

Efficient Adsorptive of Carbofuran Via Tailored Porous Polyacrylonitrile Film Incorporated Ti-MIL Coordination Polymer

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Abstract

Carbofuran is largely applied insecticide which resulted in its wide spreading in ground/surface water and food products and consequently investigation of efficient techniques for removal of carbofuran is extensively considered. Herein, facile approach for removal of carbofuran was developed via exploitation of highly adsorptive porous film based on polyacrylonitrile (PAN) and NH₂-MIL-Ti as a coordination polymer. NH₂-MIL-Ti@P-PAN film was prepared by immobilization of NH₂-MIL-Ti within the pre-prepared porous (P-PAN) film. The pore diameter of PAN film was estimated to be 8.5 – 51.2 µm. The removal of carbofuran from the porous film was systematically studied and fitted to both pseudo 2nd ordered and Langmuir models. Results showed that Langmuir maximum removal of carbofuran was largely enhanced from 292.2 mg/g for P-PAN to 489.5 – 690.1 mg/g for NH₂-MIL-Ti@P-PAN. Thus, by increasing the amount of immobilized NH₂-MIL-Ti@P-PAN in the film, the adsorption capacity of carbofuran was markedly improved, reaching a 2.4 times higher when 30% NH₂-MIL-Ti is immobilized. Importantly, after six reusing times, the removal of carbofuran by 30% NH₂-MIL-Ti@P-PAN film was decreased by only 12.5%. The overall results attest that the fabricated NH₂-MIL-Ti@P-PAN film could be efficiently used for trace removal of various insecticides and other environmental applications.

Introduction

Nowadays, carbamates are the most widely applicable type of insecticides attributing to that, among the alternative insecticides, organochlorines are disadvantageous with long-lasting residues persisting, and organophosphates (OPs) are known to be highly toxic leading to delay the neurotoxicity problems. Carbofuran (Furadan) as one of carbamates is large scaled-exploitable in forestry and agriculture as a wide-spectrum systemic acaricide, nematicide, and insecticide. Therefore, its application resulted in its wide spreading in atmospheric air, food products, groundwater and surface water are polluted with carbofuran and its metabolic products [1–4], which might affect the health of life-being. Carbofuran is a white, crystalline solid compound with a melting point of 150-152°C, water solubility of 700 ppm at 25°C, vapor pressure 2 x 10~5 m Hg at 33°C, and specific gravity 1.18 at 20°C/20°C. Carbofuran is chemically identified as 2,2-dimethyl-7-coumaranyl-N-methylcarbamate, or 2,2-dimethyl-2,3-dihydro- 7-benzofuranyl-N-methylcarbamate, or methyl carbamic acid 2,3-dihydro 2,2-dimethyl-7-benzofuranyl ester, or 2,3-dihydro-2,2-dimethyl-7-benzofuranol methylcarbamate. Additionally, carbofuran chemical formula is known as C₁₂H₁₅NO₃, while, its molecular weight is 221.26. Carbofuran exhibited high toxic effects to human beings via the oral administration and inhalation route, that subsequently resulted in pose a dangerous threatening to people who are immediately in contact with it (in industrialization, plants formulation and in cropping).

Adsorptive removal of various types of insecticides from the surrounding environmental media is the most applicable technique[5]

. Referring to numerous approaches that were considered with investigating of different adsorbing reagents like, monetite, quartz, calcite, kaolinite, gold nanoparticles [6]

, alumina, wheat straw, mesoporous carbon, graphene-based materials

[7]and activated carbon that were exploited as adsorptive removing reagent for insecticides [8–18]

. The poor application of such reported adsorbing reagents could be attributed to their solidified form and high costing (such as gold nanoparticles). Many other adsorbing reagents including nanocellulose [19], poly-vinyl-amine/nanocellulose composite [20] and hydrocalumite-iron oxide/dodecyl sulfate composite [21] are used for removing of different types of insecticides.

On the other hand, for removal of carbofuran, several adsorbents were reported in literature such as indian soils, sugarcane bagasse bio-char, animal bone meal, tea waste bio-chars, magnetic peanut shell, activated carbon, date seed activated carbon, modified maize cobs waste, steam-activated biochar, palm oil fronds activated carbon, magnetic sugarcane bagasse, mesoporous activated carbon, steel industry wastes, activated carbon from rice straw and rice straw-derived activated carbon [22–28]. All of these applicable adsorbents were exhibited quite low adsorption capacity ranged in (0.9 – 312.5 mg/g), in addition to, their existence in powder form, resulted in difficulty for their commercial application. Whereas, the adsorption capacity was very low, resulting in making the investigation of highly adsorbent/costless materials is extensively considered.

Recently, different coordination polymeric structures (CPs) were widely applicable in adsorptive removing of insecticides, such like Al-CP, Zr-CP, Zn-CP and Cu-CP [29–34]. Liu et al., investigated that, cyclodextrin/garphene oxide/FeO/Cu-CP composite can be applied in adsorptive removing of neonicotinoid with adsorption capacity of 1.8 – 3.1 mg/g [29]. More superior adsorptive action for carbon nano-tubes@Zn-CP composite, Zn-CP and quaternary amine treated Zn-CP as identified for removing of prothiofos, ethione & phosphate, respectively [30–32]. In accordance to our knowledge, no research approaches were interested in adsorptive removal of cabrofuran using coordination polymers including film [35]

Using of reusable films for insecticides removal was advantageous with higher recoverability. Hence, the importance of the present approach is designing of a highly applicable Ti-CP@porous polyacrylonitrile ($\text{NH}_2\text{-MIL-Ti@P-PAN}$) film for efficient removal of carbofuran insecticide. The prepared film was examined by scanning electron microscope, X-ray diffraction and infra-red spectroscopy. The removal of carbofuran onto the synthesized film was investigated. The adsorption kinetic, isotherm and recyclability of carbofuran were all examined.

Experimental

Chemicals and materials

Titanium iso-propoxide ($\text{TiC}_{12}\text{H}_{28}\text{O}_5$, 99%), 2-aminoterephthalic acid ($\text{C}_8\text{H}_7\text{NO}_4$, 99%), N, N-dimethylformamide (DMF, $\text{C}_3\text{H}_7\text{NO}$, 99.9%), ethanol ($\text{C}_2\text{H}_6\text{O}$, 99.9 %), methanol (CH_4O , 99.9%), benzoic acid ($\text{C}_7\text{H}_6\text{O}_2$, 99.5%) and Carbofuran ($\text{C}_{12}\text{H}_{15}\text{NO}_3$, analytical standard) were all purchased from Sigma-Aldrich and used without purification. Acrylic fabric wastes as source for polyacrylonitrile were purchased from Misr El-Mahalla for Spinning and Weaving, Egypt.

Process

Polyacrylonitrile film (PAN) was synthesized from acrylic fabric wastes as follows: 10 g of acrylic fabric wastes was dissolved in 100 mL DMF at 60°C for 2 hours. The colloid was added and casted on glass slide via a membrane applicator. The film was formed by impregnation in distilled H_2O as coagulating bath of for 1 hour at room temperature. The obtained PAN film was taken out and dried at ambient conditions prior to be used.

