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Amino-functionalized Al-MIL-53 for dimethoate pesticide removal from wastewater and their intermolecular interactions

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ABSTRACT

Aluminum-organic framework was reformed with various amount of amino-group (Al-(BDC)_x(BDC-NH₂)_{1-x}, x = 0.00, 0.25, 0.50, 0.75 and 1.00). The technique used to modify the aluminum-based metal-organic framework was the mixed bonding method. All prepared metal-organic frameworks exhibited the same structure as that of Al-MIL-53. The surface areas of amino-functionalized aluminum-based metal-organic framework showed (S_{BET} = 866, 1105, 1260, 1100 and 1060 m²g⁻¹) for Al-BDC, [Al-(BDC) _{0.75}(BDC-NH₂)_{0.25}], [Al-(BDC) _{0.5}(BDC-NH₂)_{0.75}] and Al-BDC-NH₂, respectively. Amino groups have a great effect on organ-ophosphorus insecticide dimethoate adsorption capability. Pesticide adsorption capacities of Al-BDC, [Al-(BDC) _{0.75}(BDC-NH₂)_{0.25}], [Al-(BDC) _{0.5}(BDC-NH₂)_{0.25}], [Al-(BDC) _{0.5}(BDC-NH₂)_{0.25}], [Al-(BDC) _{0.5}(BDC-NH₂)_{0.75}] and Al-BDC, NH₂)_{0.5}], [Al-(BDC) _{0.25}(BDC-NH₂)_{0.75}] and Al-BDC-NH₂)_{0.5}], [Al-(BDC) _{0.5}(BDC-NH₂)_{0.75}] and Al-BDC-NH₂)_{0.5}], [Al-(BDC) _{0.5}(BDC-NH₂)_{0.75}] and Al-BDC-NH₂)_{0.5}], [Al-(BDC) _{0.5}(BDC-NH₂)_{0.75}] and Al-BDC-NH₂)_{0.5}], [Al-(BDC) _{0.5}(BDC-NH₂)_{0.75}] and Al-BDC-NH₂)_{0.5}] is the best absorbent Al-MOF ratio to reduce dimethoate residue in wastewater. Monte Carlo simulation was used for evaluation of the dimethoate adsorption mechanism.

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1. Introduction

Metal-organic frameworks (MOFs) have great importance in various applications due to their advantages such as large pore size and high surface area [1]. Unusual properties of MOFs play an important role in various applications like gas storage [2], light emission [3–5], catalysis [6–8], and water treatment [9–12]. The "breathing" or "opening the gate," is the operation of adsorption/desorption attitude. Recent efforts have concentrated on the breathing properties engineering for MOFs materials [13]. Aluminum(III)-based MOFs among the numerous MOFs, could be used as a promising adsorbents for water treatment because they are stable in water [14–16].

MIL-53(AI) contains $AIO_4(OH)_2$ octahedron and the carboxyl groups of terephthalic acid in which they are self-assembled to form a 3D framework structure with 1D diamond holes. The well-known MIL-53 was well investigated for gas adsorption due to its breathing properties. The researchers worked on two types of modifications for engineering breathing properties of MIL-53, the first is the action of cation substitution (AI, Fe, Ga, Cr) on the properties of breathing for MIL-53 [17] and the second is the effect of different linkers in the flexibility of MIL-53 [18,19].

Recently, MOFs play an effective role for the reduction of toxic chemicals such as pesticide from water, for example, graphene oxide/

