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A CRITICAL REASSESSMENT OF A PHOSPHONATE-CONTAINING GLYCIDYL METHACRYLATE-METHYL METHACRYLATE ION EXCHANGER: SYNTHESIS, CHEMICAL STABILITY AND CHROMIUM(VI)/LEAD(II) SORPTION

Kanat A. Sadykov¹ , Nesipkhan A. Bektenov¹ , Yulia Yu. Gavronskaya^{2*} ¹Abai Kazakh National Pedagogical University, Almaty, Kazakhstan²Herzen State Pedagogical University of Russia, St. Petersburg, Russia* Corresponding author's e-mail: gavronskaya20.07@mail.ru

ABSTRACT

The previously reported performance of a phosphonate-containing ion exchanger derived from glycidyl methacrylate (GMA), methyl methacrylate (MMA), and 1-hydroxyethylidene-1,1-diphosphonic acid (HEDP; termed OEDP in the source publications) contains two unresolved issues: an incorrect chemical-stability calculation and a mechanistically unsupported explanation of chromium (VI) removal by an acidic cation exchanger. This critical reassessment includes previously unpublished, author-retained archival characterization data but reports no newly performed experiments. It re-examines the reported synthesis, recovered original Fourier-transform infrared (FTIR) spectra and elemental-analysis results, static exchange capacity (SEC), and chromium (VI) and lead (II) sorption data and compares the corrected results with recent phosphonate-based sorbents. Among the tested synthesis conditions, a copolymer: HEDP mass ratio of 1.0:1.0 at 90 °C for 10 h gave an 80% yield and the highest reported SEC, 5.92 mmol g⁻¹. Recalculation showed that 87.67-90.20% of the initial SEC was retained after a single exposure to H₂O₂, HNO₃, NaOH, or H₂SO₄; the corresponding loss was 9.80-12.33%, rather than less than 7% as previously stated. The reported lead (II) capacity was 40.4 mg g⁻¹, with 97% removal and an equilibrium time of 8 h. The reported chromium (VI) values were Cr 40.3 mg g⁻¹, 96% removal, and 2.5 h to equilibrium. Lead(II) binding is chemically consistent with proton exchange and coordination at phosphonate oxygen atoms. By contrast, chromium (VI) is present mainly as anionic species at pH 3.7-3.8, so conventional cation exchange cannot explain its removal. Mechanistic verification requires separate determination of chromium (VI) and total chromium, X-ray photoelectron spectroscopy (XPS), redox-potential monitoring, and surface-charge measurements. The archived modified-material analysis reports 12.84 wt.% phosphorus, while the recovered FTIR traces support epoxide consumption and phosphorus-containing functionalization. The reassessment corrects the numerical error and distinguishes this previously unpublished archival evidence from unconfirmed linkage geometry; no nuclear magnetic resonance (NMR) spectrum is available.

Keywords: HEDP; Phosphonate ion exchanger; Chromium (VI); Lead (II); Critical reassessment.

1 INTRODUCTION

The problem addressed in this critical reassessment is the reliability of previously published performance claims for a phosphonate-containing ion exchanger prepared from glycidyl methacrylate (GMA), methyl methacrylate (MMA), and 1-hydroxyethylidene-1,1-diphosphonic acid (HEDP; termed OEDP in the source publications). In the source papers, the stated loss of static exchange capacity (SEC) after chemical treatment is inconsistent with the reported before-and-after values, and chromium(VI) removal was attributed to an acidic cation exchanger without measurements that distinguish anion uptake from chromium reduction or precipitation. These issues affect both the numerical assessment of stability and the proposed sorption mechanism.

Two established sorbent strategies are relevant to this problem. Phosphonate and aminophosphonate materials remove metal cations through acid-base exchange and coordination at oxygen-donor sites, whereas strongly basic anion-exchange resins remove chromium (VI) oxyanions such as HCrO₄⁻, CrO₄²⁻, and Cr₂O₇²⁻ [1, 2]. These approaches are not interchangeable. Cation binding depends on ligand protonation, porosity, swelling, and competition from other ions. In chromium

(VI) systems, a decrease in chromium (VI) concentration alone cannot distinguish adsorption from reduction to chromium (III) unless total chromium and oxidation state are also determined.

GMA is particularly suitable for staged synthesis because its two functional groups are consumed in different reactions. During radical copolymerization, the methacrylate carbon-carbon double bond forms the polymer backbone. Under controlled conditions, the pendant oxirane (epoxide) ring remains intact and can subsequently be opened in a separate post-polymerization reaction to introduce chelating ligands. For example, iminodiacetate- and iminophosphonate-functionalized poly (GMA) showed neodymium (III) capacities of 0.74-0.84 mmol g⁻¹ [3]. In another study, GMA grafted onto polystyrene and subsequently modified with aminophosphonate groups sorbed lanthanum (III) up to 288.69 mg·g⁻¹ at pH 6 [4]. These examples demonstrate the synthetic value of retaining the epoxide ring for a second, chemically distinct functionalization step.

Reported capacities nevertheless vary widely. A phosphonated sepiolite-poly (GMA) hybrid bound copper (II) up to 134.5 mg·g⁻¹ [5]. Two aminophosphonate sorbents showed lead (II) capacities of 0.494 and 0.694 mmol g⁻¹ and were evaluated over five desorption cycles [6]. Other reported values reached 1.28-1.40 mmol·g⁻¹ for neodymium (III) at pH 4.5 [7] and 6.5 mmol g⁻¹ for scandium (III) at 50 °C [8]. These results cannot be ranked directly because the target ion, initial concentration, pH, temperature, matrix architecture, and criterion used to define limiting capacity differ among studies.

Mechanistic assignment requires more than Fourier-transform infrared (FTIR) spectroscopy. FTIR can show the appearance or disappearance of functional-group bands, but it cannot unambiguously identify the coordinating atom, binding geometry, or chromium oxidation state after contact. Equilibrium and kinetic measurements, X-ray photoelectron spectroscopy (XPS), elemental or solution mass balances, and regeneration tests are needed to support such assignments [1]. In swellable phosphonate networks, polymer-chain mobility and ligand accessibility must also be considered, particularly under strongly acidic conditions [9].

The GMA-MMA-HEDP ion exchanger was described in two 2022 publications. The first reported its preparation conditions, yield, FTIR band assignments, and SEC [10]; the second reported chromium (VI) and lead (II) sorption [11]. The authors' unpublished 2022 working manuscript additionally preserves the original precursor and ion-exchanger FTIR plots, proposed structural formulas, and elemental-analysis values that were omitted from the final published article. Re-examination identified two specific limitations: the percentage loss of SEC after chemical treatment had been calculated incorrectly, and the removal of anionic chromium (VI) species had been interpreted without oxidation-state, redox, or surface-charge controls.

Accordingly, the present study recalculates chemical stability from the reported source data, standardizes capacity units, distinguishes experimental capacity from a demonstrated maximum capacity, separates experimental observations from mechanistic hypotheses, compares published data under their reported experimental conditions, and proposes a minimum experimental validation programme.

