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In situ remediation of persistent organic pollutants in soil using retrievable sorbents composed of cotton fabrics decorated with UiO-66-NH_3^+ metal-organic frameworks

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ABSTRACT

Sorbent amendment is a convenient method for the *in situ* remediation of soil, but it is limited by the difficulty in recovering the sorbent from soil. This work aimed to introduce a novel method for the remediation of contaminated soils that relies on the *in situ* removal of contaminants from soil by retrievable sorbents. The remediation process is based on adding cotton fabric sheets decorated with a metal-organic framework (MOF) in a contaminated soil matrix and mixing to sorb the contaminants. Then, the MOF-modified cotton fabric, carrying the sorbed pollutants, is easily retrieved from the soil. As a demonstration, a zirconium (Zr)-based MOF (UiO-66-NH_3^+, MOR-1) was irreversibly immobilized on polydopamine (PDA)-decorated cotton fabrics (MOR-1@PDA-cotton fabric) and used to remediate a soil contaminated with organic ultraviolet (UV) filters, as model hydrophobic persistent organic pollutants, namely, 2-hydroxy-4-methoxybenzophenone, 2-ethylhexyl 4-methoxycinnamate, isoamyl 4-methoxycinnamate, 2-ethylhexyl 4-(dimethylamino)benzoate, 3-(4-methylbenzylidene)camphor, and 2-ethylhexyl 2-cyano-3,3-diphenylacrylate. The results showed that 1.88 cm^2 MOR-1@PDA-cotton fabric g^{-1} soil can remove 43%–90% of the UV filters within 60 d of application in moist (> 50% moisture) soil. Notably, by eluting the adsorbed UV filters from the MOR-1@PDA-cotton fabric with methanol, the sorbent could be reused up to 5 times. Not least, the sorbent exhibited good stability in aqueous and acidic media, which is an essential feature for its safe disposal. Overall, the developed method proposes a new approach to *in situ* soil remediation, paving the way for future applications exploring nanosorbent materials incorporated into bulk supports.

Key Words: intraparticle mass transfer diffusion, MOR-1, nanosorbent, reusability, safe disposal, soil amendment, ultraviolet filter

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INTRODUCTION

Soil is a valuable, non-renewable natural resource that is subject to widespread degradation due to anthropogenic activities (Payá Pérez and Rodríguez, 2018). For this reason, soil amendment and remediation have been at the forefront of academic research for many years, leading to various technologies based on two distinct methodological approaches: *ex situ* and *in situ* treatments (Tomei and Daugulis, 2013; Kuppusamy *et al*., 2016a, b; Koul and Taak, 2018; Golia *et al*., 2024). *Ex situ* treatment (such as solid washing/flushing, wet oxidation, electrochemical separation, thermal treatment, and solidification/stabilization) is a highly invasive method that is based on excavating the soil, transporting it in specialized facilities, extracting the pollutants, and then restabilizing the soil so that it can be safely returned to the field (Tomei and Daugulis, 2013; de Voogt, 2016; Kuppusamy *et al*., 2016b; Hussain *et al*., 2022). Although efficient, *ex situ* methods entail high operational and investment costs and significant energy requirements (de Voogt, 2016; Hussain *et al*., 2022). *In situ* methods, on the other hand, are minimally invasive, enabling the remediation of soils in the field without needing soil transportation or using specific infrastructures, *e.g*., soil flushing tanks (Kuppusamy *et al*., 2016a; Koul and Taak, 2018; Payá Pérez and Rodríguez, 2018; Hussain *et al*., 2022). As a result, they present cost-effective and relatively straightforward alternatives to *ex situ* methods. Moreover, they offer high versatility since they can be utilized for contaminant removal (*e.g*., phytoremediation), degradation (*e.g*., bioremediation), or immobilization (*e.g*., sorbent amendments) (Kuppusamy *et al*., 2016a; Koul and Taak, 2018; Hussain *et al*., 2022).

Among *in situ* remediation methods, sorbent amendment is an appealing option that involves adding and mixing micro-sized particles of sorbent materials, such as activated carbon, biochar, zeolites, and metal-organic frameworks (MOFs), into the soil. These particles bind and immobilize contaminants effectively, reducing their infiltration and bioretention and lowering their uptake and bioavailability

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to living organisms (Derakhshan Nejad *et al*., 2018; Guo *et al*., 2020; Murtaza *et al*., 2023). The limitation of this method is that the micro-sized sorbent firmly adheres to soil particles and cannot be physically separated and recovered from the soil. Although this would not be an issue if contaminant immobilization on the sorbent was permanent, several studies have shown that the efficiency of sorbents to retain contaminants diminishes over time. This degradation can occur due to the degradation of the sorbent or (bio)chemical transformation of the pollutants on the sorbent surface, leading to leaching back into the soil and inducing adverse, mid- and long-term, ecotoxic effects on living organisms (Kupryianchyk *et al*., 2011; Wang *et al*., 2021).