https://doi.org/10.1016/j.molliq.2020.114852 0167-7322/© 2020 Elsevier B.V. All rights reserved. cyclodextrin composite was decorated by iron oxide then the novel composite was incorporated with copper-organic framework (Cu-BTC) through coordinating organic ligand with inorganic metal node and it was used for uptake of neonicotinoid pesticide. The novel composite shows high pesticide adsorption uptake for example imidacloprid (3.11 mg g^{-1}), thiamethoxam (2.88 mg g^{-1}), acetamiprid (2.96 mg g^{-1}) , nitenpyram (2.56 mg g^{-1}) , dinotefuran (1.77 mg g^{-1}) , and thiacloprid (2.88 mg g^{-1}) [20]. Graphene oxide was successfully decorated with zirconium-based producing UiO-67/GO nanocomposite. It has been applied as an adsorbent for the uptake of glyphosate from polluted water. Glyphosate was adsorbed very well on the surface and in the pore of the novel nanocomposite displaying high adsorption uptake at 482.69 mg g^{-1} [21]. Zeolitic imidazolate framework-8 (ZIF-8) and multi-walled carbon nanotube (MWCN) were mixed well via the incorporation process producing novel nanocomposite (ZIF8@MWCNT). Phosphate has high adsorption capacity from polluted water as a result of using ZIF8@MWCNT and its maximum adsorption value reached 203 mg g^{-1} . The mechanism of adsorption almost depend on hydrogen bonding and Zn-O-P interaction, the mechanism was confirmed by both of the theoretical and experimental characterizations [22]. UiO-66 was modified to produce quaternary amine anionic-exchange MOFs (UiO-66-NMe³⁺). The adsorption capacity of modified MOFs toward 2,4-D reached 279 mg g⁻¹. The electrostatic interactions between quaternary amine groups from UiO-66-NMe³⁺ and organic molecules from 2,4-D has mainly confirmed the mechanism of adsorption [23]. Very recently, ZIF-8 and ZIF-67 were

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used to remove ethion and prothiofos from contaminated water. ZIF-8 and ZIF-67 have higher adsorption uptake of prothiofos (366.7 and 261.1 mg g^{-1}) than the adsorption uptake of ethion (279.3 and 210.8 mg g^{-1}), respectively [24].

The famous organophosphorus insecticide dimethoate with the chemical name 0,0-dimethyl S-methylcarbamoylmethyl phosphorodithioate was large-scale used phosphorus insecticides for the killing of insects that made damage of plant [25–27]. The miss used of dimethoate lead to the accumulating the pesticide in water, food, and soil. The maximum residue limits of dimethoate in water reached to 0.02 mg·L⁻¹ as recorded by the European Union [28]. So, it is necessary to remove the overdose of dimethoate residues from water. Our article aimed at introducing various contents of the amine groups into the framework of Al-MOF by a mixed-linkers strategy and studied the dimethoate insecticide adsorption performance. The results have revealed that 50% of amine contents played a positive role in the dimethoate adsorption capacity of Al-MOF.

2. Materials and methods

2.1. Chemicals

AlCl₃, terephthalic acid (H₂BDC, >97%, Alfa-Aesar), 2aminoteraphthalic acid (H₂BDC–NH₂, greater than 97%), and *N*,*N*dimethyformamide (98%) were used as it is. Dimethoate pesticide was extracted from commercial sources using pet. Ether, acetonitrile and chloroform by separating funnel. Silica gel column was used for purifying dimethoate insecticide by using hexane: ethyl acetate (4:1) for elution. R_f value of dimethoate in the solvent system hexane: acetone (20:80) is 0.75. The maximum absorbance of dimethoate was recorded by UV spectrophotometer (JASCO) with wave length λ = 272.5 nm. The structure of dimethoate is shown in Fig. 1.

2.2. Synthesis of Al-MOFs modified with different molar ratio of amine groups

Al-BDC was synthesized according to the following procedure, 1.066 g (8 mmol) of AlCl₃, 1.328 g (8 mmol) of terephthalic acid were dissolved in 10 mL of DMF. The mixture was refluxed at 125 °C for 8 h. The product was filtered off, washed with DMF. The raw product was then dispersed in 400 mL mixture of methanol/water (50/50, v/v). The mixture was heated at 100 °C for 12 h, followed by filteratio, washing and drying. Al-BDC-NH₂ was synthesized by adding 1.066 g (8 mmol) of AlCl₃ to 1.448 g (8 mmol) 2-aminoterephthalic acid in presence of DMF and the mixture was heated at 125 °C for 8 h. the obtained solids were washed and dried as a previous procedure. The mixed linker samples were synthesized in the molar ratios of terephthalic acid (BDC) to 2-aminoterephthalic acid (BDC-NH₂) as 3: 1, 1: 1 and 1: 3 in the initial reaction solution, the resultants were labeled as [Al-(BDC) $_{0.75}$ (BDC-NH₂) $_{0.75}$], [Al-(BDC) $_{0.5}$ (BDC-NH₂) $_{0.5}$], [Al-(BDC) $_{0.25}$ (BDC-NH₂) $_{0.75}$], respectively (Fig. 2).

