



Mechanisms of mercury removal from water with highly efficient MXene and silver-modified polyethyleneimine cryogel composite filters

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Abstract

Safeguarding aquatic ecosystems and human health requires effective methods for removing pollutants. Mercury (Hg) is a very toxic pollutant with a global presence and is highly mobile and persistent. Here, innovative materials were prepared for separating Hg(II) from water, and the mechanisms underlying the efficient uptake of Hg species have been investigated. The sorbents include silver (Ag) nanoparticles and multilayered $\text{Ti}_3\text{C}_2\text{T}_x$ MXene, both incorporated into the structure of a three-dimensional polyethyleneimine porous cryogel (PEI) that acts as a scaffold holding and exposing nano active sites involved in the removal of Hg. Specifically, Ag particles were deposited onto MXene phases, and the resulting composite was embedded in the macroporous PEI polymer (PEI/MXene@Ag cryogel). The composite has beneficial properties regarding Hg removal: 99% of Hg was separated from waste within 24 h in batch studies. The maximum removal capacity of Hg reached 875 mg/g from HgCl_2 , and 761 mg/g and 1280 mg/g from $\text{Hg}(\text{OAc})_2$ and $\text{Hg}(\text{NO}_3)_2$ salts by PEI/MXene@Ag. The Hg uptake stems from the composite's relatively large specific surface area, layered porous channels, and highly dispersed Ag nanoparticles in the multilayered $\text{Ti}_3\text{C}_2\text{T}_x$ MXene. The matrix in the water samples that were treated with the composite did not hinder the uptake of Hg by PEI/MXene@Ag. The high effectiveness achieved for the removal of Hg, combined with rapid adsorption kinetics, high efficiency, and selectivity, positions it as an efficient solution. Future work should address upscaling its preparation for increasing readiness towards mitigating Hg in surface water.

Keywords Nano · Ag · Hg · Polyethyleneimine · Water treatment

1 Introduction

Heavy metal pollution is a problem in aquatic ecosystems worldwide [1, 2]. According to the World Health Organization (WHO) and the United States Environmental Protection Agency (USEPA), the concentration of heavy metals in large bodies of water, such as the Half Park Lake (North America), the Danube River (Europe), the Nile River (Africa), the Pearl River (Asia), and the Matanza-Riachuelo (South America), exceed threshold values of toxicological concern [3]. The negative impacts of widespread heavy metal pollution in water are affecting every continent, and their bioaccumulation may affect the entire food chain [4–6].

Mercury (Hg) is one of the most toxic and common heavy metals, and its industry emissions threaten human health [7–10]. There are various approaches for removing Hg from water. These typically include adsorption, precipitation, electrolysis, ion exchange, membrane purification, or solvent extraction [11–13]. Among them, adsorption can

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be efficient, simple, and cost-effective; hence, it is suitable for large scale uses [14–16]. Activated carbon (AC), zeolites among others, have been widely used as adsorbents for Hg, although they often offer slow removal kinetics, poor adsorption capacity, and pH dependence for this metal. New composites are trying to overcome these challenges [17, 18], and there is a current technology gap for sustainable water treatment technologies with high performance that allow meeting regulations for regulated and emerging pollutants.

Composites that efficiently remove Hg and other heavy metals can rely on advantageous properties of nanomaterials [19]. For instance, a composite consisting of 2D molybdenum disulfide nanosheets (2D MoS₂) in a 3D cellulose structure almost completely removed Hg(II) from aqueous solutions [20]. The incorporation of 2D MoS₂ into a 3D sorbent improved the adsorption capacity offered, prevented aggregation of the nanosheets, and facilitated reusing the composite. Highly branched graphene oxide nanosheets incorporated onto a polyethyleneimine aerogel became efficient for treating Hg from freshwater (81% Hg removal at 50 µg Hg/L) thanks to its large number of oxidized functional groups and high specific surface area [21]. However, using nanomaterials in water treatment also entails limitations such as poor water dispersibility and self-aggregation, toxicity, and limited selectivity when treating pollutants [22].