Novelty of the present reassessment. The present study combines analytical reassessment with previously unpublished archival evidence. It presents, for the first time, the FTIR spectra of the GMA-MMA precursor and the modified ion exchanger, their proposed structural formulas, and elemental-analysis results. Chemical stability is recalculated from the published initial and final static exchange capacity values, revealing losses of 9.80-12.33%. The speciation of chromium (VI) at pH 3.7-3.8 indicates that its reported removal cannot be explained by conventional cation exchange. The previously published lead and chromium sorption data are converted into molar and charge-equivalent units. Experimental uptake measured at a single initial concentration, C₀, is distinguished from a fitted maximum sorption capacity (q_m). In addition, a minimum experimental framework is proposed to distinguish adsorption, chromium (VI) reduction, precipitation, and cation complexation. The archival data are identified as previously unreported historical measurements rather than newly performed experiments. The proposed bonding geometry is not presented as experimentally confirmed.

2 MATERIALS AND METHODS

2.1 Basis and scope of the reanalysis

No new synthesis, sorption, FTIR, or elemental-analysis experiments were performed for this reassessment. The reanalysis combines the experimental results reported in references [10] and [11] with the authors' original, unpublished 2022 working manuscript. The archived document retains two historical FTIR traces, proposed structural schemes, and elemental-analysis values that were not included in the final published version of reference [10]. The acid modifier is designated here by the widely used abbreviation HEDP; the source publications use OEDP for the same compound. Published observations, previously undisclosed archival observations, and present-work recalculations are identified separately.

2.1.1 Preparation of the GMA-MMA precursor

The published protocol and the original working manuscript describe free-radical copolymerization of GMA and MMA in N,N-dimethylformamide (DMF) at 90 °C in sealed molybdenum-glass ampoules under argon. Crystalline benzoyl peroxide was used at 0.1 wt% of the combined monomer mass. Soluble copolymer was purified by two reprecipitations from its DMF solution into ethanol; crosslinked material was washed with 1,4-dioxane to remove residual monomers. The samples were vacuum-dried at room temperature to constant mass [10].

The archived precursor was represented by the idealized repeat-pair formula $C_{12}H_{18}O_5$ ($M_r = 242$), corresponding to one GMA-derived unit plus one MMA-derived unit, i.e., a formal 1:1 molar structural model. This model must not be confused with a documented monomer charge: neither the published article nor the recovered draft states the experimentally weighed GMA:MMA feed ratio, the individual monomer masses, the DMF volume, the polymerization time, or the final solids concentration. One original precursor reaction sketch also bears an 80 °C annotation that conflicts with the 90 °C experimental paragraph; the explicit written protocol is reported here, but this discrepancy and the missing charge data require verification against the laboratory notebook.

2.1.2 HEDP modification procedure

Post-polymerization modification was conducted in DMF in a three-neck flask equipped with a mechanical stirrer, thermometer, and dropping funnel. A 35 wt.% HEDP/OEDP acid preparation was placed in the flask, and a GMA-MMA solution in DMF was introduced gradually under vigorous stirring. The tested copolymer: HEDP mass ratios were 1.0:0.5, 1.0:1.0, 1.0:2.0, and 1.0:3.0. The mixture was heated at 90 °C until gel formation, transferred to a porcelain dish, cured at 90 °C for 10 h, ground, and sieved to collect granules of 0.25-1.00 mm [10].

The 1.0:1.0 copolymer-to-acid ratio yielded the highest reported SEC (5.92 mmol g^{-1}) at an 80% product yield. Absolute copolymer and acid quantities, DMF volume, addition rate, stirring speed, gelation time, post-cure washing, and the basis used for the 35 wt.% acid calculation are not preserved in either source. Full numerical reproducibility therefore still requires the original laboratory notebook.

In the source study, FTIR spectra were recorded on a Nicolet 5700 spectrometer (Thermo Electron, USA) using potassium bromide (KBr) pellets. Static exchange capacity was determined by titration with 0.1 mol L^{-1} NaOH in accordance with the cited standard procedure. Chemical stability was evaluated after a single exposure to 10% H_2O_2 , 1 mol L^{-1} HNO_3 , 5 mol L^{-1} NaOH, or 2.5 mol L^{-1} H_2SO_4 .

2.1.3 Recalculation and comparison

The retained fraction of SEC was calculated as $R = (SEC_{\text{after}}/SEC_{\text{initial}}) \times 100\%$, and capacity loss as $100 - R$. The source unit meq g^{-1} is numerically equivalent to millimoles of charge per gram; the revised manuscript reports this quantity as mmol g^{-1} . Lead(II) capacity was converted from mg g^{-1} to mmol g^{-1} using a molar mass of 207.2 g mol^{-1} . For chromium(VI), the source publication reported the mass of elemental chromium per gram of ion exchanger.

The amount of chromium and the corresponding notional charge equivalent were therefore calculated separately. Literature data were compared only when the principal experimental conditions were available. Values measured for different ions, pH Svalues, temperatures, initial concentrations (C_0), and solution-volume-to-sorbent-mass ratios were not treated as directly rankable. Values measured at a single C_0 were described as experimental capacities rather than maximum capacities (q_m) unless a concentration series had reached saturation and an isotherm had been fitted.

3 RESULTS AND DISCUSSION

3.1 Analytical framework of the reassessment

Figure 1 summarizes the analytical framework: preparation of the epoxy-containing GMA-MMA matrix, functionalization with HEDP, recalculation of exchange-capacity retention, and critical interpretation of lead (II) and chromium (VI) sorption.