Porous polyacrylonitrile (P-PAN) film was obtained in two step processes. Acrylic fabric wastes (10 g) were solubilized in dimethyl formamide (100 mL) at 60°C for 2 hours, then 0.5 g of benzoic acid was added. The colloid was stirred for 2 h at 60°C to be casted by membrane applicator. The film was completely formed by doping in the coagulation water bath. The immobilized benzoic acid was eliminated from the obtained film by formation of water soluble sodium benzoate form through doping in 100 mL of 5 N sodium hydroxide for 1 hour. The P-PAN film was taken out, washed with distilled H_2O and then dried at ambient conditions.

Titanium-based coordination polymer ($\text{NH}_2\text{-MIL-Ti}$) was individually synthesized and then immobilized within the synthesized P-PAN film with two different weights (10% & 30%). $\text{NH}_2\text{-MIL-Ti}$ was prepared according to the previously reported method in literature [36]. The freshly synthesized $\text{NH}_2\text{-MIL-Ti}$ was firstly dispersed in 50 mL ethanol and then P-PAN film was immersed under stirring for half hour. The resulted $\text{NH}_2\text{-MIL-Ti}@P\text{-PAN}$ film was removed for rinsing with distilled H_2O and consequent drying prior to analysis and application.

Instrumental analyses and characterization

The immobilized Ti & $\text{NH}_2\text{-MIL-Ti}$ CP in the film were detected from weight difference before and after the elimination of $\text{NH}_2\text{-MIL-Ti}$. CP was removed from film by dissolving in ammonia in accordance to the previously reported methodology [37]. Taking in account the chemical construction of $\text{NH}_2\text{-MIL-Ti}$, Ti contents were calculated by normalization to the $\text{NH}_2\text{-MIL-Ti}$ contents.

The morphological features of P-PAN and $\text{NH}_2\text{-MIL-Ti}@P\text{-PAN}$ films were shown by HR Quanta FEG 250 scanning electron microscopy with field emission gun. Analyses were performed using energy dispersive X-ray detector attached to microscope. Diffractograms were detected using Malvern PANalytical X'PertPRO diffractometer ($\lambda = 1.5406 \text{ \AA}$). Diffraction angles were estimated at $3.5^\circ - 80^\circ$. Spectral results

of Fourier Transformation Infrared (FTIR) for the prepared films were measured via FT/IR 6100 JASCO spectrometer. The results was detected with absorption mode in the spectral range of 4000 – 400 cm⁻¹.

Removal of Carbofuran

The synthesized films (PAN, P-PAN, 10% NH₂-MIL-Ti@P-PAN and 30% NH₂-MIL-Ti@P-PAN) were employed in removal of carbofuran insecticide. The adsorption isotherms were estimated at 30°C and the kinetics parameters were followed up to 150 minutes. Carbofuran adsorption was carried out by adding 75 mg of film within 100 mL of carbofuran (50 – 2000 ppm). After removal, carbofuran residues was estimated via JASCO UV 630spectrophotometer. Each adsorption experiment was determined for 2 times and average value was only considered. The recyclability of the films in carbofuran adsorption was considered via re-using of the prepared films. After the first application, the used films was removed and the adsorbed carbofuran particles were leached out from film surface by dissolution in acetonitrile. Films were then dried at ambient conditions to be re-applied in the subsequent cycle. The recovered films were used in the higher cycle of carbofuran adsorption and the re-application was carried out for 4 repetitive cycles.

Results And Discussion

Characterization of the synthesized films

Porous P-PAN film was firstly synthesized to perform as the porous structure with highly efficient adsorption sites. The immobilized benzoic acid was removed by sodium hydroxide forming porous structure PAN film. The film of NH₂-MIL-Ti@P-PAN was obtained with 10% and 30% CP contents. The mechanism of NH₂-MIL-Ti@P-PAN synthesis could be hypothesized as suggested in Figure 1. The nitrile groups of PAN molecules can by chemically interacted with the Ti-CP through several interactions. The nitrogen atom of nitrile groups in PAN may form coordination and hydrogen bonds with the titanium atom and hydrogen of amino groups in the Ti-CP, respectively [38]. Moreover, π - π interactions can take a place between the groups of nitrile in PAN and aromatic nucleus of 2-aminoterephthalic acid in Ti-CP.

The content of Ti-CP within the P-PAN films were estimated and recorded in Table 1. The evaluated contents of Ti-CP were 106.5 mg/g for 10% NH₂-MIL-Ti@P-PAN film and 288.2 mg/g for 30% NH₂-MIL-Ti@P-PAN film. The real contents (10.65 % and 28.85%) of Ti-CP are quite close to that theoretically added. The amounts of Ti metal in the films were evaluated by using the chemical structure of NH₂-MIL-Ti. Ti₈C₄₈H₃₄O₃₆N₆ is the chemical formula for NH₂-MIL-Ti and consequently, the percentage of Ti in the Ti-CP is 23.2%. Based on such calculations, the Ti contents were calculated to be 24.7 and 66.9 mg/g in case of 10% NH₂-MIL-Ti@P-PAN and 30% NH₂-MIL-Ti@P-PAN films, respectively.

Table 1
Material contents for the obtained films.

Film	Ti-CP (mg/g)	Ti (mg/g)
P-PAN	0.0	0.0
10% NH ₂ -MIL-Ti@P-PAN	106.5	24.7
30% NH ₂ -MIL-Ti@P-PAN	288.2	66.9

The synthesized films (P-PAN, 10% NH₂-MIL-Ti@P-PAN and 30% NH₂-MIL-Ti@P-PAN) were examined under the electronic microscope. Figure 2 showed that highly porous structure was observed for PAN after removing of organic acid. The surface of P-PAN film is beehive like shaped. The diameter of the seen pores was measured and was ranged in 8.5 – 51.2 µm which confirmed the macro porous structure of the produced film. The pore diameter can be divided to two regions of 8.5 – 22.6 µm and 31.8 – 51.2 µm. For NH₂-MIL-Ti@P-PAN film, crystalline Ti-CP were densely distributed over the surface of the P-PAN film and filled the small pores. Crystalline disc structure of NH₂-MIL-Ti was seen onto the P-PAN film surface with size dimensions of 84.0 – 98.0 x 167.9 – 654.1 nm. The amount of NH₂-MIL-Ti onto the surface of P-PAN film was increased by increment of the impregnated ratio from 10–30%. The EDX analysis showed the signals of C and N for P-PAN film. While, the signals of O and Ti were both recorded besides those of C & N in case of NH₂-MIL-Ti@P-PAN film which further confirmed the incorporation of Ti-CP within the film.

