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Research Article

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Efficacy of Single-Walled Carbon Nanotubes and Titanium Dioxide Nanoparticles as Remediators of the Aquatic Environment from Pendimethalin Residues

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Abstract

Pesticides are useful in increasing the quantity and quality of agricultural products. However, over-application or misuse would accumulate their residues in the environments, which might pose threats to non-target organisms and humans. Therefore, this study investigated the sorption of herbicide, pendimethalin (PD) onto titanium dioxide nanoparticles (TiO_2NPs) and single-walled carbon nanotubes (SWCNTs) surfaces in aqueous solutions. Several experiments were conducted to study the contact time of the nanoparticles with different concentrations of PD under laboratory conditions. The experiments were done at 25 ºC and pH values 7.0. Sorption results were then fitted using Langmuir and Freundlich isotherm models. Quantities of 0.5 to 2.5 µg/ml of TiO_2NPs and 50.0 µg/ml of SWCNTs exhibited 100.0% and 99.8% removal of PD, respectively. Small amounts of PD (0.5-2.5 µg/ml) were completely removed (100%) by TiO2NPs and SWCNTs particles. Isotherms displayed adsorption capacities of 1.850 and 2.304 µg/g for TiO2NPs and SWCNTs, respectively, which highlight the elevated potential of cleaning the environment from pendimethalin residues.

Keywords: Titanium Dioxide Nanoparticles; Single-Walled Carbon Nanotubes; Adsorption; Pendimethalin Removal; Water.

Introduction

Pesticides are widely used for various agricultural activities [1, 2]. Extensive use of pesticides might result in the accumulation in the environment, which would impose risks to water resources [3, 4]. As documented in the literature, the inappropriate discarding of unfilled pesticide containers, wash of spray machines and equipment, and unrestricted effluents from manufacturing places are the major causes of contamination of surface water and rivers with pesticides [5]. Pesticides, for example, herbicides are widely used in controlling weeds in various orchards, crops, and vegetables. However, their extensive use has turned back into aquatic sources (canals, lakes, or rivers) [6].

The herbicides exert diverse side effects on the aquatic ecosystem [7]. Pendimethalin herbicide is a selective herbicide that is applied to control annual and commonly broadleaf grasses in most crops e.g. fruits, grapes, vegetables, oilseeds, cereals, and ornamentals [8]. It might contaminate surface water from foliar practice, drift, runoff from rainfall events, and through soil leaching after application. Once in the aquatic system, it goes through microbially-mediated metabolism and volatilization with a half-life of 21 days [7, 9]. Although it has a low leaching pattern to groundwater, it was detected in numerous biota, including fish, and aquatic invertebrates. Consequently, the widespread use of PD may harmfully disturb endangered species of terrestrial, aquatic plants, fish, and birds. Impacts on non-target organisms e.g. terrestrial and semi-aquatic plants are anticipated to be moderate [10, 11]. Moreover, contamination of water resources with PD could induce threats to human health.

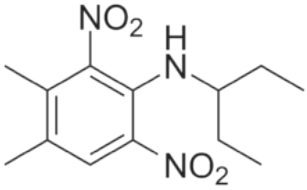
Thus, remediation of pesticides from the ecosystems through the employment of appropriate methods is a vital goal. Various techniques were reported to be suitable to remediate pesticides contamination e.g. photocatalytic deprivation, coupling of Photo-Fenton, biological and chemical oxidation, aerobic decomposition, ozonation, adsorption, and nanofiltration membrane techniques [12-14]. Nanotechnology was used to clean water from pollutants and organic contaminants [15, 16]. For example, nano-enabled water conduct techniques based on membrane filters fabricated from carbon nanotubes (CNTs), nanoporous ceramics, and magnetic nanoparticles were assayed for pesticides' removal [17-21]. Titanium dioxide nanoparticles (TiO2NPs) were examined to remove phenol and dyes from aqueous solutions. Also, CNTs were used to remove pesticides from aquatic environments [22-28].

Consequently, the present study aimed to investigate the effectiveness of TiO_2NPs and Single-Walled Carbon Nanotubes (SWCNTs) in the removal of PD residues from aqueous solutions under different laboratory conditions with the maximization of contact time, concentration of herbicide, and adsorbent dose.

