Sorption of recalcitrant phosphonates in reverse osmosis concentrates and wastewater effluents – influence of metal ions
Asya Drenkova-Tuhtan, Emily K. Sheeleigh, Eduard Rott, Carsten Meyer and David L. Sedlak

ABSTRACT
Magnetic microparticles functionalized with tailored ZnFeZr oxyhydroxide adsorbent were used for the reversible sorption of orthophosphate and recalcitrant organo-phosphonates from wastewater. The loaded particles were harvested magnetically from water, regenerated in an alkaline solution and reused numerous times. The applicability of the technology to treat brackish water reverse osmosis concentrates was tested under controlled synthetic conditions by investigating the influence of typical metals (Ca^{2+}, Pb^{2+}, Cu^{2+}) on the removal of common phosphonates (HEDP, NTMP, EDTMP), and vice versa. When present at equimolar concentrations, metal cations enhanced the adsorption of phosphonates and were co-adsorbed at pH 4.0–4.5 (with removals of 83–93% for Pb^{2+} and 53–73% for Cu^{2+}), likely through ternary complex formation. In the absence of metals, at pH > pH_{PZC} ∼ 7 (the material point of zero charge), a drop in adsorption efficiency was observed for orthophosphate and all phosphonates. Thus, at pH 7, an increased adsorbent dose (>0.1 g/L) was necessary to remove 1 mg/L NTMP-P in 30 min. The reusability and effluent polishing potential of the ZnFeZr particles was demonstrated in a pilot test with municipal wastewater throughout 55 adsorption/desorption cycles without any drop in performance. Consistent removal of the non-reactive phosphorus species to ultra-low concentrations (<0.05 mg/L P_{tot}) and complete orthophosphate elimination (<0.005 mg/L PO_{4-P}) was maintained under optimal conditions.

Key words | antiscalants, brackish water desalination, effluent polishing, eutrophication, magnetic adsorbents, reversible sorption

HIGHLIGHTS
- Magnetic engineered particles were used for reversible sorption of orthophosphate and phosphonates from synthetic reverse osmosis concentrate and municipal wastewater.
- Metals (Ca^{2+}, Pb^{2+}, Cu^{2+}) enhanced the adsorption of phosphonates (HEDP, NTMP, EDTMP) and were co-adsorbed at pH 4.
- Reusability of the adsorbent was demonstrated in a pilot test with municipal wastewater throughout 55 cycles without any drop in performance.

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INTRODUCTION

Phosphonates are organophosphorus compounds widely used as complexing agents in many industrial sectors as antiscalants in drinking water membrane filtration and reverse osmosis (RO) desalinations plants, bleach stabilizers in the paper and textile industries, hardness stabilizers in cooling plants. They are also used as additives in household detergents and cleaning agents. Despite their good elimination (80–95%) in municipal wastewater treatment plants (Nowack 1998; Rott et al. 2020a), considerable amounts of phosphonates are regularly discharged into receiving water bodies, posing a risk of eutrophication due to their photolytic and catalytic degradation to bioavailable orthophosphate or accumulation in river sediments (Rott et al. 2020b).

A significant number of the coastal global population relies on desalination of brackish groundwater for the public drinking water supply (Ziolkowska & Reyes 2016). Phosphonates are commonly used as antiscalants in brackish water desalination via RO (Nowack 2003; Boels et al. 2012). Phosphonate antiscalants are added prior to desalination to prevent the formation of CaCO$_3$, CaSO$_4$, SiO$_2$, and BaSO$_4$ scales. After desalination, however, antiscalants in RO concentrates impede intermediate mineral precipitation (Greenlee et al. 2010). Thus, phosphonate removal from RO concentrates is attractive for various reasons: (1) certain treatment strategies for a more sustainable desalination process, such as intermediate demineralization and resource recovery from the RO concentrates, are hindered by the present antiscalants (Gabelich et al. 2011); (2) when discharged to the environment, metal-catalyzed oxidation may lead to the formation of bioavailable orthophosphate and subsequent eutrophication (Nowack 2005) or phosphate accumulation in sediments with uncertain long-term consequences (Rott et al. 2020b); (3) recovery and reuse of the phosphonates can reduce chemical costs and make RO desalination more cost-efficient.

Various methods have been researched for the removal of phosphonates from aqueous media, such as UV/Fe$^{II}$, UV/Fenton (Rott et al. 2017) or coagulation and biological treatment (Wang et al. 2020). However, these methods have the disadvantage of accumulating significant amounts of chemical or biological sludge, which must be treated and disposed of at additional cost. Sorption-based methods are a better alternative due to the high phosphate uptake capacity (even at low P concentrations) and selectivity of the adsorbent materials, no waste sludge production, easy operation, low costs, option for regeneration and reuse of the adsorbents, and recovery and reuse of the phosphonates.

Previous research has focused mostly on ferric hydroxide adsorbent materials, due to their low cost and availability (Nowack & Stone 1999; Martínez & Farrell 2017). In our recent work we reported that an engineered zinc–iron–zirconium (ZnFeZr) oxyhydroxide material outperforms ferric hydroxide in phosphate adsorption (Rott et al. 2018). This was proposed as an advancement of a technology already tested for the removal and recovery of orthophosphate from wastewater with reusable, magnetically separable microparticles (Mandel et al. 2015) modified with the tailored ZnFeZr oxyhydroxide adsorbent (Drenkova-Tuhtan et al. 2017; Schneider et al. 2017). In addition to orthophosphate, the ZnFeZr-coated particles were also able to remove and recover the two commonly used phosphonates (Figure 1) nitrioltrismethylene-phosphonic acid (NTMP) and diethylenetriaminepentakis-(methylene phosphonic acid) (DTPMP) from a synthetic NTMP solution and a DTPMP-rich membrane concentrate.
Moreover, successful reusability of the engineered particles was demonstrated in industrial wastewater and complete phosphonate removal below the limit of detection (<LOD) was maintained even after 30 cycles of particles reuse.

