mainly determined by hydrophobic interactions with supplementary hydrogen bonding effects. Meanwhile, the IBP adsorption was mostly attributed to both hydrophobic interactions and electrostatic interactions. Fig. 4 shows a schematic diagram of the proposed adsorption mechanisms of PhACs by MOF.

3.4. Regeneration of used MOF

The regeneration of used MOF is an important parameter in practical and commercial applicability (Bhadra et al., 2017; Lv et al., 2018; Seo et al., 2017). We used acetone to perform desorption of PhAC-doped MOF for regeneration, a procedure that has been reported previously (Seo et al., 2017). Fig. 5 shows the regeneration abilities of MOF for PhACs removal over four successive adsorption-desorption cycles. Acetone successfully removed PhACs from the MOF, so the q_e value almost completely recovered after regeneration following each of the four cycles. That is, MOF can be used as highly efficient and recyclable adsorbents for the removal of PhACs from wastewater.

We then carried out FTIR/XPS analysis to support our regeneration data by comparing virgin and regenerated MOF in terms of chemical properties (Jun et al., 2018a; Jun et al., 2019c). We analyzed the FTIR spectra of the virgin, CBM/IBP powder, CBM/IBP-doped MOF, and regenerated MOF to clarify the adsorption and desorption phenomena, as shown in Fig. 6. FTIR spectra of the virgin MOF showed a similar pattern with the previous study (Jun

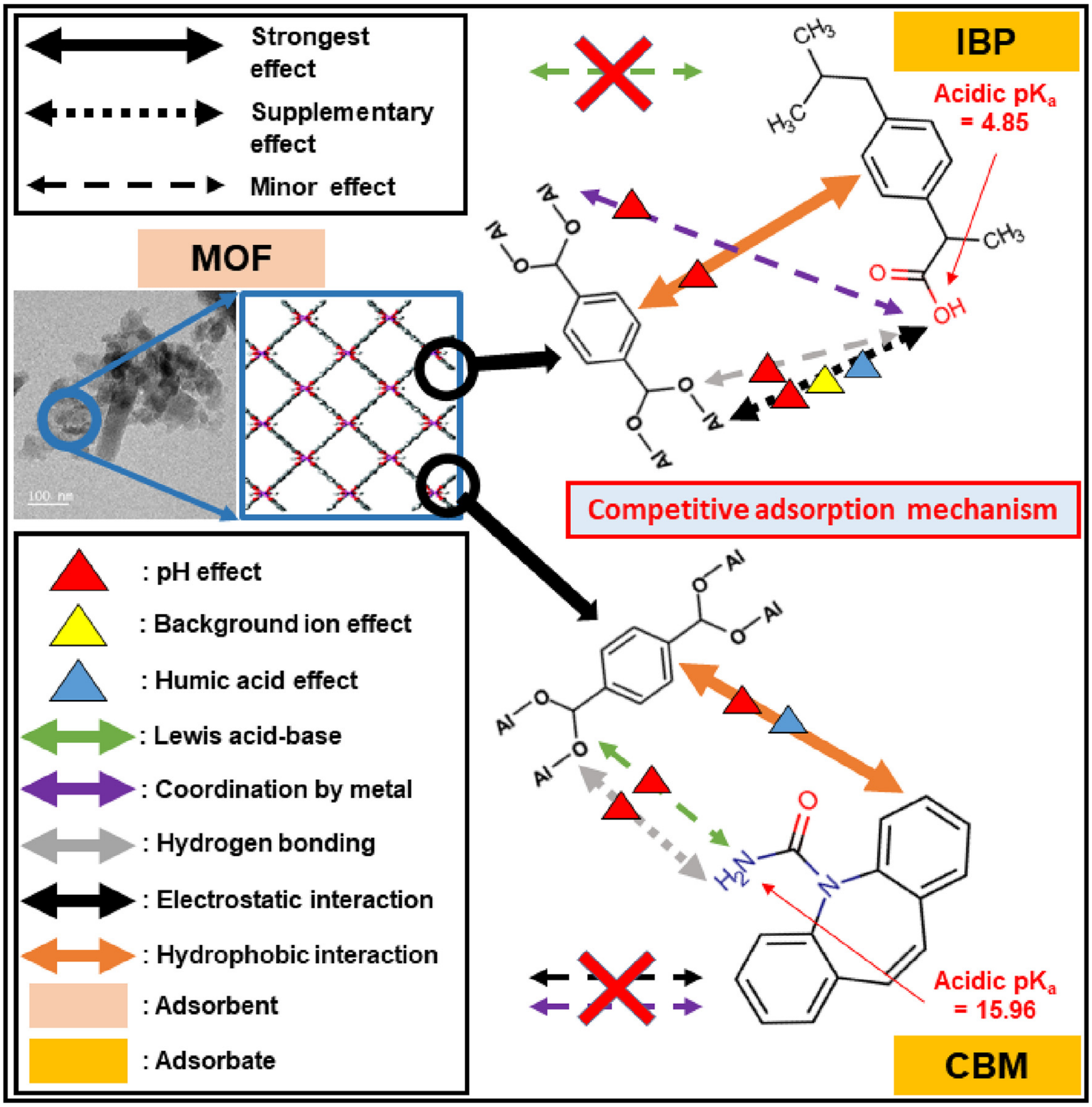

Fig. 4. Proposed schematic diagram related to adsorption mechanisms of PhACs by MOF.