2.3. Characterization of composite

The phase purity and crystallinity of Al-BDC, $[Al-(BDC)_{0.25}(BDC-NH_2)_{0.75}]$, $[Al-(BDC)_{0.5}(BDC-NH_2)_{0.5}]$, $[Al-(BDC)_{0.75}(BDC-NH_2)_{0.25}]$



Fig. 1. Structure of dimethoate.

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Fig. 2. Synthesis of Al-MOFs with different amino contents.

and Al-BDC-NH₂ were characterized using X-ray diffraction (XRD) patterns (X'Pert MPD Philips diffractometer; the used monochromated was Cu K_{α}). The nanostructure morphology of modified amino functionalized Al-MOFs was tested by scanning electron microscope and transmission electron microscope (SEM: Hitachi SU-70, JP and TEM: Hitachi H-9000 (JP)). To confirm the formation of novel ratios of nanocomposites, the functional groups like amino, carbonyl, CH aliphatic, and aromatics were tested by infrared spectroscopy (FTIR, Matson 5000).

2.4. Batch adsorption experiments

The adsorption experiments were performed in 15 mL glass centrifuge tubes under varying experimental conditions which included initial concentration and reaction time. During the combined trials 0.04g modified Al-MOFs and 20 mg L⁻¹ dimethoate pesticide concentration was stirred at 303 K for up to 8 h. Through the experiment, the sample vials were removed periodically from the reaction vibration schedule at specific time intervals and centrifuged. The aqueous solution was extracted three times by 10 mL chloroform and dried over sodium sulphate anhydrous. Three replicated experiments were conducted. The absorbance of dimethoate was recorded with UV spectrophotometer (JASCO) at $\lambda = 272.5$ nm and the concentration of the mixed contaminants before and after the reaction were measured by the peak area.

The amount of dimethoate insecticide adsorbed onto Al-MOFs under different conditions was calculated according to Eq. (1).

$$Q_t = \frac{(C_o - C_t)V}{m} \tag{1}$$

where Q_t (mg·g⁻¹) is the adsorption concentration quantity of Al-MOFs, *t* is the time of dimethoate adsorption. C_0 is the initial concentration of dimethoate insecticide and C_t (mg·L⁻¹), is the residual concentration of dimethoate insecticide at time *t*. Both V and m are the liquid volume (L) and mass of Al-MOFs (g), respectively. The removal efficiency (R) of dimethoate insecticide is calculated in accordance with Eq. (2):

$$\%R = \frac{(C_o - C_t)}{C_o} \ 100 \tag{2}$$

2.5. Monte Carlo (MC) simulation

The MC simulation was performed using the BIOVIA Materials Studio 2017 package (Accelrys Software Inc.). The monoclinic I2/*m* crystal structure of NH₂-MIL-53(Al) was taken from Isaeva et al. [29]. Using this structure, the other MIL-53(Al) with different amino contents were constructed and shown in Fig. 3. The dimethoate molecule and MOFs were optimized by the Universal forcefield [30]; and the QEq charge method [31] was applied. The adsorption of dimethoate onto MOFs (001) and (100) surfaces was carried out using MC simulation, in which the Metropolis MC method finds the lowest-energy structures. The Universal force field/QEq was also used in the MC simulation. The MOF (001) and (100) surfaces were cleaved using $3 \times 2 \times 2$ and $4 \times 2 \times 2$ supercells of the optimized structures, respectively. A 20 Å-thick vacuum slab was created above the MOF surfaces.

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Fig. 3. The optimized structures of Al-BDC (a), $[Al-(BDC)_{0.75}(BDC-NH_2)_{0.25}]$ (b), $[Al-(BDC)_{0.5}(BDC-NH_2)_{0.5}]$ (c), $[Al-(BDC)_{0.25}(BDC-NH_2)_{0.75}]$ (d), $Al-BDC-NH_2$ (e), and dimethoate using Universal forcefield.

The Legnnard-Jones and Coulombic forces were used for creation electrostatic and the van der Waals interactions, respectively. The optimizations and MC simulation were performed by Forcite and Adsorption modules, respectively. The convergence tolerance qualities were, respectively, ultrafine and fine for the optimization and MC simulation. The summation method for the van der Waals interaction was atom based in both optiomization and MC simulation, while for the electrostatic interaction was atom-based in case of the optimization of dimethoate and Ewald in MOFs optimization and MC simulation. The Adsorption Locator module gives the adsorption energy (ΔE_{ads}).