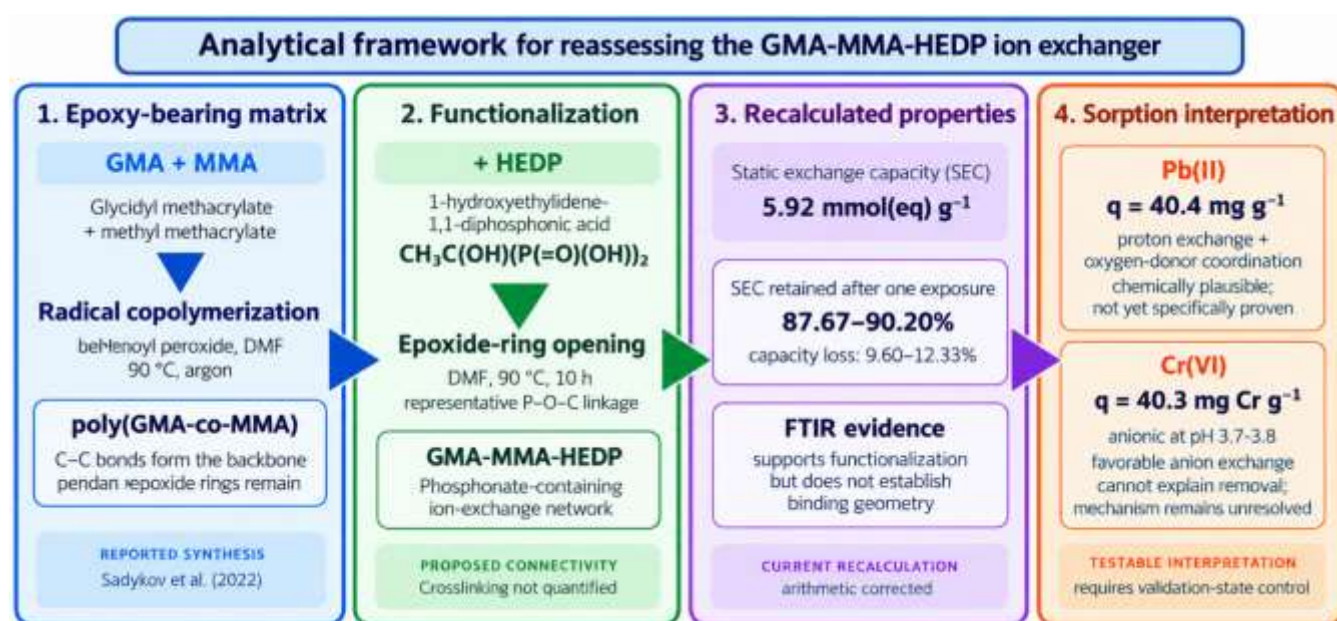


Figure 1 - Analytical framework for reassessing the phosphonate-containing GMA-MMA-HEDP ion exchanger. The schematic was created for the present work; synthesis and SEC data are based on Sadykov et al. [10], and lead (II)/chromium (VI) data are based on Bektenov et al. [11]

The framework explicitly separates reported measurements from interpretation. Synthesis conditions, FTIR observations, SEC, and capacity loss are supported by numerical source data or the present recalculation. Proton exchange and oxygen-donor coordination are proposed for lead(II), whereas the mechanism of chromium(VI) removal remains unresolved because anionic chromium species cannot be retained by a conventional acidic cation-exchange pathway.

Formation of the Phosphonate-Containing Ion Exchanger

The representative reaction in Figure 2 shows proposed opening of the pendant GMA epoxide ring by HEDP and formation of a P–O–C linkage. Reaction at more than one phosphonic-acid site could create interchain bridges and convert the soluble precursor into a crosslinked network. This pathway is chemically plausible, and the recovered archival elemental analysis reports 12.84 wt.% phosphorus. However, epoxide conversion, formulation-specific phosphorus balances, XPS data, and ^{31}P nuclear magnetic resonance spectra remain unavailable; therefore, the exact P–O–C connectivity and interchain bridging cannot be independently confirmed.

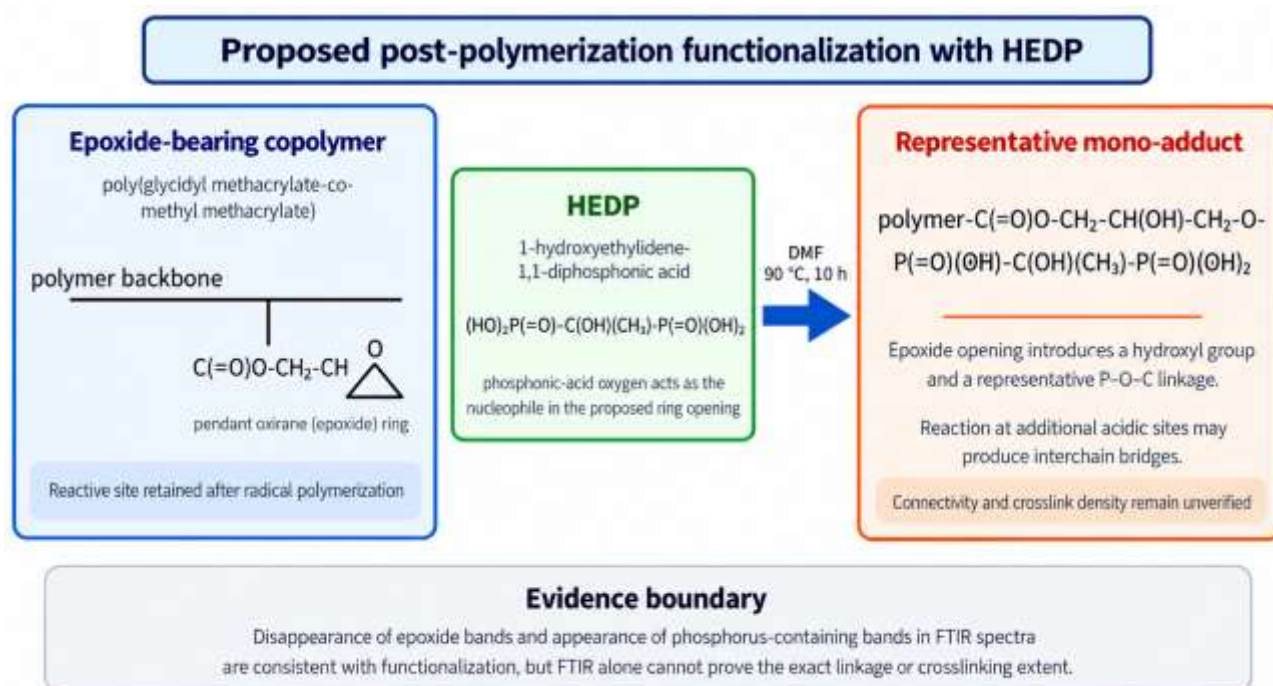


Figure 2 - Proposed post-polymerization functionalization of the GMA-MMA copolymer with HEDP. The schematic was newly drawn for this reassessment from the reaction proposed by Sadykov et al. [10]; the exact linkage and crosslink density remain unconfirmed

3.2 Recovered archival structural formulas

The original 2022 working manuscript preserves the proposed constitutional formulas of the epoxy-bearing GMA-MMA precursor and the HEDP-modified ion exchanger. These author-retained schemes were not included in the final published version of reference [10]. Figures 3 and 4 reproduce their structural content as historical proposed models; the m and n labels do not establish the experimental GMA:MMA feed composition, and the drawings do not independently prove linkage geometry or network architecture.

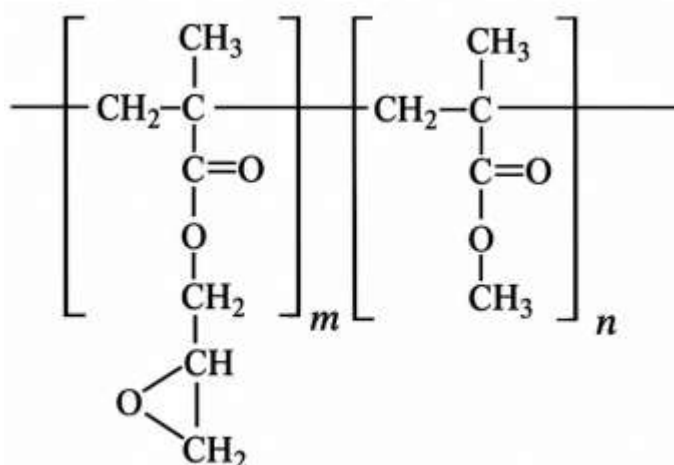


Figure 3 - Previously unpublished archival structural representation of the GMA-MMA copolymer. The retained oxirane group is shown on the GMA-derived unit; m and n denote unspecified repeat counts.

