

Removal of multiple contaminants from agricultural water using versatile filtration media

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Abstract

Agricultural runoff contains a mixture of particulate and dissolved contaminants that are difficult to remove simultaneously using conventional filtration media. Here, we developed multifunctional reactive filter media by functionalizing sand with Fe-, Al-, and Mg-based phases, with Mg recovered from mine tailings through acid dissolution. Seven modified media were compared with unmodified sand using real agricultural runoff in column filtration experiments. The modified media consistently outperformed unmodified sand. Phosphorus removal reached 99%, producing effluent concentrations below 0.5 mg P L⁻¹, whereas total organic carbon and turbidity removals reached 89% and 95%, respectively. The media also retained dissolved metals. Among the tested materials, the S-Mg-Al-Fe medium achieved the highest overall performance, with an initial nitrate removal of approximately 74% and >99% glyphosate removal. Repeated filtration experiments showed sustained treatment performance over 20 filtration cycles, whereas pH-dependent tests and surface characterization revealed a chemically heterogeneous interface, suggesting the contribution of complementary contaminant-retention mechanisms. These findings demonstrate that multicomponent surface functionalization can transform conventional sand into a multifunctional filtration medium capable of simultaneously removing diverse contaminants from agricultural waters. The study further illustrates how mine-derived materials can be integrated into decentralized treatment technologies, linking water quality improvement with resource recovery.

Keywords: Agricultural waters, Modified sand, Filter media, Mine tailings, Phosphorus removal, Organic matter removal, Dissolved metals, Adsorption.

Introduction

Diffuse pollution from agricultural activities represents a major cause of surface-water degradation worldwide. Intensive agricultural practices promote the simultaneous transport of nutrients, dissolved organic matter, suspended solids, and metals into aquatic systems, contributing to eutrophication, water-quality deterioration, and biodiversity loss¹⁻³. In agricultural watersheds, pesticides can also be transported to surface waters, raising additional concerns for water quality⁴.

Given their diffuse nature and large volumes, agricultural waters often remain untreated before reaching receiving environments. Consequently, there is a growing need for decentralized treatment technologies that can address multiple contaminants under variable field conditions while limiting operational demands. Passive treatment systems have attracted increasing attention because of their simplicity and suitability for decentralized implementation^{5,6}.

Granular sand filtration is widely used for water treatment because of its simplicity, low cost, and operational robustness. Although conventional sand filtration efficiently removes suspended particles, its performance for dissolved contaminants remains limited due to the low chemical reactivity of silica surfaces^{7,8}. This limitation represents a major challenge for the treatment of agricultural waters, where phosphorus, dissolved organic matter, and metals are often present in soluble forms.

To enhance the reactivity of granular filtration systems, several studies have investigated the modification of filtration media using metal-based active phases. Recent studies have highlighted the potential of passive treatment systems incorporating metal (hydr)oxide-based reactive materials to enhance the retention of dissolved contaminants in runoff waters and support decentralized water treatment applications^{5,6}. Iron (Fe)- and aluminum (Al)-based materials exhibit strong affinities toward phosphorus and dissolved metals through adsorption and precipitation mechanisms⁹⁻¹¹. In addition, multifunctional metal oxide systems have demonstrated promising capacities for the simultaneous removal of diverse contaminants¹². However, most studies have focused on single- or binary-component systems, and the potential complementary roles of multiple active phases in hybrid filtration media remain insufficiently understood.

Magnesium-rich materials derived from mine tailings may also serve as reactive amendments while providing a pathway for the beneficial reuse of mineral residues. Acid dissolution releases Mg^{2+} that can be incorporated during media preparation and may contribute to surface reactions or mineral precipitation under suitable conditions^{11,13}. However, whether Mg, Fe, and Al can be combined to create multifunctional filtration media capable of retaining chemically diverse contaminants under realistic conditions remains largely unresolved.

Here, we asked whether multicomponent surface functionalization could convert conventional sand into a reactive interface capable of retaining both particulate matter and chemically diverse dissolved contaminants. A filtration system combining Fe-, Al-, and Mg-based phases, with Mg partly derived from mine tailings, was developed for this purpose (Fig.1). Seven modified media were compared with unmodified sand for the removal of turbidity, total organic carbon,

phosphorus, and dissolved metals from real agricultural runoff. Nitrate and glyphosate removal were then examined using the best-performing medium (S-Mg-Al-Fe). Repeated filtration over 20 cycles, pH-dependent tests, rinsing experiments, and SEM-EDS and XPS analyses were used to evaluate performance persistence, chemical stability, and surface properties. Rather than isolating the contribution of individual components, this study evaluates whether multicomponent functionalization creates complementary contaminant-retention pathways. More broadly, this work explores multicomponent surface functionalization as a strategy for transforming conventional granular media into reactive interfaces for decentralized water treatment.