Our earlier research showed that phosphonate adsorption efficiency dropped significantly at pH > pH_{PZC} \approx 7 (the point of zero charge of the ZnFeZr adsorbent). However, the presence of calcium (Ca^{II}) considerably improved the adsorption of both NTMP and DTPMP at pH > pH_{PZC}, proving that metals are able to co-adsorb and facilitate phosphonate adsorption (Rott et al. 2018). Nevertheless, the adsorption of other metals possibly present in RO concentrates (e.g. Pb^{II} and Cu^{II}) onto the ZnFeZr material surface has not yet been investigated. To predict the suitability of the ZnFeZr adsorbent to remove phosphonate antiscalants from RO concentrates, a better fundamental understanding is needed of how the presence of metals impacts the adsorbent performance.

Firstly, this study examines the orthophosphate and phosphonate removal as a function of pH and adsorbent dose, using synthetic solutions of PO_{4}, HEDP, NTMP and EDTMP (Figure 1). The section on the effect of pH is a modified recapitulation of previously published data (Rott et al. 2018), selecting and representing only the aforementioned phosphonates, the understanding of which is important for interpreting the further results.

Secondly, this study investigates the extent to which three divalent metal ions (Ca^{II}, Pb^{II}, Cu^{II}), typically present in RO concentrates and with diverse electronic characters, influence phosphonate adsorption, and whether they adsorb to the particles themselves. We demonstrate under controlled synthetic conditions the influence of Ca^{II}, Pb^{II} and Cu^{II} on the removal of the common phosphonates NTMP, HEDP and EDTMP. And vice versa: the influence of the three phosphonates on the removal of the metals Pb^{II} and Cu^{II}.

Thirdly, in a pilot test with real municipal wastewater we investigate the long-term reusability of the magnetic ZnFeZr adsorbent and its ability to consistently remove and recover recalcitrant phosphorus species at pH \sim 7 from a secondary clarifier effluent with high concentrations of Ca^{2+} and Na^{+} cations. For this purpose, total phosphorus (TP or P_{tot}) and the easily removable dissolved reactive phosphorus, i.e. orthophosphate (dRP or PO_{4}-P), were measured. The recalcitrant species were calculated as the difference between the two and defined as the non-reactive phosphorus fraction \Delta P = P_{tot} - PO_{4}-P, which includes the dissolved non-reactive phosphorus (dNRP), dominated by organo-phosphonates and the particulate total phosphorus (pTP). In previous research we proved that the proportion of phosphonates in wastewater treatment plant (WWTP) effluents can be significant, namely 10–40% of the dNRP fraction in the effluent (Rott et al. 2020a). The successful removal of this non-reactive \Delta P fraction over numerous cycles of adsorbent regeneration and reuse proved the ability of the magnetic sorbents to achieve ultra-low P concentrations and polish the effluent.

Finally, this study interprets the findings from the pilot test with municipal wastewater to the applicability of the technology for treating real brackish water RO concentrates.

**MATERIALS AND METHODS**

**Concept of the proposed technology using magnetic ZnFeZr-coated adsorbent particles for phosphorus removal and recovery**

The proposed technology combines nanocomposite magnetic particles (Fe_{3}O_{4} nanoparticles embedded in a SiO_{2} matrix) with a tailored adsorbent material (ZnFeZr oxyhydroxide) for the selective removal of dissolved phosphorus...
from pre-treated wastewater followed by its concentration in a purer liquid matrix as a source for further P recovery (Drenkova-Tuhtan et al. 2017). The adsorbent deposited on the carrier magnetic particles (ZnFeZr@MP) has a Zn:Fe:Zr molar ratio of 6:1:1 and was selected from >70 tested combinations of metal oxides, hydroxides, and oxyhydroxides due to its higher adsorption capacity, selectivity, stability, and P recovery potential (Schneider et al. 2017). The fraction of the ZnFeZr adsorbent was about 30 wt% of the whole composite particle. The particles were prepared and stored as a thick dark suspension with ~40 g/L dry matter. In the rest of the text, the term ‘adsorbent’ always refers to the ZnFeZr oxyhydroxide component of the composite particles.

The engineered composite particles (size ~25 μm, surface area ~75 m²/g) are magnetically extracted from water after 20 min reaction, regenerated in an alkaline NaOH solution (where phosphorus desorption, concentration and recovery take place) and reused. The technology offers the dual benefit of phosphorus elimination down to <0.005 mg/L PO₄-P (orthophosphate) and <0.05 mg/L Ptot (total phosphorus) concentrations, obviating any eutrophication risk, and the option for subsequent recovery of the valuable nutrient.

A more detailed schematic overview of the technological concept can be found in Figure S1 in the Supplementary Information.

Chemical reagents and synthetic phosphonate solutions

For the experiments investigating the pH and adsorbent dosage effects (Figures 2 and 3, respectively), stock solutions with 1 g/L of each phosphonate (HEDP, NTMP, EDTMP) or orthophosphate (PO₄-P) were used to prepare 1 mg/L P solutions with deionized water of phosphonate-P (corresponds to 16.1 μM HEDP, 10.8 μM NTMP, 8.1 μM EDTMP) or orthophosphate-P (32.3 μM H₃PO₄).

For the experiments on the influence of dissolved metals (Figures 4 and 5), all glassware was first acid washed in 10% HNO₃. Phosphonate stock solutions (0.01 M) were prepared by dissolving the phosphonate into 0.01 M NaNO₃. Metal stock solutions (0.01 M) were prepared by dissolving the metal nitrate into 1% HNO₃ to minimize metal adsorption to glass. The stock solutions were diluted with deionized water to reach 10 μM concentration for both the phosphonates (HEDP, NTMP, EDTMP) and the metals (CaII, PbII, CuII). A background concentration of 0.01 M NaNO₃ was used to maintain a constant ionic strength.