Source: authors' original 2022 working manuscript, not the published figure set of reference [10]

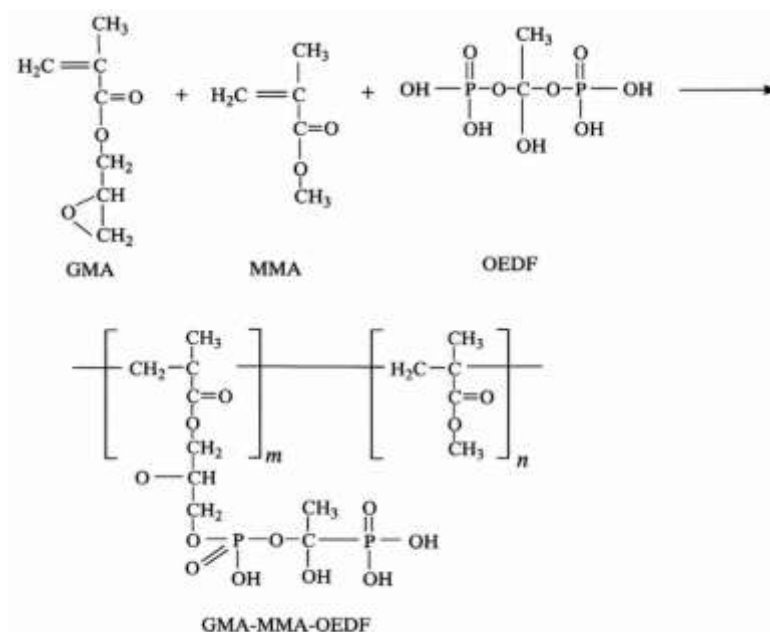


Figure 4 - Previously unpublished archival proposed structure of the GMA-MMA-HEDP ion exchanger. OEDF is the historical source notation for the same HEDP/OEDP modifier. The schematic is a constitutional hypothesis rather than proof of the exact P-O-C linkage. Source: authors' original 2022 working manuscript

3.3 Recovered FTIR spectra and evidence-based assignments

The authors' unpublished working manuscript retained both original Nicolet 5700/KBr-pellet FTIR plots, although neither graph appeared in the final published article. Figures 5 and 6 reproduce those historical spectra over approximately 4000-400 cm^{-1} . They are previously unreported archival measurements, not newly acquired spectra. Peak values in Table 1 are read from the labels visible on the retained plots and are distinguished explicitly from values mentioned only in the earlier source narrative.

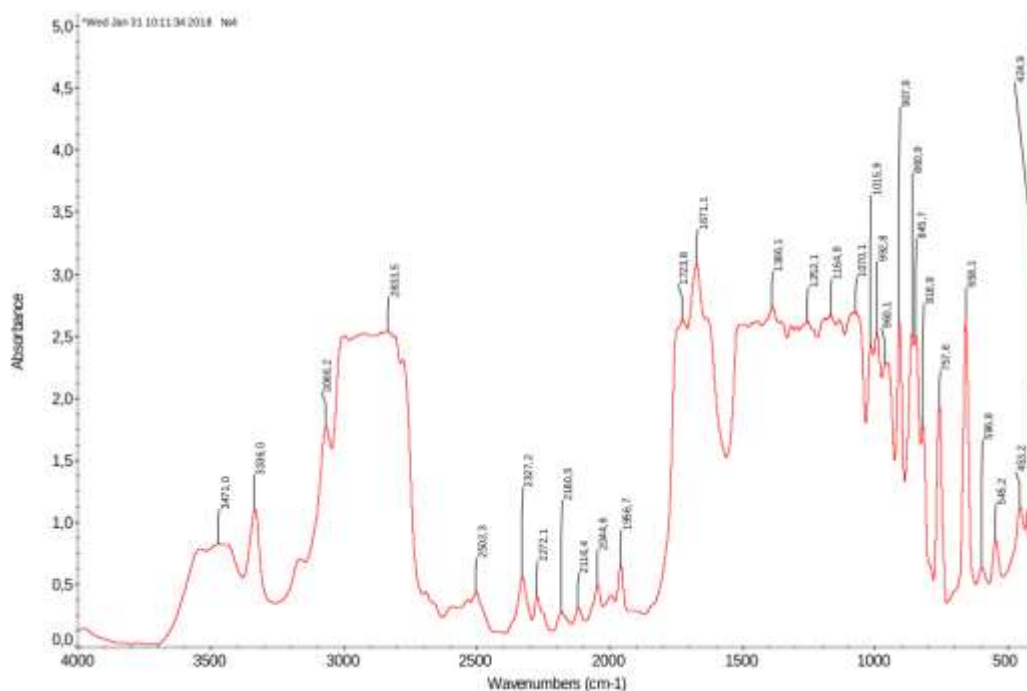


Figure 5 - Previously unpublished archived FTIR spectrum of the initial GMA-MMA copolymer, recorded using a Nicolet 5700 spectrometer and a KBr pellet. The spectrum was recovered from the authors' original 2022 working manuscript; it was absent from the final published article [10]