A promising family of 2D materials for water purification is MXenes. Despite that they were only discovered in 2011, MXenes can remove heavy metals from water [23–25]. Furthermore, there is evidence of its safety relevant to humans for some of its uses [26]. The 2D structure of MXenes, along with their abundant polar functional groups (-OH, -F, and -O), and very good dispersibility, are advantageous for the removal of both organic and metals from water [27]. Compared to other 2D structures, MXenes possess in situ reductive-adsorption capacity and can selectively remove Hg from wastewater [28–32]. Despite the potential safety of the nanomaterials used in this work, using nanomaterials dispersed in water for removing pollutants in the natural environment would not be a practical approach, and its risks do not outweigh the benefits [33]. Therefore, nanomaterials such as MXenes can be embedded in monoliths that would be employed to hold free nanoparticles. Cryogels are polymers with large interconnected macropores ranging in size from tens to several hundreds of micrometers, and their properties as nano-enablers are well established [34–36]. In this study, monolith filter cryogels will be prepared to maximize the removal of Hg as well as holding nanomaterials that would provide active sites involved in such removal. For the cryogel synthesis, the polyethyleneimine (PEI) was used as the main polymeric compound, due to the presence of primary, secondary, and tertiary amines, which are well-known metal chelating groups [37–40]. The study will focus

on understanding mechanisms that drive the removal of Hg from water with Ti₃C₂T_x MXene doped with silver nanoparticles while embedded in cryogels. Nanosilver (Ag) can amalgamate Hg in hyperstoichiometric ratios, and this can add additional capacity for Hg removal [41]. The significance of this study is identifying the important properties that need to be preserved and maximized when upscaling the sorbent, and simplifying it, to enhance its impact and applicability.

2 Materials and methods

2.1 Materials

Dimethylacrylamide (DMAAm, 99%); N, N'-methylenebisacrylamide (BisAAM, 99%), polyethyleneimine (PEI, 99%); N, N, N', N'-tetramethylethylene-1,2-diamine (TEMED, 99%); allylamine (98%); phosphoric acid (H₃PO₄, ≥ 85%); sodium hydroxide (NaOH, ≥ 98%); ammonium persulfate (APS, 98%); hydrofluoric (HF, ≥ 48%); Hg(II) chloride (HgCl₂, ≥ 99.5%); mercury (II) acetate (Hg(OAc)₂, 97%); mercury (II) nitrate monohydrate (Hg(NO₃)₂ • H₂O, ≥ 98.5%); and silver nitrate (AgNO₃, > 99%), dimethyl sulfoxide (DMSO, ≥ 99.9%) were purchased from Sigma-Aldrich (Germany). Ti₃AlC₂ MAX phase (99%) was purchased from Carbon-Ukraine LTD. All experiments were performed with ultrapure water (Puris Eco RO 1600-M, South Korea).

2.2 Synthesis of PEI cryogel

PEI cryogels were prepared according to previous work [32]. Briefly, TEMED and APS acted as the catalyst and initiator, respectively. Allylamine and PEI were the monomers; BisAAM was the crosslinker, and the functional group precursor was DMAAm. Water (18.5 mL) was purged with N₂ for 30 min and separated in two beakers. In one of them, 10 mL of the H₂O with low air content, 260 mg of BisAAM, and 250 mg of PEI were stirred at room temperature until their full dissolution. In parallel, a second beaker, a fraction of the purged H₂O (8.5 mL), and allylamine (0.3 mL) were mixed with concentrated H₃PO₄ (0.24 mL). Further, the solutions in both beakers were mixed, and the pH was adjusted to 7.5 by adding 5 M NaOH dropwise. TEMED (0.03 mL) was added to it, and the mixture was placed in an ice bath to reach 2–3 °C. Finally, 0.80 mL of 5% APS was added to the monomeric solution; the mixture was homogenized manually, and it was quickly transferred to plastic syringes (which had their narrow aperture sealed) placed in a refrigerated/heating circulator (F34 HE, Julabo, USA) filled with ethanol kept at – 12 °C for proceeding with the polymerization step. The mixture remained in the cryostat for 24 h

to become cryogel monoliths. These were taken out from the syringes, thawed at room temperature, and washed several times in water to remove unreacted compounds. Following, they were frozen, lyophilized, and kept at room temperature and for future use.