Retrieval of the sorbent after deployment was suggested as a viable means to remove contaminants and prevent leaching. However, this is not technically feasible because most sorbent materials are produced in powder form (*i.e*., micro or nanoparticles), which firmly attach to and assimilate into the soil matrix. One proposed approach is to use magnetic sorbents that can be recovered from soil with an external magnetic field. In practice, however, the magnetic (micro/nano) sorbents also bind strongly to the soil particles and cannot be physically separated by magnetism. The dispersion of the soil-sorbent mixture in water and then magnetic separation of the sorbent is the only way to overcome this problem. However, excavating large amounts of soil and dispersing it in water tanks for *ex situ* treatment entails high costs and generates large amounts of secondary waste, such as significant volumes of potentially contaminated water (Chen *et al*., 2022; Yuan *et al*., 2023; Liu *et al*., 2024). A more effective and practical solution proposed by our group is using granular magnetic sorbents (Gouma *et al*., 2022b). Due to their large size, granular sorbents do not assimilate with soil particles. Thus, they can be directly retrieved from the solid matrix with an external magnetic field, producing a sorbent-free soil matrix. From our experience, the limitation of this method lies in the need for a relatively high amount of sorbent ($\geqslant$ 10%, weight/weight) to achieve efficient remediation and in the change of soil pH, which may affect the activity of living (micro)organisms and enhance the hydrolysis of organic compounds.

In this study, we proposed an *in situ* soil remediation method that relies on nanosorbent materials incorporated onto bulk solid supports for the minimally invasive, *in situ* removal of organic contaminants from soil. A MOF was used as a sorbent material due to its high surface area, good stability, and excellent adsorption properties. We have already shown that a zirconium (Zr)-based MOF, UiO-66-NH_3^+(MOR-1, $Zr_6O_4(OH)_4(NH_3^+\text{-BDC})_6Cl_6$, where BDC is terephthalate), immobilized on fabrics can effectively extract ultraviolet (UV) filters from water. Therefore, we used MOR-1 as an efficient sorbent for UV filters as model non-polar compounds, which exhibit a wide range of physicochemical properties (Gouma *et al*., 2022a). Cotton fabric sheets were utilized as bulk support for the MOF due to their lightweight nature, low cost, and availability in variable qualities. Additionally, cotton fabrics occupy minimal storage space and can be easily collected after use. By combining MOFs and cotton fabrics, we developed a hybrid sorbent and evaluated its use for remediation of non-polar persistent organic pollutants in soil. Moreover, based on the excellent stability and inertness of the MOF, post-treatment of the sorbent (reuse and disposal) was also evaluated. This study introduced a minimally invasive *in situ* soil remediation method that enabled the removal of pollutants from soil, instead of their immobilization, and paves the way towards the exploitation of bulk-supported nanosorbents for the improvement of soil quality with a procedure that combined ease of use and on-site capabilities.

MATERIALS AND METHODS

Materials

Cotton fabric sheets were purchased from local stores, washed with water and acetone, and air-dried. Zirconium chloride ($>$ 99.5%, metal basis), glacial acetic acid ($\geqslant$ 99.7%), and 2-aminoterephthalic acid (99%) were obtained from Alfa-Aesar, Germany. Six organic UV filters, *i.e*., 2-hydroxy-4-methoxybenzophenone (BZ3), 2-ethylhexyl 4-methoxycinnamate (EMC), 2-ethylhexyl 4-(dimethylamino) benzoate (EDP), 3-(4-methylbenzylidene) camphor (MBC), isoamyl 4-methoxycinnamate (IMC), and 2-ethylhexyl 2-cyano-3,3-diphenylacrylate (OCR), were used in this study, and their purity and suppler information are provided in Table I. High-performance liquid chromatography grade methanol and water were purchased from Scharlab, Spain. Anhydrous Na_2SO_3 was purchased from J.T. Baker Chemical, UK, and ethyl acetate ($>$ 99.5%) was procured from Honeywell, USA. The synthesis of polydopamine (PDA)-coated cotton fabrics decorated with MOR-1 (MOR-1@PDA-cotton fabrics) was performed according to the procedure described in our previous work (Gouma *et al*., 2022a).

Non-polluted soil was collected from the 20–25 cm soil layer of a remote area and air-dried. To remove debris and large particles, the soil was sieved through a 2-mm stainless steel sieve and manually milled for homogenization. The particle size distribution of the soil, determined by dry-sieving with stainless steel sieves, was: 1–2 mm 17.6%, 0.5–1 mm 38.4%, 0.25–0.5 mm 21.2%, 0.063–0.25 mm 15.4%, and $<$ 0.063 mm 7.4%. The other properties of the soil were as follows: electrical conductivity, 188 $\pm$ 21 μS cm^{-1}; pH, 7.6 $\pm$ 0.3; soil organic matter, 81 $\pm$ 17 g kg^{-1}; and $CaCO_3$, 160 $\pm$ 25 g kg^{-1}.