The chemicals HEDP·H₂O (>95%) and NTMP (>97%) were obtained as solids from Sigma-Aldrich (St. Louis, Missouri, USA). The phosphonate EDTMP was purchased as a solid (~5.3% water of crystallization) from Zschimmer
& Schwarz Mohsdorf (Burgstädt, Germany) and, for the metal experiments (≥98%) from VWR International (Pasadena, California, USA). Ortho-phosphoric acid (H₃PO₄, ≥99.5%), sodium hydroxide (NaOH, ≥99%) and sulfuric acid (H₂SO₄, 95–97%) were purchased from Merck KGaA (Darmstadt, Germany). Hydrochloric acid (HCl, 32%) was obtained from VWR Chemicals (Fontenay-sous-Bois, France) and from Sigma-Aldrich (2N HCl). Metal nitrate salts, Ca(NO₃)₂·4H₂O, Pb(NO₃)₂, and Cu(NO₃)₂·3H₂O, (≥99.95%) were purchased from Sigma-Aldrich. Sodium nitrate (NaNO₃, ≥95%) was purchased from ThermoFisher Scientific (Fair Lawn, New Jersey, USA).

Analytical methods

Dissolved orthophosphate concentrations were determined after membrane filtration (0.45 μm) with ammonium molybdate following the international standard DIN-EN-ISO-6878, measured with spectrophotometer Shimadzu UV-1800 and presented as elemental PO₄-P (mg/L). Total phosphorus (P_\text{tot}) concentrations were measured according to DIN 38405-11 after acidic digestion of the samples. The difference ΔP = P_\text{tot}−Po₄-P (mg/L) represents the non-reactive phosphorus fraction (dissolved and particulate) in the domestic WWTP effluent. In the synthetic phosphonate solutions, the respective phosphate concentration was determined indirectly also as ΔP = P_\text{tot}−Po₄-P.

For the experiments investigating the influence of metal ions on phosphonate adsorption, the metal and phosphonate (as P_\text{tot}) concentrations were determined via inductively coupled plasma mass spectrometry (ICP-MS; Agilent 7700) after filtration through 0.45 μm nylon filter. The metal concentrations in the domestic wastewater were analyzed after microwave digestion in HNO₃/H₂O₂ with ICP-MS NexION-350X (Perkin-Elmer) following DIN-EN-ISO-17294-1.

Electrical conductivity was measured with a WTW-TetraCon-925 probe and a WTW-Multi-3,430 device. Temperature and pH were measured with a Greisinger-3,551 pH–temperature meter and a Greisinger-GE-117 pH electrode. All other standard wastewater parameters in Table 1 were analyzed following the respective DIN standards (more details in the Supplementary Information).

Lab-scale experiments with synthetic phosphonate solutions

Experimental procedure 1 – effect of pH and adsorbent dose on phosphonate adsorption

In these tests, 250 mL of each 1 mg/L phosphonate-P or phosphate-P containing synthetic solution was mixed with a fixed adsorbent dose 0.03 g/L (Figure 2) or varying dose 0.03–1.0 g/L (Figure 3) under magnetic stirring at room temperature (20 °C) for 30 min. Within the pH range of 4–13, the adsorption equilibrium was reached after 24 hours.
to 12, the target pH value was adjusted with HCl or NaOH in each reactor immediately after adding the adsorbent and maintained until the end of the experiment. After 30 min adsorption, the P-loaded magnetic particles were harvested at the bottom of each reactor using a handheld NdFeB-magnet N42, 40 × 20 × 20 mm (Supermagnete Webcraft GmbH, Germany). Samples for analysis were taken from the clear supernatant and were membrane-filtered (0.45 μm) before measuring the total phosphorus concentration in the filtrate.

Adsorption efficiency $E_{\text{ads}}$ (%) was calculated as follows:

$$E_{\text{ads}} = \left( \frac{C_0 - C_t}{C_0} \right) \times 100$$  \hspace{1cm} (1)

where $C_0$ and $C_t$ are the initial P concentration and the P concentration at time $t$ in the solution (mg/L).

The fitting curves in Figures 2 and 3 depicting the adsorption efficiency as a function of pH and adsorbent dose were fitted with the logistic function model (LFM), described in the Supplementary Information (Equation (S1)).

**Experimental procedure 2 – effect of metals on phosphonate adsorption**

This set of experiments was carried out in 15 mL plastic vials at room temperature. Six controls (each phosphonate HEDP, NTMP, or EDTMP, and each metal Ca$^{II}$, Pb$^{II}$, or Cu$^{II}$ added to the adsorption vessel, without adsorbent), six baseline conditions (each phosphonate plus adsorbent, each metal plus adsorbent), and nine test conditions (a phosphonate plus a metal plus adsorbent) were prepared in duplicate. The metal ion and phosphonate were added to the adsorption vessel first, in a 1:1 ratio (both at 10 μM concentrations), followed by 0.03 g/L adsorbent. Before introducing the adsorbent, the suspension was stirred for 1 hour to ensure homogeneity. The adsorption vessels were equilibrated for 24 hours on a mechanical tube rotator (∼25 rpm). Over this time, the pH of the vessels with phosphonate only and adsorbent increased from ∼5.5 to 6.5–7.0. For the vessels to which acidified metal nitrates were added, the pH was lower, increasing from ∼3.5 to 4.0–4.5 over 24 hours (vessels with both metal and phosphonate, or with only a metal). The solutions were then filtered through 0.45 μm nylon syringe filters before elemental analysis with ICP-MS. Phosphonate and metal adsorptions to the ZnFeZr particles were calculated according to Equation (1), where $C_0$ is the elemental phosphorus and metal

![Figure 5](image-url) | Effects of 10 μM concentration of metals (left of dotted line versus right of dotted line) and phosphonates (white versus gray bars) on the dissolution of Zn from the ZnFeZr absorbent particles. Same conditions as in Figure 4.

