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Adsorption of Haloacetonitriles (HANs) by Metal-Organics Frameworks (MOFs)

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ABSTRACT

This research investigated adsorption efficiency of HANs by using Dichloroacetonitrile (DCAN) as a represent on metal organic frameworks (MOFs; ZIF-8, MIL-53(Al), HKUST-1) and carbonized metal organic frameworks (C-MOFs; C-ZIF-8, C-MIL-53(Al), C-HKUST-1) comparing with powder activated carbon (PAC). ZIF-8, MIL-53(Al) were synthesized via room temperature method, and HKUST-1was synthesized via solvothermal method. Original MOFs were carbonized in tube furnace with N_2 flow at 900 $^{\circ}$C. The synthesized materials were characterized the crystallized pattern by X-ray diffraction (XRD). The screening experiment was studied to select the potential adsorbents C-MOFs. As a result, C-ZIF-8, C-MIL-53(Al) and PAC which process high adsorption capacities of DCAN, were selected for kinetic and isotherm study. The adsorption kinetics and isotherm were studied to examine the adsorption mechanism under batch condition. According to the results, the adsorption rate and capacity of C-ZIF-8 exhibited the higher amount than C-MIL-53(Al) and PAC. Pseudo-second order models were applied for adsorption kinetic models. The adsorption isotherm was fitted with Langmiur and Fruendlich models.

Keywords : Haloacetonitriles (HANs), Metal-Organic Framework (MOFs), Carbonization, Adsorption

INTRODUCTION

1. Haloacetonitriles (HANs)

Conventional water treatment plant has been designed to remove contaminants in order to supply high quality water; i.e. coagulation and flocculation, sedimentation, filtration and disinfection. For disinfection process, chlorine is considered as the most widely use disinfectant due to its efficiency, cost, and convenient for operation. On the other hand, when aqueous free chlorine reacts with natural organic matter (NOM), disinfection by products (DBPs) can be formed in treated water. Epidemiological studies of DBPs show that potential health risks from DBPs include cancer and reproductive developmental effects, with bladder cancer, showing the most consistency in human epidemiologic studies from several countries [1, 2]

DBPs are several organic and inorganic compounds which had found in disinfected water. Although above 700 of DBPs have been identified in water, there are few of major halogenated DBPs which are commonly study such as Trihalomethanes (THM), Haloacetic acids HAAs). Especially, HANs which is included to be emerging water pollutants. HANs are generally detected at much lower concentrations than carbonaceous DBPs (C-DBPs). HANs are a relatively new class of nitrogenous disinfection by-products (N-DBPs), which has higher genotoxicity and cytotoxicity than the relatively THMs or HAAs.

2. Metal-Organic Framework (MOFs) and Carbonization process

From the review of Bin Li in 2016 [8], Metal–organic frameworks (MOFs), also known as coordination polymers, represent an interesting type of solid crystalline materials that can be straight forwardly self-assembled through the coordination of metal ions/clusters with organic linkers, which mimic the porous nature of zeolite materials. MOFs materials can succeed in the functions of both site, metal ions/clusters and organic linkers, hence MOFs can provide special properties such as electronic, magnetic and optical properties of such inorganic and organic building units to develop multifunctional materials. MOFs also can be used as gas storage and separation, optical materials, chemical sensing, catalysis, and biomedicine.

Considering the ability of MOFs for gas storage, many researchers [9, 10] have found that MOFs are efficiency material for H_2 storage by their extremely high porosities, pore volume and surface areas. Thus, MOFs are challenging to use for liquid storage in HANs adsorption process. However, application as a adsorbent for removal of contaminants in aqueous phase of MOFs still has many problem due to their stability against hydrolysis reaction in water condition. Hence, improving stability of porous structure of MOFs and reducing release of metal from MOFs framework should be concerned. Carbonization under nitrogen flow is one of the most popular modified method that can enhance adsorption efficiency for MOFs, due to increasing of surface area and strengthen porous structure as well as increase of active functional groups on carbonized materials. Thus, this research has selected carbonization method to modify selected MOFs and investigated the effect of carbonization on adsorption kinetics and isotherms of HANs in aqueous phase. Toward many studies about MOFs carbonization [11, 12], carbonization with N_2 flow at 900°C was selected for material modification in this research. Various types of original MOFs were selected in this study such as ZIF-8, MIL-53 and HKUST-1, UiO-66 and MIL-88B, and then four type of MOFs were carbonized under nitrogen flow at 900 $^{\circ}$C (C-MIL-53, C-ZIF-8, C-HKUST-1 and C-MIL-88B) and investigated adsorption capacity for HANs.