Contaminated soil was prepared by spiking a methanolic solution of UV filters (BZ3, IMC, MBC, OCR, EDP, and

TABLE I

Organic ultraviolet filters used in this study

Name	Abbreviation	Purity	Supplier
		%	
2-Hydroxy-4-methoxybenzophenone	BZ3	98	Sigma-Aldrich, Germany
2-Ethylhexyl 4-methoxycinnamate	EMC	99.8	Sigma-Aldrich, Germany
2-Ethylhexyl 4-(dimethylamino)benzoate	EDP	98	Sigma-Aldrich, Germany
3-(4-Methylbenzylidene)camphor	MBC	99.7	Guinama S.L., Spain
Isoamyl 4-methoxycinnamate	IMC	99.3	Haarmann and Reimer Parets del Vallés, Spain
2-Ethylhexyl 2-cyano-3,3-diphenylacrylate	OCR	> 98	F. Hoffman-La Roche Ltd., Switzerland

EMC) into the soil under mixing to achieve a concentration of 5 mg kg^{-1} for each UV filter (total 30 mg kg^{-1} for all UV filters). The slurry was initially aged overnight in an air-sealed vessel while mixed in an orbital shaker (100 r min^{-1}) and then dried under room conditions (*ca.* 18–20 °C, *ca.* 50%–60% humidity). The slurry was mixed with a glass rod to facilitate drying and homogenization, allowing UV filters to reach a pseudo-equilibrium with the soil.

MOR-1@PDA-cotton fabric characterization

Powder X-ray diffraction (PXRD) pattern of the synthesized MOR-1@PDA-cotton fabric was recorded on a diffractometer (Bruker, USA) with CuK_α radiation ($\lambda = 0.154\ 184$ nm). Fourier-transform infrared (FTIR) spectrum was collected on a Spectrum Two spectrometer (PerkinElmer, USA). Surface morphology was observed with a scanning electron microscope (SEM) (Thermo Fisher Scientific, USA).

Batch adsorption experiments of UV filters on MOR-1@ PDA-cotton fabrics

Rectangle MOR-1@PDA-cotton fabrics and PDA-coated cotton fabrics (PDA-cotton fabrics) (2.2 cm × 3.0 cm) with a surface area of 13.2 cm^2 (6.6 cm^2 on each side) were added in an aqueous solution containing 5 mg L^{-1} UV filter and stirred at 100 r min^{-1} for 30 min in an orbital shaker. At a given time interval, an aliquot of 100 μL solution sample was withdrawn and analyzed for UV filter with a high-performance liquid chromatograph (Shimadzu, Japan) composed of an LC-20AD high-pressure solvent delivery pump, a DGU-20A3 degasser, a CTO-10 A column oven, and an SPD-10AV UV/visible detector. Analysis was performed by injecting 20 μL sample in a thermostated (45 °C) Hypersil ODS C18 column (250 mm length, 4.6 mm inner diameter, 5 μm particle size) obtained from MZ Analysentechnick (Germany) under isocratic flow (1 mL min^{-1}) conditions using methanol and water at a mixing ratio of 75:25 (volume/volume) as a mobile phase. Peak area was recorded at 313 nm for all UV filters.

Adsorption kinetics was analyzed using the Ho-Mckay pseudo-second-order (PSO) kinetic model:

$$q_t = \frac{kq_{\mathrm{e}}^2 t}{1 + kq_{\mathrm{e}} t} \quad (1)$$

where q_t (mg cm^{-2}) and q_{e} (mg cm^{-2}) are the amounts of UV filter adsorbed on MOR-1@PDA-cotton fabric or PDA-cotton fabric at time t (min) and at equilibrium, respectively, and k (cm^2 mg^{-1} min^{-1}) is the PSO rate constant. The diffusion mechanism in the adsorption of UV filters on MOR-1@PDA-cotton fabric and PDA-cotton fabric was examined using the intraparticle diffusion (IPD) model of Weber-Morris:

$$q_t = Kt^{0.5} + C \quad (2)$$

where K (mg cm^{-2} min$^{-0.5}$) is the IPD rate constant and C (mg cm^{-2}) is an empirical parameter related to the thickness of the boundary layer.

Soil remediation experiments with MOR-1@PDA-cotton fabric

The efficiency of MOR-1@PDA-cotton fabric in removing UV filters from soil was optimized by varying sorbent surface area, soil moisture content, and remediation time. In each experiment, remediation efficiency was calculated as the concentration of UV filters remaining in the remediated soil. Experiments were performed in Amber glass vessels to avoid direct light exposure and minimize moisture fluctuations throughout the experiment, as occurs in natural soils (except for surface soil, which was directly exposed to light and air). Although UV filters are persistent organic compounds that are not readily biodegraded by microorganisms, NaN_3 was added to the soil as a biocide at 500 mg kg^{-1} to inhibit microbial activity and growth (Han *et al.*, 2015; Gouma *et al.*, 2022b). In this manner, the remediation efficiency of MOR-1@PDA-cotton fabric could be calculated unaffected by random variations in environmental conditions (light and moisture fluctuations and microbial degradation) that could lead to false positive results.

For the sorbent surface area experiment, MOR-1@PDA-cotton fabrics of surface areas from 6.3 to 50.2 cm^2 (or 0.32–2.51 cm^2 g^{-1} soil) were added to 20 g contaminated soils (50% moisture) for a remediation time of 10 d. For the soil moisture experiment, 50.2 cm^2 MOR-1@PDA-cotton fabrics were added to 20 g contaminated soils of 50% and 100% moisture for a remediation time of 10 d. For the remediation time experiment, 50.2 cm^2 MOR-1@PDA-cotton fabrics were added to 20 g contaminated soils (100% moisture) for 5–60 d of remediation. The cotton fabric was mixed with the soil and incubated. Weekly, a glass rod was used to plow the soil, and the gross weight of each vessel was measured to calculate moisture loss. When the gross weight decreased by more than 10% of the initial weight recorded at the beginning of the experiment, a small aliquot of distilled water was added dropwise and mixed with the soil to restore moisture content and maintain constant humidity throughout the remediation period. Finally, the MOR-1@PDA-cotton fabric sorbent was pulled out of the soil. Then, both the soil and the MOR-1@PDA-cotton fabric were dried in air. A schematic representation of the method is shown in Fig. S1 (see Supplementary Material for Fig. S1). The extraction of UV filters from the soil matrix was performed by ultrasound-assisted solvent extraction as described in our previous work (Gouma *et al*., 2022b).