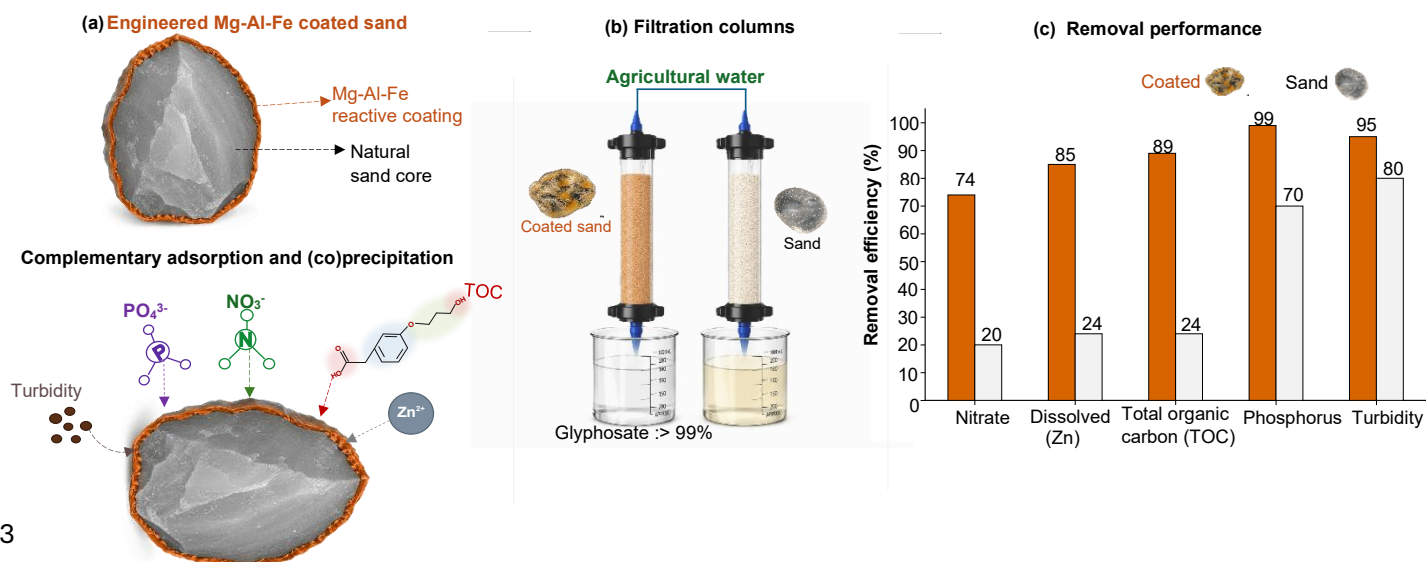


Fig.1. Concept and performance of the Mg–Al–Fe-modified sand. **(a)** Schematic illustration of the engineered Mg–Al–Fe-coated sand highlighting the reactive coating and the simultaneous removal of phosphorus, nitrate, dissolved metals, total organic carbon (TOC), and suspended solids. **(b)** Photograph of laboratory-scale column filtration systems packed with Mg–Al–Fe-modified and unmodified sand treating agricultural water. **(c)** Comparison of the removal efficiencies for turbidity, phosphorus, nitrate, total organic carbon (TOC), and dissolved metals, demonstrating the superior performance of the Mg–Al–Fe-modified sand.

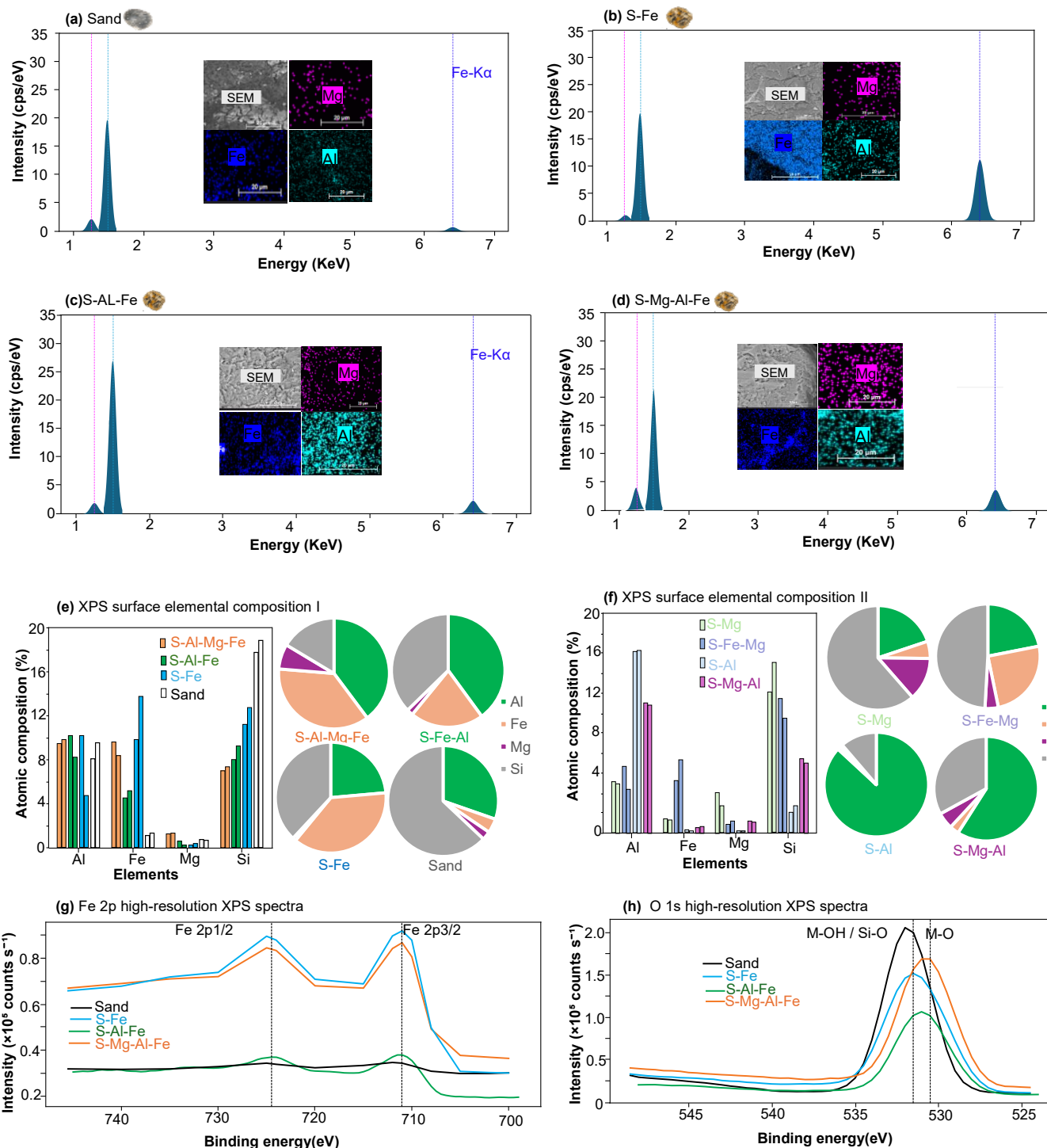
Results and Discussion

Surface characterization of the optimized filtration medium

The morphology, elemental composition, and surface chemistry of the filtration media were characterized using SEM-EDS and XPS (Fig.2). SEM images revealed substantial morphological changes following surface functionalization. Compared with the relatively smooth surface of unmodified sand, the modified media exhibited rougher and more heterogeneous surfaces, consistent with the deposition of reactive phases on the silica substrate. Similar surface transformations have been reported following the deposition of metal-(hydr)oxide coatings on granular filtration materials^{14,15}. EDS spectra and elemental mapping confirmed the presence of Fe, Al, and Mg and showed that these elements were distributed across the analyzed regions of the modified grains. Although EDS is inherently semi-quantitative and spatially limited, the observed distributions support the successful incorporation of these elements onto the sand surface. Similar elemental patterns have been associated with reactive surface layers in engineered filtration media^{14,16}.