Materials and Methods

Chemicals

Tested nanomaterials: TiO_2NPs and SWCNTS were obtained from Nano Laboratory of Dream Land Campus, 6th October City, Egypt. Sodium sulfate anhydrous (Na_2SO_4) was purchased from BDH Laboratory Supplies, BH 151T, England, while dichloromethane and n-hexane were supplied by Merck KGaA, 64271 Darmstadt, Germany. Herbicide, pendimethalin (PD), IUPAC name: 3,4-dimethyl-2,6-dinitro-N-penton-3-ylaniline (Stomp® 40% EC) was obtained from Star Kim Company for Agrochemicals, Egypt [11].



Characterization of NPs

Nanoparticles of TiO2 and SWCNTS were validated using Scanning Electron Microscopic (SEM) (JOEL, model JSM 5300, Japan) under great perseverance and electron fillemental gun of 120 Kev. Trace amounts of NPs have been covered with copper grids to visualize their dimension and form. Another aliquot of TiO2NPS was achieved on X-ray Electron Dispersive Analysis (EDA) instrument (X-ray Oxford detector unit, model 6697, England) to check the purity of NPS. The SWCNTs were scanned using the Elemental Analysis Instrument at Micro Analytical Center, Cairo University to obtain carbon percent in the prepared particles. Solutions of both NPs were subjected to Dynamic Light Scattering (DLS) (DTS Nano v 5.2; Malvern Zeta sizer Nano ZS, Malvern Instruments, UK) for positive charges measuring. The suspensions of studied NPs were sonicated for 20 min at 40W before being checked.

Removal of PD from Aqueous Solution

Sorption Experiments

TiO2NPs and SWCNTs were tested as remediators of aqueous solutions from PD residues. Each of NPs (0.5, 1, 2.5, 12.5, 25, and 50 µg/ml) doses were incubated with each of PD concentrations (0.5, 1, 2.5, 12.5, 25, and 50 µg/ml) for 0, 1, 3, 6, 12, and 24 hrs at 250 rpm shaking. The experiment was replicated 3 times. At the end of incubation, the samples were centrifuged for 5 min and the supernatant was taken for the herbicide residue analysis. pH value was constant (7.0) during the experiment. The removal efficiency was estimated and fitted in relationship with NPs concentration.

Adsorption isotherm was estimated through equations of Langmuir and Freundlich models. Linear pattern of Langmuir isotherm model was as follows:

$$\frac{1}{x/m} = \frac{1}{qmax} + \frac{1}{qmax\,b} + \frac{1}{C}$$

Where: b is a constant that increases with increasing the molecular size, *qmax* is the adsorbed amount on the surface (µg/g), x is the weight substance adsorbed (µg), *m* is the adsorbent weight (g), and C is PD concentration remained in the solution (µg/ml) [29].

The model can be stated in relation to equilibrium limitation (*qm*), which is a dimensionless constant discussed as an equilibrium parameter [30].

$$qm = \frac{1}{1 + bC}$$

The value of *qm* indicates the type of isotherm, where if $qm>1$ the isotherm is unfavorable, $qm=1$ it is linear, $0<qm<1$ it is favorable, and $qm=0$ it is irreversible.

Freundlich isotherm was calculated from the equation:

$$Log\ q. = \log K + \frac{1}{n} x \log C$$

K and n represent constants depending on temperature status [31].

GC-MS residue analysis of PD

Each solution (200 ml) was extracted with 20 ml of dichloromethane (2 times), dried over Na_2SO_4 anhy. and vaporized to dryness at 30 ℃. Then, PD residue was re-dissolved in 1 ml of n-hexane and directed to gas chromatographic-mass spectrometry (GC-MS) quantification. The GC-MS instrument (Agilent technologies 7890D GC and Agilent technologies 5977A MSD) equipped with HP5MS column (30 m×0.25 mm×0.25 µm film thickness) was used. The injection temperature was set at 280 °C. Operation of the GC-MS instrument was set according to in the following program: column temperature started at 80 °C for 6 min, followed increase to 215 °C at 15 °C/min (hold for 1 min), then to 230 °C at 5 °C/min and finally to 290 °C at 5 °C/min (hold for 2 min), respectively. The carrier gas was at a flow rate (1.1 ml/min). Herbicide, PD was documented by mass spectral scans and retention time (Rt) using the total ion current as a monitor to give a Total Ion Chromatogram (TIC) of the standard material. The standard curve of PD was constructed using 0.5, 1, 5, 10, 20, and 40 µg/ml. The analytical method was validated via recovery experiment and precision (coefficient of variation of the results obtained in triplication). The limits of detection (LOD) and quantification (LOD) values were established according to the criteria itemized by Thier and Zeumer [32, 33].