The XRD for the as-synthesized films were shown in Figure 3 for more confirmation to the successive preparation of the as-required films. For P-PAN film, two diffractions at $2\theta = 17.2^\circ$ (strong) and 29.3° (weak) characterized for (100) and (110) crystalline indices of PAN [39, 40]. NH₂-MIL-Ti powder showed many characterized diffractions at $2\theta = 6.6^\circ$, 9.8° and 11.7° , 15.3° , 16.7° , 18.0° , 19.6° , 21.6° , 22.7° and 25.4° which were strongly matched with the diffractions in literature [41, 42]. For NH₂-MIL-Ti@P-PAN films, the diffraction patterns of NH₂-MIL-Ti were observably obtained beside those of PAN which further confirming the successive immobilized of NH₂-MIL-Ti in the P-PAN film. The intensity of NH₂-MIL-Ti diffraction was higher in case of impregnation higher Ti-CP contents.

The chemical interaction between P-PAN and NH₂-MIL-Ti in the as-synthesized films was illustrated via FTIR spectra (Figure 4a). From the plotted spectra, it could be depicted that, P-PAN film was shown with three main absorption peaks at $2918\text{-}2844\text{ cm}^{-1}$, $2240/1728/1659\text{ cm}^{-1}$ and $1443\text{-}1226\text{ cm}^{-1}$. The detected peaks are attributed to the aliphatic C-H, the nitrile group and CH₂ & CH₃ groups which referring to the chemical structural of PAN [43, 44]. For NH₂-MIL-Ti powder, four prime peaks were recorded for NH group at 3427 cm^{-1} , OH groups at 3318 cm^{-1} , carboxylate group of 2-aminoterephthalic acid at $1659/1537\text{ cm}^{-1}$ and Ti-O bond at 752 cm^{-1} [45, 46]. In case of NH₂-MIL-Ti@P-PAN film, the

characterized absorption peaks of NH₂-MIL-Ti were significantly observed beside that of PAN. The intensities of the absorption peaks for NH₂-MIL-Ti became stronger at impregnation higher Ti-CP content in the film. These spectral mapping data are further support the data of XRD diffraction and microscopic observations.

Removal of carbofuran

The so-prepared films (PAN, P-PAN, 10% NH₂-MIL-Ti@P-PAN, 30% NH₂-MIL-Ti@P-PAN) were employed in the adsorptive removing of carbofuran insecticide. Firstly, FTIR spectral mapping data (Figure 4b) were illustrated for approval of the adsorption processing using the prepared films. After adsorption of carbofuran onto the NH₂-MIL-Ti@P-PAN film, three new base absorption peaks were observed at 3356 cm⁻¹, 2972 cm⁻¹, 1519 cm⁻¹ and 868 cm⁻¹. These peaks are characterized for NH, CH aliphatic, C=C of aromatic and CH aromatic for the carbofuran molecule [26, 28]. Moreover, the amide-C=O was overlapped with that for CN of PAN. These interoperations affirmed the adsorption of carbofuran onto the as-applied NH₂-MIL-Ti@P-PAN film.

The adsorptive removal of carbofuran was systematically monitored via the investigation of the characteristic absorption peak at 290 nm. Adsorption capacities of the carbofuran were detected with time and plotted in Figure 5. The plotted data showed that, adsorption of carbofuran using the synthesized films was enhanced by prolonging the duration and the adsorption was fast in the first adsorption hour, to be subsequently slowed down with prolonged duration. The adsorption capacities of carbofuran onto the applied films were followed the order of PAN < P-PAN < 10% NH₂-MIL-Ti@P-PAN << 30% NH₂-MIL-Ti@P-PAN. Whereas, within only 2.5 hours, almost all carbofuran were removed by using 30% NH₂-MIL-Ti@P-PAN film. In the first hour, the removal amounts of carbofuran were 86.6, 126.6, 180.0 and 300.0 mg/g when PAN, P-PAN, 10% NH₂-MIL-Ti@P-PAN and 30% NH₂-MIL-Ti@P-PAN films were applied, respectively. The removal amounts of carbofuran onto the corresponding film were increased up to 110.0, 153.3, 220.0 and 360.0 mg/g, respectively after 2.5 hours of contact time. The lowest removal capacity was recorded for PAN due to the limited interaction with carbofuran and absence of porous structure. While, the removal was slightly improved by formation of porous film of P-PAN. The adsorption of carbofuran onto the exploitable P-PAN film was progressively increased by immobilization of NH₂-MIL-Ti. Removal was observably enhanced by increment the impregnated NH₂-MIL-Ti, owing to increasing of the reactive adsorptive sites.

Eventually, the kinetic parameters for adsorption removal of carbofuran onto the synthesized films were carried out for nonlinear model of pseudo-1st ordered and pseudo-2nd ordered (Figure 5). For examination the fitting of adsorption data, the value of correlation coefficient (R^2) and Chi-squared test (χ^2) were measured and all parameters were tabulated in Table 2. Attributing to higher values of R^2 and smaller values of χ^2 , the adsorption of carbofuran onto the films was well described by pseudo-2nd ordered modelling which means that the removal of carbofuran depended on the concentration of carbofuran and amount of applied film. Additionally, attributing to the observable increasing of

adsorption sites, the rate constant (k_2) was considerably reduced from 2.9×10^{-4} L/mg.min for P-PAN film to 1.3×10^{-4} L/mg.min for 30% NH₂-MIL-Ti@P-PAN film. This observation could mean that the rate of carbofuran removal using the synthesized films was accelerated by 55% when 30% of NH₂-MIL-Ti immobilized within the P-PAN film.

Table 2
Adsorption parameters of adsorption kinetics and isotherm for carbofuran onto the synthesized films.

Model	Parameter	PAN	P-PAN	10% NH ₂ -MIL-Ti@P-PAN	30% NH ₂ -MIL-Ti@P-PAN
	Q _e exp. (mg/g)	110.0	153.3	220.0	360.0
Pseudo-first order	Q _e (mg/g)	105.3 ± 1.9	148.8 ± 1.8	211.4 ± 3.1	347.4 ± 6.9
	K ₁ × 10 ⁻³ (min ⁻¹)	32.4 ± 2.3	35.6 ± 1.7	36.1 ± 2.2	40.9 ± 3.6
	R ²	0.98	0.99	0.99	0.98
	χ ²	12.6	11.6	37.4	213.7
Pseudo-second order	Q _e (mg/g)	127.1 ± 1.4	177.3 ± 1.1	250.8 ± 1.6	403.4 ± 4.9
	K ₂ × 10 ⁻⁴ (L/mg.min)	2.9 ± 0.2	2.4 ± 0.1	1.7 ± 0.1	1.3 ± 0.1
	R ²	0.99	0.99	0.99	0.99
	χ ²	1.5	1.1	2.6	29.2
Freundlich isotherm	n	2.9 ± 0.5	2.5 ± 0.2	2.2 ± 0.1	2.7 ± 0.3
	K _F	12.5 ± 2.2	12.8 ± 2.9	15.5 ± 2.8	45.2 ± 5.4
	R ²	0.92	0.97	0.98	0.96
	χ ²	223.5	225.1	326.2	2005.9
Langmuir isotherm	Q _{max} (mg g ⁻¹)	160.8 ± 4.2	292.2 ± 5.8	489.5 ± 13.3	690.1 ± 13.1
	K _L × 10 ⁻³ (mg/L)	4.7 ± 0.4	3.0 ± 0.2	2.6 ± 0.2	5.1 ± 0.3
	R ²	0.99	0.99	0.99	0.99