**Table 1** | Characteristics and chemical composition of the municipal secondary effluent wastewater used in the WWTP effluent polishing pilot tests

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Value range</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>–</td>
<td>7.3 ± 0.26</td>
</tr>
<tr>
<td>Temperature</td>
<td>°C</td>
<td>15.1 ± 2.9</td>
</tr>
<tr>
<td>Conductivity</td>
<td>mS/cm</td>
<td>1.195 ± 0.420</td>
</tr>
<tr>
<td>TSS</td>
<td>mg/L</td>
<td>10.5 ± 7.5</td>
</tr>
<tr>
<td>Total P</td>
<td>mg/L</td>
<td>0.99 ± 0.91</td>
</tr>
<tr>
<td>PO$_4$-P</td>
<td>mg/L</td>
<td>0.441 ± 0.38</td>
</tr>
<tr>
<td>COD</td>
<td>mg/L</td>
<td>21.0 ± 13.0</td>
</tr>
<tr>
<td>TOC</td>
<td>mg/L</td>
<td>7.79 ± 2.07</td>
</tr>
<tr>
<td>HCO$_3$-</td>
<td>mg/L</td>
<td>45.4 ± 7.9</td>
</tr>
<tr>
<td>NH$_4$-N</td>
<td>mg/L</td>
<td>0.56 ± 0.53</td>
</tr>
<tr>
<td>NO$_3$-N</td>
<td>mg/L</td>
<td>7.1 ± 3.9</td>
</tr>
<tr>
<td>NO$_2$-N</td>
<td>mg/L</td>
<td>0.20 ± 0.09</td>
</tr>
<tr>
<td>SO$_4$-S</td>
<td>mg/L</td>
<td>28 ± 12</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>mg/L</td>
<td>260 ± 150</td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>mg/L</td>
<td>89 ± 24</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>mg/L</td>
<td>182 ± 82</td>
</tr>
<tr>
<td>K$^+$</td>
<td>mg/L</td>
<td>19.2 ± 5.7</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>mg/L</td>
<td>14.0 ± 3.8</td>
</tr>
<tr>
<td>Si</td>
<td>mg/L</td>
<td>13.3 ± 10.4</td>
</tr>
<tr>
<td>Total Fe</td>
<td>mg/L</td>
<td>0.47 ± 0.4</td>
</tr>
<tr>
<td>Zn$^{2+}$</td>
<td>mg/L</td>
<td>0.22 ± 0.1</td>
</tr>
<tr>
<td>Zr$^{4+}$</td>
<td>mg/L</td>
<td>0.13 ± 0.12</td>
</tr>
<tr>
<td>Al$^{3+}$</td>
<td>mg/L</td>
<td>0.36 ± 0.18</td>
</tr>
<tr>
<td>Cd</td>
<td>mg/L</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Cr</td>
<td>mg/L</td>
<td>0.002 ± 0.001</td>
</tr>
<tr>
<td>Cu</td>
<td>mg/L</td>
<td>0.033 ± 0.031</td>
</tr>
<tr>
<td>Pb</td>
<td>mg/L</td>
<td>0.002 ± 0.001</td>
</tr>
</tbody>
</table>
concentrations measured in their respective controls (no adsorbent present) and $C_i$ is the concentration measured after 24 hours of equilibration with the adsorbent.

**Pilot-scale adsorbent reusability experiments for polishing a municipal secondary effluent**

The wastewater for these experiments was collected from the effluent of the Municipal Sewage Treatment Plant for Education and Research at the ISWA Institute, University of Stuttgart, Germany. The wastewater composition is summarized in Table 1. The high concentrations of the metals Ca$^{2+}$ (65-113 mg/L) and Na$^+$ (100-264 mg/L) are important in the context of phosphonate adsorption and may facilitate a more efficient P-removal process, as discussed later in this paper.

At an earlier research stage, pilot tests were performed to verify the proof of concept and demonstrate a successful 50-times upscaling of the technology by treating 1.5 m$^3$ effluent wastewater spiked with orthophosphate (Drenkova-Tuhtan et al. 2017). In this work, the same pilot setup was used for polishing the effluent by removing the recalcitrant phosphorus species. For this purpose, the pilot plant (Figure S2, Supplementary Information) was designed and equipped with a 200 L adsorption reactor, commercial drum magnetic separator with permanent magnets (Steinert Elektromagnetbau GmbH, Cologne, Germany), buffer tank for intermediate storage of the treated effluent, second-stage filtration unit through a high-gradient magnetic separator (HGMS) with permanent magnets (non-commercial design), magnetic plate $30 \times 30$ cm for further concentration of the particle suspension flushed from the HGMS, and associated peripheral equipment. Phosphorus desorption and regeneration of the adsorbent particles were carried out in a smaller 30 L desorption reactor. Afterwards the regenerated particles were magnetically separated and reintroduced into the adsorption reactor for the next cycle. The collected effluent wastewater was treated ‘as was’, without spiking it with additional phosphate. The goal of the research presented was to test the particles’ ability to remove phosphorus from a low-concentrated medium (0.08-1.9 mg/L $P_{\text{tot}}$) by adjusting the reaction parameters and demonstrate the potential for advanced elimination of recalcitrant P species and polishing of secondary wastewater effluents.

Adsonption efficiency $E_{ads}$ (%) was calculated following Equation (1).

Based on earlier research findings (Drenkova-Tuhtan et al. 2016; Drenkova-Tuhtan et al. 2017), phosphorus desorption and simultaneous regeneration of the ZnFeZr adsorbent was performed in a 1M NaOH solution (pH ≥ 13). Repetitive reuse of the desorption solution throughout all adsorption/desorption cycles could guarantee a minimum 10-times enrichment with phosphorus compared to the initial P concentration in the wastewater. The declining electrical conductivity of the NaOH solution was an indicator that its regeneration capacity was being exhausted. Desorption efficiency $E_{des}$ (%) was calculated as the ratio of the desorbed to the previously adsorbed phosphorus:

\[
E_{des} = \frac{q_d}{q_a} \times 100
\]

where $q_d$ is the desorbed and $q_a$ is the initially adsorbed phosphorus (mg/g).

**RESULTS AND DISCUSSION**

**Effect of pH on phosphonate removal at a fixed adsorbent dosage**

This section is a modified recapitulation of previously published data (Rott et al. 2018), selectively representing the effect of pH on adsorption only of the phosphonates that are the focus of this paper (HEDP, NTMP, EDTMP) and PO$_4$, the understanding of which is important for the interpretation of the results.

The point of zero charge of the engineered ZnFeZr adsorbent was found to be at pH$_{pzc}$ ≈ 7 in our earlier research (Rott et al. 2018). The plots in Figure 2 show that in the alkaline range at pH > pH$_{pzc}$ ≈ 7, a drop in adsorption efficiency was detected for all investigated phosphonates (HEDP, NTMP, EDTMP) and PO$_4$, the sharpest drop was at pH 6–8. This can be attributed to electrostatic repulsion between the increasingly negatively charged adsorbent surface and the presence of more negatively charged phosphate/phosphate species with increasing pH.