XPS analysis further confirmed surface enrichment in Fe, Al, and Mg relative to unmodified sand. High-resolution spectra provided additional insight into the chemical environments of the surface species. The Fe 2p spectra exhibited signals in the 710-725 eV region consistent with Fe-containing (hydr)oxide phases, whereas only weak Fe-related signals were observed for unmodified sand. The O 1s spectra contained contributions in the 530-532 eV region that can be assigned to metal-oxygen (M-O), siloxane (Si-O-Si), and hydroxylated surface groups (M-OH/Si-OH). Such hydroxylated, metal-enriched surfaces can provide reactive sites for ligand exchange, electrostatic interactions, and surface complexation^{11,15}. Taken together, the SEM-EDS and XPS results indicate the formation of a chemically heterogeneous reactive interface incorporating Fe-, Al-, and Mg-based surface functionalities. These characteristics are consistent with the existence of complementary contaminant-retention pathways, although the specific contribution of each element to the removal of individual contaminants cannot be resolved from these analyses alone.

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Fig.2. (a–d) EDS spectra and elemental maps of Mg, Al and Fe for Sand, S-Fe, S-Al-Fe and S-Mg-Al-Fe, with the corresponding SEM images. (e–f) Surface elemental composition determined by XPS for the eight filter media; values represent the mean of duplicate measurements ($n = 2$). (g–h) High-resolution XPS spectra of the Fe 2p and O 1s regions for the three best-performing filter media (S-Fe, S-Al-Fe and S-Mg-Al-Fe) and the unmodified Sand control, revealing the chemical environments of Fe-, Si- and O-containing surface species.

Overall filtration performance of modified media

The filtration performance of the different media was evaluated using real agricultural runoff (Fig. 3). Across the tested operating conditions, all modified media outperformed unmodified sand for turbidity, total organic carbon (TOC), phosphorus, and dissolved metals. Media containing combined Fe, Al, and Mg phases generally exhibited the highest overall treatment performance across the measured parameters.

Effluent turbidity was substantially reduced by all modified media (Fig. 3a), with removal efficiencies ranging from 79 to 95% (maximum 95% for S–Mg–Al–Fe), compared with 57% for unmodified sand. These values fall within the upper range reported for functionalized granular filters under runoff conditions^{7,8} and are consistent with enhanced particle retention following surface functionalization. A similar trend was observed for TOC (Fig. 3b), where removal efficiencies ranged from 31 to 70% (maximum 70% for S–Mg–Al–Fe), compared with 25% for unmodified sand. This behavior is consistent with interactions between dissolved organic matter and hydroxylated Fe- and Al-containing surfaces^{13,17,18}.

Phosphorus removal was particularly effective (Fig. 3c), reaching 96–99% (maximum 99% for S–Mg–Al–Fe), compared with 70% for unmodified sand. These performances are comparable to or exceed those reported for iron-modified sands^{9,19}. Similar phosphorus removal performance was reported by Que-Trépanier et al.²⁰ using Fe-modified recycled glass media for agricultural drainage water treatment. Together with the findings of Lapointe et al.²¹, these observations support the effectiveness of metal-functionalized granular media for phosphate retention. Adsorption onto Fe- and Al-(hydr)oxide surfaces is a plausible mechanism, whereas Mg-associated precipitation may also contribute; however, this pathway was not isolated experimentally.

The removal of dissolved metals (Fig. 3d) also improved substantially. Fe concentrations decreased by 37–73% depending on the medium (maximum 73% for S–Al), compared with 17% for unmodified sand, whereas Zn removal ranged from 56 to 87% (maximum 87% for S–Mg–Al–Fe), compared with 24% for unmodified sand. Aluminium was released from unmodified sand (–15% removal) and, to a lesser extent, from S–Al (–4%), whereas the other modified media achieved removal efficiencies of up to 83%. These trends are consistent with metal immobilization through adsorption and surface complexation^{22,23}. Overall, the Fe–Al–Mg combinations provided the most balanced performance across the measured parameters. The results show that multicomponent surface functionalization can transform weakly reactive sand into a multifunctional reactive interface capable of retaining chemically diverse contaminants. Adsorption, surface complexation, particle retention, and precipitation represent plausible

complementary retention pathways^{24,25}, consistent with the multifunctional treatment materials reported by Abi Farraj et al.²⁶.