Stability, reusability, and safe disposal evaluation of MOR-1@PDA-cotton fabric

After retrieving the MOR-1@PDA-cotton fabric from the soil, the UV filters were eluted with methanol after 15 min of agitation. Then, the PXRD and FTIR patterns of MOR-1@ PDA-cotton fabric were measured and compared to those of the pristine MOR-1@PDA-cotton fabric to evaluate sorbent stability. The reusability of the sorbent was evaluated by reusing the sorbent several times. To enable a direct comparison, 10 g of soil, spiked with the same UV filter concentration, was remediated with MOR-1@PDA-cotton fabric (50.2 cm^2) for 15 d. After use, the UV filters were eluted, and the sorbent was reused in new soil. The stability of UV filters adsorbed on MOR-1@PDA-cotton fabrics was evaluated by leaching tests to assess the potential hazards associated with the disposal of the UV filter-loaded sorbent phase. First, MOR-1@PDA-cotton fabrics were immersed in a 20-mL solution containing a mixture of UV filters (1 mg L^{-1} each UV filter) for 1 h under orbital shaking (150 r min^{-1}) to establish equilibrium. Then, the leaching of UV filters was examined by immersing the UV filter-loaded fabrics into i) distilled water, ii) a dilute acetic acid solution (pH *ca*. 4), and iii) a 0.05 mol L^{-1} NaOH solution while agitated (50 r min^{-1}) for 24 h.

RESULTS AND DISCUSSION

Characteristics of MOR-1@PDA-cotton fabrics

The efficiency of the synthetic method for immobilizing MOR-1 particles on cotton fabrics has been demonstrated and optimized in our previous works, along with extensive characterization data on the properties of the MOR-1-coated cotton fabrics (Gouma *et al*., 2022a; Pournara *et al*., 2022; Moisiadis *et al*., 2023). In this work, we only confirmed the successful synthesis through PXRD and FTIR analyses, while SEM evidenced the formation of MOR-1 particles. The diffraction peaks of MOR-1 at 2θ of 7.3°, 8.5°, and 12° corresponded to (111), (200), and (220) planes, respectively (Fig. 1a). The peaks at 13.5°, 15.3°, and 21.5° corresponding to pure cotton were present in the PDA-cotton fabrics (Gouma *et al*., 2022a). The characteristic FTIR peaks at 1 572 and 1 380 cm^{-1} corresponded to the asymmetric and symmetric stretching modes of the COO– group, respectively (Fig. 1b). The peaks at 761 and 656 cm^{-1} were assigned to the Zr–O bond (Yao *et al*., 2019). Finally, SEM images confirmed the successful immobilization of the octahedral MOR-1 particles on the cotton surface (Fig. 1c, d).

Thermogravimetric analysis of the MOR-1@PDA-cotton fabric showed that cotton fabric residues remaining after thermal treatment led to an irreproducible determination of the net amount of MOR-1 (as zirconium dioxide) that was deposited on the cotton. Since it was not possible to separate cotton residues from zirconium dioxide, the amount of MOR-1 deposited on cotton was determined gravimetrically by weighing the cotton sheet before and after the deposition of MOR-1. Although this procedure is not as accurate as thermogravimetric analysis, we calculated the average weight from 200 individual MOR-1@PDA-cotton fabrics to accomplish a good approximation. Through this procedure, the estimated amount of MOR-1 deposited per 25.75 cm^2 surface area of cotton was 25.6 $\pm$ 5.0 mg. This means that approximately 1.00 $\pm$ 0.04 mg MOR-1 was deposited per 1 cm^2 cotton fabric, indicating a relatively high surface coverage of the cotton sheets, which is advantageous for remediation. The Brunauer-Emmett-Teller specific surface area of MOR-1@PDA-cotton fabric, *ca*. 581 m^2 g^{-1} (Pournara *et al*., 2022), however, was significantly lower than that of MOR-1 powder, *ca*. 1 100 m^2 g^{-1} (Rapti *et al*., 2016), possibly because the PDA coating may partially cover the immobilized MOR-1 particles. Moreover, the water contact angle of the modified cotton was less than 20°, indicating the high hydrophilicity of the material.