2.3 Synthesis of MXene

Ti_3AlC_2 (1 g) MAX phase was gently dispersed in HF (10 mL of 48 wt%) in a plastic bottle and stirred for 24 h at room temperature as earlier reported [42]. The etched MXene was washed with 3.5 L of water via repeated centrifugation-decantation at 3500 rpm until the pH of the supernatant reached approximately ~6–7. To increase the interlayer spacing of multi-layer MXene, the washed $\text{Ti}_3\text{C}_2\text{T}_x$ was suspended in DMSO and left stirring for 24 h. The DMSO/MXene suspension was washed via repeated ($\times 15$) centrifugation-decantation at 3500 rpm. The obtained MXene sediment was filtered with 0.45- μm PVDF filter paper (Milli-Q, USA), vacuum dried, and preserved in a desiccator at room temperature for further studies.

2.4 Synthesis of MXene@Ag composite

Dry MXene (200 mg) was suspended in water (170 mL), and the suspension was mixed with 30 mL of aqueous solution of AgNO_3 (100 mg). The mixture was stirred for 10 min at 300 rpm and washed through centrifugation (for 5 min at 3500 rpm in 96% ethanol for three times). The sediment was washed in water twice. The solid residue (MXene@Ag flakes) was filtered with 0.45- μm PVDF filter paper (Milli-Q, USA), vacuum dried for 24 h, and used for further characterization. Freshly prepared MXene@Ag colloidal solutions (therefore where the filtration step had been omitted) were used without drying for cryogel modification.

2.5 Synthesis of PEI/MXene@Ag composite

For the superficial deposition of MXene@Ag onto the cryogel walls, the cryogel monoliths (20 mg) were immersed in 10 mL of MXene@Ag colloidal solution and left shaking for 24 h. The resulting material was washed with water to remove any MXene@Ag residues from the cryogel pores. The modified composites were freeze-dried and stored in a desiccator at room temperature for further use. The same procedure was used to modify cryogels with raw MXene.

2.6 Characterization

The surface chemistry of the dry material was characterized with IR. Specifically, an ATR-FTIR spectrophotometer (Cary 600 Series, Agilent Technologies) was used in the range of 4000–400 cm^{-1} with a resolution of 4 cm^{-1}

and a scanning speed of 1 $\text{cm}^{-1} \text{ s}^{-1}$. Before the acquisition, the synthesized materials were lyophilized and ground into fine powder with a mortar. To evaluate the morphology and elemental composition of the samples, they were examined with scanning electron microscopy (SEM) (Zeiss Crossbeam 540, Germany), operating at 5–20 kV. The SEM was coupled with energy-dispersive X-ray (EDX) spectrometry. High-resolution transmission electron microscopy (HRTEM) (JEM-2100 LaB6 HRTEM, JEOL, Japan), operating at 80 kV, was used to assess pre-ground powdered samples that had been suspended in alcohol and sonicated to avoid agglomeration. A 10 μL drop of the suspension was placed on a 300-mesh carbon-coated copper grid, and the sample was dried overnight. Compositional data from bare MXenes and modified cryogel composites was obtained with X-ray diffraction (XRD), using an X-ray diffractometer (Rigaku SmartLab, Japan) with a HyPix-3000 high-energy resolution 2D HPAD detector. Materials were scanned in the range from 5 to 70° with a diffraction angle of 2θ at 40 kV and 40 mA. X-ray photoelectron spectroscopy (XPS) measurements were conducted on a VG-Microtech Mutilab 3000 device equipped with a 9 channeltrons hemispherical electron analyzer and X-ray radiation source with Mg and Al anodes. The binding energies (BE) were calibrated by a C1s core level at 284.8 eV as a reference. The analysis of the zeta potential of the samples was done as follows: briefly, each sample with a mass 10 mg was added to 10 mL aqueous solution with adjusted pH (from 1 to 10). The pH value was adjusted by adding 1 M HCl or 1 M NaOH. After 24-h shaking, the pH was measured and readjusted if needed. Upon reaching stable pH values, the surface charge of each sample was analyzed with a Malvern Zetasizer Pro model.

2.7 Mercury adsorption experiments

The performance of the prepared composites for Hg adsorption was done by mixing 10 mg of materials with various Hg concentrations and volumes. Different Hg salts were tested independently as sources of Hg. The total amount of Hg was quantified with inductively coupled plasma-mass spectrometry (ICP-MS) (iCAP RQplus, Thermo Fisher, USA). Kinetic adsorption experiments were carried out as follows: 10 mg of the synthesized material, 20 mL 10 mg/L of Hg from independent salts (HgCl_2 , $\text{Hg}(\text{OAc})_2$, or $\text{Hg}(\text{NO}_3)_2$) adjusted to pH 3. The adsorption experiments were left stirring at room temperature. For the analysis of Hg at every time point, 30 μL of solution was collected, diluted, and analyzed to record the residual concentration of Hg. For isotherm studies, like in kinetic studies, 10 mg of the composites were mixed with 20 mL of Hg in solution. Here, the levels of Hg were 100–1000 mg/L. These solutions were prepared from the above mentioned salts and left for 24 h under the stirring. To analyze the speciation of Hg ions with pH, 100 mg/L