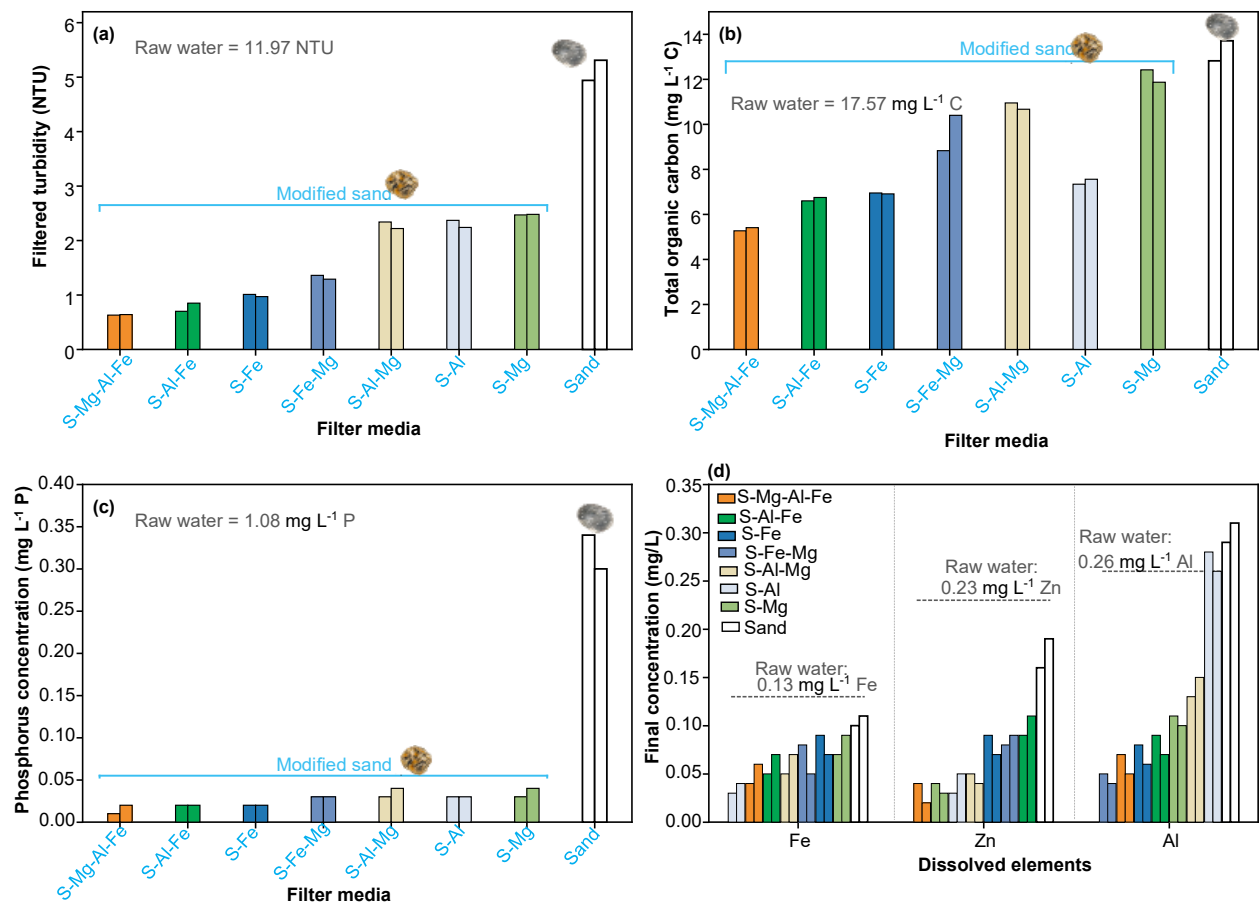


Fig. 3. Removal efficiencies for **a**, turbidity; **b**, total organic carbon (TOC); **c**, total phosphorus; and **d**, dissolved metals (Fe, Zn and Al) after filtration of real agricultural runoff through unmodified sand and seven modified sand media. The media were functionalized using Fe-, Al- and Mg-based phases, with Mg partly derived from mine tailings. Bars represent the mean of duplicate experiments (n = 2), and individual replicate values are shown as separate data points. Negative removal values indicate net release from the filtration medium.

Selection and breakthrough behaviour of optimized filtration media

The persistence of treatment performance was evaluated over 20 successive filtration cycles using normalized concentrations (C/C_0) (Fig. 4). Breakthrough curves provide a dynamic assessment of fixed-bed filtration and adsorption systems by describing the evolution of effluent concentrations relative to influent conditions^{27,28}. Although no universal breakthrough criterion exists, $C/C_0 \approx 0.5$ is commonly used as an operational indicator of substantial performance decline and partial media saturation.

The 20-cycle filtration experiments revealed clear differences in treatment persistence between unmodified sand and the selected modified media (S-Fe, S-Al-Fe, and S-Mg-Al-Fe). While unmodified sand showed progressive performance deterioration, the modified media maintained substantially lower C/C_0 values throughout the experimental period. The evolution of C/C_0 over successive cycles provides insight into the persistence of treatment performance under repeated loading conditions. Differences among media may reflect variations in particle retention, physicochemical interactions, and the availability of reactive surface sites within the porous media^{25,29}. Because complete breakthrough was not observed for several media, the results provide an assessment of treatment persistence within the tested window rather than a determination of ultimate media capacity or service life.

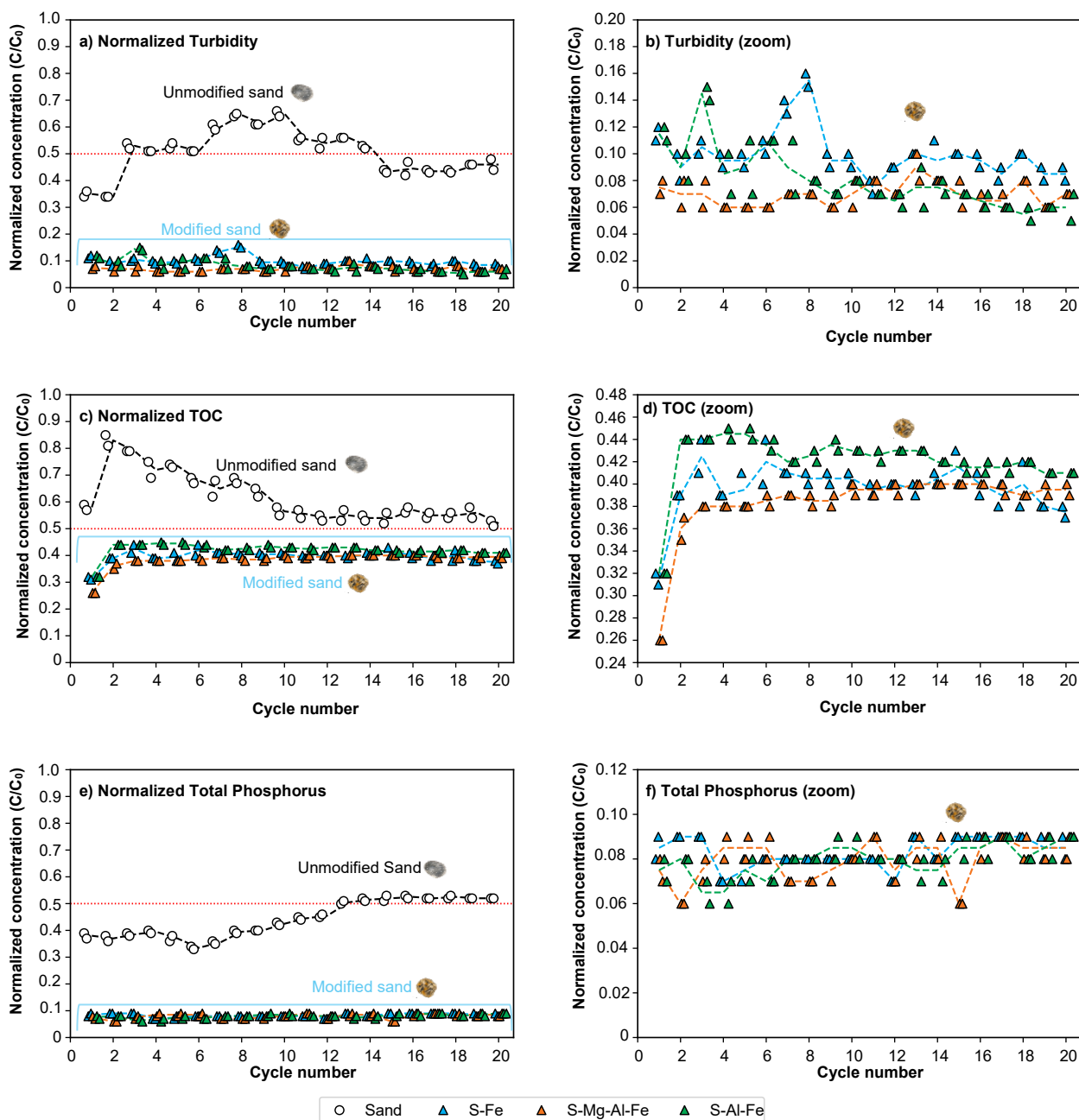
For turbidity (Fig. 4a-b), unmodified sand rapidly approached $C/C_0 \approx 0.5$, indicating a progressive loss of particle-retention capacity. In contrast, S-Fe, S-Al-Fe, and S-Mg-Al-Fe maintained low normalized concentrations ($C/C_0 \approx 0.10$ – 0.15) throughout the experiment, with no pronounced upward trend. These results indicate sustained particle retention during repeated operation and are consistent with previous observations for surface-functionalized granular filtration materials^{7,8}. A similar pattern was observed for TOC (Fig. 4c-d). For unmodified sand, C/C_0 gradually increased to approximately 0.55–0.65, whereas the modified media stabilized at values of approximately 0.35–0.45 following an initial equilibration period. The lower and more stable normalized concentrations observed for the modified media indicate more persistent TOC retention within the investigated period. This behaviour is consistent with interactions between dissolved organic matter and hydroxylated Fe- and Al-containing surface functionalities.^{11,13,15} However, the results do not permit determination of the total adsorption capacity of the media.