Results

NPs Characterization

SEM images of TiO2NPs showed spherical particles with dimensions from 12 to 65 nm (Figure 1a), while the SWCNTs showed singular tubules with sizes ranging from 15 to 56 nm (Figure 1b). Also, the X-ray EDA pattern of TiO2NPs plotting was presented in Figure 1c displaying dominantly TiO2 (100%) of the total content, while the elemental analysis of SWCNTs samples displayed that C atoms about 97.0% of the total content. The average zeta potential of TiO2NPs in-vehicle solutions was -20.5 mv (Figure 1d), while the value of SWCNTs was 4.7 mv (Figure 1e).

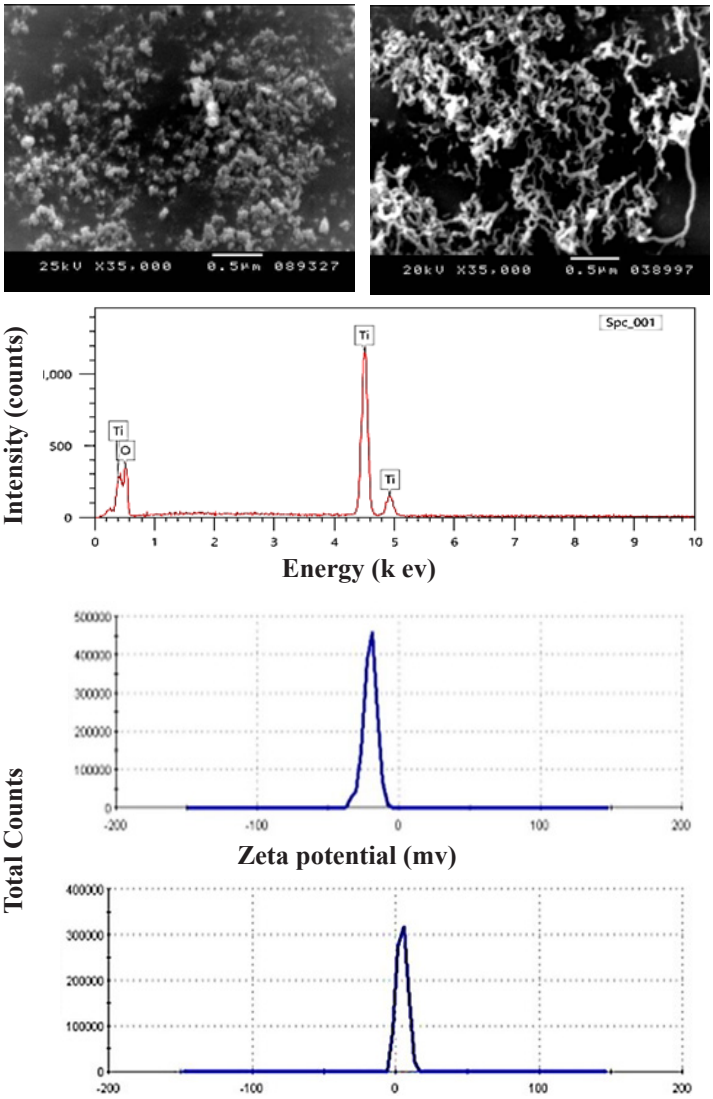


Figure 1: Characterization profiles of nanoparticles on **SEM** (a) TiO_2NPs and (b) SWCNTs, **EDA** pattern of (c) TiO_2, and **DLS** (d) TiO_2 and (e) SWCNTs.

GC-MS Method Quality Control Characteristics

The used analytical method was suitable and efficient for the determination of PD residues in water samples (Table 1). Recovery percentages of PD from water were 94.75±5.41 and 95.91±6.08% for spiked doses of 0.5 and 5.0 µg/l, respectively. Inter-assay and intra-assay precision values were 6.18 and 4.07 %, respectively. Accuracy, recovery, and RSD% met the acceptable criteria range according to World Health Organization requirements [34]. Moreover, RSD values were below 20%, and the data were corrected for obtained recovery percentage values. Method detection limits: LOD and LOQ were 1.98 and 6.01 µg/l, respectively. Moreover, separation of PD was conducted at Rt 16.54 min with R2 value of 0.9916 (Figure 2).