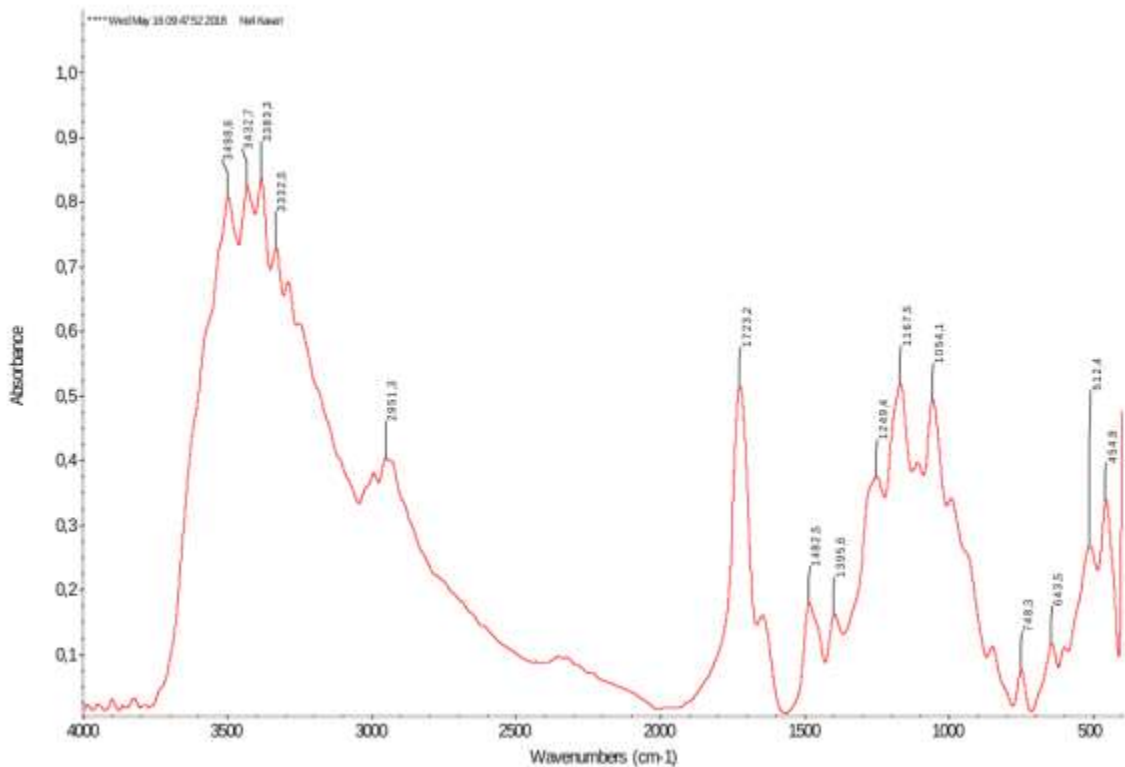


Figure 6 - Previously unpublished archived FTIR spectrum of the GMA-MMA-HEDP (GMA-MMA-OEDP) ion exchanger, recorded using a Nicolet 5700 spectrometer and a KBr pellet. Reproduced from the authors' original 2022 working manuscript; no new measurement was performed [10]

The precursor trace contains an ester C=O band at 1723.8 cm⁻¹ and oxirane-associated labeled features at 907.9 and 845.7 cm⁻¹. The modified trace retains the ester band at 1723.2 cm⁻¹ and shows a broad O-H region at approximately 3498.6-3332.5 cm⁻¹ together with bands at 1249.4, 1167.5, and 1054.1 cm⁻¹, where P-O/P=O and ester C-O contributions overlap.

Table 1. Comparison of labeled bands on the recovered precursor and HEDP-modified FTIR traces

Region	GMA-MMA trace, cm ⁻¹	Modified trace, cm ⁻¹	Evidence-based interpretation
O-H	3471, 3336	3499, 3433, 3383, 3333	Broader hydroxyl environment after acid treatment; this region is not specific for covalent attachment.
Ester C=O	1723.8	1723.2	The methacrylate ester carbonyl is retained after modification.
Oxirane markers	907.9, 845.7	No matching labeled markers	Loss of these labeled oxirane features is consistent with epoxide-ring opening; conversion is not quantified.
C-O / P-O	1252.1, 1164.9, 1070.1	1249.4, 1167.5, 1054.1	The region changes but persists; the approximately 1250 cm ⁻¹ feature cannot truthfully be described as disappearing.
Low-frequency	757.6	748.3, 643.5	A changed low-wavenumber region provides supportive but non-exclusive evidence.
Source prose	Reported: 1267, 703	Exact values not labeled in trace	Historical source-text assignments are retained transparently but cannot be verified from the archived plot labels.

**Source: Peak labels were transcribed from the authors' previously unpublished archived spectra (Figures 5 and 6). The separately identified 1267/703 cm⁻¹ values come from the earlier written description [10], not from visible labels on the recovered trace.*

The source prose additionally reports bands at 1267 and 703 cm^{-1} , but those exact numbers are not labeled on the recovered modified-material plot. Conversely, a band near 1250 cm^{-1} is visible in both spectra; it should not be described as having disappeared. Because the archived traces have different absorbance scales and no instrument-export numerical files are available, they support qualitative functional-group comparison rather than quantitative epoxide conversion. cm^{-1}

3.4.1 Previously unpublished elemental-analysis evidence

The same original working manuscript records calculated and found elemental compositions for both materials. The precursor was modeled as $\text{C}_{12}\text{H}_{18}\text{O}_5$ ($M_r = 242$), and the modified material as $\text{C}_{14}\text{H}_{26}\text{O}_{12}\text{P}_2$ ($M_r = 448$), corresponding formally to addition of one HEDP molecule, $\text{C}_2\text{H}_8\text{O}_7\text{P}_2$, to the proposed GMA-MMA repeat pair. These formulas are idealized constitutional models, not measured molecular-weight distributions or proof of an alternating copolymer sequence.

Table 2. Previously unpublished calculated and found elemental composition from the authors' archived working manuscript

Material	Proposed formula M_r	C, %	H, %	O, %	P, %
GMA-MMA precursor	$\text{C}_{12}\text{H}_{18}\text{O}_5$ $M_r = 242$	59.50 / 59.33	7.43 / 7.55	33.05 / 33.07	Not reported
GMA-MMA-HEDP	$\text{C}_{14}\text{H}_{26}\text{O}_{12}\text{P}_2$ $M_r = 448$	37.50 / 38.03	5.80 / 6.05	42.86 / 43.06	13.84 / 12.84

**Source: Authors' original, unpublished 2022 working manuscript. Values are transcribed as recorded; analytical replicates, uncertainty, the instrument used, and whether oxygen was measured directly or obtained by difference are not preserved.*

The found phosphorus content of 12.84 wt.% directly establishes that the analyzed modified sample contained phosphorus and is 1.00 percentage point below the 13.84 wt.% value calculated for the proposed idealized adduct. This corresponds to approximately 4.15 mmol g^{-1} . If the archived elemental result and the reported SEC of 5.92 mmol g^{-1} refer to the same formulation, their conditional ratio is approximately 1.43 titratable charge equivalents per phosphorus atom. Batch identity, modifier leaching, exact P-O-C connectivity, substitution degree, and interchain crosslink density remain unverified.

Neither the published papers nor the recovered archival manuscript contains a ^1H , ^{13}C , or ^{31}P NMR spectrum, and no NMR measurements were performed for the present reassessment. Because the modified product is an insoluble crosslinked ion exchanger, definitive follow-up would require solid-state ^{13}C and ^{31}P magic-angle-spinning NMR, supplemented by XPS and modifier-leaching controls. FTIR together with elemental phosphorus supports functionalization, but the linkage and bridging shown in Figures 2 and 4 remain proposed rather than independently confirmed.

3.4.2 Effects of reagent ratio, curing temperature and time

Table 3. Reported synthesis conditions and static exchange capacity of the GMA-MMA-HEDP ion exchanger

Copolymer:HEDP mass ratio	Temperature, $^{\circ}\text{C}$	Time, h	Yield, %	SEC with 0.1 mol L^{-1} NaOH, mmol g^{-1}
1.0:0.5	90	10	75	3.11
1.0:1.0	90	10	80	5.92
1.0:2.0	90	10	80	5.10
1.0:3.0	90	10	79	5.03

**Source: Data adapted from Sadykov et al. [10]. The table was reformatted, terminology was standardized, and $\text{meq}\cdot\text{g}^{-1}$ was expressed as the numerically equivalent mmol g^{-1}*

The highest SEC among the tested formulations was not obtained at the largest HEDP dosage. Increasing the copolymer:HEDP mass ratio from 1.0:0.5 to 1.0:1.0 increased SEC from 3.11 to 5.92 mmol g⁻¹. Further increases in the HEDP fraction reduced SEC to 5.10 and 5.03 mmol g⁻¹, while the reported yield remained 79-80%. Network densification and reduced accessibility of phosphonate groups are possible explanations, but this hypothesis requires swelling, porosity, gel-fraction, and formulation-specific phosphorus-content measurements.