DCAN (Dichloroacetonitriles) was selected as representative HANs due to its highly effect on human health. Adsorption screening, kinetics and isotherms were investigated and compared with commercial powdered activated carbon (PAC).

METHODOLOGY

1. Materials synthesis

A. Synthesis of ZIF-8

ZIF-8, synthesized in a purely aqueous system. Zinc nitrate hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$) (5 mmol) and 2-methylimidazole (mIm) (40 mmol) are dissolved in separate 100 mL portions of methanol. The two clear solutions are combined and stirred rapidly for 1 h, during which time the combined solution became cloudy due to the precipitation of nanoparticles (NPs) of ZIF-8. The ZIF-8 colloid is separated from the solution by three times of centrifugation at 14,000 rpm for 15 min and resuspension of the nanoparticles in ethanol. The solvent is removed using rotary evaporation, and the product is further dried at room temperature in a desiccator with reduced pressure. [15]

B. Synthesis of MIL-53(Al)

MIL-53 (Al), A solution containing 8 mmol aliquot of $Al(NO_3)_3$, 4 mmol 1,4-benzenedicarboxylic acid and 8 mmol sodium hydroxide are mixed with in a 100 mL distilled water at room temperature for 24 h and washed three times with deionized water. Pore of materials are activated by DMF solvent exchange at 150 ℃ for 24 h. The solution is transferred to a Teflon lined stainless steel autoclave and heated at 150 ℃ for 3 days. The synthesized light-yellow MIL-53(Al) solid is washed with methanol to remove the DMF solvent from the pores of the material. And then the methanol is substituted with water (1 g of MIL-53 in 0.5 l of water) and the light-yellow powder is dried at 60 $^{\circ}$C for 12 hours.

C. Synthesis of HKUST-1

Basically, 0.875 g of $Cu(NO_3)_2{\bullet}H_2O$ are dissolved in 12 mL of DI water and 0.42 g of trimesic are dissolved in 12 mL of ethanol. Subsequently, both solutions is mixed, kept under stirring with magnetic stirrer of 60 min and then placed in Teflon-lined autoclave at 120 $^{\circ}$C in oven for 16 hours. Finally, turquoise crystals are collected and dried at 120 $^{\circ}$C for 10 hours. [16]

D. Powder activated carbon (PAC)

PAC in this study was purchased under brand “Shirasaki S10”.

2. Carbonization

Three kinds of the carbonized MOFs were prepared by the direct pyrolysis of MIL-53, ZIF-8 and HKUST-1. A ceramic boat containing the MOF powder was placed in a tube furnace. The furnace was heated from room temperature to 900 $^{\circ}$C under N_2 flow at the rate of 60mL/min with 10°/min and maintained for 1 h. then cooling down to room temperature at the rate 1°C/min. Corresponding to MIL-53, ZIF-8 and HKUST-1, the obtained samples are denoted as C-MIL-53, C-ZIF-8 and C-HKUST-1, respectively.

3. Characterization

Powder X-ray Powder Diffraction (PXRD) for proving the synthesis MOFs with references MOFs with phase identification of a crystalline material and can provide information on unit cell dimensions.

4. Adsorption experiment

A. Reagent preparation

Reagent water is defined as purified water which does not contain any measurable quantities of any target analyzes or any other interfering species. This research use DI water 18 mΩ from Elga purelab ultra water distiller.

Phosphate buffer stock is prepared by mixture of 10 g of potassium phosphate (KH_2PO_4) and 5.8 g of dipotassium phosphate (K_2HPO_4) then stirring for 1 hour in 100 mL of DI water, both buffer salts should be in granular form and of ACS grade or better. After that the solution is kept in bottle with screw cap for dilution. Fresh phosphate buffer was diluted from 10 mL phosphate buffer stock in to 1000 mL of DI water for 0.01 M phosphate buffer.

B. Adsorbates

DCAN stock were prepared by using Dichloroacetonitrile (DCAN) from Sigma-Aldrich, CAS No.: 3018-12-0. The stock was mixed in acetone by calculated volume for stock of 500 ppm. Then stock was diluted with phosphate buffer to 1 ppm for fresh initial concentration.