Model	Parameter	PAN	P-PAN	10% NH ₂ -MIL-Ti@P-PAN	30% NH ₂ -MIL-Ti@P-PAN
	χ^2	19.7	21.6	82.5	157.6

The nonlinear isotherm fitting for carbofuran adsorption onto the as-synthesized films was investigated in accordance to Langmuir and Freundlich modelling (Figure 6). While, the calculated parameters of both isotherms and the estimated R² & x² were all presented in Table 2. According to the values of x² and R², the adsorptive removal of carbofuran was well fitted to Langmuir isotherm rather than Freundlich modelling. Langmuir isotherm clarified that the adsorption of carbofuran onto the applied films performed through monolayer formation [47]. The calculated maximum capacities (Q_{max}, mg/g) for carbofuran adsorptive removal were greatly enlarged from 160.8 mg/g for PAN to 292.2 mg/g for P-PAN and to 489.5 – 690.1 mg/g for NH₂-MIL-Ti@P-PAN, respectively. The maximum carbofuran adsorption capacity of P-PAN film was enhanced by 1.7 and 2.4 times at incorporation of 10% and 30% NH₂-MIL-Ti, respectively. The obtained findings approved the superiority of 30% NH₂-MIL-Ti@P-PAN film in the removal of carbofuran.

Adsorptive removal of carbofuran onto the applied films can be described by physical and chemical adsorption. The physical adsorptive removal might be carried out by the pores of P-PAN film and pores of NH₂-MIL-Ti as a kind of coordination polymer which characterized by its porous framework. The higher adsorption capacity of P-PAN than that of PAN confirmed this hypothesis. For chemical adsorption, the reactive groups of films (CN of P-PAN and COO & Ti in CP) could be chemically interacted with the functional groups of carbofuran (N, O) as suggested in Figure 7. Coordinating bonds formed between Ti in film and N & O in carbofuran, while, N of CN and O of COO in the film interacted by H-bonds with H of N in carbofuran [26, 37, 38]. Furthermore, the aromatic ring of 2-aminoterphthalic acid can compose π – π interactions with the benzene ring of carbofuran [26, 48, 49]. Due to the several functional groups as reactive sites, NH₂-MIL-Ti@P-PAN film exhibited extremely greater adsorptive removal of carbofuran comparing to P-PAN film. This postulation further emphasized by the observable increment in the adsorptive removal capacity of carbofuran with increasing the immobilized content of NH₂-MIL-Ti from 10–30% in the film. In accordance to Langmuir isotherm, monolayer adsorption was implemented by a limit of adsorption in the active sites of film including pores and the accessible functional groups [50]. Consequently, each active site in the applied film was full by only one carbofuran molecule resulting of one layer. The pseudo 2nd ordered model declared that the carbofuran adsorption onto the applied film was relied on the contents of the active sites (pores and functional groups) and the concentration of carbofuran [47]. Subsequently, the adsorptive removal capacity of carbofuran could be further improved by immobilization much higher NH₂-MIL-Ti content within the film.

In order to highlight the superiority of the currently prepared NH₂-MIL-Ti@P-PAN film in the adsorptive removal of carbofuran (690.1 mg/g), comparative overview for series of adsorbents in literature was presented in Table 3. Many of the summarized adsorbent materials (indian soils, slow pyrolyzed

sugarcane bagasse biochar, animal bone meal, tea waste biochars, magnetic peanut shell, granular activated carbon, commercial activated carbon) showed very low adsorption capacity for carbofuran (0.9 – 97.1 mg/g) [22–28]. Much high carbofuran adsorption was obtained (137.0 – 312.5 mg/g) at using date seed activated carbon, modified maize cobs waste, steam-activated biochar, palm oil fronds activated carbon, magnetic sugarcane bagasse, mesoporous activated carbon, steel industry wastes, activated carbon from rice straw and rice straw-derived activated carbon [28, 51–58]. However, the presently synthesized 30% NH₂-MIL-Ti@P-PAN film exhibited extremely greater carbofuran adsorption than that of all the adsorbents reported in Table 3 by factor of more than 2. Additionally, NH₂-MIL-Ti@P-PAN film was advantageously characterized by the recyclability efficiency. Therefore, the currently obtained NH₂-MIL-Ti@P-PAN film is an excellent adsorptive film for removal of carbofuran with higher applicability and hence it could be more desirable for removal of different insecticides.

Table 3
Adsorption capacity for carbofuran onto different adsorbents reported in literature.

Adsorbent	Q_{\max} (mg/g)	Reference	Reference
30% NH₂-MIL-Ti@P-PAN	690.1	Current work	Current work
Indian soils	0.9 – 4.9	18	Krishna, K. R., & Philip, L., 2008
Slow pyrolyzed sugarcane bagasse biochar	3.6 – 18.9	21	Vimal, V., et al., 2019
Animal bone meal	18.5	20	Roudani, A., et al., 2014
Tea waste biochars	22.8 – 54.7	22	Mayakaduwa, S., et al, 2016
Magnetic peanut shell	89.3	23	Toledo-Jaldin, H. P., et al., 2020
Granular activated carbon	96.2	17	Salman, J., & Hameed, B., 2010
Commercial activated carbon	97.1	19	Salman, J., et al., 2011a
Date seed activated carbon	137.0	52	Salman, J., et al., 2011b
Modified maize cobs waste	149.2	51	Foo, K., 2016
Steam-activated biochar	160.8	56	Mayakaduwa, S., et al., 2017
Palm-oil-fronds-activated carbon	164.0	54	Salman, J. M., 2013
Magnetic sugarcane bagasse	175.0	23	Toledo-Jaldin, H. P., et al., 2020
Mesoporous activated carbon	193.1 – 205.0	50	Njoku, V., et al., 2014
Steel industry wastes	208.0	49	Gupta, V. K., et al., 2006
Activated carbon from rice straw	296.5	55	Chang, K.-L., et al., 2011
Rice straw-derived activated carbon	222.2 – 312.5	53	Chang, K.-L., et al., 2014

Recoverability

The four synthesized films (PAN, P-PAN, 10% NH₂-MIL-Ti@P-PAN and 30% NH₂-MIL-Ti@P-PAN) were utilized in the study the recyclability for carbofuran adsorption up to six repetitive cycles. Figure 8 showed that carbofuran adsorption by the applied films was slightly reduced after reusing which is due to the

leaching of some of NH₂-MIL-Ti from the film during the adsorption/desorption process. For 30% NH₂-MIL-Ti@P-PAN film, the adsorptive removal capacity was decreased from 360 mg/g to 315 mg/g after six reusing cycles which means that the adsorption of carbofuran was lowered by only 12.5 % when re-using for six repetitive cycles. These could explain that the employed NH₂-MIL-Ti@P-PAN film exhibited a superior recyclability in carbofuran removal that approved its wide exploitability in removing of insecticides. The synthesized NH₂-MIL-Ti@P-PAN film might be promisingly employed in removal of toxic & hazardous materials from water with highly applicability which support its application in environmental purposes.