The recovered working manuscript also preserves two one-factor curing series. At a fixed 10 h curing time, temperatures of 40, 60, 90, and 120 °C yielded SEC values of 2.05, 4.21, 5.91, and 5.03 mmol g⁻¹, respectively. At 90 °C, curing for 6, 10, 24, and 48 h yielded 4.05, 5.92, 5.08, and 4.53 mmol g⁻¹, respectively. These archived values independently support 90 °C and approximately 10 h as the optimum among the tested conditions; the 0.01 mmol g⁻¹ difference between 5.91 and 5.92 in the two source tables cannot be evaluated without replicate statistics.

3.4.3 Corrected calculation of chemical stability

Recalculation changes the interpretation of chemical stability. The retained fraction of the initial SEC was 90.20% after NaOH, 88.51% after H₂O₂, 88.18% after HNO₃, and 87.67% after H₂SO₄. The corresponding losses were 9.80, 11.49, 11.82, and 12.33%. The previously stated loss of “no more than 7%” is inconsistent with the source SEC values. The available evidence supports resistance to one chemical exposure but does not establish durability during repeated operation.

Table 4. Recalculated static exchange capacity retained and lost after a single exposure to chemical reagents

Parameter	10 % H ₂ O ₂	1 mol L ⁻¹ HNO ₃	5 mol L ⁻¹ NaOH	2.5 mol L ⁻¹ H ₂ SO ₄
Initial SEC, mmol g ⁻¹	5.92	5.92	5.92	5.92
SEC after treatment, mmol g ⁻¹	5.24	5.22	5.34	5.19
SEC retained, %	88.51	88.18	90.20	87.67
SEC loss, %	11.49	11.82	9.80	12.33

*Source: Initial and post-treatment SEC values are from Sadykov et al. [10]. Percent SEC retained and percent SEC loss were recalculated in the present work.

3.4.4 Chemical Interpretation of material stability

The largest calculated SEC loss occurred after H₂SO₄ exposure and the smallest after NaOH exposure; the difference was 2.53 percentage points. Because replicate measurements and standard deviations were not reported, it is not possible to determine whether this difference represents a reagent-specific effect or ordinary experimental variability. The defensible conclusion is that approximately 88-90% of the initial SEC remained after one exposure.

The cause of the SEC decrease has not been established. Plausible processes in acidic media include hydrolysis of P-O-C bonds, leaching of physically retained HEDP, and network contraction. Strong alkali may increase phosphonate ionization and swelling but can also hydrolyse ester groups in the polymer matrix. H₂O₂ may oxidize the organic component. These possibilities could be distinguished by monitoring mass change, phosphorus and total organic carbon in wash solutions, FTIR/XPS spectra, and granule integrity.

A single contact with a reagent is insufficient for technological assessment. Working capacity should be measured over repeated sorption-desorption cycles. Comparable aminophosphonate studies evaluated at least five cycles and reported both desorption efficiency and residual sorption capacity [6, 8]. Equivalent cyclic data are not available for GMA-MMA-HEDP.

3.4.5 Previously published Cr(VI) and Pb(II) sorption results

Table 5 reorganizes the source sorption data and adds the molar and charge-equivalent values calculated in the present reassessment. The reported quantities are used for mechanistic analysis and are not presented as new experimental results.

The reported capacity of 40.4 mg g⁻¹ (Pb(II)) corresponds to 0.195 mmol g⁻¹ (Pb(II)), or 0.390 meq g⁻¹. This value is 6.6% of the titratable acid-base capacity of 5.92 meq g⁻¹. The difference is not contradictory: NaOH titration measures accessible acidic protons, whereas lead(II) sorption is also constrained by pH 3.5, metal concentration, diffusion, and coordination geometry.

For chromium(VI), 40.3 mg g⁻¹ (Cr(VI)) corresponds to 0.775 mmol g⁻¹ (Cr(VI)). If all chromium is notionally assigned to dichromate, this equals 0.388 mmol g⁻¹ (Cr₂O₇²⁻), or 0.775 meq g⁻¹. At pH 3.7–3.8, chromium(VI) occurs mainly as HCrO₄⁻, with a concentration-dependent contribution from Cr₂O₇²⁻; CrO₄²⁻ is less important under these acidic conditions. An acidic phosphonate cation exchanger should not exchange these anions by a conventional cation-exchange mechanism. The previous interpretation therefore requires verification.

Table 5. Previously published sorption data and present-work conversions for GMA-MMA-HEDP

Parameter	Chromium (VI)	Lead (II)
Feed salt	K ₂ Cr ₂ O ₇	Pb(NO ₃) ₂
Initial concentration, C ₀	105.0 mg L ⁻¹	104.6 mg L ⁻¹
pH	3.7-3.8	3.5
Reported equilibrium time	2.5 h	8.0 h
Reported experimental capacity, q	40.3 mg L ⁻¹	40.4 mg L ⁻¹
Converted amount	0.775 mmol g ⁻¹	0.195 mmol g ⁻¹
Charge-equivalent capacity	0.775 mmol g ⁻¹ (notional, if retained as Cr(VI))	0.390 mmol g ⁻¹
Reported removal	96%	97%

*Source: C₀, pH, equilibrium time, q, and removal are from Bektenov et al. [11]. Molar and charge-equivalent values were calculated in the present work; the table layout is new.

Several pathways remain possible: partitioning of anions into the polar polymer phase, ion-pair formation at locally protonated sites, reduction of chromium(VI) to chromium(III) followed by coordination, or precipitation/coprecipitation. None has been demonstrated. Required controls include separate measurement of total chromium and chromium(VI), Cr 2p XPS, redox potential, zeta potential, and a blank experiment without the ion exchanger.

3.4.6 Pb(II) binding mechanism

At pH 3.5, phosphonic-acid groups are only partly deprotonated. A limiting overall reaction can be written as 2≡R-P(=O)(OH)₂ + Pb²⁺ ⇌ [≡R-P(=O)(OH)-O]₂Pb + 2H⁺, where ≡R denotes the polymer matrix. Figure 7 visualizes this proposed combination of proton exchange and Pb-O coordination.

The dashed contact indicates possible auxiliary hydroxyl/ether oxygen coordination. The denticity and geometry have not been established experimentally. The real complex may be monodentate, bidentate, or oxygen-bridged, and hydroxyl or ether oxygen atoms generated by epoxide-ring opening may also contribute.