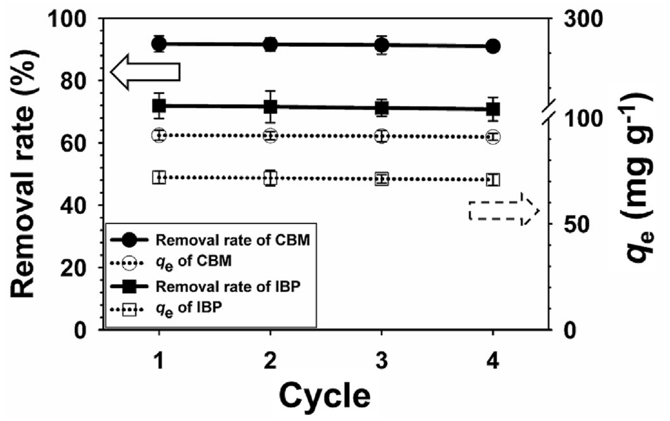

Fig. 5. Regeneration ability of MOF for PhACs removal in four successive cycles of adsorption and desorption.

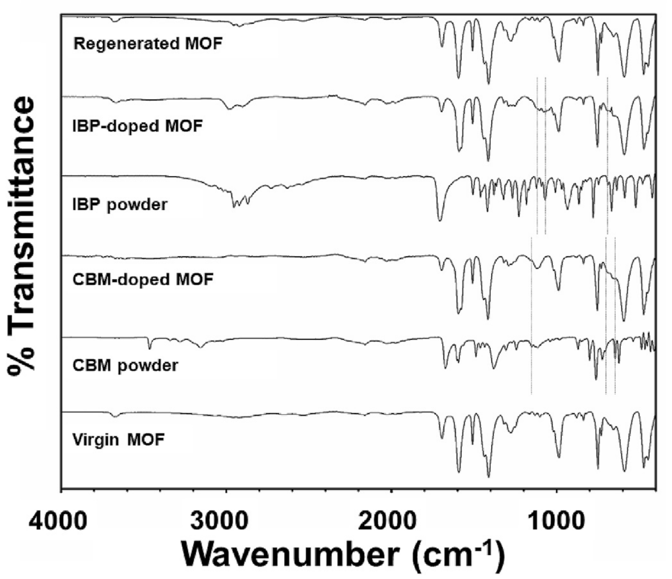

Fig. 6. Investigation of before and after adsorption of PhACs on MOF via FTIR determination.

et al., 2019b). For example, the intrinsic peaks of Al-based MOF such as C-O-Al and Al-O bond were confirmed at 987 and 600 cm^{-1}, respectively (Jun et al., 2019b). The new peaks at 1,153/852/800 (Di Profio et al., 2011) and 1,123/1,070/689 cm^{-1} (Zhao et al., 2016) indicate the adsorption of CBM and IBP by the MOF, respectively. Subsequently, acetone solution almost completely desorbed the adsorbates from adsorbent, so the FTIR spectra of the regenerated MOF were very similar to those of the virgin MOF. We measured the XPS spectra of the virgin and regenerated MOF to support our FTIR results. The C 1s spectra of the virgin and regenerated MOF were deconvoluted into major peaks based on the results of a previous study, as follows (Liu et al., 2018): (i) O−C=O bond (~289 eV), (ii) C−O−C bond (~287 eV), (iii) C-C/C=C bond (~285 eV), and (iv) Al−C carbide (~283 eV), as described in Fig. S2 (a) and (b). The areas of the C-C/C=C, C-O-C, and O-C=O bonds normalized by the Al-C bond are summarized in Table S3. The XPS spectra and normalized area of the regenerated MOF exhibited similar patterns to the virgin MOF. Hence, these XPS results were highly correlated to the FTIR results. Lastly, the performance results of IBP and CBM in this study were comparable or better than other MOF-based adsorbents as shown in Table S4.

4. Conclusions

We applied a novel MOF as an effective adsorbent for the removal of selected PhACs. We characterized the MOF using a porosimeter, XRD, SEM-EDS, TEM, and the zeta potential to explain its physico-chemical properties. We carried out an adsorption kinetic and isotherm study of the MOF with respect to the removal of PhACs, and the results were in good agreement with the pseudo-second-order kinetic model and Langmuir isotherm model, respectively. We carried out adsorption of the PhACs according to four water chemistry conditions, as follows: (i) solution temperature, (ii) solution pH, (iii) ionic strength/background ions, and (iv) existence of HA. Based on experimental results of four water chemistry factors, the adsorption mechanisms of CBM and IBP were mainly determined by hydrophobic interaction with supplementary hydrogen bonding effect and both hydrophobic interactions and electrostatic interactions, respectively. Furthermore, we clarified the regeneration capabilities of the MOF based on FTIR/XPS and carried out four cycles of regeneration tests to confirm its practical utility. The MOF presented is a promising adsorbent for removing PhACs from wastewater, as its performance is superior to that of commercial PACs and it has good reusability qualities. Therefore, the specific water chemistry factors to determine q_e of CBM and IBP in this study would be practically helpful for future readers who will work on the treatment of PhAC containing wastewater.

Acknowledgements

This research was funded by the Korea Ministry of Environment (The SEM projects; 2018002470005, South Korea) and the National Science Foundation (OIA-1632824, USA). This research was also supported by the Korea Environment Industry & Technology Institute (KEITI) through Plant Research Program, funded by Korea Ministry of Environment (MOE) (1485016267, South Korea). The authors would also like to thank KBSI at Daegu for microscopic measurements (SEM and TEM) and Dr. Namguk Her at the Korea Army Academy at Youngcheon for data analysis.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2019.06.208.

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