HgCl₂, Hg(OAc)₂, and Hg(NO₃)₂ solutions were used, and the study was supported with Visual MINTEQ 3.1 program. To simulate realistic conditions for the treatment of environmental samples with various co-existing ions, tap water without any purifications was spiked with 10 mg/L Hg from solutions from the salts HgCl₂, Hg(OAc)₂, and Hg(NO₃)₂ with further pH adjustment to 3 using HCl or HNO₃. Hg-spiked tap water solutions (50 mL) were mixed with 10 mg of PEI, PEI/MXene, and PEI/MXene@Ag samples and left for stirring for 24 h. To compare the efficiency of synthesized materials with commercial adsorbents for the removal of Hg ions, the H⁺-form ion-exchange resin (Merck), NaY synthetic zeolites (Sigma-Aldrich), and activated carbon (GUNT) were used. Flow-through experiments were carried out to evaluate the effectiveness of Hg removal in dynamic mode. The synthesized samples were cut into disks (6 mm thickness, 8 mm in diameter) of ~14–16 mg, and these were used for filtering 5 mg Hg/L aqueous solutions filtered through the monolith with the help of a peristaltic pump. The flow rates of the filtrate solution were 2.5–5 mL/min, depending on the experiment. Every minute, the filtered solutions were collected and analyzed by ICP-MS. All experiments were performed in duplicate, and the average values with their error bars (corresponding to the standard deviation) are presented in Figs. 3, 4, 5, and 6.

2.8 Applied adsorption models

The results of isotherm experiments were used to evaluate the fitting of experimental adsorption data to widely used Langmuir and Freundlich models. The linearized equation of the Langmuir sorption isotherm [43] is given in Eq. (1):

$$\frac{C_{eq}}{q_{eq}} = \frac{1}{q_m K_L} + \frac{C_{eq}}{q_m} \quad (1)$$

In Eq. (1), C_{eq} and C_0 (mg/L) are the equilibrium and initial concentration of Hg ions in solution, respectively, q_{eq} and q_m are the equilibrium and maximum adsorption capacities in mg/g wet sorbent, while K_L is the Langmuir constant (L/mg). The linear form of the Freundlich sorption (Eq. 2) isotherm is as follows [44]:

$$q_{eq} = \log K_F + \frac{1}{n} \log C_{eq} \quad (2)$$

In Eq. (2), C_{eq} (mg/L) and q_{eq} (mg/g) are the concentration and adsorption capacity at the equilibrium, and n (dimensionless) and K_F are constants (units depend on the $1/n$).

In order to evaluate the behavior of the adsorption kinetics, pseudo-first order and pseudo-second order models were fit to the experimental data [45]:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (3)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

In Eqs. (3) and (4), q_{eq} and q_t are the amount (mg/g) of Hg adsorbed at equilibrium and at a given time, t , in min, respectively. The pseudo-first-order constant k_1 (min⁻¹) and the calculated q_e can be obtained from the slope and intercept of the $\ln(q_e - q_t)$ versus t graph. The pseudo-second-order constant k_2 (g·mg⁻¹·min⁻¹) and q_e can be calculated from the t/q_t versus t graph.

The breakthrough curve is plotted from the normalized instantaneous Hg concentration in solution (C_t/C_0), and C_0 is the initial concentration of Hg ions. When designing a fixed-bed adsorption column, important parameters are the breakthrough time (t_b) and exhaustion time (t_s) that can be deduced from the breakthrough curve. The breakthrough time (t_b) is the point at which the concentration of Hg at a given time is divided by its initial concentration (C_t/C_0) = 0.05, while the exhaustion time (t_s) is when C_t/C_0 = 0.95. The total amount of adsorbed Hg ions (q_{total}) and the maximum adsorption capacity (q_m) can be calculated with Eqs. (1) and (2), respectively, as indicated elsewhere [46].