UV filter-adsorption performance of MOR-1@PDA-cotton fabric

Before its application to soil remediation, the adsorption kinetics and efficiency of the MOR-1@PDA-cotton fabric were evaluated using batch adsorption experiments and compared to PDA-cotton fabric and pure cotton. For pure cotton, adsorption was trivial and irreproducible. Therefore, no kinetic data could be extrapolated. The kinetic data for the adsorption of UV filters on MOR-1@PDA-cotton fabric and PDA-cotton fabric are shown in Fig. 2. For both sorbents, adsorption was very fast, reaching equilibrium within 5 min, which is a significant advantage for environmental

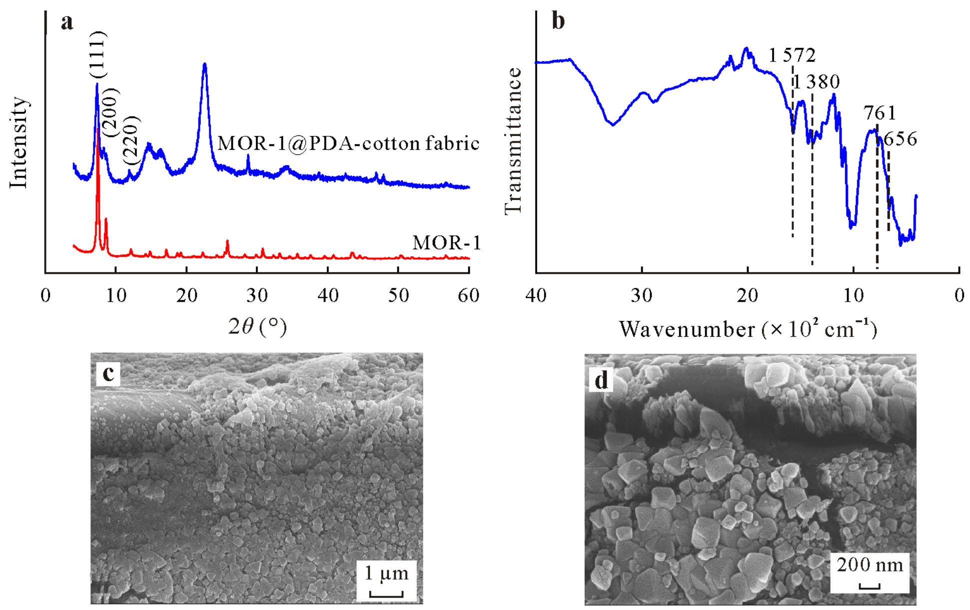

Fig. 1 Powder X-ray diffraction spectra of a Zr-based metal-organic framework (MOR-1) and polydopamine (PDA)-coated cotton fabric decorated with MOR-1 (MOR-1@PDA-cotton fabric) (a), Fourier-transform infrared spectrum of MOR-1@PDA-cotton fabric (b), and scanning electron microscope images of MOR-1@PDA-cotton fabric (c and d).

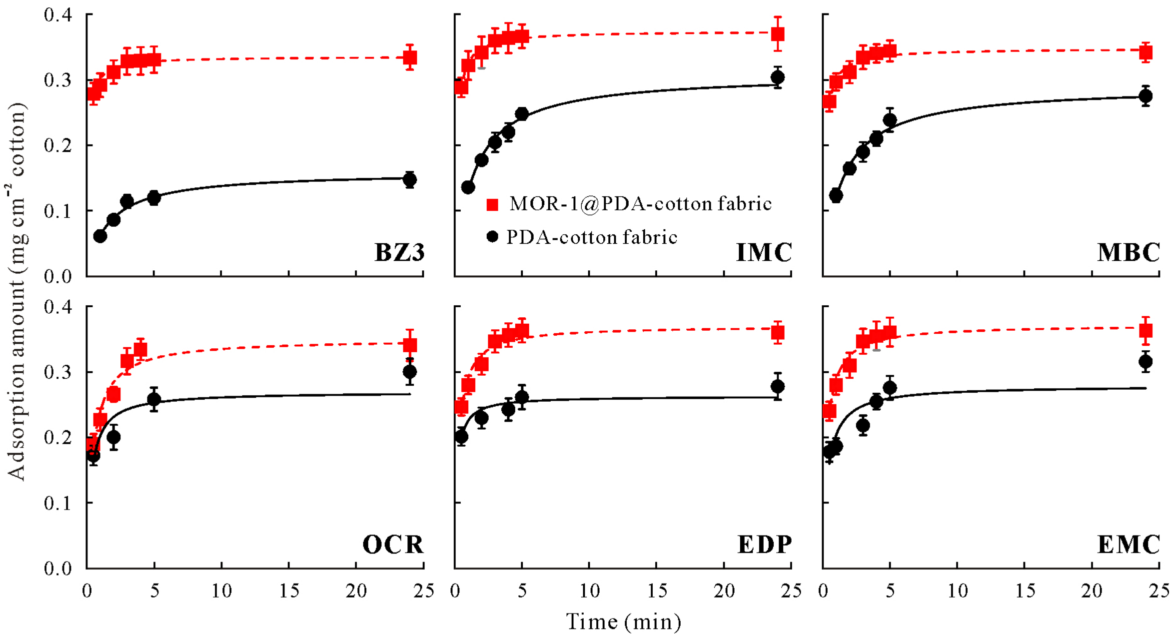

Fig. 2 Adsorption kinetics of six ultraviolet filters, 2-hydroxy-4-methoxybenzophenone (BZ3), isoamyl 4-methoxycinnamate (IMC), 3-(4-methylbenzylidene) camphor (MBC), 2-ethylhexyl 2-cyano-3,3-diphenylacrylate (OCR), 2-ethylhexyl 4-(dimethylamino)benzoate (EDP), and 2-ethylhexyl 4-methoxycinnamate (EMC), on polydopamine (PDA)-coated cotton fabric (PDA-cotton fabric) and PDA-cotton fabric decorated with a Zr-based metal-organic framework (MOR-1@PDA-cotton fabric) and their fitting with the Ho-Mckay pseudo-second-order kinetic model. Error bars are standard deviations of the means ($n = 3$).