The most pronounced differences were observed for phosphorus (Fig. 4e-f). Unmodified sand approached C/C_0 values of approximately 0.40–0.50, whereas the modified media maintained very low normalized concentrations ($C/C_0 \approx 0.03$ – 0.10) throughout the experiment, without evidence of phosphorus breakthrough during the 20-cycle test. Reported breakthrough criteria for phosphate removal by Fe-based materials vary depending on operating conditions and performance objectives⁹. The low normalized concentrations observed here therefore indicate that phosphorus breakthrough was substantially delayed relative to unmodified sand within the experimental window, although they do not define the ultimate treatment capacity or field-scale lifetime of the media. Among the tested materials, S-Mg-Al-Fe consistently exhibited the lowest normalized

221 concentrations and the greatest resistance to performance decline across the evaluated parameters.
222 The improved persistence observed for the Fe–Al–Mg medium is consistent with the presence of
223 multiple active phases contributing to contaminant retention during repeated operation.

224 Overall, S–Fe, S–Al–Fe, and S–Mg–Al–Fe maintained the removal of suspended matter, dissolved
225 organic matter, and phosphorus more effectively than unmodified sand throughout the 20-cycle
226 experiment. These findings demonstrate that multicomponent surface functionalization
227 substantially improves treatment persistence under repeated loading conditions. The observed
228 behaviour is consistent with complementary contaminant-retention pathways operating at
229 multicomponent reactive interfaces^{13,29}.

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Dashed lines show average values; individual points show duplicates. Red dotted line indicates $C/C_0 = 0.5$.

Fig. 4. Breakthrough behaviour of the selected filtration media. **(a,b)** Turbidity, **(c,d)** total organic carbon (TOC), and **(e, f)** total phosphorus (TP) expressed as normalized concentrations (C/C_0) over successive filtration cycles, with the corresponding enlarged views. The red dashed line ($C/C_0 = 0.5$) represents the commonly adopted breakthrough threshold. Experimental conditions: agricultural runoff collected in Quebec (Canada); turbidity 12.0 NTU, TOC 23.7 mg L⁻¹, TP 4.86 mg L⁻¹, initial pH 7.85, flow rate 3 mL min⁻¹ (1 m h⁻¹), and 20 filtration cycles. Data are presented as mean ± standard deviation ($n = 2$).

Effect of pH on filtration performance and media stability

pH strongly influenced the performance of the selected filtration media for turbidity, phosphorus, and total organic carbon (TOC) removal (Fig. 5). The observed trends reflect the pH-dependent surface chemistry of metal (hydr)oxides, including protonation and deprotonation of surface hydroxyl groups and changes in electrostatic interactions with colloidal and dissolved species.

For turbidity (Fig. 5a), the modified media generally maintained high removal efficiencies (>85–90%) across a broad pH range, indicating stable filtration performance and effective colloidal retention. A pronounced deviation was observed for S–Fe at pH 10, where residual turbidity increased sharply and exceeded the raw-water value (~14 NTU). This behaviour may result from the deprotonation of $\equiv\text{Fe}-\text{OH}$ groups to $\equiv\text{Fe}-\text{O}^-$ above the point of zero charge, producing a more negatively charged surface and reducing affinity for negatively charged colloidal particles¹³. Alkaline conditions may also promote the remobilization of fine particles or partial detachment of Fe-rich (hydr)oxide coatings through weakened particle–surface interactions within the porous medium²⁵.

Phosphorus removal (Fig. 5b) remains highly effective under acidic to neutral conditions (pH 4–7), with low effluent concentrations (<0.5 mg L⁻¹). At higher pH, a slight decrease in performance is observed, which can be attributed to electrostatic repulsion between negatively charged phosphate species (HPO_4^{2-} , PO_4^{3-}) and deprotonated oxide surfaces, as well as competition with hydroxide ions for reactive sites. These trends are consistent with the behaviour of Fe- and Al-based filtration media reported in the literature^{9,19}.

For TOC removal (Fig. 5c), the modified media consistently outperform unmodified sand across the entire pH range. A slight decrease in removal efficiency is observed at high pH, particularly for S–Fe. This behaviour is consistent with a reduced affinity between dissolved organic matter and deprotonated metal surfaces, as electrostatic interactions, surface complexation and ligand-exchange processes become less favourable¹³.

Rinsing experiments using ultrapure water at controlled pH (Fig. 5d) provide further insight into the intrinsic stability of the retained organic matter, independently of filtration processes. Under these conditions, the observed behaviour primarily reflects pH-induced desorption mechanisms and changes in surface interactions. Unmodified sand shows a significant increase in TOC release with increasing pH, exceeding 3–4 mg L⁻¹ at pH 10, indicating the presence of weakly bound organic fractions that are readily mobilized under alkaline conditions. In contrast, the modified media exhibit limited TOC release (<1 mg L⁻¹), confirming stronger binding of organic matter on Fe/Al-rich surfaces. A slight increase is observed for S–Fe at high pH, consistent with reduced stability of Fe-related surface interactions under alkaline conditions. The contrasting desorption behaviour may be explained by the deprotonation of surface hydroxyl groups ($\equiv\text{Me}-\text{OH} \rightarrow \equiv\text{Me}-\text{O}^-$) at high pH, which reduces the affinity of organic matter for the media surface.

However, Fe/Al-containing media remained substantially more resistant to TOC desorption than unmodified sand, indicating stronger organic-matter retention under alkaline conditions. Similar alkaline desorption behaviour has been reported for modified filtration and metal-oxide systems^{11,13,17}. Overall, pH was a key factor governing both treatment efficiency and media stability. S-Fe was more sensitive to alkaline conditions, whereas S-Al-Fe and S-Mg-Al-Fe maintained high removal efficiencies and low TOC release, highlighting their greater chemical robustness under variable pH conditions.

