Hydrophobic Nanomaterials for Remediation of Phthalate-Contaminated Soil and Water (Postprint)

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Abstract

Phthalate ester pollution in Xinjiang farmland soils and surrounding lake and river sediments is extremely severe. Owing to arid climatic conditions, existing microbial remediation technologies are often unsuitable for treating phthalate ester contamination caused by plastic mulch films in Xinjiang. Consequently, there is an urgent need to develop remediation technologies and materials for phthalate ester-contaminated soils and water bodies. Based on the principle that strong surface hydrophobicity of applied materials confers excellent adsorption performance for phthalate esters, three types of nanoparticles (BN, SiO_2, Fe_3O_4) were modified via polydopamine polymerization to obtain materials with favorable hydrophobicity, and the modified materials were characterized by SEM-EDS, ATR-FTIR spectroscopy, Raman spectroscopy, N_2 adsorption-desorption isotherms, etc. Using dibutyl phthalate, a common phthalate ester in Xinjiang plastic mulch film-contaminated soils, as the target pollutant for adsorption performance experiments, the results demonstrated that: the developed modified materials exhibited favorable adsorption performance for dibutyl phthalate, with an equilibrium adsorption capacity reaching $218.63\ \mathrm{mg \cdot g^{-1}}$; adsorption could achieve equilibrium within 220 min, and the adsorption kinetics conformed to the pseudo-second-order kinetic equation; the adsorption isotherm could be well fitted by both Langmuir and Freundlich models, with the latter demonstrating superior correlation; and the materials maintained favorable adsorption performance under pH conditions ranging from 2 to 12 and sodium chloride salinity up to 4%. This material possesses broad application prospects for remediating phthalate ester-contaminated soils, sediments, and water bodies in arid regions.

Full Text

Effects of Salinity and pH Value on Adsorption of Dibutyl Phthalate in Mulching Farmland Soil to Nanomaterial Adsorbent

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Abstract: Plastic film mulching is the most intensively applied practice in agricultural production in Xinjiang Uyghur Autonomous Region, causing serious phthalate pollution in farmland soil and lake or river sediments. Traditional bioremediation technologies face strong challenges in this area due to the extremely arid climate, making it urgent to develop remediation technologies and materials suitable for arid regions. In this study, three kinds of nanoparticles (BN, SiO_2, and Fe_3O_4) were modified through dopamine polymerization to serve as hydrophobic materials, considering the strong hydrophobicity required for effective phthalate adsorption. The materials were characterized by SEM-EDS, ATR-FTIR spectroscopy, and Raman spectroscopy. The results showed that the adsorbent exhibited excellent adsorption capacity for dibutyl phthalate (DBP), with equilibrium adsorption capacity reaching as high as 218.63 $\mathrm{mg \cdot g^{-1}}$, and equilibrium could be achieved within 220 minutes. The adsorption kinetics followed the pseudo-second-order kinetic equation. Both the Langmuir and Freundlich models could satisfactorily describe the adsorption isotherms. Strong DBP adsorption capability could be maintained under pH values ranging from 2 to 12 and at salinity levels up to 40 $\mathrm{g \cdot L^{-1}}$. This nanomaterial adsorbent demonstrates great potential for remediation of phthalate pollution in farmland soil and lake or river sediments.

Keywords: field film pollution; phthalate; hydrophobicity; nanoparticle; adsorption; Xinjiang

1. Materials and Methods

1.1 Adsorbent Preparation and Characterization The modified adsorbent was prepared by coating $BN/SiO_2/Fe_3O_4$ nanoparticles with a polydopamine layer. Scanning electron microscopy (SEM) analysis revealed that the composite particles exhibited a core-shell structure with distinct morphological features. Energy-dispersive X-ray spectroscopy (EDS) confirmed the elemental composition, showing characteristic signals for boron, silicon, iron, oxygen, and nitrogen from the polydopamine coating.

Attenuated total reflectance Fourier-transform infrared (ATR-FTIR) spectroscopy identified key functional groups: the B-N stretching vibration appeared at 1421 cm^{-1}, Si-O bonds at 781 cm^{-1}, and Fe-O bonds at 669 cm^{-1}. Additional peaks at 3000 cm^{-1} indicated N-H stretching from the polydopamine layer, while a weak signal at 2318 cm^{-1} suggested S-H groups from residual precursors. Raman spectroscopy further confirmed the presence of BN with its characteristic peak at 1365 cm^{-1}.

1.2 Adsorption Experiments 1.2.1 Batch Adsorption Procedure

A stock solution of DBP was prepared at 5 $mg \cdot L^{-1}$ by dissolving appropriate amounts of DBP in methanol (1% v/v) and diluting with ultrapure water. Batch adsorption experiments were conducted by adding a fixed amount of adsorbent (typically 100 mg) to 50 mL of DBP solution in 100 mL conical flasks. The mixtures were agitated in a temperature-controlled shaker at 25°C and 150 rpm.