remediation. Except for the high affinity of the sorbent for UV filters, adsorption kinetics may have been improved by the fabric substrate that facilitates the flow of water through its large pores (60–100 μm) without causing redirection or reverse flow, as is the case with impermeable substrates or solid sorbents (Kabir *et al*., 2017), facilitating mass transfer (Kabir *et al*., 2017; Gouma *et al*., 2022a). The Ho-Mckay PSO kinetic model could optimally describe the adsorption kinetics for all six UV filters. In this kinetic model, the adsorption rate depends on the adsorption capacity rather than the adsorbate concentration. Hence, this model can also estimate the equilibrium adsorption capacity (Wankasi, 2013; Sahoo and Prelot, 2020). The data in Table II show that the equilibrium adsorption capacities of the examined UV filters

TABLE II

Measured and model-estimated adsorption amounts at equilibrium (q_e) and parameter values of the Ho-Mckay pseudo-second-order (PSO) kinetic model and the intraparticle mass transfer diffusion (IPD) model of Weber-Morris for the adsorption of ultraviolet (UV) filters (5 mg L^{-1}) on polydopamine (PDA)-coated cotton fabrics decorated with a Zr-based metal-organic framework in an aqueous solution

UV filter[a)]	Measured q_e	PSO kinectic mode[b)]			IPD model[c)]			
					1st stage		2nd stage	
		q_e	k	R^2	K	R^2	K	R^2
	—— mg cm^{-2}	——	cm^2 mg^{-1} min^{-1}		mg cm^{-2} $min^{-0.5}$		mg cm^{-2} $min^{-0.5}$	
BZ3	0.34	0.33	26.2	0.93	0.04	0.97	0.002	0.89
EDP	0.36	0.37	9.9	0.95	0.08	0.97	–[d)]	–
EMC	0.36	0.37	9.2	0.97	0.08	0.96	0.001	0.99
IMC	0.37	0.37	17.4	0.99	0.05	0.91	0.001	0.99
MBC	0.34	0.34	18.1	0.96	0.05	0.94	–	–
OCR	0.34	0.35	6.1	0.94	0.11	0.99	0.002	0.99

[a)] BZ3 = 2-hydroxy-4-methoxybenzophenone; EDP = 2-ethylhexyl 4-(dimethylamino)benzoate; EMC = 2-ethylhexyl 4-methoxycinnamate; IMC = isoamyl 4-methoxycinnamate; MBC = 3-(4-methylbenzylidene)camphor; OCR = 2-ethylhexyl 2-cyano-3,3-diphenylacrylate.
[b)] k = PSO rate constant; R^2 = coefficient of determination.
[c)] K = IPD rate constant.
[d)] The fitting was represented by a straight line, so there was no 2nd stage.

ranged from 0.34–0.37 mg cm^{-2} of MOR-1@PDA-cotton fabric. Compared to PDA-cotton fabric (Table SI, see Supplementary Material for Table SI), the adsorption capacity in the presence of MOR-1 increased by 12%–56%, proving the contribution of MOR-1 in improving the removal efficiencies. As 1 cm^2 of cotton fabric contained approximately 1 mg MOR-1, the adsorption capacity of 0.34–0.37 mg cm^{-2} cotton fabric is very satisfactory considering that a 1 000-cm^2 cotton fabric or 1 g MOR-1 may adsorb 340–370 mg UV filters.

When the adsorption data were fitted with the intraparticle mass transfer diffusion model of Weber-Morris (Eq. 2), q_t as a function of $t^{0.5}$ was not represented by a straight line (Fig. S2, see Supplementary Material for Fig. S2), meaning that intraparticle diffusion was not the rate-limiting step in the adsorption of UV filters. Since the intraparticle diffusion rate constant (K) in the first stage was higher than that in the second stage (Table II), the second stage (*i.e.*, film diffusion) was the rate-limiting step in the adsorption process, which means that the external surface of the sorbent was the primary site for adsorption. This is reasonable since the sizes of UV filters were estimated to be $\geqslant$ 1.0 nm (Fig. S3, see Supplementary Material for Fig. S3), which were larger than the pores of MOR-1 (0.8–0.9 nm) (Rapti *et al*., 2016).