Table 1: Percentages of recovery, coefficients of variation (CV %), LOD and LOQ, and linearity parameters of PD determined using GC-MS.

Parameter		Value
Recovery (%)±RSD[$]	0.5 (µg/l)	94.75±5.41
	5.0 (µg/l)	95.91±6.08
*CV (%)	Inter-assay Intra-assay	6.18 4.07
[δ]Method limits (µg L^{-1})	LOD LOQ	1.98 6.01
Linearity	Slope Intercept R^2	0.000006±0.00000012 -0.0000002 0.9916

$RSD=relative standard deviation. *Inter– and intra-assay precision data obtained from the analysis of the concentrations of the standard material of PD herbicide in fortified water. [δ]Method detection and quantification limits were calculated from the signal-to-noise (S/N) ratios of the samples with the lowest concentration level of PD (LOD = S/N×3.3, LOQ = S/N×10). LOD and LOQ were calculated using the following equations: σ/S and σ/S, where σ is the standard deviation of the y-intercept and S is the slope of the corresponding calibration curve.

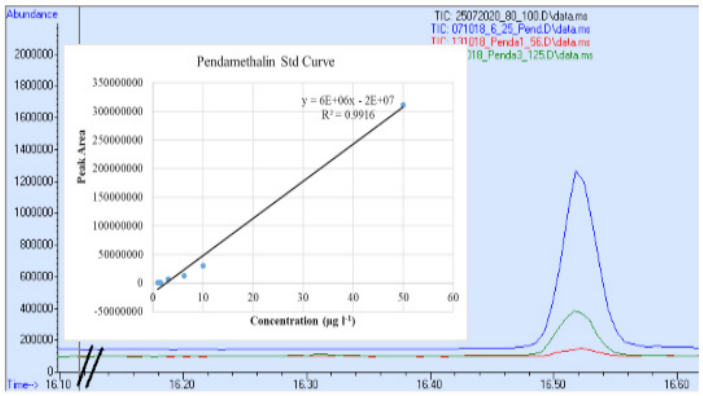


Figure 2: Separation and the calibration curve of PD that was analyzed using GC-MS on HP 5MS separation column

Influence of interaction time on PD removal

The time effect on PD elimination from the aqueous solutions was conducted through changing periods of shaking adsorbate and adsorbent in the range of 0-24 hr as illustrated in Figure 3. TiO_2NPs exhibited the greatest removal percentage of PD (93.34%) after 1 hr and the trend was declined during later stages of time as the following 87.82, 87.90, 84.12, and 78.25% after 3, 6, 12, and 24 hr, respectively. In the case of SWCNTs, the highest removal percentage (100.0%) was found after periods from zero-time to 6 hr, followed by a decline to (90.4%) after 12 hr and to 89.18% after 24 hr.

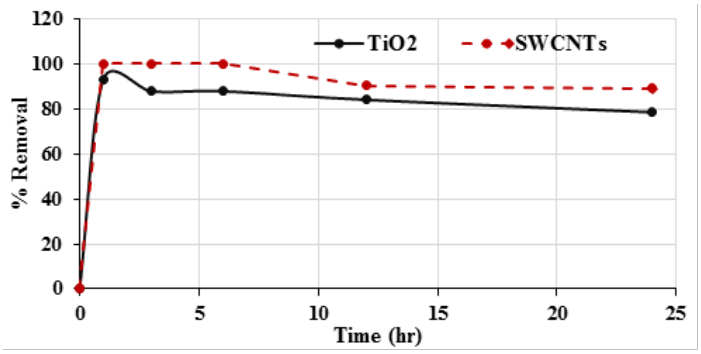


Figure 3: Time interaction between nanoparticles (TiO_2NPs and SWCNTs at 50 µg/ml) and PD on the removal of PD at a concentration of 50 µg/ml from water.