3. Results and discussion

3.1. Characterization of the adsorbent

Fig. 4 shows the PXRD patterns of Al-BDC, $[Al-(BDC)_{0.75}]$ (BDC-NH₂)_{0.25}], $[Al-(BDC)_{0.5}(BDC-NH_2)_{0.5}]$, $[Al-(BDC)_{0.25}(BDC-NH_2)_{0.75}]$ and Al-BDC-NH₂. It is clear that all amine-modified Al-MOFs exhibited similar PXRD patterns to that of Al-MIL-53, which indicates that the amine-modified Al-MOFs have been synthesized successfully and they exhibit the same 20 at 8.5°,10.2°, 12.4°, 15.0°, 17.4°, and 26.2°, which are characterized by MIL-53-NH₂ [32].

The SEM images (Fig. 5a–e) suggest that highly crystalline Al-MOFs particles were formed. It can be found that some long strips with 5 μ m size of Al-BDC crystals were clearly visible, and most of them were an octahedral shape, which was uniformly dispersed and was not aggregation. From TEM analysis (Fig. 5a–e), the surface of Al-BDC-NH₂ seemed much rougher than that of Al-BDC and the length of Al-BDC-NH₂ particle was shortened to 100 nm. EDX analysis shows the presence of Al³⁺, carbon, oxygen, and nitrogen for the prepared materials.

The FT-IR spectra of Al-BDC, $[Al-(BDC)_{0.75}(BDC-NH_2)_{0.25}]$, $[Al-(BDC)_{0.5}(BDC-NH_2)_{0.5}]$, $[Al-(BDC)_{0.25}(BDC-NH_2)_{0.75}]$ and $Al-BDC-NH_2$ are appeared in Fig. 6. In the spectrum of Al-BDC, the bands at 1589 cm⁻¹ and



Fig. 4. PXRD patterns of Al-BDC, [Al-(BDC) $_{0.75}$ (BDC-NH $_{2}$) $_{0.25}$], [Al-(BDC) $_{0.5}$ (BDC-NH $_{2}$) $_{0.5}$], [Al-(BDC) $_{0.25}$ (BDC-NH $_{2}$) $_{0.75}$] and Al-BDC-NH $_{2}$.

1410 cm⁻¹ are related to the carboxylate (COO-) asymmetric and symmetric stretching vibrations of terephthalate (BDC). The absorption peak of about 3424 cm⁻¹ might be attributed to -OH stretching vibration. In the FT-IR spectrum of Al-BDC-NH₂, a series of peaks at the range of 1400–1700 cm⁻¹ were involved in carbonyl groups that coordinated with A1⁺³ and the carbonyl groups of DMF molecule which adhered to channels of the sorbent. Specifically, the absorption peaks at 1400 and 1440 cm⁻¹ should be the symmetry stretching vibration of carbonyl group; the peaks at 1500 and 1600 cm⁻¹ might be the dissymmetry

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Fig. 5. SEM, TEM and EDX of Al-BDC, [Al-(BDC) 0.25(BDC-NH₂)0.75], [Al-(BDC) 0.5(BDC-NH₂)0.5], Al-(BDC) 0.75(BDC-NH₂)0.25 and Al-BDC-NH₂.

stretching vibration of the carbonyl group, the peaks at 3380 and 3500 cm^{-1} were $-\text{NH}_2$ stretching vibration. Al—O shows peaks at $1000-1100 \text{ cm}^{-1}$, making sure that Al atom was coordinated to O atom in the framework [33].

The BET surface area of Al-BDC, [Al-(BDC) $_{0.25}$ (BDC-NH₂) $_{0.75}$], [Al-(BDC) $_{0.5}$ (BDC-NH₂) $_{0.5}$], Al-(BDC) $_{0.75}$ (BDC-NH₂) $_{0.25}$ and Al-BDC-NH₂ were examined by nitrogen adsorption-desorption test. The BET surface areas of Al-BDC, [Al-(BDC) $_{0.25}$ (BDC-NH₂) $_{0.75}$], [Al-(BDC) $_{0.75}$ (BDC-NH₂) $_{0.75}$], [Al-(BDC) $_{0.5}$ (BDC-NH₂) $_{0.25}$, and Al-BDC-NH₂ were 866, 1105, 1260, 1100 and 1060 m²g⁻¹, respectively.