Conclusion

Highly adsorptive porous film of NH₂-MIL-Ti@P-PAN was successively synthesized by immobilization of NH₂-MIL-Ti CP within the pre-prepared porous polyacrylonitrile film. The obtained films were investigated by SEM, XRD and FTIR. The estimated pore diameter of PAN film was 8.5 – 51.2 µm. The adsorption of carbofuran insecticide onto the obtained films was systematically studied. The adsorption of carbofuran was fitted to Langmuir isotherm and pseudo 2nd ordered model. The maximum adsorptive removal of carbofuran onto films was extensively enlarged from 160.8 mg/g for PAN to 292.2 mg/g for P-PAN and to 489.5 – 690.1 mg/g for NH₂-MIL-Ti@P-PAN. The removal capacity of P-PAN film was improved by factor of 2.4 at immobilization of 30% NH₂-MIL-Ti, respectively. The applied NH₂-MIL-Ti@P-PAN film exhibited quite good recyclability, and the carbofuran adsorptive removal capacity was lowered by only 12.5 % after 6 repetitive applied cycles. Regarding to the conventional techniques for removal of carbofuran mentioned in literature, the prepared NH₂-MIL-Ti@P-PAN film showed advantageous properties of high adsorptive removal efficiency, and recyclability. Thus, the exploited porous film could be described as successfully functionalized in removal of insecticides and hazardous materials and could be promisingly applicable in other environmental applications.

Declarations

Compliance with ethical standards

The authors declare that they have no conflict of interest

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Conflict of Interest

The authors declare no conflict of interest.

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Figures

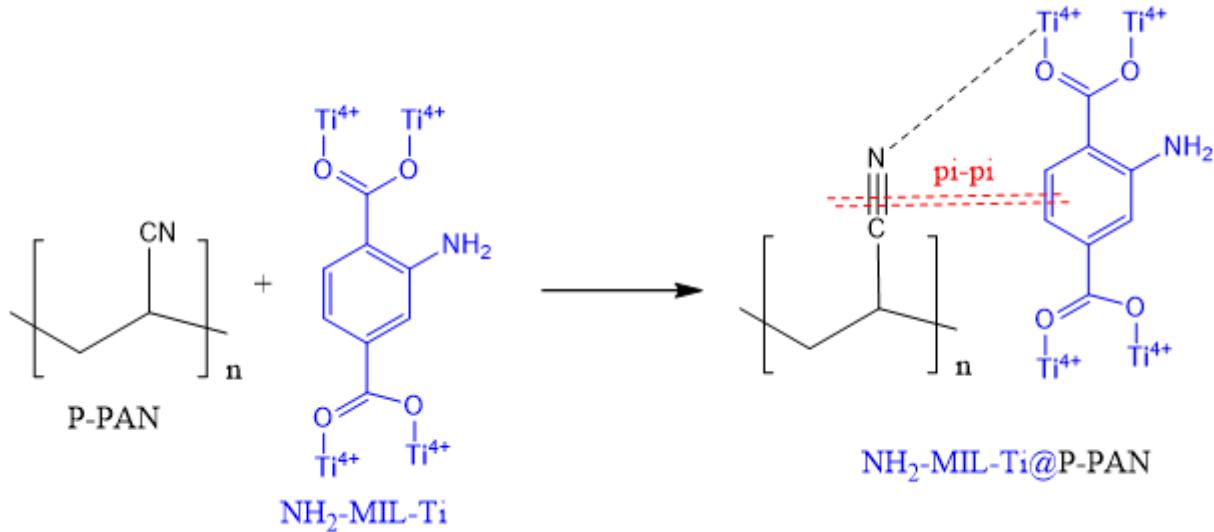


Figure 1

Preparation scheme of NH₂-MIL-Ti@P-PAN film.

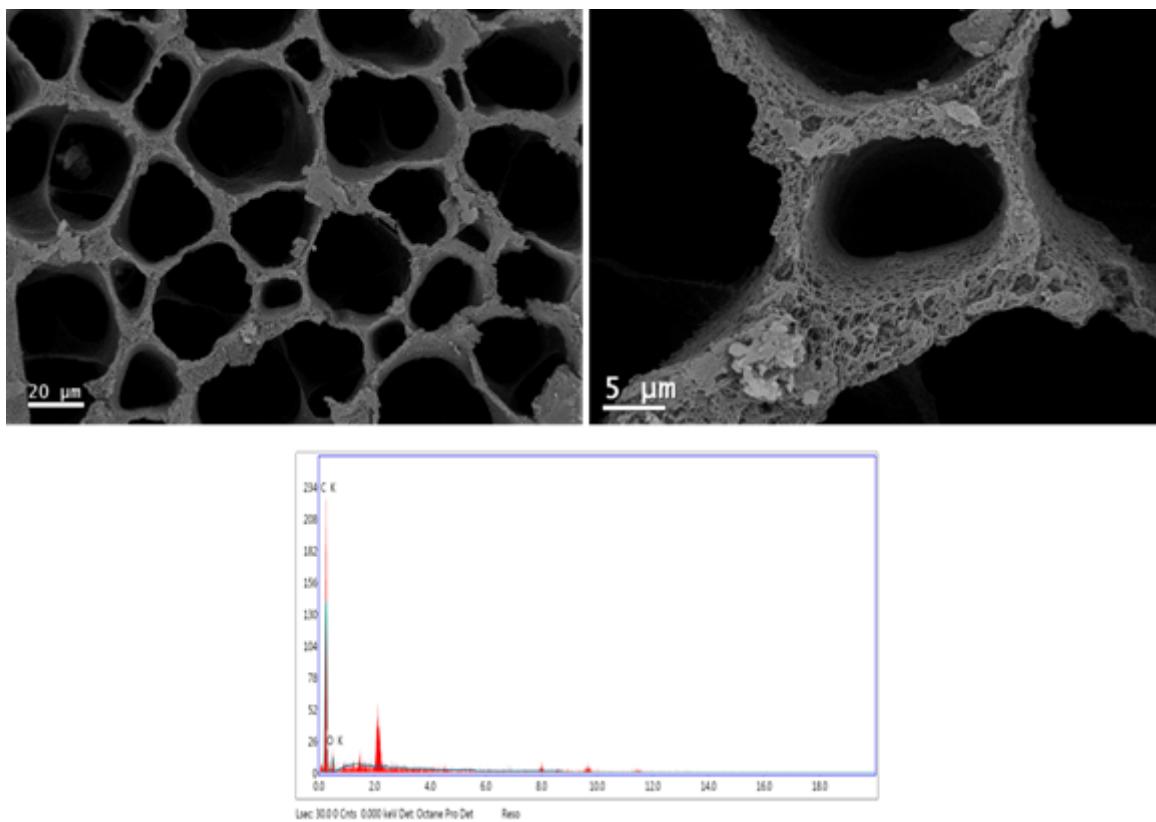


Figure 2

Scanning micrographs for the synthesized films; [a] P-PAN, [b] 10% NH₂-MIL-Ti@P-PAN and [c] 30% NH₂-MIL-Ti@P-PAN. EDX analysis are presented below the micrographs