$$q_{total} = QC_0 A = QC_0 \int_{t=0}^{t=t_{total}} \left(1 - \frac{C_t}{C_0}\right) dt \quad (5)$$

$$q_m = \frac{q_{total}}{M} \quad (6)$$

In Eqs. (5) and (6), t_{total} is the total duration of the filtration, C_0 and C_t (mg/L) are Hg concentrations (mg/L) at the initial and at specific time points, M is the mass of sorbent in the column, Q is the filtration flow rate (mL/min), and A is the area under the breakthrough curve. The total amount of Hg (q_{total}) adsorbed by the column can be calculated from Eq. (7):

$$m_{total} = C_0 Q t_{total} \quad (7)$$

The removal of Hg from the initial solution, expressed as percentage (%), can be calculated with Eq. (8).

$$q_{total} = \frac{q_{total}}{m_{total}} \times 100 \quad (8)$$

The efficiency of the adsorption zone in the column, so-called mass transfer zone (MTZ), was calculated with Eq. (9) [47], where, Z is the total depth of the adsorbent in the column (mm).

$$MTZ = Z \times \left(1 - \frac{t_b}{t_s}\right) \quad (9)$$

The total effluent volume (V_s) and breakthrough volume (V_b) can be obtained by Eqs. (10) and (11), respectively.

$$V_s = Q \times t_s \quad (10)$$

$$V_b = Q \times t_b \quad (11)$$

Three models, namely Adam-Bohart's, Thomas's, and Yoon-Nelson's, were used to adjust the experimental data of flow-through experiments. The Adams-Bohart model assumes that the rate of adsorption is proportional to both the concentration of the adsorbing species and the residual capacity of the adsorbent. The Adams-Bohart model is only used for the description of the initial part of the breakthrough curve and is expressed as linear Eq. (12) [48]:

$$\ln \frac{C}{C_0} = k_{AB} C_0 t - N \frac{H}{U_0} \quad (12)$$

where k_{AB} (mL/mg/min) is the rate constant of the Adams-Bohart model, H (cm) is the bed depth, N_0 (mg/L) is the maximum ion adsorption capacity per unit volume of adsorbent column, and U_0 (cm/min) is the linear velocity of influent solution. A linear relationship between C/C_0 and time is obtained for the relative concentration up to $C/C_0 = 0.5$, and thus, the values of N_0 and k_{AB} were calculated as intercept and slope of the line.

Thomas's model is one of the most widely used column performance models which allows predicting the relationship between concentration and time. It is presented in Eq. (13) [49]:

$$\frac{C}{C_0} = \frac{1}{1 + \exp\left(\frac{k_{TH} q_m}{F} - k_{TH} C_0 t\right)} \quad (13)$$

where C_0 is the initial concentration of metal ions, C is that concentration at time t (mg/L), Q_0 is the maximum adsorption capacity of the adsorbent (mg/g), q_m is the amount of adsorbent (g), F is the flow rate (mL/min), t is the time of the experiment (min), and k_{TH} is the Thomas' model constant (mL/mg/min). Yoon-Nelson's model (Eq. (14)) does not require detailed data about the characteristics of the adsorbate or from the physical proportions of the adsorption bed [50].

$$\frac{C}{C_0} = \frac{\exp[k_{YN}(t - \tau)]}{1 + \exp[k_{YN}(t - \tau)]} \quad (14)$$

where k_{YN} is Yoon-Nelson's model constant (min^{-1}), and τ is the time (min) required for 50% adsorbate breakthrough.

3 Results and discussion

The structure and composition of the material will affect the efficiency of Hg removal. The design of future approaches for Hg removal from environmental samples will be informed by research aiming at finding fundamental information such as the work presented here.

3.1 Morphology and structure of synthesized materials

The morphology of the PEI/MXene@Ag cryogel composite is presented in Fig. 1. The SEM micrographs display a macroporous 3D channeled network for both the pure cryogel and the composite (Fig. 1A–E). Both the MXene and modified sorbent MXene@Ag presented multi-layer structure with typical accordion-like morphology of the MXenes (Fig. 1B, C), indicating that the etching of Al from the initial MAX phase was successful. After the modification of the composite, the MXene@Ag particles were found in the interior of the porous structure of the cryogel as well as on the surface (Supplementary, Figure S1). The composite had aggregates of Ag particles on the surface and between the MXene layers (Supplementary, Figure S2) as confirmed by EDX.