The fitting of the kinetic data to the Ho-Mckay PSO kinetic model and the fact that adsorption occurred on the external surface of the sorbent can be attributed mainly to the NH_2-BDC^{2-} ligands of MOR-1 and the PDA reactive sites, which are all capable of forming strong hydrogen bonds and enabling π-stacking interactions (Ma *et al*., 2013; Hu *et al*., 2015; Pournara *et al*., 2022; Li *et al*., 2023). Pearson correlation analysis of the maximum adsorption capacities (q_{max}) and the PSO rate constants (k) with the logarithm of the partition coefficients ($\log K_{ow}$) of the UV filters indicated that less hydrophobic UV filters exhibited faster adsorption kinetics ($r = -0.87$, $P < 0.05$) and that adsorption capacity was not related to hydrophobicity. On the other hand, the positive correlations observed for both q_{max} ($r = 0.49$, $P > 0.05$) and k ($r = 0.45$, $P > 0.05$) of PDA-cotton fabric (although not statistically significant) suggested that hydrophobic interactions also contributed to the adsorption of UV filters to PDA-cotton fabric. Even though hydrophobic interactions are relatively more potent than other weak intermolecular forces and are spontaneous (Israelachvili, 2011), the high surface area of MOR-1 (*ca*. 581 m^2 g^{-1} for the MOR-1 immobilized on cotton fabric) offered a significant number of available reactive sites for the adsorption of UV filters by weak intermolecular forces (hydrogen bonds and π-stacking interactions), which increased the adsorption capacity.

Performance of MOR-1@PDA-cotton fabrics in soil remediation

The removal efficiency of UV filters in relation to the surface area of the MOR-1@PDA-cotton fabrics is depicted in Fig. 3a. From these data, it can be inferred that increasing the surface area of the sorbent from 6.3 to 50.2 cm^2 per 20 g of soil (or 0.32–2.51 cm^2 g^{-1} soil), the removal efficiency of UV filters improved for surface area up to 1.88 cm^2 g^{-1} soil. This was also verified by analysis of variance (ANOVA) analysis, which showed that there was a significant ($P < 0.01$) difference in the mean removal efficiency with increasing sorbent area ($F = 18.4 > F_{critical/0.01} = 4.43 > F_{critical/0.05} = 2.87$). This was due to the larger contact area of the sorbent with the soil and the higher mass of MOR-1, which increased the available adsorption sites and reached a plateau at higher values.

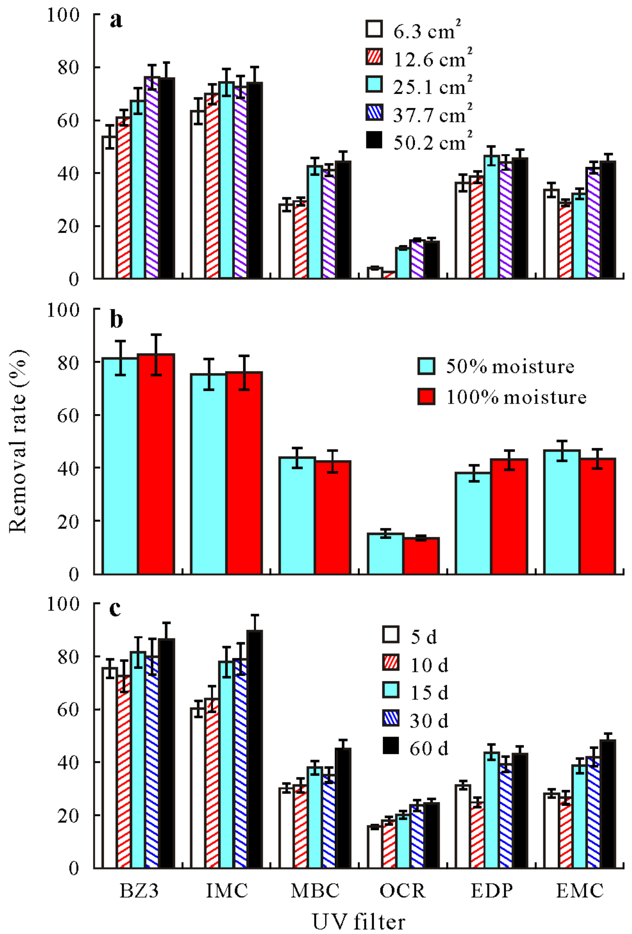

Fig. 3 Effects of the surface area of the sorbent, polydopamine-coated cotton fabric decorated with a Zr-based metal-organic framework (a), soil moisture content (b), and remediation time (c) on the removal rates of six ultraviolet (UV) filters from a UV filter-spiked soil in laboratory incubation experiments. The concentration of each UV filter was 5 mg kg^{-1}. Error bars are standard deviations of the means (n = 3). BZ3 = 2-hydroxy-4-methoxybenzophenone; IMC = isoamyl 4-methoxycinnamate; MBC = 3-(4-methylbenzylidene)camphor; OCR = 2-ethylhexyl 2-cyano-3,3-diphenylacrylate; EDP = 2-ethylhexyl 4-(dimethylamino)benzoate; EMC = 2-ethylhexyl 4-methoxycinnamate.

Soil moisture is an essential parameter because it serves as an interface that enables the mass transfer of contaminants from soil particles to the sorbent. Therefore, the effect of soil moisture was evaluated at two levels to assess its impact on the remediation efficiency. The results presented in Fig. 3b showed that moisture had no significant ($P > 0.05$) influence on the removal efficiency. This is advantageous because it indicates that the sorbent can be used effectively over various soil moisture conditions, including water-saturated soils such as those found in wetlands, river or lake shores, and sediments.