3.2. Adsorption isotherms

Plotting the dimethoate concentration with the amount of dimethoate adsorbed onto Al-MOFs at a constant temperature $(30 \,^{\circ}\text{C})$ gives us adsorption isotherm. The importance of the adsorption isotherm comes from the best information on the adsorbent uptake and the reaction mechanism. The excessively used adsorption models are the Freundlich and Langmuir models. The Langmuir model proved that dimethoate is uptake as a monolayer and all adsorption centers are the same. The Langmuir model has been written as non-linear equation (Eq. (3)):

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Fig. 6. FTIR spectra of Al-BDC, [Al-(BDC) 0.25(BDC-NH₂)0.75], [Al-(BDC) 0.5(BDC-NH₂)0.5], Al-(BDC) 0.75(BDC-NH₂)0.25 and Al-BDC-NH₂.

$$Q_e = \frac{Q_m k_L C_e}{1 + k_L C_e} \tag{3}$$

where $C_{\rm e}$ represents the equilibrium concentration of dimethoate, $Q_{\rm e}$ is the equilibrium adsorption capacity, $Q_{\rm m}$ is the highest adsorption capacity of Al-MOFs and $K_{\rm L}$ is the Langmuir constant. The experimental $C_{\rm e}$ and $Q_{\rm e}$ are given in the Supporting Materials. In comparison, the Freundlich experimental model (Eq. (4)) does not make any assumptions about surface adsorption and adsorption is considered heterogeneous.

$$Q_e = k_F C_e^{\frac{1}{n}} \tag{4}$$

where Q_e is the equilibrium adsorption capacity, C_e is the dimethoate equilibrium concentration; K_F is Freundlich adsorption equilibrium constant, n is an empirical parameter. The 1/n has a value between 0 and 1 and it shows the effect of concentration on adsorption strength.

At 30 °C, R² (coefficient of determination) values for dimethoate was respectively 0.921 and 0.980 for the Langmuir and Freundlich equations using Al-MOFs and 0.968 and 0.997 in the case of Al-MOFs (Table 1). This meaning that Langmuir model is perfect fitting with data of Al-MOFs (Fig. 7). Table 1 showed that the adsorption of dimethoate pesticide by Al-MOFs was more consistent with the Langmuir adsorption model. These findings proof that the adsorption mechanism is monolayer adsorption of dimethoate insecticide onto the surface of Al-MOFs. To determine the best isothermal models, a Chi-square (χ 2) statistic was used to evaluate the data and it was calculated for both models [34–36]. The values of χ^2 show that the Langmuir isotherm model was the best model because the χ^2 values are very smaller than the values when using the Freundlich model. The values of χ^{2} , maximum adsorption capacities, and R^2 were presented in Table 1. The values of R^2 and χ^2 give the best explanation of dimethoate pesticide adsorption onto MOFs.

3.3. Kinetics analysis

The adsorption capacities of different amino ratio of modified Al-MOFs were tested over time to calculate the kinetic parameters. The data of effect of time was fitted in both a pseudo-first-order and a pseudo-second-order kinetic model (Table 2 and Fig. 8) by using the following equations:

The non-linear equation of the pseudo-first-order model is written as follow:

$$Q_t = Q_e \left(1 - \exp^{-k_1 t} \right) \tag{5}$$

The non-linear equation of the pseudo-second-order model is written as follow:

$$Q_t = \frac{k_2 Q_e^2 t}{1 + k_2 t Q_e} \tag{6}$$

where q_e and q_t of Al-MOFs are the adsorption capacity at equilibrium at time t, respectively; k_1 and k_2 are the rates constant of the pseudo-firstorder, pseudo-second-order kinetic model, respectively. The kinetics results for dimethoate show the best fit for the pseudo-second-order kinetic model with R² about 0.999 (Table 2). The best-fitting of kinetic models can be determined by using the Chi-square statistic (χ^2) [34]. It is concluded that when χ^2 has a small number, this meaning the data from the model are similar to the experimental data. Table 2 exhibited that, the Chi-square statistic values for a pseudo-second-order model are less than the values corresponding to the first-order model. This means that a pseudo-second kinematic model is more suitable for describing insecticide absorption in MOFs.

Several adsorbing materials were used to sorption of dimethoate from wastewater. Table 3 shows the maximum sorption capacities of dimethoate onto different adsorbent materials. Up to now, the

Table 1

Parameters of isotherm for adsorption of dimethoate onto Al-MOFs.