The adsorption affinity at pH 6 followed the order: HEDP > PO$_4$ > EDTMP > NTMP. This implies that HEDP and PO$_4$ were preferentially adsorbed compared to the nitrogen-containing aminophosphonates, most likely due to their lower molecular weight and lower phosphorus content. The adsorption data for all P compounds were fitted with the LFM and plotted as solid-line curves in Figure 2. The mathematical equations and the $r^2$-values of the fitting curves are summarized in Table S1 in the Supplementary Information.
The flattest curve can be assigned to the best-adsorbed phosphonate, HEDP, which has two phosphate groups (Figure 1) and dissociates only into two (di- and tri-) negatively charged species within the investigated range pH 4–12. According to Popov et al. (2001), only after both phosphate groups are fully deprotonated, i.e. at pH > 13, will the aliphatic hydroxyl group in HEDP dissociate, meaning that the hydroxyl group does not have a significant impact on the phosphate complexation at pH < 13.

Likewise, at pH 4–12, ortho-phosphoric acid also dissociates only into two species (mono- and di-protonated) and exhibits a high removal efficiency, similar to HEDP, especially at pH 6–8 where a considerable decline in adsorption was observed among the aminophosphonates NTMP and EDTMP.

At neutral pH, the aminophosphonates dissociate into species with different negative electric charges, as depicted by the gray dashed-line curves in Figure 2. For example, NTMP (three phosphate groups and one amino group) is present as $-3/-4$ negatively charged species, and EDTMP (four phosphate groups and two amino groups) dissociates into $-4/-5$ charged species at pH 7. Nevertheless, both phosphonates had comparably low adsorption efficiencies in the neutral pH range, which validates the assumption that the surface charge of the adsorbent (defined by the point of zero charge) and not the number of dissociated phosphate species is critical for whether phosphate adsorption does or does not occur.

At pH > 8 the adsorption of all phosphonates and phosphate was either negligible or not detected at all. However, in our earlier research (Rott et al. 2018) we could prove that the presence of more than 0.5 mM Ca$^{II}$ (20 mg/L Ca$^{II}$) can significantly improve the adsorption of NTMP and DTPMP, especially in the alkaline pH range. In this work, we further investigate the effect of metals, including Ca$^{II}$, on phosphate adsorption and test the reusability of the adsorbent particles in a real wastewater effluent containing ~100 mg/L Ca$^{II}$.

**Effect of pH on NTMP removal at various adsorbent dosages**

For this experiment, only NTMP (1 mg P/L synthetic solution) was investigated, used as a representative phosphonate with three phosphate groups and a molecular weight of 299.05 g/mol, which is between HEDP (two phosphate groups, 206.03 g/mol) and DTPMP (five phosphate groups, 573.20 g/mol).

Our earlier research (Rott et al. 2018), we demonstrated that the engineered ZnFeZr@MP was highly efficient at removing NTMP, with a maximum load of ~20 mg NTMP-P/g (215 μmol NTMP/g) at room temperature, pH 6 and 30 min contact time. The adsorption kinetics at pH < pH$_{PZC}$ = 7 was fast, reaching equilibrium in ~30 min, and followed the pseudo-second-order kinetics model, which typically indicates chemisorption. Furthermore, NTMP adsorption onto ZnFeZr oxyhydroxide proved to be an endothermic process most accurately modeled using the Freundlich isotherm equation, implying multilayer adsorption. Experimental data, model equations and fitting curves of the previously researched NTMP adsorption kinetics and isotherms for the custom ZnFeZr adsorbent are published elsewhere (Rott et al. 2018) and for the convenience of the reader, also included in the Supplementary Material (Figure S3, Tables S2 and S3 and Equations (S3)–(S6)).

In this work, the effect of pH on NTMP removal at four different adsorbent dosages relevant for the further experiments is shown in Figure 3.

The plot in Figure 3 shows that at the lowest adsorbent dosage of 0.03 g/L ZnFeZr@MP there is a sharp drop in NTMP adsorption efficiency from ~60% at pH 6 (~90% at pH 5) down to ~15% at pH 7. As already mentioned, pH 7 corresponds to the point of zero charge of the material, at which there were far fewer protonated OH groups on the adsorbent surface, suggesting that the weaker electrostatic interactions at pH 7 resulted in a slower adsorption compared to pH 6. Nevertheless, the weaker interaction at pH 7 could be compensated by increasing the adsorbent dosage to >0.1 g/L ZnFeZr@MP, as the higher adsorbent concentration provided more protonated OH groups which improved the NTMP removal efficiency to >90% at pH 7. The rapid adsorption at pH 7 and >0.1 g/L ZnFeZr@MP implies a low activation barrier, which increases considerably with an increase in pH value. The higher adsorbent dosages of 0.4 g/L and 1.0 g/L had a marginal effect on improving the NTMP removal at pH > 10.

The engineered ZnFeZr adsorbent consists of metals with valencies of two- (Zn$^{2+}$), three- (Fe$^{3+}$) and four- (Zr$^{4+}$) in the form of metal oxides/hydroxides (Schneider et al. 2017). The different oxidation states of the elements can greatly influence the surface charge of the adsorbent (by forming more protonated OH groups at pH < pH$_{PZC}$) and facilitate its electrostatic interactions with the dissociated phosphate species. The most common physico-chemical mechanisms of NTMP adsorption onto metal oxide/hydroxide surfaces with protonated or deprotonated OH groups involve either simple electrostatic attraction to the protonated OH groups, ligand exchange with the OH groups or...
covalent bonding with the metallic cations via inner-sphere complexation. In the case of NTMP, binding onto hydroxide surfaces via bidentate complexes is energetically more favorable than monodentate complexes (Martínez & Farrell 2017).

For practical adsorbent applications in real municipal or industrial wastewater effluents, a neutral pH – 7 value must be considered. Based on the results in Figure 3, for wastewater with P concentrations around 1 mg/L, a minimum of 0.1 g/L ZnFeZr@MP adsorbent should be dosed to overcome the thermodynamic limitations at neutral pH and achieve >90% P-removal efficiency. For more complex wastewaters with high concentration of competing ions, organics and suspended solids, the adsorbent dose needs to be increased correspondingly.