Appropriate NPs amounts in the removal of PD

The efficient amounts of tested NPs on the removal of PD (50 µg/ml) were examined by testing varying the amount of the NPs as illustrated in Figure 4. The results showed that the removal competence of TiO_2NPs increased with increasing amounts from 0.5 to 2.5 µg/ml reaching 100.0%. While quantities from 12.5 to 50 µg/ml resulted in removal percentages from 98.19 to 87.17%. Regarding SWCNTs, an increasing pattern was noticed where the concentrations of 0.5, 1, 2.5, 15.5, 25, and µg/ml exhibited removal of 0.16, 66.6, 73.1, 94.41, 97.8, and 99.8%, respectively.

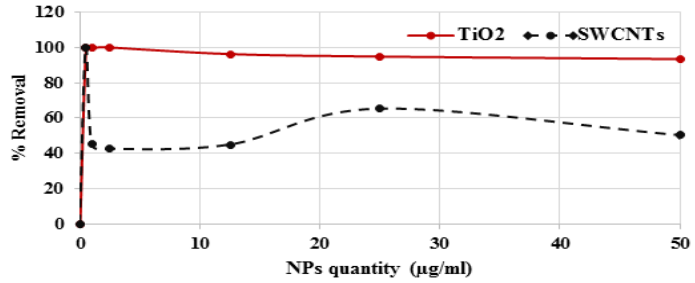


Figure 4: Effects of NPs amounts on PD removal from aqueous solutions.

The greatest amount of PD that could be removed using the tested NPs

The greatest amount of the tested nanoparticles was tested against varying amounts of PD to examine their removal efficiency of the herbicide from aqueous solutions (Figure 5). Examined dose of TiO_2NPs exhibited the greatest removal percentage (100%) for PD in concentrations: zero-2.5 µg/ml, followed by 98.19% for 12.5 µg/ml, 95.0% for 25.0 µg/ml, and 87.17% for 50.0 µg/ml. In case of SWCNTs, the greatest removal percentage (100%) was recorded for PD concentrations: zero and 0.5 µg/ml, followed by 97.85% for 1.0 µg/ml, 94.38% for 2.5 µg/ml, 73.0% for 12.5 µg/ml, respectively. The amount of 50.0 µg/ml of SWCNTs didn't remove PD from the aqueous solutions.

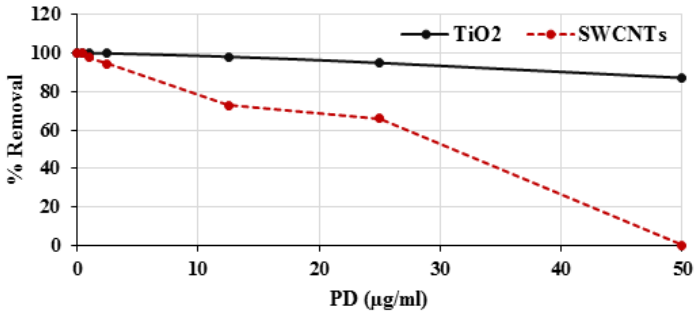


Figure 5: Influence of PD quantities on removal competence of the used NPs in aqueous solutions.

Langmuir and Freundlich Equilibrium Isotherms

Adsorption isotherms were designated by a sorption line, categorized by firm factors whose values were related directly to the surface properties. The affinity of the sorbent sorption equilibrium was recognized when the dose of the sorbate in the bulk solution was in dynamic balance with that at the sorbent interface [35]. Equilibrium isotherm was conducted using the two models of Langmuir and Freundlich. Isotherm characteristics for sorption of PD by TiO_2NPs and SWCNTs were reported in Table 2. The value of 1/n of Freundlich isotherm indicated that both nanoparticles were favorable for the removal of PD. On the other hand, the value of qm of Langmuir isotherm showed that TiO_2NPs (1.877) were unfavorable but SWCNTs (0.482) were favorable in the removal of PD. It can be concluded that Freundlich isotherm was more adaptive than Langmuir, where the adsorption capacity displayed values: 1.850 and 2.304 µg/g for TiO_2NPs and SWCNTs, respectively. Thus, SWCNTs were more effective in the uptake of PD compared to TiO2NPs from aqueous solutions.