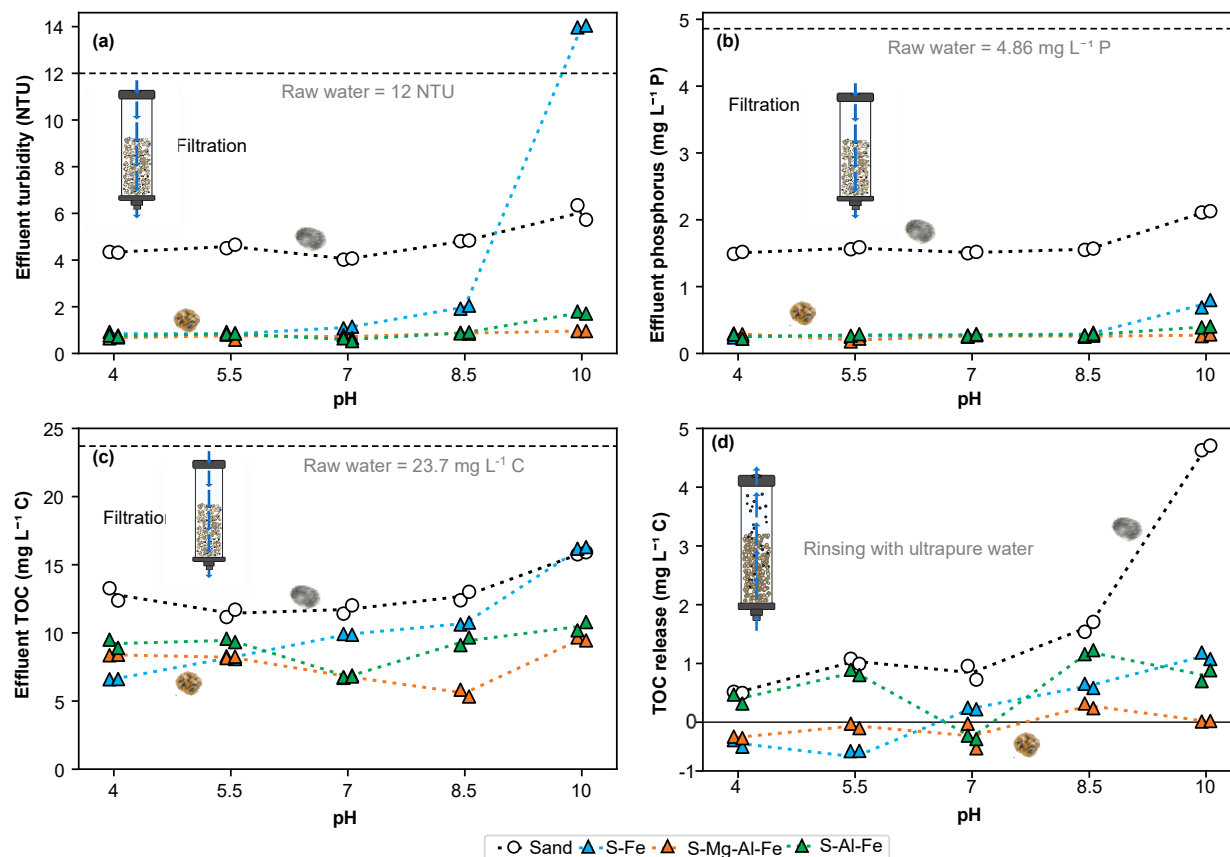


Fig. 5. Effect of pH on filtration performance and TOC release behaviour. **(a)** Effluent turbidity, **(b)** total phosphorus (TP), **(c)** total organic carbon (TOC), and **(d)** TOC release during rinsing with ultrapure water as a function of pH. Experimental conditions: agricultural runoff collected in Quebec (Canada); turbidity 12.0 NTU, TOC 23.7 mg L⁻¹, TP 4.86 mg L⁻¹, flow rate 3 mL min⁻¹ (1 m h⁻¹), and pH adjusted to 4, 5.5, 7, 8.5, and 10 before filtration. Rinsing experiments were performed using ultrapure water adjusted to the same pH values to evaluate potential TOC release from the filtration media. Horizontal dashed lines in **(a–c)** indicate the initial raw-water concentrations, whereas the horizontal solid line in **(d)** indicates zero TOC release. Data are presented as duplicate measurements (n = 2); dotted lines represent the mean values. Negative TOC release values reflect analytical variability following blank correction and are interpreted as negligible release.

Selection of the optimal filtration medium

The selection of the final filtration medium was based on screening experiments, followed by targeted optimization and validation under real agricultural runoff conditions (Fig. 3–Fig. 5). The S–Mg–Al–Fe medium provided the most balanced performance across the measured parameters and was further optimized by increasing the volume of functionalization solution from 8 mL (moderately coated sand) to 12 mL (highly coated sand).

For an initial TOC concentration of 18 mg L^{-1} (Fig. 6a), both configurations reduced TOC relative to unmodified sand. The highly coated sand produced effluent concentrations of $2\text{--}6 \text{ mg L}^{-1}$, whereas concentrations after sand filtration remained above 13 mg L^{-1} . The improved removal is consistent with a greater availability of reactive surface sites for interactions with dissolved organic matter^{17,30}.

The short-term chemical stability of the optimized medium was assessed by monitoring Fe, Al, and Mg relative to their raw-water concentrations of 0.19 , 0.11 , and 2.75 mg L^{-1} , respectively (Fig. 6b). Effluent Fe and Al concentrations remained below their influent values over the tested cycles, providing no evidence of net release under these conditions. A slight increase in Mg indicates limited dissolution or release from the medium. These observations provide no evidence of significant release from the functionalized medium under the tested conditions. However, longer-term leaching tests are still required to evaluate the durability of the medium.

Under higher loading conditions ($\text{TOC} \approx 49.9 \text{ mg L}^{-1}$; turbidity $\approx 42 \text{ NTU}$), the highly coated sand maintained effluent TOC concentrations between 6 and 15 mg L^{-1} over multiple cycles (Fig. 6c–d). Turbidity remained below 2 NTU , whereas values after sand filtration were approximately 20 NTU and increased gradually. These results are consistent with complementary contributions from physical retention and surface interactions in the functionalized medium^{7,8}.