**Effect of metal ions on the adsorption of phosphonates**

In our earlier work (Rott et al. 2018), we demonstrated that the presence of metals such as CaII can significantly increase the removal of phosphonates by the ZnFeZr@MP adsorbent in the neutral and alkaline pH range. A similar positive effect of metal ions on the adsorption of phosphonates onto goethite was observed by others (Nowack & Stone 1999).

In this work, we further investigate the effect of other metals on phosphonate adsorption (Figure 4(a)), specifically PbII and CuII, which are particularly relevant for RO concentrates produced during treatment of industrial and agricultural waters. Moreover, the inverse scenario, i.e. the influence of phosphonates on the adsorption of metals, is also investigated (Figure 4(b)).

Phosphonate adsorption in the metal-free solutions (open circles in Figure 4(a)) was similar to that observed in the previous experiments at pH 6.5–7.0 (Figure 2), with adsorption efficiencies of ~70% for HEDP, 25% for NTMP, and 30% for EDTMP. The addition of an acidified metal nitrate (solid circles in Figure 4(a)) corresponds to an increase in adsorption, with near-complete removal of HEDP and two to three times higher adsorption of NTMP and EDTMP, compared to the metal-free condition.

The higher adsorptions observed here are most likely to be explained by the fact that metal salt addition caused a drop in pH. The reduction in pH associated with metal salt addition produced an expected increase in phosphonate adsorption, in line with the results discussed in the previous section. The measured adsorptions of ~90–100% for HEDP, ~50–65% for NTMP, and ~70–90% for EDTMP closely align with those presented in Figure 2 at pH 4.0–4.5. This is because at pH values below the point of zero charge (pH_{pzc} ≈ 7.0) of the ZnFeZr adsorbent, the presence of metal cations would not be expected to enhance electrostatic interactions between the positively charged adsorbent surface and negatively charged phosphate groups. Similarly, Nowack & Stone (1999) examined the effect of Ca and Cu on the adsorption of NTMP, HEDP, and EDTMP to the iron (hydr)oxide goethite and found that equimolar concentrations had negligible effects.

**Effect of phosphonates on the adsorption of metals**

The more useful results from this set of experiments concern the adsorption of metals to the ZnFeZr particles. The first finding is that metal ion adsorption increased significantly in the presence of phosphonates, as shown in Figure 4(b). Due to poor sensitivity to calcium ion concentrations, ICP-MS data for Ca was excluded. Equimolar concentrations of phosphonates roughly doubled the PbII and CuII adsorption efficiency from ~40% to 83–93% and ~30% to 53–73%, respectively.

Addition of phosphonate did not significantly alter the solution pH (all metal-containing solutions had equilibrium pH values of ~4.0–4.5). Thus, three main adsorption mechanisms are possible. First, some PbII and CuII ions likely co-adsorbed with the phosphonates, which have two to three negatively charged phosphate groups in this pH range. Phosphonates and metals can co-adsorb as ternary complexes, which have been described for surface-phosphate-Ca complexes for ferric (hydr)oxides (Nowack & Stone 1999; Martínez & Farrell 2017). This mechanism is favored at low pH values, where the predominant metal species in solution are the free metal cation and organic complexes, while carbonate or hydroxyl complexes become significant at high pH (Sposito 2016). Secondly, metal cations can physically adsorb via electrostatics, but unfavorable positive/positive charge interactions would reduce the plausibility of this mechanism. Finally, ion exchange can occur, where Pb and Cu swap with other metals in the surface structure. The long equilibration times employed here (24 hours versus 30 min in the previous experiments) were likely long enough for dissolution reactions of the adsorbent precursor metals (e.g. Zn) to become important (Nowack & Stone 1999).

Further results summarized in Figure 5 show that in the presence of all three metals, dissolved Zn concentrations of ~20–25 μM were observed in the supernatant, indicating some chemical instability of the engineered composite particles under these conditions and risk of dissolution of the particle precursors. Dissolved Fe was also detected, but at much lower concentrations (<0.01–1 μM).
Phosphonate concentrations encountered in RO systems (desalination and treatment of WWTP effluents for potable reuse) are variable and dependent on source type, but are typically within an order of magnitude of the 10 μM concentrations used here. For example, phosphonate antiscalant concentrations in brackish water RO concentrates are reported to be 10–50 μM (McCool et al. 2012; Greenlee et al. 2014), while representative concentrations in municipal WWTP influents tend to be ~1 μM, with higher levels observed in plants receiving significant inputs from the textile industry (Nowack 1998, 2003). On the other hand, 10 μM concentrations of Ca, Pb, and Cu are less representative of typical RO concentrates, where Ca can be 10^2–10^5 times higher (millimolar range) and in municipal wastewater Pb is 10^2–10^3 times lower (nanomolar range).

Even though the metal concentrations in these experiments do not model authentic RO concentrates, they do allow us to investigate the extent to which the electronic character of the metal ion affects its interaction with the ZnFeZr oxyhydroxide surface and its influence on phosphonate adsorption. Moreover, Cu^{2+}, a transition metal with a partially filled d-orbital, and Pb^{2+}, a ‘soft shell’ metal with a full d-orbital, are more strongly chelated by phosphonates than Ca^{2+}, which is a ‘hard-sphere’ metal with a noble gas configuration. Hard sphere metals are less able to displace waters of hydration to form inner-sphere complexes (Benjamin 2005). Additionally, Cu^{3+} and Pb^{2+} have higher stability constants with phosphonates than Ca^{2+} (Popov et al. 2001; Nowack 2003). Such differences, however, did not result in any clear impacts on (1) the metal ion’s influence on phosphonate adsorption, (2) the metal’s absorption to the ZnFeZr surface, or (3) possible ion exchange and resulting Zn dissolution. Further experiments should address how more realistic metal:phosphonate ratios impact phosphate and metal adsorption, as well as Zn dissolution on shorter contact times.