At predetermined time intervals, 5 mL aliquots were withdrawn and immediately filtered through 0.45 m membrane filters. The filtrate was then extracted using a liquid-liquid microextraction method: 1 mL of filtrate was mixed with 50 L of extraction solvent, vortexed for 30 seconds, and the organic phase was collected for analysis. For quality control, all samples were filtered through 0.22 m filters before instrumental analysis.

1.2.2 Analytical Methods

DBP concentrations were determined using gas chromatography-mass spectrometry (GC-MS, Agilent 7890B/5977A GC/MS) equipped with an HP-5 capillary column (30 m × 0.25 mm × 0.25 m). The injection volume was 1.0 L in splitless mode. The oven temperature program started at 50°C (held for 1 min), increased to 280°C at $30°C \cdot min^{-1}$ (held for 1 min), then to 280°C at $8°C \cdot min^{-1}$ (held for 3 min), with a final hold at 285°C for 5 min. The injector temperature was maintained at 250°C and the ion source at 230°C. The carrier gas was high-purity helium ($ 99.999^{-1}$.

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2. Results and Discussion

2.1 Characterization of the Modified Adsorbent SEM-EDS analysis [Figure 1: see original paper] demonstrated that the adsorbent possessed a heterogeneous structure with particle sizes distributed around 700 nm for SiO_2, 300 nm for Fe_3O_4, and 300 nm for BN components. The polydopamine coating created a uniform surface layer that enhanced the hydrophobicity while maintaining the magnetic properties of the Fe_3O_4 core.

The ATR-FTIR spectra [FIGURE:2(a)] confirmed successful modification, with characteristic absorption peaks at 1421 cm^{-1} (B-N stretching), 781 cm^{-1} (Si-O-Si asymmetric stretching), and 669 cm^{-1} (Fe-O stretching). The Raman spectra [FIGURE:2(b)] showed the E_2g vibrational mode of BN at 1365 cm^{-1}, confirming the integrity of the boron nitride structure after modification. The presence of broad bands in the 3000-3500 cm^{-1} region indicated N-H and O-H groups from the polydopamine coating, which contributed to the adsorption mechanism.

2.2 Adsorption Performance 2.2.1 Adsorption Kinetics

The adsorption kinetics of DBP onto the modified adsorbent showed rapid initial uptake followed by gradual approach to equilibrium [Figure 5: see original paper]. Equilibrium was established within 220 minutes, with an adsorption capacity of 28.44 $mg \cdot g^{-1}$ under the experimental conditions. The kinetic data were well-fitted by the pseudo-second-order model ($R^2 = 0.803$), with a calculated equilibrium capacity of 8.01 $mg \cdot g^{-1}$, indicating that chemisorption processes dominated the adsorption mechanism.

2.2.2 Adsorption Isotherms

Adsorption isotherms were measured at 25°C across a range of initial DBP concentrations [Figure 6: see original paper]. The equilibrium data were analyzed using both Langmuir and Freundlich models. The Langmuir model yielded a maximum monolayer adsorption capacity of 246.9 $mg \cdot L^{-1}$ with a correlation coefficient (R^2) of 0.95, while the Freundlich model gave a 1/n value of 0.07 and Kd of 16.70, also with $R^2 = 0.95$. The good fit of both models suggests that adsorption occurred through a combination of monolayer coverage and heterogeneous surface binding.

TABLE:1 Isothermal parameters of DBP adsorption to the adsorbent

Model	Parameter 1	Parameter 2	R^2	Kd
Langmuir	246.9 ($mg \cdot L^{-1}$)	0.07	0.95	16.70
Freundlich	0.87	0.95	13.82	-

2.2.3 Effect of pH

The adsorbent demonstrated remarkable stability across a wide pH range [Figure 8: see original paper]. When the pH was varied from 2 to 12, the adsorption capacity remained relatively constant, decreasing only slightly under strongly acidic or alkaline conditions. This pH independence is advantageous for practical applications in diverse environmental matrices, as it eliminates the need for pH adjustment.

2.2.4 Effect of Salinity

Salinity effects were investigated using NaCl solutions ranging from 0 to 40 $g \cdot L^{-1}$ [Figure 7: see original paper]. The adsorption capacity showed moderate sensitivity to ionic strength, with a slight decrease at higher salinities. However, even at 40 $g \cdot L^{-1}$ salinity, the material retained significant adsorption capability (approximately 220 $mg \cdot g^{-1}$), demonstrating its suitability for saline environments typical of arid region soils.

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3. Conclusion

This study successfully developed a polydopamine-modified $BN/SiO_2/Fe_3O_4$ nanocomposite adsorbent for DBP removal from contaminated soil and water. The material exhibited excellent adsorption performance with equilibrium capacities up to 218.63 $mg \cdot g^{-1}$, rapid kinetics (equilibrium within 220 min), and robust performance across extreme pH (2-12) and high salinity (40 $g \cdot L^{-1}$) conditions. The pseudo-second-order kinetic model and both Langmuir and Freundlich isotherm models accurately described the adsorption behavior. These characteristics make the adsorbent particularly suitable for remediation of phthalate pollution in the arid agricultural environments of Xinjiang, where traditional bioremediation is limited by climatic conditions.

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