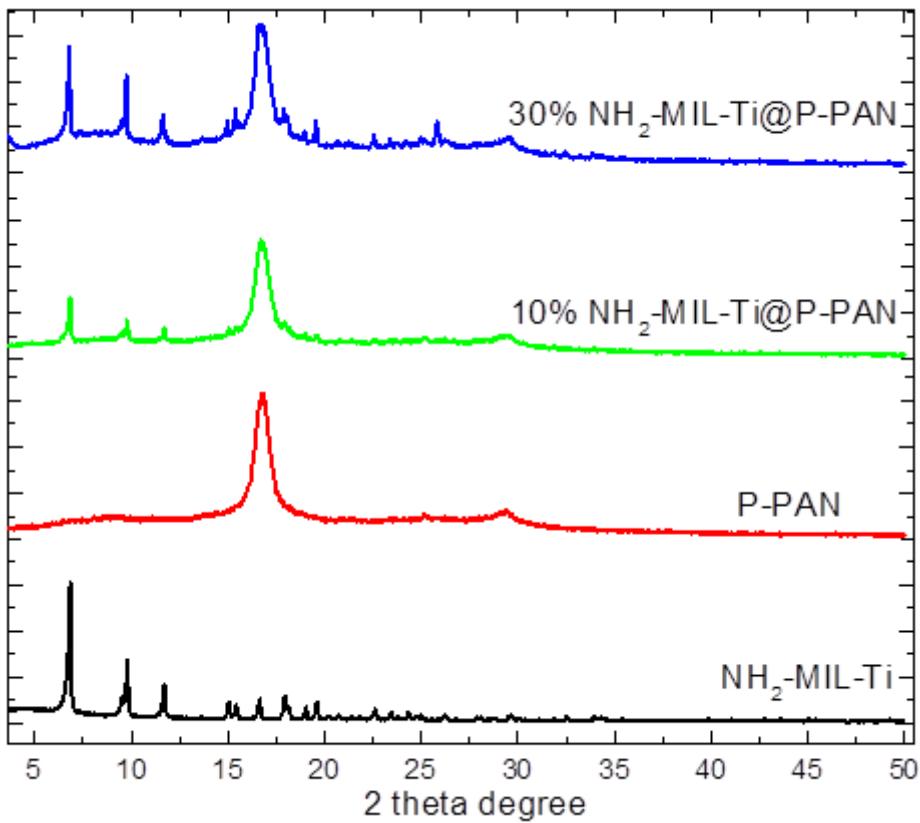


Figure 3

X-ray diffraction of the synthesized films.

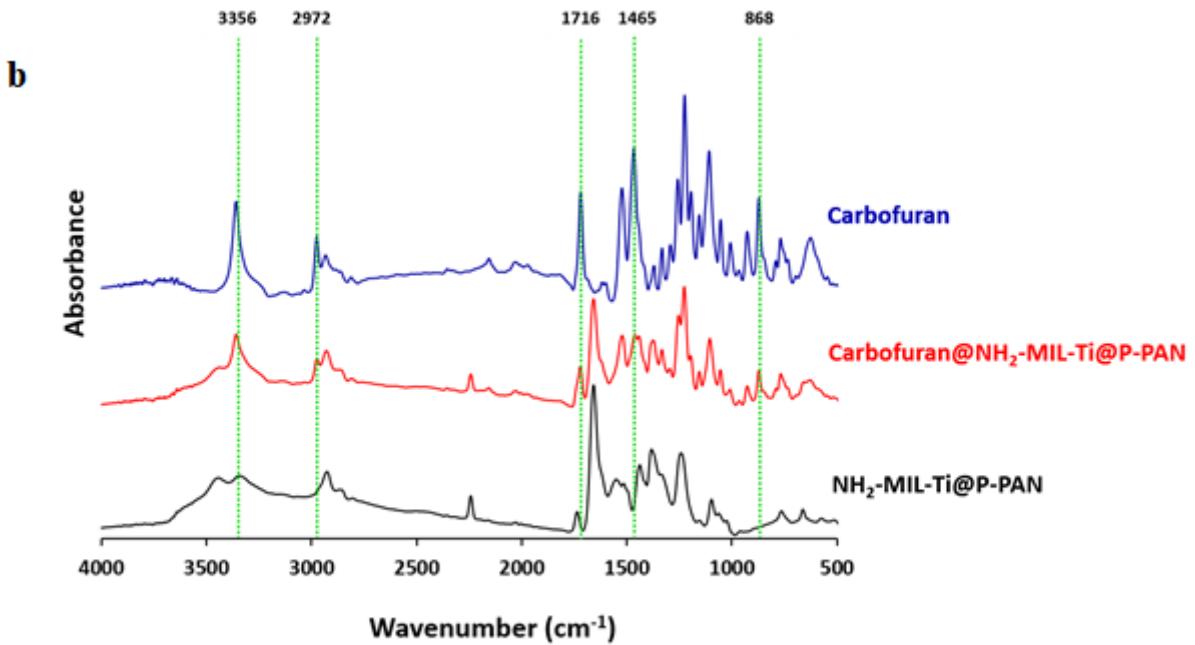
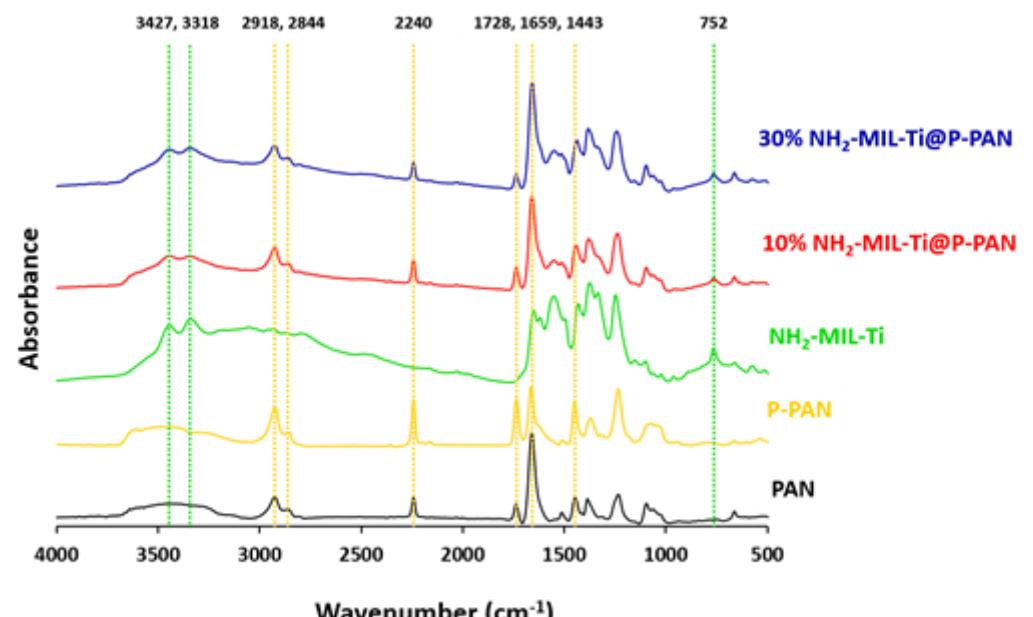


Figure 4

FTIR spectra for; [a] the synthesized films and [b] film after carbofuran adsorption.