Nitrate removal decreased from 74% to approximately 60% over successive cycles (Fig. 6e). Although lower than the removal achieved for phosphorus, nitrate retention remained substantial throughout the experiment. The gradual decline in performance suggests progressive occupation of available retention sites during repeated operation^{25,31}. Given the well-recognized challenges associated with nitrate removal from water and the need for specialized adsorbents or catalytic systems in many treatment approaches^{32,33}. The observed removal demonstrates the capacity of the multicomponent medium to retain nitrate under repeated filtration conditions. While the relative contribution of Fe, Al, Mg, and the grafted anionic polyacrylamide could not be distinguished, nitrate retention was maintained even after multiple filtration cycles.

Glyphosate removal (Fig. 6f) was evaluated for the highly coated sand in a single filtration cycle. From an influent concentration of $4.1 \pm 0.5 \text{ } \mu\text{g L}^{-1}$, the effluent concentration remained below the detection limit ($\text{LOD} = 0.05 \text{ } \mu\text{g L}^{-1}$), corresponding to $>99\%$ removal. The strong affinity of phosphonate groups for Fe- and Al-containing surfaces through ligand-exchange reactions provides a plausible explanation for this performance^{9,19}. Similar behaviour has been reported for glyphosate retention in Fe- and Al-rich environmental systems^{4,34}. However, the present

experiment does not establish the retention mechanism or the long-term capacity of the medium for glyphosate removal.

Among the tested configurations, the highly coated sand exhibited the most favourable balance between contaminant removal and operational performance. Based on these results, it was selected for subsequent validation and future field-oriented evaluation.

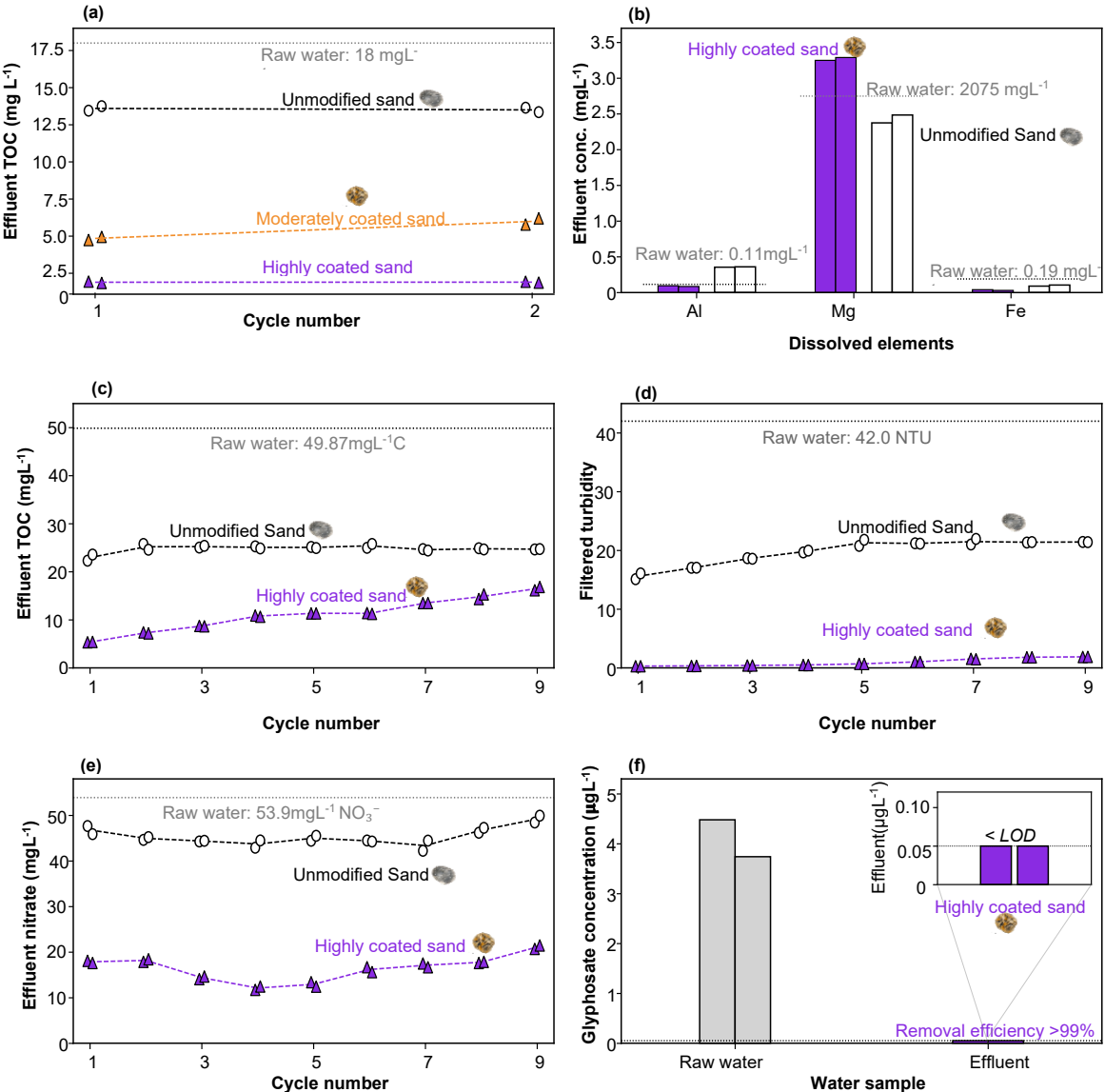


Fig.6. Removal performance, chemical stability, and glyphosate attenuation of the optimized Mg–Al–Fe filtration medium. **(a)** TOC removal during two filtration cycles using agricultural runoff (initial TOC = 18 mg L⁻¹) and comparing unmodified sand, moderately coated sand, and highly coated sand. **(b)** Effluent Fe, Al, and Mg concentrations demonstrating the chemical stability of the optimized medium. **(c–e)** TOC, turbidity, and nitrate removal over nine filtration cycles using highly loaded agricultural runoff. **(f)** Glyphosate removal by the highly coated sand; effluent concentrations remained below the detection limit (LOD = 0.05 μg L⁻¹). Moderately and highly coated sands were prepared using 8 and 12 mL of functionalization solution, respectively. Data are presented as mean ± standard deviation (n = 2).

Taken together, the results demonstrate that surface functionalization substantially improved treatment performance relative to unmodified sand under the tested conditions. Among the evaluated configurations, the highly coated sand consistently provided the most balanced and persistent performance across the measured parameters. High and sustained removal efficiencies were achieved for turbidity, TOC, and phosphorus, while nitrate removal remained substantial despite a gradual decline during repeated filtration cycles. The superior performance of the highly coated sand highlights the benefits of increasing the degree of surface functionalization to improve contaminant retention and treatment longevity. The highly coated sand also maintained stable treatment performance under varying pH conditions and showed no evidence of significant Fe or Al release during the experimental period. In addition, glyphosate removal exceeded 99% in a single-cycle validation test, indicating a strong potential for retaining phosphonate-containing contaminants commonly encountered in agricultural environments. In addition, glyphosate removal exceeded 99% in a single-cycle validation test, indicating a strong potential for retaining phosphonate-containing contaminants commonly encountered in agricultural environments.