The difference between 5.92 meq g⁻¹ determined by NaOH titration and 0.390 meq g⁻¹ for Pb(II) is not a conversion error. The two experiments measure different quantities. Moreover, one Pb²⁺ ion may occupy several oxygen-donor sites, and some acidic groups may be inaccessible to the metal at the selected pH and phase ratio. The proposed mechanism can be tested by recording Pb 4f, P 2p, and O 1s XPS spectra before and after sorption, measuring proton release, and evaluating competition from Ca²⁺, Mg²⁺, Cu²⁺, Ni²⁺, and Zn²⁺. Shifts in P 2p/O 1s binding energies together with a Pb-O spectral component would support inner-sphere coordination rather than simple electrostatic retention.

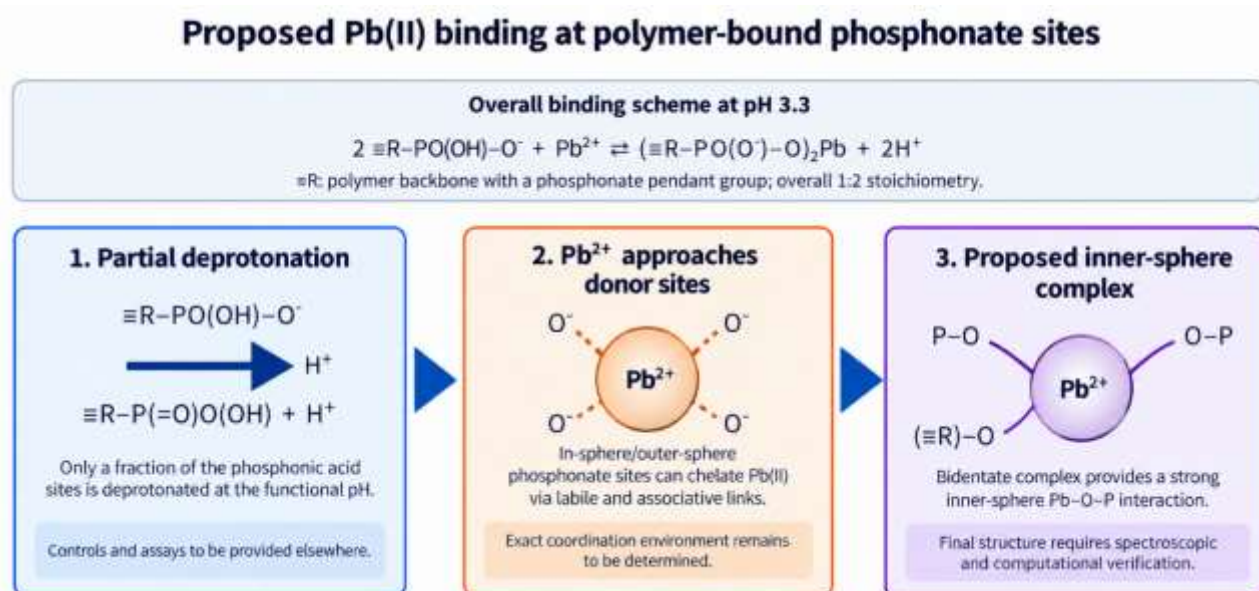


Figure 7 - Proposed, testable pathway for lead(II) binding at polymer-bound phosphonate sites. Solid Pb-O contacts represent the limiting coordination model

3.5 Testable sorption hypotheses

3.5.1 Cr(VI) sorbent speciation

At pH 3.7-3.8, the initial chromium(VI) occurs mainly in anionic forms. If chromium remains as chromium(VI), the notional charge capacity is 0.775 mmol g⁻¹. If it is reduced to chromium(III), the same amount of chromium corresponds to 2.33 mmol g⁻¹ of positive charge. Both values are below the total SEC, but neither calculation establishes the mechanism.

The reduction hypothesis has the greatest effect on interpretation: $\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$. Electrons could, in principle, be supplied by oxidizable matrix fragments or impurities, but the source experiments did not test this possibility. Without oxidation-state control, a decrease in chromium(VI) concentration cannot automatically be described as dichromate-anion sorption.

Verification should include chromium(VI) and total chromium in the initial and equilibrium solutions, redox potential, Cr 2p XPS, electron paramagnetic resonance (EPR) or ultraviolet-visible (UV-Vis) spectroscopy, zeta potential as a function of pH, and a control with unmodified GMA-MMA. If chromium(III) appears as chromium(VI) decreases, the process should be described as reduction followed by complexation rather than direct ion exchange.

3.5.2 Criteria for valid comparison of sorbents

Capacities expressed in mg g⁻¹ are useful for comparing the same ion but are unsuitable for direct comparison among metals with different molar masses. Molar uptake should be expressed in mmol g⁻¹, whereas charge exchange should be expressed in meq g⁻¹. Even after conversion, comparisons remain conditional on pH, ionic strength, temperature, C_0 , solution-volume-to-sorbent-mass ratio, and the equilibrium criterion.

Table 6 therefore summarizes results obtained under different conditions; it is not a ranking.

Functional-group chemistry determines only part of sorption performance. Phosphonate oxygen atoms are hard donor sites and generally interact more strongly with hard and intermediate cations, particularly trivalent ions. Protonated amine groups can bind anions. Access to these sites is controlled by porosity and swelling; consequently, materials with similar SEC values may differ substantially in experimental capacity and equilibration time.

The experimental values reported for GMA-MMA-HEDP are lower than several published capacities for Pb(II), La(III), Nd(III), Cu(II), and Sc(III). This does not demonstrate that the matrix is intrinsically inferior. Bektenov et al. [11] used an initial concentration of approximately 100 mg L⁻¹, which is insufficient to establish a saturated isotherm. The value of 40.4 mg g⁻¹ should therefore be described as an experimental capacity at the selected C_0 , not as a demonstrated q_m . A concentration

series, nonlinear model fitting, and parameter confidence intervals are required.

FTIR alone is also insufficient to support a selectivity claim. For the MTS9500 resin, differences in iron(III), aluminium(III), and magnesium(II) binding were investigated using XPS and interaction-energy calculations [14-17]. Equivalent evidence is unavailable for GMA-MMA-HEDP. The defensible statement is therefore narrower: the material contains phosphonate sites and binds metal cations, whereas selectivity remains to be tested in multicomponent solutions.

Zeng et al. [13] provide a useful mechanistic comparison. They related high uptake not only to phosphonic-acid ligands but also to polymer-network mobility and tested the interpretation using FTIR, XPS, controlled experiments, and density functional theory (DFT). Although one recovered archival measurement reports 12.84 wt.% bulk phosphorus, formulation-resolved phosphorus balances, P/O chemical states, and direct evidence of metal coordination remain unavailable for GMA-MMA-HEDP. Ligand protonation and competition among ions must therefore remain explicit variables in any selectivity claim.