C. Adsorption experiment

Adsorption of the prepared adsorbents was carried out in batch experiments. The adsorption capacity of these materials (MIL-53, ZIF-8, HKUST-1, C-MIL-53, C-ZIF-8, C-HKUST-1 and PAC) were evaluated by adsorption of a DCAN aqueous mixture. A DCAN stock was prepared in phosphate buffer at initial concentration of 500 ppm then stock was diluted to 1 ppm. In screening adsorption study, a specific amount of adsorbents (0.010 g) was put in the 1 ppm aqueous DCAN mixture (50 ml) was mixed in a 200 mL amber glass bottle with screw cap. The adsorption study was continued by shaking in rotary shaker at 200 rpm for 24 h at room temperature (25±2 ℃). For kinetic experiments, three adsorbents were selected (C-MIL-53, C-ZIF-8 and PAC). A specific amount of adsorbents (0.010 g) was put in the aqueous DCAN mixture (50 ml) having fixed concentrations at 1 ppm. The mixture was shook and maintained for a fixed time (0 min - 24 h) at room temperature (25±2℃). For isotherm experiments, three adsorbents were also selected (C-MIL-53, C-ZIF-8 and PAC). A specific amount of adsorbents (0.010 g) was put in the aqueous DCAN mixture (50 ml) having fixed concentrations from 50 ppb to 500 ppb. The mixture containing the adsorbents were mixed for equilibrium time at room temperature (25±2℃). All experiments, a solid part was withdrawn and filtered through 0.22 μm nylon syringe filter after reaching determined time. Then the remaining mixture was kept for the extraction by the EPA method 551.1 [17]

D. Extraction and analytical method

HANs will extract according to the EPA method 551.1, sample is extracted by liquid-liquid extraction. A 25 mL of sample are filled in the 40 mL amber glass vial with screw cap and silicone septum. After that 5 g. of Na_2SO_4 is added and mixed by vortex for 2 min, then 2.5 mL of MTBE is added and mixed by vortex for 3 min. The solution is standing for 5 min for separation, 1 mL of organic layer is transferred to glass amber GC vial with septum crimping cap and analyze by GC/ECD.

GC/ECD will set with HP-1 column Serial No. US4760541H from Agilent Technologies System. Nitrogen and helium act as carrier gases with back split inlet, ratio 100:1 and flow 150 mL/min at 200°C with pressure 7.38 psi. Oven is set at 45°C at initial, ramp1 at 150°C for 2 min and post run at 200°C for 1 min. Detector is set at 250°C with N_2 makeup flow at 45°C.

RESULTS AND DISCUSSIONS

1. Materials characterizations

Powder X-ray diffraction (PXRD) was analyzed by SmartLab X-ray diffractometer, Riguka with 40 kV, 30 mA by SC-70 detector compared to the calculation pattern. From Fig. 1, the results showed that both X-ray diffraction peaks line up with the spectra simulated from single crystal X-ray diffraction patterns.

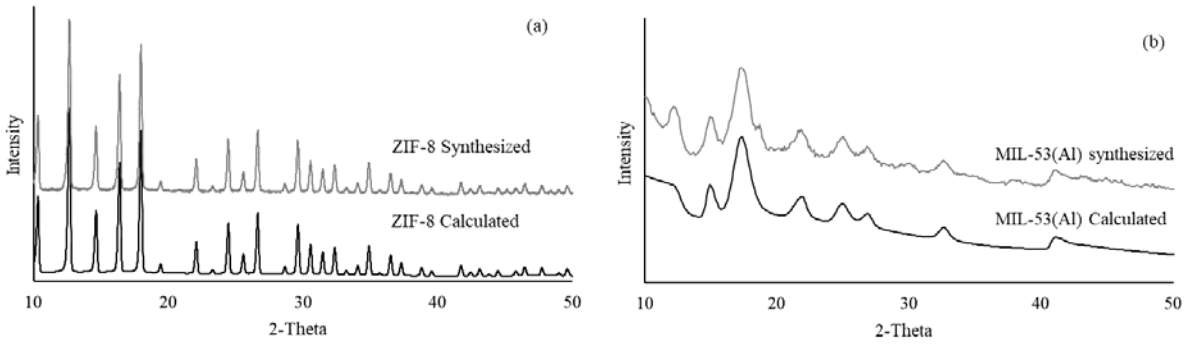

Figure 1 (a) Comparison XRD pattern of ZIF-8 calculation and synthesized ZIF-8, (b) Comparison XRD pattern of MIL-53 calculation and synthesized MIL-53