The amorphous cryogel structure from PEI/MXene can be appreciated with TEM in Fig. 2A. TEM is especially important for observing the distribution and size of metal nanoparticles. For the PEI/MXene@Ag composite, the particles on the surface of the cryogel were 10 to 30 nm; a representative detail of the composite is given in Fig. 2B. The composites were also examined with XRD before and after modification with Ag and MXene nanoparticles (Fig. 2C). The X-ray patterns obtained for $\text{Ti}_3\text{C}_2\text{T}_x$ MXene had characteristic peaks for (004) and (008) at 2θ 21.16° and 27.68°, respectively [51] (Fig. 2C), and the MXene@Ag composite has four major diffraction peaks which can be indexed to the (111), (200), (220), and (311) planes of the face-centered-cubic Ag single crystal [52]. The composites' surface chemistry was examined with high-resolution XPS (Fig. 2D). A comparative analysis of the XPS spectra from PEI/MXene@Ag composite and pristine PEI helps to observe characteristic peaks in the PEI/MXene@Ag composite attributed to the elements Ti, C, O, and Ag (Fig. 2E). For example, in the Ag 3d region, two peaks are observed at 367.3 eV and 373.3 eV from the presence of Ag 3d_{5/2} and 3d_{3/2} spin-orbit pairs, respectively [53]. The presence of MXene in the composite is indicated by peaks in the Ti 2p region characteristic of the Ti-C bond at 455.03 eV and Ti-C-F/O at 456.04 eV, also in the C1s region (Supplementary, Figure S3). A peak at 281.95 eV