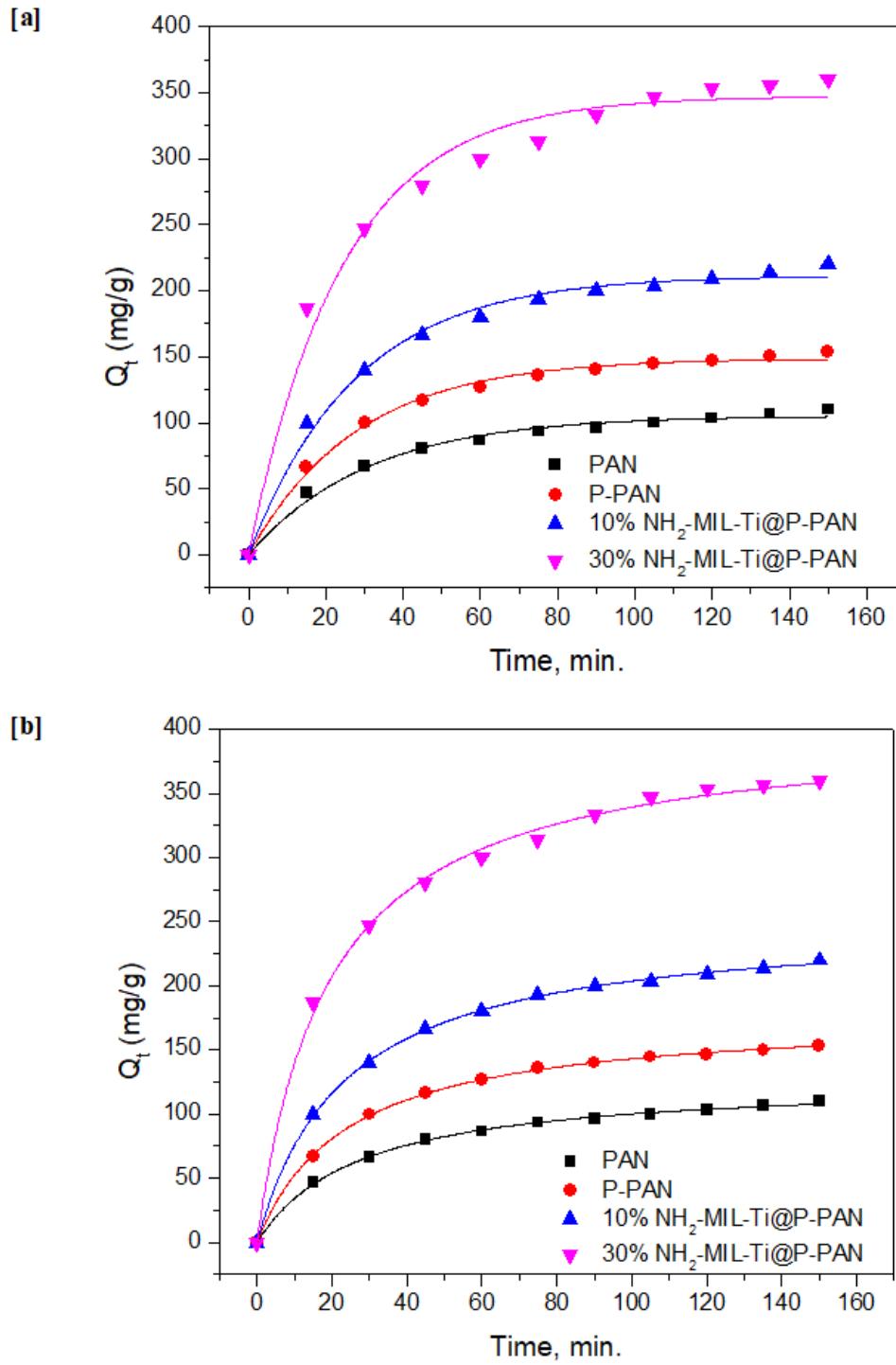
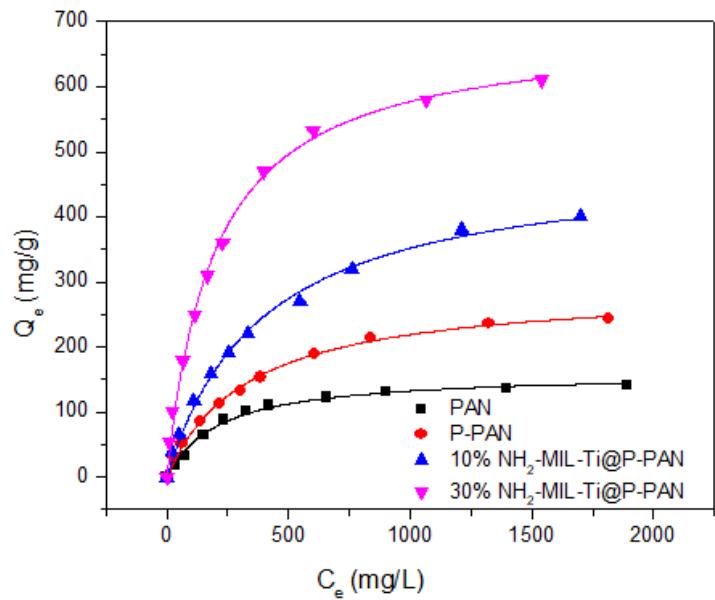


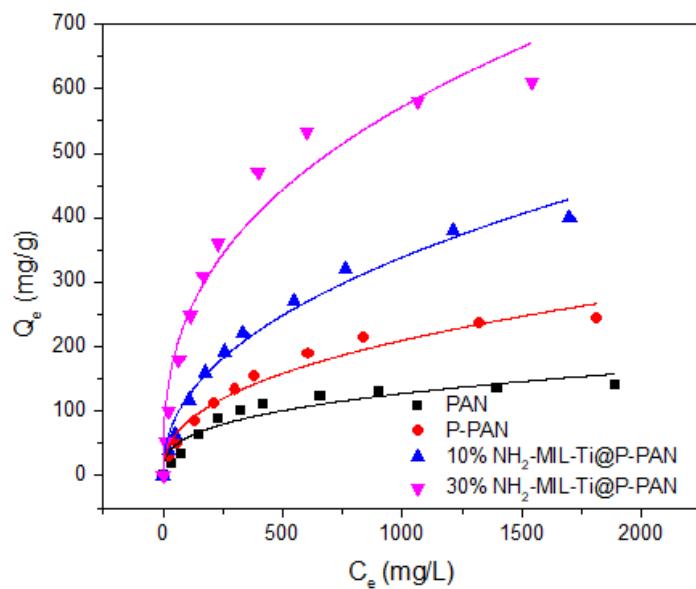
Figure 5

Adsorption kinetic of Carbofuran insecticide onto the synthesized films (PAN, P-PAN, 10% NH₂-MIL-Ti@P-PAN and 30% NH₂-MIL-Ti@P-PAN); [a] pseudo-first order and [b] pseudo-second order.