Some economic aspects will be considered in the future studies as well. For many desalination facilities, antiscalants account for a significant fraction of the chemical costs. Following multiple cycles of adsorbent regeneration, antiscalants could be recovered from the desorption solution and reused, which will reduce the chemical costs. Moreover, many heavy metals (e.g. Cu^{2+}, Pb^{2+}) are toxic and subject to disposal and discharge regulations. This applies to liquid RO concentrate disposal (to WWTPs, ocean or surface water discharge, deep well injection) and landfiling of salt solids. Removal of metal toxicants is often required to obtain disposal permits and avoid fines.

Polishing of municipal WWTP effluents through removal and recovery of recalcitrant non-reactive phosphorus species with magnetic adsorbent particles

This set of experiments demonstrates the reusability of the magnetic ZnFeZr adsorbent particles in real secondary effluent from a municipal WWTP. The purpose of these tests is to verify the scalability of the technology and its suitability for the removal and recovery of recalcitrant phosphorus species, including phosphonates, from municipal wastewater. These test results can serve as a good approximation for the applicability of the ZnFeZr adsorbent in other phosphate-containing matrices, such as RO concentrates.

The chart in Figure 6(a) shows the phosphorus concentration (mg/L) in the raw wastewater as it was collected from the effluent of the microstrainers at the final WWTP treatment stage. The lighter part of the beige bars represents the dissolved orthophosphate portion (PO₄-P). The upper darker part equals all other phosphorus containing compounds (ΔP), i.e. the non-reactive phosphorus fraction NRP (dissolved and particulate) that could not be removed by chemical precipitation, where up to 40% of the dNRP may be attributed to phosphonates (Rott et al. 2020a). The sum of both (PO₄-P + ΔP) adds up to the total phosphorus concentration in the wastewater to be treated in inflow adsorption reactor (P_{tot,in}). Some fluctuations can be noticed, especially in cycles 2, 3, 19, 20 and 43, where the PO₄-P concentrations were unusually high due to some operational problems with the chemical precipitant dosing units and malfunction of the microstrainers. Under normal operational conditions, the effluent total phosphorus concentration was usually below 0.2 mg/L.

In an analogous manner, the blue bars in Figure 6(a) show the concentration of the same parameters in wastewater but after treatment with the particles. The light blue bars represent the dissolved orthophosphate (PO₄-P) and the dark blue fraction is the non-reactive ΔP in the treated wastewater. They both add up to the total phosphorus concentration in outflow adsorption reactor (P_{tot,out}).

Figure 6(b) summarizes the P-adsorption efficiencies (%) in every individual cycle. The gray bars show the desorption efficiency, while the adsorption efficiency is plotted as circles for all different fractions: PO₄-P (black), P_{tot} (gray) and ΔP (white). The vertical lines across the charts correspond to changes in the reaction conditions throughout the cycles, described at the bottom of the figure.

Earlier research (Drenkova-Tuhtan et al. 2017; Rott et al. 2018) showed fast P-adsorption kinetics on the
Figure 6 | Advanced phosphorus elimination from municipal effluent via cyclic regeneration and reuse of magnetic particles with 31 wt% ZnFeZr adsorbent. (a) $P_{\text{tot, in}}$ ($\Delta P$) concentrations in the inflow wastewater to be treated at inflow adsorption; and outflow $P_{\text{tot, out}}$ concentrations after treatment with the particles; (b) adsorption/desorption efficiencies in each cycle. $\Delta P = P_{\text{tot}} - P_{\text{O}_4}\text{-}P$ is the non-reactive phosphorus (dissolved and particulate); (c) concentration of phosphate ions in the 1M NaOH desorption solution and reduction of its conductivity as an indicator of depleting particle regeneration capacity.
ZnFeZr particles and compliance with the pseudo-second-order kinetics model, implying that chemisorption dominates the phosphate/phosphonate uptake process. The Freundlich isotherm model fitted the adsorption data best, implying multilayer coverage and heterogeneous adsorbent surface. Maximum sorption capacity in secondary effluent wastewater at 24 °C and neutral pH was 75.8 mg PO₄-P/g. However, adsorbent loading should not exceed 10 mg P/g to guarantee effluent concentrations <0.005 mg/L PO₄-P.

Based on earlier research findings, the contact time in all adsorption and desorption cycles was set to 20 min, adsorption pH was maintained neutral (pH ∼ 7), while desorption took place in 1M NaOH at highly alkaline pH ∼ 13. Initially an adsorbent dose of 0.2 g/L (0.6 g/L particles with 31 wt% ZnFeZr adsorbent) was introduced into the system, in accordance with Figure 3 results. Considering the low phosphorus concentration in wastewater (Table 1: 0.99 ± 0.91 mg/L P_total), it was assumed that particles could handle several loading cycles without regeneration. However, the first four cycles (Figure 6(c)) showed a quick drop in adsorption performance from ~80% in cycle 1 down to ~10% in cycle 5.

From cycle 5 on the desorption process was started in a 1M NaOH solution (pH ∼ 13), which was reused until the end of cycle 28. Adsorption values improved significantly, especially for PO₄-P to > 90%. This trend continued until cycle 15, when adsorption dropped to ~20% due to unexpectedly higher total phosphorus concentration in the raw wastewater (P_0 > 1 mg/L). Another problem was the steadily increasing phosphorus concentration in the desorption solution due to its repetitive reuse, which reached almost 4 mg/L in cycle 15. Part of this phosphorus got trapped within the particles (even though the desorption solution was pumped out of the system) and was carried over into the next adsorption cycle, thus increasing the initial P concentration. Therefore, decision was made to start washing the particles with water from cycle 15, which improved the adsorption performance.

Another spike in the inflow P concentration in cycles 19 and 20 reduced the efficiency again, requiring an increase in particle dosage. From cycle 21, the adsorbent dosage was raised to 1 g/L (corresponding to 3.2 g/L particles), which resulted in a significant performance improvement with > 95% or even complete PO₄-P removal until the end of the experiment. P_total and δP adsorption efficiencies fluctuated around and above 50%, and whenever PO₄-P was the dominant fraction in wastewater, the P_total removal values were close to 100% (cycles 41–53).