2. Adsorption study for HANs removal

Adsorption study for the removal of DCAN. The synthesized materials (MIL-53, ZIF-8, HKUST-1, C-MIL-53, C-ZIF-8, C-HKUST-1 and PAC) were evaluated for their adsorption capabilities with DCAN as model pollutant in aqueous phase. The adsorption percentages were calculated by Eq. 1. The conventional MOFs showed adsorption percentages of 5.48, 8.93 and 6.95 percent, respectively, and the carbonized MOFs prepared by carbonization of MOFs at 900 °C showed adsorption capacities of 16.35, 92.45, 3.06 and 70.51 percent respectively. These results show that carbonized ZIF-8 has showed the highest potential to adsorb DCAN in aqueous solution, followed by PAC and C-MIL-53. The C-ZIF-8 shows an interesting adsorption capacity for DCAN with 5083.48 μg g^{-1} which is almost 9 times of conventional ZIF-8. In addition, higher than the amount adsorbed by PAC which is a commercial adsorbent.

$$\%removal = \left(\frac{C_o - C_e}{C_o}\right) \times 100 \qquad \text{(Eq. 1)}$$

$$q = \frac{(C_o - C_e)}{M} \times V \qquad \text{(Eq. 2)}$$

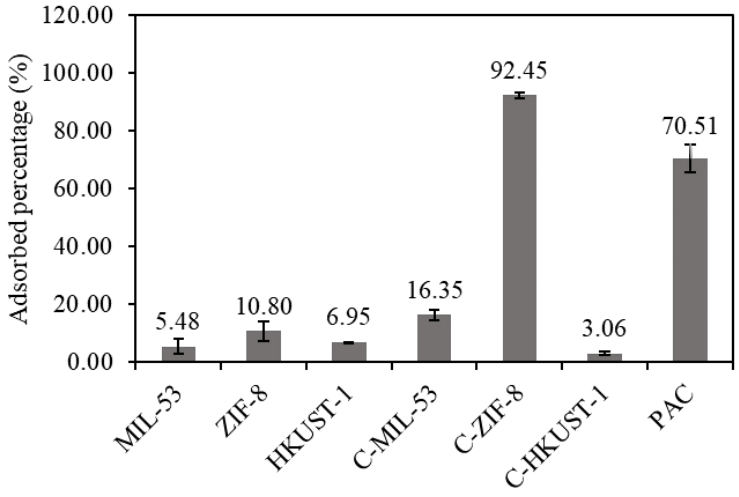

Figure 2 Adsorption percentages of MIL-53, ZIF-8, HKUST-1, C-MIL-53, C-ZIF-8, C-HKUST-1 and PAC

2. Adsorption kinetic

There are several adsorption kinetic models for defining the controlling mechanism of DCAN adsorption from aqueous solution. Pseudo-first order and Pseudo-second order models are widely used for the adsorption processes. The adsorption kinetics calculation was performed for C-MIL-53, C-ZIF-8 and PAC to compare the findings for different type of adsorbent. Table 1 is showed the kinetic parameters. The experimental data was analyzed by comparing the calculated q_t against time from the two kinetic models. All adsorbents fitted the pseudo-second order model well and shows a better fit for the experimental data when comparing r^2 (Table 1) to the pseudo-first order model. The calculated adsorption capacity from the model is also very close to the experimental value (Fig. 4). These results confirm the suitable of the pseudo-second order equation.

3. Adsorption isotherm

Adsorption isotherms of C-MIL-53, C-ZIF-8 and PAC were showed in figure 4. C-ZIF-8 exhibited the highest adsorption capacity comparing with PAC. Porosity of large particle and rigid framework like ZIF-8 are suggested to be more stable after carbonization upto 900 $^{\circ}$C comparing with MIL-53(Al) which has flexible pore structure and small particle. Hence, adsorption of DCAN on C-ZIF-8 was significantly higher than C-MIL-53(Al).