Conclusion

Multicomponent functionalization converted conventional sand into a reactive filtration medium capable of retaining a broad range of contaminants from real agricultural runoff. Among the tested formulations, S–Mg–Al–Fe consistently provided the most balanced performance across turbidity, organic carbon, phosphorus, and dissolved metals. Following optimization, the highly coated sand also achieved substantial nitrate removal and > 99% glyphosate removal during validation experiments. Repeated-filtration and pH-stability assessments further demonstrated greater treatment persistence and retention stability than unmodified sand within the tested operating window, indicating the capacity of the developed medium to maintain performance under variable water-quality conditions.

Surface characterization confirmed the incorporation of Fe-, Al-, and Mg-containing functionalities and the formation of a chemically heterogeneous reactive interface. These surface characteristics were associated with enhanced contaminant retention and are consistent with the coexistence of complementary retention pathways acting on chemically diverse contaminants. The superior performance of the Fe–Al–Mg formulation highlights the advantages of combining multiple active phases within a single filtration medium. In addition to improving treatment performance, the incorporation of Mg partly derived from mine tailings introduces a resource-recovery dimension, demonstrating how industrial by-products can be integrated into the development of advanced treatment materials.

The present findings demonstrate the potential of multicomponent surface functionalization as a practical strategy for enhancing the treatment capacity of conventional granular media. The ability of the developed material to simultaneously attenuate nutrients, dissolved organic matter, trace metals, and glyphosate highlights its relevance for decentralized agricultural water-treatment applications. Further work should focus on long-term breakthrough behaviour, media durability, regeneration potential, and field-scale validation, as well as on improving the understanding of the respective roles of Fe, Al, and Mg phases in contaminant retention. Such investigations would support the optimization of media composition and facilitate the transition of this approach toward full-scale implementation.

Materials and methods

Filtration media preparation

Commercial silica sand (ActiSAND®, Veolia; $D_{50} = 160 \mu\text{m}$) was modified with iron (Fe), aluminum (Al), and magnesium (Mg) phases. Briefly, 180 g of sand were mixed with 100 mL of ultrapure water, followed by the addition of either 8 mL or 12 mL of the functionalization solution, corresponding respectively to moderately coated sand and highly coated sand. When multiple metals were used, the total volume was equally distributed among the corresponding precursor solutions. The modification solutions consisted of ferric chloride (PIX 311; 13.36% Fe), aluminum sulfate (8.3% Al), and a magnesium-rich solution obtained by acid dissolution of calcined mine tailings. The pH of the suspension was then adjusted to 7.5–8.0 using NaOH and HCl.

To promote material fixation, a polyacrylamide solution was prepared by dissolving 0.1 g of an anionic polyacrylamide (Hydrex 3511) in 200 mL of deionized water under stirring for 15 min, after which 100 mL were added to the suspension. The modified filter media were dried at 90 °C for 24 h, whereas unmodified sand was used as the control. Eight filter media were prepared using different combinations of Fe, Al, and Mg.

Surface characterization

The morphology and elemental composition of selected media were analyzed using scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM–EDS, TUM300). In addition, surface chemical composition was investigated using X-ray photoelectron spectroscopy (XPS, Escalab 250Xi, Thermo Fisher Scientific) to better understand the nature of the functionalized phases.

Column filtration experiments

Filtration experiments were carried out using borosilicate glass columns (XK 16/20, Cytiva) equipped with flow adapters (AC 16, Cytiva). Columns were operated in parallel to ensure identical hydraulic conditions. Each column (length 20 cm; internal diameter 16 mm) was packed as a dual-layer system. A bottom layer of 16 g of support sand (600 μm) was used to ensure proper drainage and flow distribution. This was overlain by 26 g of test media ($\sim 125 \mu\text{m}$), consisting of either modified or unmodified sand. A geotextile membrane (80 μm) was placed at the base to prevent material loss. Agricultural drainage water was introduced at the top of the column using a syringe pump (Kd Scientific) at a constant flow rate of 3.0 mL min⁻¹, corresponding to a slow filtration regime. Each filtration cycle corresponded to 50 mL of treated water. Effluent samples were collected for analysis. All experiments were performed in duplicate ($n = 2$), and results are reported as mean $\pm$ standard deviation.

Water sampling and analysis

Raw water was collected from different points within an agricultural drainage system and used without significant pre-treatment in order to preserve field-representative conditions. Turbidity

was measured using a nephelometric turbidimeter (TL2350, HACH). Total organic carbon (TOC) was analyzed using a TOC analyzer (FormacsHT, SKALAR) following method 5310 C (persulfate oxidation with UV irradiation). Dissolved metals were quantified using inductively coupled plasma mass spectrometry (ICP-MS). The pH was measured using a calibrated pH meter (pH/CON 510 Series, OAKTON). Orthophosphates were analyzed using an automated colorimetric method based on ascorbic acid (MA. 303 – P 1.0) with a spectrophotometer (VARIAN), and nitrates were measured by ion chromatography (IC). Glyphosate analysis was carried out in a specialized laboratory at the Université de Montréal (UdeM).

Durability and regeneration tests

The filtration media were collected after column experiments to assess their stability and desorption behaviour as a function of pH. The influence of pH on the release of organic matter was investigated over a pH range from 4 to 10. After 10 or 20 filtration cycles with raw water, the media were removed from the columns and air-dried at room temperature. Each sample (26 g) was then divided into aliquots of approximately 5 g. Each aliquot was placed in a beaker containing 100 mL of ultrapure water, with the pH adjusted to the target value using NaOH (to increase pH) and HCl (to decrease pH). The samples were then stirred at room temperature for 5 min and left to settle for 30 s to allow particle settling. The supernatant was collected for total organic carbon (TOC) analysis, used as an indicator of organic matter desorption and the stability of interactions between the media and organic compounds.

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AUTHORSHIP CONTRIBUTIONS

Lovenie Victor: conceptualization, validation, formal analysis, investigation, data curation, visualization, and writing—original draft.

Mathieu Lapointe: conceptualization, data curation, methodology, validation, resources, review & editing, visualization, supervision, project administration, and funding acquisition.

491 **ADDITIONAL INFORMATION**

492 M.L. has applied for a patent on the use of functionalized media for water treatment. The authors
493 declare no conflicts of interest.

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