Figure 6(b) shows that from cycle 21 onwards the total phosphorus concentration in the treated wastewater was kept consistently below the eutrophication threshold of 0.05 mg/L P_total, mostly due to complete elimination of the orthophosphate (< LOD), but also due to significant reduction of the dissolved and particulate non-reactive phosphorus (ΔP). Moreover, adsorption was performed at pH ∼ 7, which corresponds to the point of zero charge of the ZnFeZr adsorbent. At neutral pH, the presence of calcium in the wastewater (Table 1: 65–113 mg/L Ca²⁺) might have facilitated the removal of the recalcitrant ΔP species, especially if dominated by phosphonates, as demonstrated in earlier research (Rott et al. 2018).

In the last few cycles (51–55) the adsorbent concentration was doubled to 2 g/L (6.4 g/L particles) to target the δP fraction. The results, however, did not show any change in performance, implying that the δP removal is not linearly proportional to the increase in particle concentration, probably due to thermodynamic limitations. Unfortunately, it was not clear what the exact composition of the non-reactive δP fraction was, i.e. if these recalcitrant species were phosphonates or other compounds. This still needs to be investigated.

The P-loaded particles were regenerated each time in the same 1M NaOH for 20 min at pH ∼ 13, where P desorption took place. Only orthophosphate (PO₄-P) could be measured due to the highly alkaline nature of the desorption samples and the limited sample volume. This is possibly the reason why some P-desorption values (gray bars in Figure 6(b)) surpassed 100%, assuming that some of the δP got transformed into orthophosphate in the alkaline medium and contributed to the higher PO₄-P values. The desorption solution was gradually concentrated with phosphate ions through its constant reuse, attaining almost eight-fold enrichment in cycle 28 (∼7.5 mg/L PO₄-P) compared to the initial concentration in wastewater (0.08–1.9 mg/L P_total). From cycle 29 until the end of the experiment, the desorption solution was replaced with a fresh 1M NaOH due to depletion. The gradual drop in performance could be detected through the linear reduction of electrical conductivity values in the NaOH solution (crosses in Figure 6(c)), indicating a depletion of its particle regeneration capacity.

The results thus far demonstrated the ability of the magnetic sorbents to successfully transfer dissolved phosphorus from a low concentrated medium (wastewater effluent with 0.06–0.82 mg/L PO₄-P) into a high concentrated NaOH solution (several mg/L PO₄-P) through multiple enrichment steps with minimal losses. Moreover, ultra-low effluent
concentrations of <0.05 mg/L P_{tot} were consistently maintained by removing a large portion of the non-reactive phosphorus ΔP, most likely including phosphonates. The final P-rich eluate reclaims an intermediate liquid product of the proposed technology. Optionally, a solid fertilizer, e.g. struvite, can be precipitated from the phosphate-rich reclaimed solution as a final step to recover the phosphorus (Drenkova-Tuhtan et al. 2017).

In contrast to municipal wastewater, typical brackish water RO concentrates would have lower PO_{4} but higher phosphate (10–50 μM) concentrations, lower organic content and higher total dissolved solids (TDS ∼1,000–2,000 ppm, mostly Na, Ca, Cl, and HCO). Extrapolating the pilot test results with municipal effluent to the applicability of the ZnFeZr particles in RO concentrates would probably require an increase in particle dose and a more concentrated NaOH solution for adsorbent regeneration. The high Ca concentration would probably enhance phosphate adsorption at neutral and alkaline pH values. Nevertheless, the possible co-adsorption of metals and other ions and their potential desorption in the final eluate should be monitored closely. The RO concentrates, however, are not expected to have a negative impact on the magnetic separability of the ZnFeZr particles.

CONCLUSIONS

This work advanced the development and application spectrum of engineered magnetically separable ZnFeZr-based micro-sorbents for the removal and recovery of PO_{4} and recalcitrant phosphorus species such as phosphonates from wastewater effluents and synthetic RO concentrates. At pH > pH_{PZC} ~ 7 (the point of zero charge of the ZnFeZr adsorbent), a sharp drop in adsorption efficiency was observed for PO_{4} and all investigated phosphonates (HEDP, NTMP, EDTMP). The adsorption affinity at pH 7 followed the order: HEDP-P > PO_{4}-P > EDTMP-P > NTMP-P. Adsorbent dose > 0.1 g/L was necessary to remove 1 mg/L NTMP-P from a synthetic solution in 30 min at neutral pH.

The presence of metals typically found in RO concentrates (Ca^{II}, Pb^{II}, Cu^{II}) enhanced the adsorption of phosphonates, likely due to the pH drop caused by the metal salt addition. At low pH values (pH < 5) and short equilibration times (~30 min), ternary complex formation led to the removal of metal cations (Pb^{II} and Cu^{II}) along with the phosphonate antiscalants in the synthetic RO concentrates. Long equilibration times (24 hours) and the presence of Ca^{II}, Pb^{II}, and Cu^{II} resulted in Zn dissolution from the particles, possibly due to ion exchange reactions with these metals.

A pilot test with secondary effluent wastewater form a municipal WWTP demonstrated the reusability and effluent polishing potential of the ZnFeZr particles over 55 adsorption/desorption cycles, achieving >90% total efficiency under optimal conditions. An adsorbent dose of 1 g/L at pH ~ 7 and 20 min contact time were sufficient to remove the non-reactive phosphorus species (including phosphonates) from the municipal wastewater and consistently maintain ultra-low effluent concentrations (<0.05 mg/L P_{tot}) over numerous cycles, avoiding the eutrophication risk to the aquatic environment. Successful adsorbent regeneration and simultaneous P desorption were performed in a constantly reused 1M NaOH, where > 10-fold P enrichment was achieved compared to the initial P concentration in the wastewater. The P-rich eluate can be reused in the process or utilized as a source for phosphorus recovery via precipitation of a solid fertilizer product, e.g. struvite.

Future studies should investigate if metals are desorbed during adsorbent regeneration at pH ~ 15. Additionally, there is a need to better understand metal adsorption to the ZnFeZr particles over a broader spectrum of pH 4–12, including the influence of phosphonates. These pH-controlled experiments should employ contact times and metal concentrations more consistent with real water treatment systems, followed by studies in authentic RO concentrates.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.
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