Table 6. Comparison of published sorption performance

Materials	Target ions	Reported value	Conditions / comments	Ref.
GMA-MMA-HEDP	Pb(II)	40.4 mg g ⁻¹ (0.195 mmol·g ⁻¹)	pH 3.5; 8 h; previously published	[11]
GMA-MMA-HEDP	Cr(VI)	40.3 mg g ⁻¹	pH 3.7-3.8; mechanism requires verification	[11]
PGMA with iminophosphonate groups	Nd(III)	0.74-0.84 mmol·g ⁻¹	capacity depends on ligand type	[3]
PS-PGMA-DETA-PA	La(III)	288.69 mg g ⁻¹	pH 6; 298.15 K	[4]
Ethylenediamine- and diethylenetriamine-derived aminophosphonate sorbents	Pb(II)	0.694 / 0.494 mmol·g ⁻¹	pH ≈ 5; 5 regeneration cycles	[6]
Phosphonated sepiolite-graft-PGMA	Cu(II)	134.5 mg g ⁻¹	Langmuir model	[5]
Aminophosphonate resin	Nd(III)	1.28-1.40 mmol·g ⁻¹	pH 4.5; equilibrium in 60 min	[7]
Phosphonate-carboxylate copolymer	Sc(III)	up to 6.5 mmol·g ⁻¹	pH 4; 50 °C; 5 cycles	[8]
GMA-ACN-PEI	Pb(II) / Cu(II)	85.6% / 77.8% removal	different GMA copolymer; Langmuir model	[13]

*Abbreviations: PS, polystyrene; PGMA, poly(glycidyl methacrylate); DETA, diethylenetriamine; PA, phosphorous acid; ACN, acrylonitrile; PEI, polyethyleneimine.

3.6 Limitations and required future experiments

This reassessment is constrained by the limitations of the source experiments. The number of replicates and standard deviations were not reported. Although the original working manuscript restores two FTIR plots, proposed structural formulas, and quantitative elemental-composition summaries, the experimentally charged GMA:MMA feed ratio, individual reagent quantities, solvent volumes, polymerization time, original numerical FTIR data files, FTIR acquisition settings, elemental-analysis replicates, epoxide conversion, and NMR spectra remain unavailable. Some values in the historical written FTIR interpretation are not labeled on the recovered plots; these discrepancies are reported explicitly rather than treated as confirmed peaks. Concentration series, desorption, and cyclic stability were not examined; HEDP leaching was not monitored; and chromium oxidation state after contact was not determined. The source sorption method also contains an internal

inconsistency: 0.05 g of ion exchanger in 20 mL of solution corresponds to 2.5 g L⁻¹ (or 0.4 L g⁻¹), whereas an ion-exchanger-to-solution ratio of 1:1000 is also stated. The laboratory record should be checked before any missing or inconsistent parameter is reused.

A minimum new experimental block should include 6-8 initial concentrations, at least three independent replicates, nonlinear Langmuir and Freundlich fits, 8-10 kinetic time points, competitive sorption, and five sorption-desorption cycles. The ion exchanger should be examined before and after contact by FTIR, solid-state ¹³C/³¹P NMR, XPS, and scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM-EDS). For chromium(VI), parallel determination of chromium(VI) and total chromium is essential. Only such a dataset can distinguish a new experimental study from further interpretation of the 2022 results.

3.6.1 Practical significance and further validation programme

Static capacity measured in a flask does not predict column performance. Translation to water-treatment conditions requires dynamic exchange capacity, breakthrough curves plotted as the effluent-to-influent concentration ratio (C/C₀) against treated volume or bed volumes, and experiments at several flow rates and bed heights. Without these measurements, the working lifetime of the ion exchanger cannot be estimated.

Distribution coefficients (K_d) and separation factors should be calculated in multicomponent solutions. For lead(II), competition from Ca(II), Mg(II), Zn(II), Cu(II), and Ni(II) is critical. For chromium(VI), oxidation-state control and direct comparison with a strongly basic anion exchanger are required. Leaching of the phosphorus-containing modifier, total organic carbon in treated water, and mechanical integrity of the granules should be measured separately.

Table 7. Minimum programme for validation of sorption properties

Validation block	Minimum design	Criterion for interpretation
Reproducibility	At least three independent experiments for each point	Mean ± standard deviation; relative error
Isotherm	6-8 initial concentrations; nonlinear fitting	q _m , equilibrium constants, RMSE/AIC, and confidence intervals
Kinetics	8-10 time points up to equilibrium	Model parameters and intraparticle-diffusion assessment
Selectivity	Binary and multicomponent solutions	K _d and separation factors
Regeneration	At least five sorption-desorption cycles	Capacity retention and desorption efficiency
Dynamic mode	Column tests at several flow rates	Breakthrough curve and dynamic capacity
Mechanism	XPS, SEM-EDS, pH/redox potential; chromium(VI) and total chromium	Surface composition, coordination evidence, and oxidation state

*Abbreviations: q_m, fitted maximum capacity; RMSE, root-mean-square error; AIC, Akaike information criterion; K_d, distribution coefficient; XPS, X-ray photoelectron spectroscopy; SEM-EDS, scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy.

The programme in Table 7 separates three questions: how much metal the ion exchanger binds, which process is responsible for binding, and how effectively the material can be regenerated. Until these questions are resolved, application of GMA-MMA-HEDP to industrial effluents should be described as a testable prospect rather than an established technology.

4 CONCLUSION

Among the tested synthesis conditions, a copolymer: HEDP mass ratio of 1.0:1.0 at 90 °C for 10 h gave an 80% yield and the highest reported SEC, 5.92 mmol g⁻¹. After one exposure to H₂O₂, HNO₃, NaOH, or H₂SO₄, 87.67-90.20% of the initial SEC remained, corresponding to a loss of 9.80-12.33%. The previously stated loss of “no more than 7%” is not supported by the source values.

For lead(II), the reported experimental capacity of $40.4 \text{ mg} \cdot \text{g}^{-1}$ is chemically consistent with proton exchange and coordination at phosphonate oxygen sites, although the proposed geometry requires XPS and proton-release evidence. For chromium(VI), the reported $40.3 \text{ mg} \cdot \text{g}^{-1}$ and 96% removal cannot be explained by conventional cation exchange because chromium(VI) is mainly anionic at pH 3.7–3.8. Separate measurement of chromium(VI) and total chromium, redox-potential monitoring, and surface analysis after contact are required.

The reassessment discloses the previously unpublished archival FTIR spectra, proposed structural formulas, and elemental-analysis result of 12.84 wt.% phosphorus; resolves the arithmetic inconsistency; and provides a species-based reinterpretation of chromium(VI) removal. The recovered evidence supports phosphonate functionalization but does not independently confirm the exact covalent linkage or establish q_m , selectivity, regeneration stability, or dynamic performance. Final evaluation requires replicated isotherms and kinetics, multicomponent tests, repeated sorption-desorption cycles, modifier-leaching measurements, and column breakthrough experiments.

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Data Availability Statement: The displayed FTIR plots, proposed structural formulas, and elemental-analysis values originate from the authors' unpublished 2022 working manuscript and were absent from published reference [10]. No new measurements were performed; numerical FTIR export files, NMR spectra, and elemental-analysis replicate records remain unavailable.

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