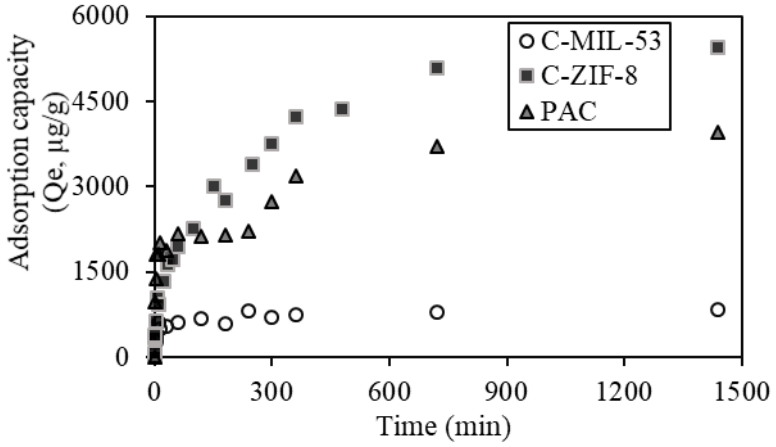

Figure 3 Adsorption capacity of C-MIL-53, C-ZIF-8 and PAC for DCAN at varies times

Table. 1 Adsorption kinetic parameters on C-ZIF-8, C-MIL-53 and PAC

Adsorbent	q_e(exp), µg g^{-1}	Pseudo-second order		
		q_m(cal), µg g^{-1}	K_2, (µg g^{-1}min^{-1})	R^2
C-ZIF-8	5083.48	5076.54	0.0002	0.9768
C-MIL53	781.81	780.65	0.0012	0.9965
PAC	3706.02	3701.39	0.0003	0.9748

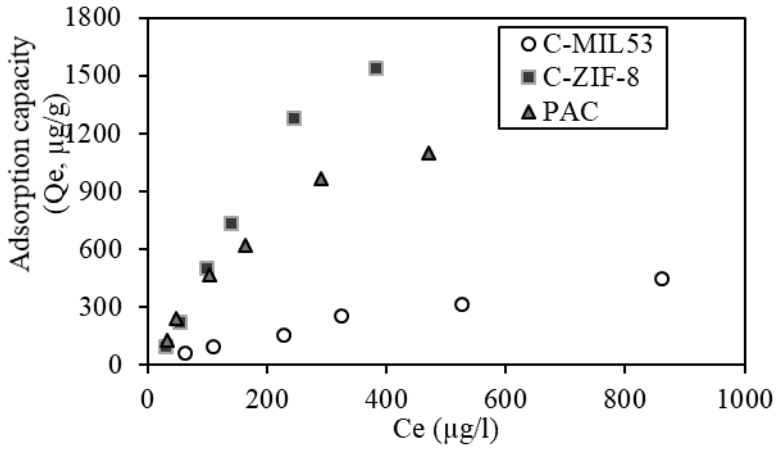

Figure 4 Adsorption capacity of C-MIL-53, C-ZIF-8 and PAC for DCAN at different concentration

Langmuir and Freundlich models are used to analyzed C-ZIF-8, C-MIL-53 and PAC data to compare the results with different type of adsorbent. Table 2 shows the calculated values of Langmuir and Freundlich model's parameters. According to the graphs and calculations the equilibrium data showed a better fit to the Langmuir equation with r^2, which are 0.9805, 0.9912 and 0.9600 respectively.

Table. 2 Adsorption isotherm parameters on C-ZIF-8, C-MIL-53 and PAC

Model	Parameter	Adsorbent		
		C-ZIF-8	C-MIL-53	PAC
Langmuir	R^2	0.9805	0.9912	0.9600
	Q_m, µg/g	1548.48	448.71	1109.96
	K_L, L/ µg	0.3208	0.9752	0.2452
Freundlich	R^2	0.9761	0.9890	0.9572
	n	0.8217	1.1026	0.8734
	K_F, L/ µg	1.113	0.7814	0.8059