[a]



[b]

**Figure 6**

Adsorption isotherm of Carbofuran insecticide onto the synthesized films (PAN, P-PAN, 10% NH₂-MIL-Ti@P-PAN and 30% NH₂-MIL-Ti@P-PAN); [a] Langmuir model and [b] Freundlich model.

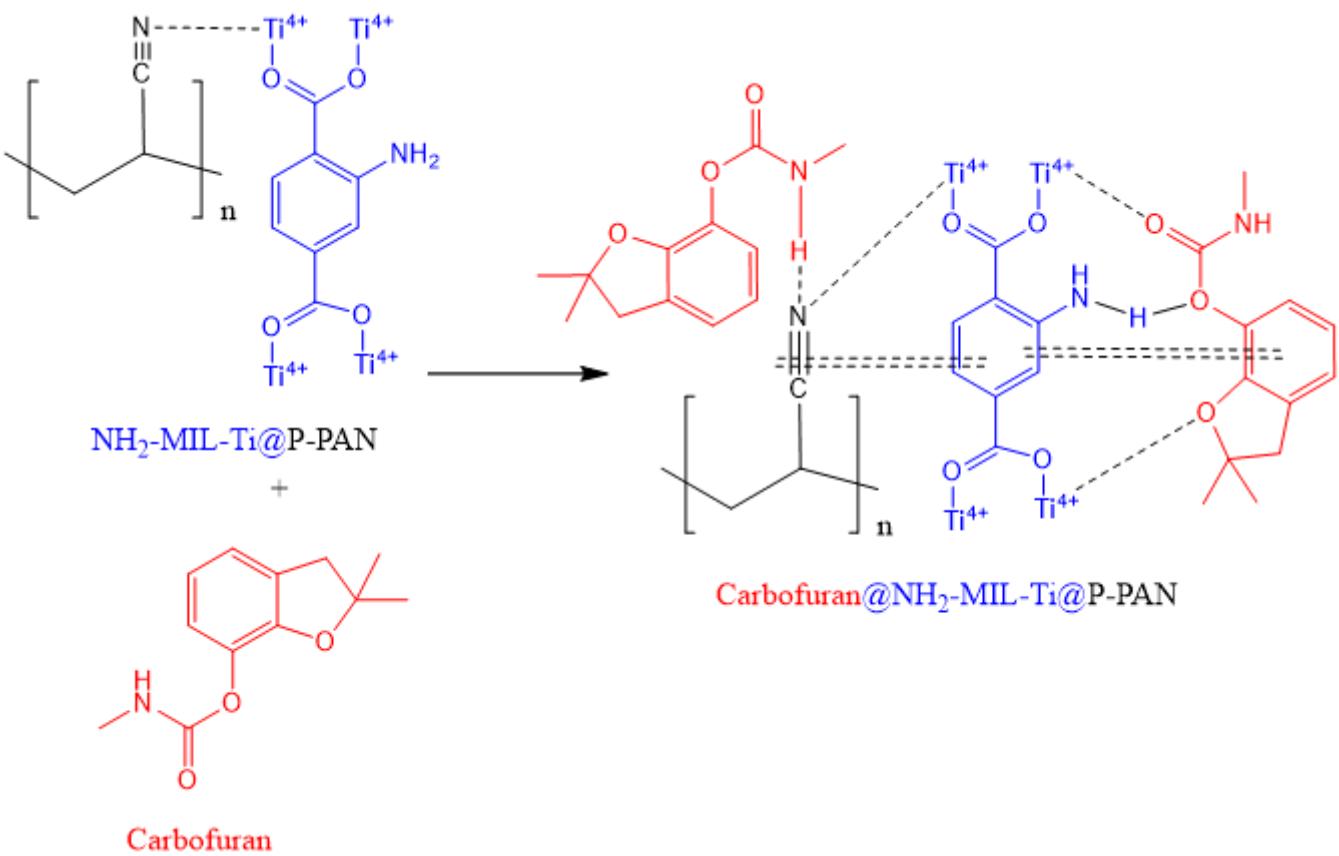


Figure 7

The suggested adsorption scheme of Carbofuran insecticide onto $\text{NH}_2\text{-MIL-Ti@P-PAN}$ film.

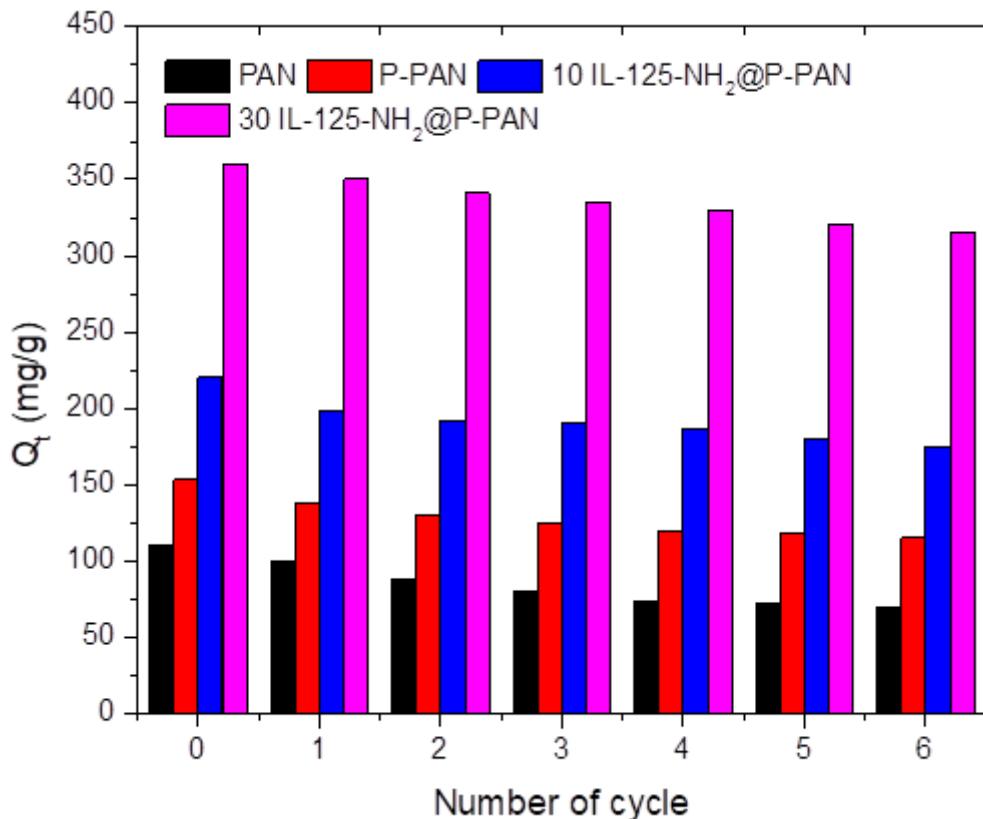


Figure 8

The effect of repetitive washings on the efficiency of NH₂-MIL-Ti@P-PAN film in the adsorption of Carbofuran.