Samples	Freundlich parameters				Langmuir parameters				
	n	K _F	\mathbb{R}^2	χ^2	$Q_m(mg \cdot g^{-1})$	K _L	\mathbb{R}^2	χ^2	
Al-BDC Al-(BDC) _{0.75} (BDC-NH ₂) _{0.25} Al-(BDC) _{0.5} (BDC-NH ₂) _{0.50} Al-(BDC) _{0.25} (BDC-NH ₂) _{0.75} Al-BDC-NH ₂	$\begin{array}{l} 9.8 \pm 0.3 \\ 8.1 \pm 2.1 \\ 4.1 \pm 0.78 \\ 7.2 \pm 1.37 \\ 6.7 \pm 2.1 \end{array}$	$\begin{array}{l} 112.98 \pm 6.9 \\ 186.83 \pm 13.9 \\ 246.01 \pm 25.9 \\ 241.85 \pm 14.6 \\ 168.07 \pm 19.1 \end{array}$	0.933 0.956 0.943 0.965 0.934	888 382.9 899.4 594.4 603.5	$\begin{array}{c} 154.8 \pm 2.1 \\ 267.2 \pm 2.4 \\ 513.4 \pm 6.3 \\ 344.7 \pm 3.3 \\ 266.9 \pm 8.4 \end{array}$	$\begin{array}{l} 1.89 \pm 0.28 \\ 2.38 \pm 0.16 \\ 1.04 \pm 0.05 \\ 4.12 \pm 0.031 \\ 1.23 \pm 0.025 \end{array}$	0.995 0.998 0.998 0.997 0.982	13.6 18.1 61.5 39.2 62.7	

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Fig. 7. Effect of pesticide concentration on Al-MOFs adsorption process and Langmuir model fitting.

synthesized $[Al-(BDC)_{0.5}(BDC-NH_2)_{0.5}]$ was almost the perfect material to adsorb dimethoate from wastewater with high capacity (513.14 mg g⁻¹). It is clear that the removal capacity of the modified Al-MOFs exceeds the maximum residue limits of dimethoate in water as recorded by the European Union [28]. Therefore, they are potential adsorbents for dimethoate removal from water.

3.4. Adsorption mechanism

Our research proved that the 3D framework structure of MIL-53(AI) can automatically adjust the size and shape of the porous channel when it absorbed hydrocarbon molecules and some polar molecules. This adjustment was called the "breathing" effect of the framework. Generally, the framework structure was not destroyed in the process of transformation. This geometrical parameter provides a better diffusion of dimethoate into micro/mesopores of the metal–organic matrices. According to the discussion, the adsorption mechanism of dimethoate in Al-MOFs can be depending on two possible factors, the first is the hydrogen bonding between MOF-amino groups and dimethoate. The second important factor is the surface areas of the synthesized Al-MOFs.

Fig. 9 shows the lowest-energy structures obtained from the adsorption of dimethoate on the studied Al-MOFs surface (001), as obtained from the MC simulations. In all obtained configurations, a phosphate oxygen atom formed hydrogen bond (HB) with the hydroxyl hydrogen of the MOFs. Intramolecular hydrogen bond between amine hydrogen and S atom of the dimethoate molecule was also observed in all investigated systems (a–e). In the Al-BDC(001) surface–dimethoate interaction (a), the carbonyl oxygen and amine nitrogen atoms of the dimethoate formed HBs with the hydrogens of water molecules coordinated to the surface Al cations. In the Al-(BDC)_{0.75}(BDC-NH₂)_{0.25}(001) surface–dimethoate interaction (b), the carbonyl oxygen atom formed HB with

Table 2

Parameters of adsorption of dimethoate onto Al-MOFs.



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Fig. 8. Effect of time on the adsorption of pesticide on to ratio of Al-MOFs and pseudosecond-order kinetic model fitting.

 Table 3

 Maximum adsorption capacities of dimethoate onto several adsorbents used in literature.