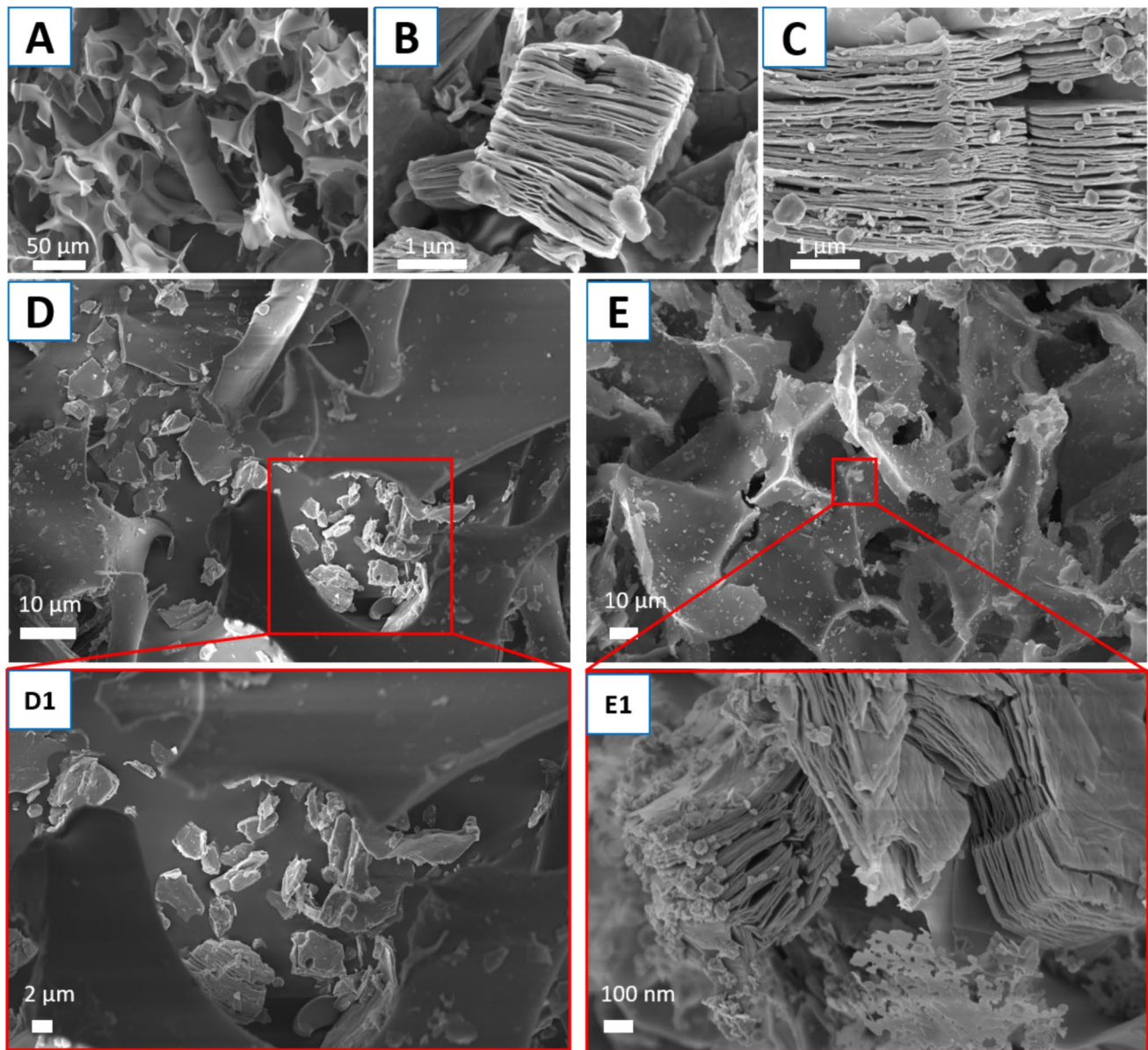


Fig. 1 Details of **A** PEI cryogel, **B** MXene, **C** MXene@Ag, **D** PEI/MXene, and **E** PEI/MXene@Ag from SEM analysis

corresponds to a single C-Ti bond [54]. On the other hand, a peak at 529.75 eV in the O 1 s region indicates vacant O positions in defective TiO_2 [55]. Thus, the analysis of the spectra obtained for the PEI/MXene@Ag composite and pristine PEI indicates successful modification, while for PEI, all peaks in the C1s and O1s regions are attributed to the presence of carbon bonds and the presence of oxygen functional groups, which is in good agreement with the literature [56]. The analysis of the surface charge of the PEI, PEI/MXene, and PEI/MXene@Ag samples by measuring zeta potential was performed, and results are presented in Figure S4 (in Supplementary). The zeta potential measurements for all samples measured from pH 1 to 10 show

positive potential values. This is due to the presence of PEI, where amine groups are protonated [57]. Despite that MXene has a negative surface charge due to the presence of the O^- , OH , and F^- groups [58], the MXene content in PEI/MXene composite did not exceed 10 wt%, which did not show an impactful decrease of zeta potential values of composites. At the acidic pH 1–2, the zeta potential values from PEI/MXene (17.1 and 20.9 mV, respectively) were higher than bare PEI (11.8 and 15.9 mV) due to the protonation of the PEI amino groups and MXene OH groups, which in good agreement with previous works [59]. Further increase of the pH decreased the zeta potential values for all samples, reaching 5–8 mV at pH 10.