Table 2: Isotherm characteristics for sorption of PD by TiO2NPs and SWCNTs from aqueous solutions

Isotherm Model	Parameter	Value	R^2
Freundlich			
TiO_2NPs	*K*	1.850	0.98
	1/n	8.04	
SWCNTs	*K*	2.304	0.90
	1/n	7.201	
Langmuir			
TiO_2NPs	*qm b*	1.976	0.98
	B	1.052	
	Qm	1.877	
SWCNTs	*qm b*	1.795	0.91
	B	3.725	
	Qm	0.482	

Discussions

The present data display the capability of the examined NPs in the removal of PD from the aqueous solutions. Moreover, SWCNTs and TiO2NPs were previously investigated to explore their capability to eliminate numerous contaminants e.g. dyes, pesticides, pharmaceuticals/drugs, and phenols from water and/or wastewater [36 - 39]. Activated carbon (AC) was used as a commercial adsorbent, independent of its excellent adsorption capacity for organic contaminants [25, 40].

In recent years, increased emphasis has been focused on the application of NMs as adsorbents to remove toxic and harmful organic substances from wastewater [12, 19]. For example, CNTs, which were discovered by Iijima in 1991 [41] are one of the most widely studied NMs as excellent adsorbents of pollutants [42, 43], independent of their hollow and layered structure and large specific surface area [44 - 46]. Carbon nanotubes (CNTs) adsorbents were classified into three types: single-walled CNTs (SWCNTs), multi-walled CNTs (MWCNTs), and functionalized CNTs (f-CNTs) [16, 47, 48]. Such materials already display an important role in the removal of several organic contaminants from water [16, 49].
Removal of pesticide residues from water sources is of particular importance regarding human health. Chen et al. [18] reported the removal of two herbicides: diuron and dichlobenil from contaminated water using MWCNTs. Also, the adsorption of diuron onto as-prepared and oxidized MWCNTs was studied by [26] with an oxidation treatment to enhance the surface area and pore volume, which resulted in increased absorption of the herbicide. Moreover, SWCNTs have demonstrated higher adsorption capacity for 4-chloro-2-methylphenoxyacetic acid (MCPA), a phenoxy acid herbicide, on the three types of MWCNTs (with average outer diameters of 15, 30, and 50 nm) and several nanoscale metal oxides (Al2O3, TiO2, and ZnO) [28]. Atrazine was cleaned from aqueous solution by AC and CNTs via kinetic and thermodynamic processes [50]. Overall, the use of CNTs for pesticide removal appears to be less studied than for other organic contaminants.

The main mechanism by which CNTs adsorb organic compounds differs depending on the properties of the compound of interest (polar vs. nonpolar). Several factors that govern the interactions between pollutants and CNTs have been proposed e.g. hydrophobic interactions, π–π stacking interactions, van der Waals forces, electrostatic interactions, and hydrogen bonding interactions might act individually or simultaneously [20]. The adsorption of six perfluorinated compounds (PFCs) on CNTs increased with C–F chain length [27]. The surface functional groups resulting from oxidative modification (hydroxyl and carbonyl groups) can also increase the hydrophilicity of CNTs resulting in increases in rejection of hydrophobic organics [51].

Moreover, metallic nanoparticles (NPs) have a high-adsorption capacity toward pollutants [52]. For example, nano-sized inorganic oxides (nano-TiO2) successfully removed phenolic compounds from contaminated water, where the effectiveness and prominence of nano-TiO2 to adsorb 4-chloro-2-nitrophenol (4C2NP) were reported. However, these particles showed reduced capacity in the removal of 4C2NP which might be explained due to the aggregation of NPs, which caused a decline in the interference area between the solution and the adsorbent [22, 53]. Also, Saritha et al. [54] utilized TiO2 powder to adsorb 4C2NP and reported that the amount adsorbed in mg/g was decreased as the amount of the adsorbent increased, which might explain the Langmuir results reported in current study.

Conclusion

The examined NPs were efficient in the sorption of the herbicide PD from aqueous solutions. Quantities from 0.5 to 2.5 µg/ml of TiO2NPs and 50.0 µg/ml of SWCNTs exhibited 100.0% and 99.8% removal of PD, respectively. Results reported herein fitted perfectly on the Freundlich adsorption isotherm model for both TiO2NPs and SWCNTs, respectively, which highlighted their potential in environmental remediation of PD residues. However, further studies are required to investigate the capability of utilizing these materials towards the removal of pesticide residues from drinking water and wastewater.

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