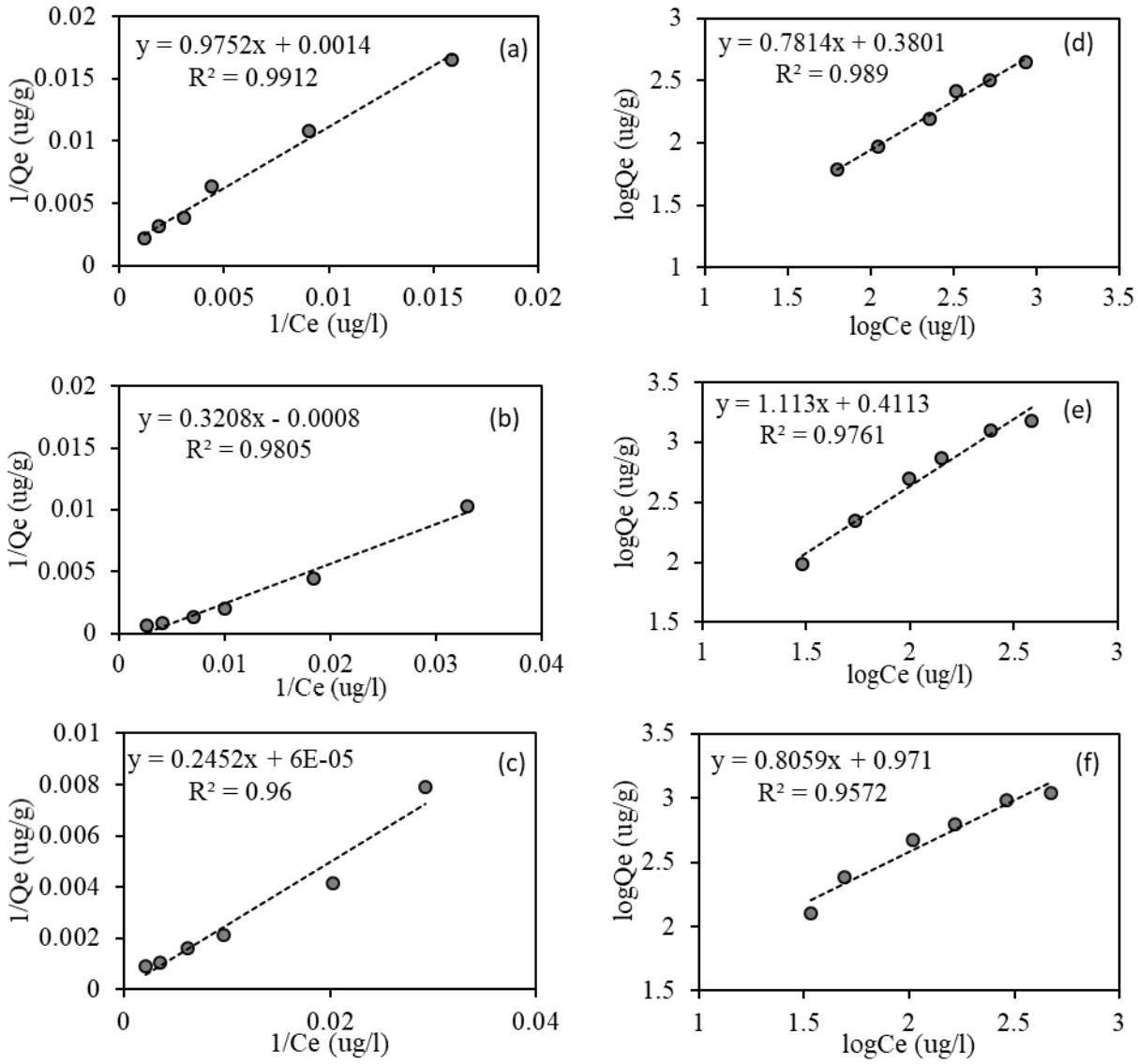

Figure 5 Adsorption isotherm of C-MIL-53, C-ZIF-8 and PAC for DCAN; (a), (b)and (c) for Langmuir isotherm model, (d), (e)and (f) for Freundlich isotherm model

CONCLUSION

In this study, the effect of carbonization on adsorption capacity of MOFs for HANs in aqueous solution was investigated. Carbonized MOFs were prepared by direct carbonization at 900 °C of MIL-53, ZIF-8, HKUST-1. Comparing carbonized MOFs with conventional MOFs, two of carbonized MOFs (C-MIL-53 and C-ZIF-8) expressed better adsorption capacity except for C-HKUST-1. The adsorption studies revealed that C-ZIF-8 had outstanding adsorption capacity of DCAN compared with other adsorbents, including PAC. The isotherm and kinetics studies showed that the adsorption process followed the Langmuir model and pseudo-second order kinetic model. This study illustrates that material modification by carbonization has significant

effect on adsorption properties of MOFs for the removal of organic pollutants from aqueous phase.

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