Adsorbent	Maximum adsorption capacity $(Q_m, mg g^{-1})$	References
[Al-(BDC) 0.5(BDC-NH2)0.5]	513.4	Present work
Gold nanospheres	456	[37]
Gold nanorods	57.1	[37]
Greek agricultural soils	11.87-25.51	[38]
KOH modified <i>Thevetia peruviana</i> shell	10.056	[39]
graphene oxide powder	89.4	[40]
single layer graphene	100.76	[40]
X-MC-EISA-800-Y	100	[41]
B-MC-EISA-800-1	164	[41]
Komchén soil	0.04	[42]
Xcanatún soil	0.0349	[42]
Chablekal soil	0.0339	[42]
Mocochá soil	0.0360	[42]

the hydrogens of water molecules bound to the surface Al cations. The amine nitrogen atom of dimethoate formed HB with the amine hydrogen atom of the MOF. In the Al- $(BDC)_{0.5}(BDC-NH_2)_{0.50}(001)$ surface-dimethoate interaction (c), a phosphate oxygen atom formed HB with amine hydrogen of the MOFs. The carbonyl oxygen and amine nitrogen atom of the dimethoate formed HBs with water hydrogen atoms of the MOF-surface. In the Al- $(BDC)_{0.25}(BDC-NH_2)_{0.75}(001)$ surface-dimethoate interaction (d), a phosphate oxygen atom formed HB with an amine hydrogen of the MOFs and the carbonyl oxygen formed also HB with another MOF-amine hydrogen. The sulfur atom with one double bond (=S) of the dimethoate formed HB with the MOF-hydroxyl hydrogen atom. The carbonyl oxygen and nitrogen atoms formed HBs

Samples	Qe exp	pseudo-first-order parameters			pseudo-second-order parameters				
		Qe	K ₁	R ²	χ^2	Qe	$\text{K}_2\times 10^{-4}$	R ²	χ^2
Al-BDC	230 ± 5.8	239.4 ± 6.8	0.629 ± 0.051	0.993	48.6	309.3 ± 20.9	19.1 ± 4.2	0.985	11.2
Al-(BDC) _{0.75} (BDC-NH ₂) _{0.25}	335 ± 6.7	326 ± 6.1	1.177 ± 0.083	0.993	93.2	380.1 ± 5.1	37.6 ± 2.4	0.998	21.3
Al-(BDC) _{0.5} (BDC-NH ₂) _{0.50}	425 ± 4.3	370.8 ± 32.1	193.2 ± 5.04	0.749	620.2	475.1 ± 14.5	44.6 ± 7.8	0.990	246.8
Al-(BDC) _{0.25} (BDC-NH ₂) _{0.75}	405 ± 3.4	336.6 ± 35.9	84.9 ± 10.271	0.657	774.6	465.8 ± 15.8	31.9 ± 5.3	0.991	214.8
Al-BDC-NH ₂	293 ± 2.3	290.1 ± 4.1	0.926 ± 0.045	0.996	32	349.5 ± 7.2	29.4 ± 2.6	0.997	30.3

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Fig. 9. The lowest-energy structures of the adsorption of dimethoate onto the MOFs (001) surface (side view): (a) Al-BDC, (b) Al-(BDC)_{0.75}(BDC-NH₂)_{0.25}, (c) Al-(BDC)_{0.5}(BDC-NH₂)_{0.25}, (d) Al-(BDC)_{0.25}(BDC-NH₂)_{0.25}, and (e) Al-BDC-NH₂, as obtained from the MC simulation.

with the MOF-water hydrogen atoms. In the case of the Al-BDC-NH₂ (001) surface–dimethoate interaction (e), the (S=) atom formed HB with the MOF-hydroxyl hydrogen atom. Hydrogen bond was formed between phosphate oxygen and MOF-amine hydrogen. Mutual hydrogen bonds were observed between a dimethoate amine group and a MOF-amine group.

The lowest-energy configurations of the adsorption of dimethoate on the studied Al-MOFs surface (100) obtained from the MC simulations are shown in Fig. 10. In all interactions (a–e), intramolecular HB between amine hydrogen and S atom of the dimethoate molecule was formed. The dimethoate-carbonyl oxygen and S atoms formed HB with the MOF-hydroxyl hydrogen in the Al-BDC (100) surfacedimethoate interaction (a). In the Al-(BDC)_{0.75}(BDC-NH₂)_{0.25}(100) surface-dimethoate system (b), the phosphate oxygen and (S=) atoms of the dimethoate formed HB hydroxyl hydrogen formed HB with the MOF-hydroxyl hydrogen atoms. Mutual HBs were also formed between the dimethoate amine group and MOF-amine group. In the Al-(BDC)_{0.5}(BDC-NH₂)_{0.5}(100) surface-dimethoate system (c), the (-S), (=S), and the carbonyl oxygen of the dimethoate formed HBs with the MOF-hydroxyl hydrogen. Besides the mutual HBs between the amine groups of both dimethoate and MOF, an HB between phosphate oxygen atom and MOF-amine hydrogen was also observed. In the Al-(BDC)_{0.25}(BDC-NH₂)_{0.75}(100) surface-dimethoate system (c), the (-S) atom and phosphate oxygen atom formed HBs with the MOFhydroxyl hydrogen. The second phosphate oxygen formed HB with the MOF-amine hydrogen, and a mutual HBs were also formed between the dimethoate-amine and MOF-amine groups. As for the Al-BDC-NH₂ (100) surface-dimethoate system (e), a mutual HBs between the amine groups of the dimethoate and MOF were formed and a phosphate oxygen and (=S) atoms formed HBs with MOF-amine hydrogen atoms. Moreover, a phosphate oxygen atom and the (=S) atom formed HBs with the MOF-hydroxyl hydrogen atoms.