Finally, the effect of remediation time was investigated. The remediation efficiency improved significantly($P < 0.05$) with increasing incubation time for all UV filters (Fig. 3c). Under the optimum conditions, a removal rate of 43%–90% can be achieved for most UV filters, except for the highly hydrophobic OCR ($\log K_{\rm ow}$ = 6.9), whose removal rate was only 25%. In agreement with the previous discussion, the removal efficiency was negatively correlated to the $\log K_{\rm ow}$ of the UV filters ($r = -0.97$, $P < 0.05$), suggesting that MOR-1@PDA-cotton fabric is more effective in the adsorption of less hydrophobic compounds. Therefore, the different efficiencies in removing the UV filters shown in Fig. 3 can be attributed to their hydrophobicity.

Another important observation was that, compared to the control treatments (contaminated soil incubated for the same time intervals without MOR-1@PDA-cotton fabric), no significant change in soil pH (ΔpH $\leqslant$ 0.5) was observed during the remediation period. This is advantageous compared to other sorbents because it does not induce secondary reactions with organic compounds (*e.g.*, protonation at acidic pH or hydrolysis under alkaline conditions) that may alter the interaction of the contaminants with the soil, the properties of the sorbent, and the efficiency of remediation (Chien *et al.*, 2018; Neina, 2019).

Reusability, stability, and safe disposal of MOR-1@ PDA-cotton fabric

The PXRD patterns and the FTIR spectra showed that the diffraction peaks and the FTIR bands of MOR-1 were maintained throughout the remediation period, indicating that MOR-1 retained its stability (Fig. S4, see Supplementary Material for Fig. S4).

In addition, the sorbent can be efficiently reused 5 times without losing efficiency for most UV filters (Fig. 4). According to ANOVA, there was no difference ($P > 0.05$) in the mean extraction efficiency across 5 reuses, which is advantageous as the sorbent can be reused to reduce the overall cost

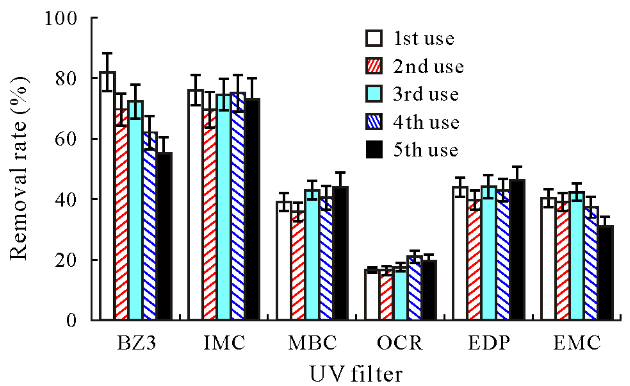

Fig. 4 Removal rates of six ultraviolet (UV) filters from UV filter-spiked soils during the 5-time reuse of the sorbent, polydopamine-coated cotton fabric decorated with a Zr-based metal-organic framework, in a laboratory incubation experiment. The concentration of each UV filter was 5 mg kg^{-1}. Error bars are standard deviations of the means (n = 3). BZ3 = 2-hydroxy-4-methoxybenzophenone; IMC = isoamyl 4-methoxycinnamate; MBC = 3-(4-methylbenzylidene)camphor; OCR = 2-ethylhexyl 2-cyano-3,3-diphenylacrylate; EDP = 2-ethylhexyl 4-(dimethylamino)benzoate; EMC = 2-ethylhexyl 4-methoxycinnamate.

of the application. After the UV filter-loaded MOR-1@PDA-cotton fabrics were immersed in distilled water, dilute acetic acid solution, and NaOH solution for 24 h, no leaching of UV filters was observed in distilled water and the diluted acetic acid solution. In NaOH, on the other hand, most UV filters leached into the solution due to NaOH digestion of the MOR-1 (Chu *et al*., 2020). Based on these results, it can be inferred that storing and disposing of contaminated cotton in non-alkaline media poses no threat to the environment.

CONCLUSIONS

This work demonstrated a new remediation method that combines the principle of *in situ* removal with sorbent amendment. Incorporating nanosorbent materials onto bulk supports addresses the challenges associated with adding nanosorbents to soil by enabling not only the easy addition of the sorbent medium into the soil to adsorb the contaminants, but also its retrieval, thus accomplishing both the adsorption of contaminants from soil and the removal of the contaminant-loaded sorbent. Using cotton fabrics decorated with MOFs, we demonstrated the remediation of soils contaminated with hydrophobic organic compounds, achieving satisfactory removal efficiencies (43%–90%) within a relatively short period (60 d) with approximately 0.2 m^2 sorbent-decorated fabric kg^{-1} soil. The remediation efficiency or the sorbent surface area requirement could likely be improved by mixing the fabrics frequently to maximize contact with soil using simple mechanical means such as those used for plowing. Notably, the sorbent can be reused several times (5 or more for some analytes), reducing remediation cost, or safely disposed of without specialized treatment. Another advantage of bulk-supported nanosorbents is that they may be used as a protective layer to sorb contaminants and prevent future pollution passively. Both applications (remediation and prevention) may be particularly interesting for managing sediments, where *ex situ* treatment methods have been the only available option, often with limited success due to the secondary implications in water quality and biota. Further research on other supported nanosorbents, their influence on the mobility of the remaining contaminants, and their use as a protective layer may unravel the full potential of the proposed remediation method.

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.

SUPPLEMENTARY MATERIAL

Supplementary material for this article can be found in the online version.

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