Fig. 10. The lowest-energy structures of the adsorption of dimethoate onto the MOFs (100) surface (top view): (a) Al-BDC, (b) Al-(BDC)_{0.75}(BDC-NH₂)_{0.25}, (c) Al-(BDC)_{0.5}(BDC-NH₂)_{0.25}, (d) Al-(BDC)_{0.25}(BDC-NH₂)_{0.25}, and (e) Al-BDC-NH₂, as obtained from the MC simulation.

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Table 4

The adsorption energies (ΔE_{ads} , kcal·mol⁻¹) of dimethoate onto Al-MOFs.

Surface	$\Delta E_{\rm ads}$, kcal·mol ⁻¹							
	Al-BDC	Al-(BDC) _{0.75} (BDC-NH ₂) _{0.25}	Al-(BDC) _{0.5} (BDC-NH ₂) _{0.50}	Al-(BDC) _{0.25} (BDC-NH ₂) _{0.75}	Al-BDC-NH ₂			
(001) (100)	-29.5 -44.3	-30.1 -44.4	-30.6 -45.0	-31.1 -45.3	-31.4 -46.1			

Table 4 includes the adsorption energies (ΔE_{ads}) values of dimethoate on the investigated Al-MOFs (001)/(100) surfaces. It is observed that the ΔE_{ads} values onto MOFs (001) surfaces are greater than those of MOFs (100) surfaces. The adsorption energies were increased with increasing the BDC-NH₂ contents due to the HBs formation between MOF-amine groups with the dimethoate molecules. Nevertheless, this behavior does not agree with the experimental dimethoate adsorption capacities of the amino-functionalized MIL-53(Al). As mentioned earlier, the surface area of the studied NH₂-MIL-53(Al) materials represents another important factor in the adsorption process. The surface areas (S_{BET}) of the Al-BDC, [Al-(BDC) _{0.75}(BDC-NH₂)_{0.25}], [Al-(BDC) _{0.5}(BDC-NH₂)_{0.5}], [Al-(BDC) _{0.25}(BDC-NH₂)_{0.75}] and Al-BDC-NH₂, are (866, 1105, 1260, 1100 and 1060) m²g⁻¹, respectively; therefore, the order of adsorption capacities matches that of the surface area.

4. Conclusions

In this study, different amine ratio MOFs (Al-BDC, [Al-(BDC) 0.75(BDC-NH2)0.25], [Al-(BDC) 0.5(BDC-NH2)0.5], [Al-(BDC) 0.25(BDC-NH₂)_{0.75}] and Al-BDC-NH₂) were successfully synthesized and tested as adsorbents to eliminate organophosphorus insecticide dimethoate from wastewater. The adsorption mechanisms were examined through Monte Carlo simulation and experimental data. The present mechanism can be linked as the combination of electrostatic interactions and hydrogen bond formation. The amino group on Al-BDC MOFs has significantly enhanced the adsorption capability of dimethoate. Furthermore, the pseudo first-order kinetic model was more appropriate with the experimental data and the isothermal Langmuir model was a better method for describing the equilibrium adsorption behavior. Therefore, the adsorption process of dimethoate onto Al-BDC MOFs mostly attributed to chemisorptions and monomolecular-layer adsorption. The maximum adsorption capacity of $[Al-(BDC)_{0.5}(BDC-NH_2)_{0.5}]$ was 513.4 mg g⁻¹, which was much greater than that of free amino Al-BDC (154.8 mg g^{-1}) and full amino Al-BDC-NH₂ (266.9 mg g^{-1}).

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi. org/10.1016/j.molliq.2020.114852.

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