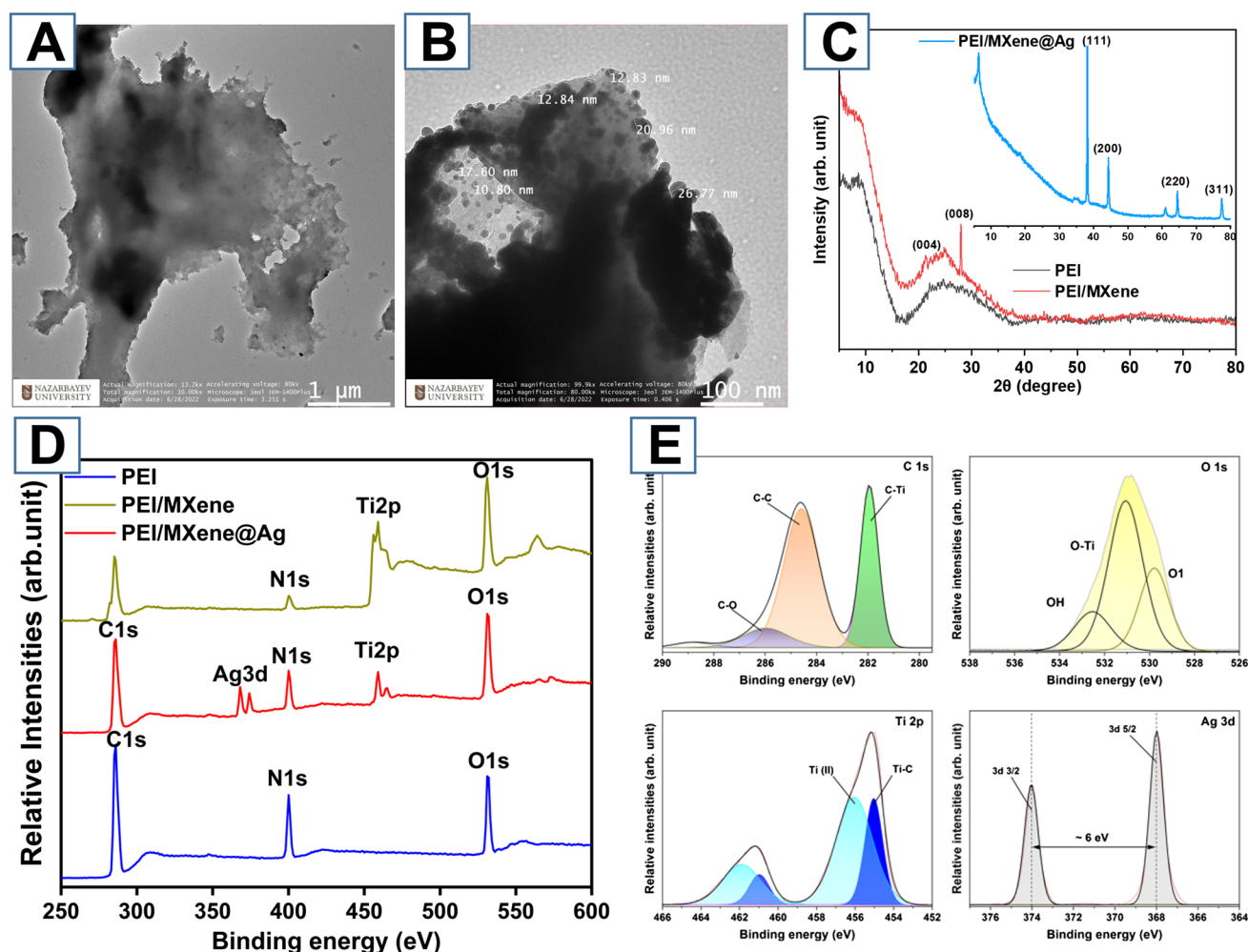


Fig. 2 TEM images of **A** PEI/MXene, **B** PEI/MXene@Ag, **C** XRD pattern, and **D** XPS spectra for all samples and **E** for PEI/MXene@Ag by elements

3.2 Mercury sorption studies

3.2.1 Mercury speciation

The occurrence of Hg species prepared from various salts, namely HgCl_2 , $\text{Hg}(\text{OAc})_2$, and $\text{Hg}(\text{NO}_3)_2$, at different pH, was predicted with Visual MINTEQ 3.1 (Fig. 3a–c). An outcome is that, to avoid the precipitation of Hg in the form of insoluble $\text{Hg}(\text{OH})_2$ onto adsorbents, it is necessary to carry out experiments at pH values < 5 when the starting salt is HgCl_2 , while for $\text{Hg}(\text{OAc})_2$ and $\text{Hg}(\text{NO}_3)_2$, the pH to mitigate precipitation should be < 3 .

3.2.2 Sorption isotherms

Sorption isotherms with initial concentrations 100–1000 mg Hg/L using HgCl_2 , $\text{Hg}(\text{OAc})_2$, and $\text{Hg}(\text{NO}_3)_2$, independently,

at pH 3, were performed to determine the maximum adsorption capacities of pristine PEI, and PEI/MXene, and PEI/MXene@Ag composites. The pH conditions of this study were chosen to avoid precipitation of insoluble Hg species and to determine the adsorption capacities of the prepared materials. The adsorption isotherms using HgCl_2 presented a synergistic effect attributed to the modification of the pristine PEI with MXene and AgNPs on (Fig. 4A). At the initial concentration (C_0) of Hg of 100 mg/L, PEI reached 145 mg/g maximum removal capacity (q_{max}), where both MXene-modified sorbents uptook Hg ions reaching ~ 200 mg/g capacity. With the increase of C_0 from 200 to 1000 mg Hg/L prepared from HgCl_2 salt, the q_{max} also increased to a maximum of 340 mg of Hg per g of PEI cryogel. For the PEI/MXene and PEI/MXene@Ag composites, both showed similar removal capacities until $C_0 = 500$ mg/L with q_{max} values ~ 690 mg/g, which is > 3 times superior to what was achieved for the bare polymer PEI. With the increase of C_0

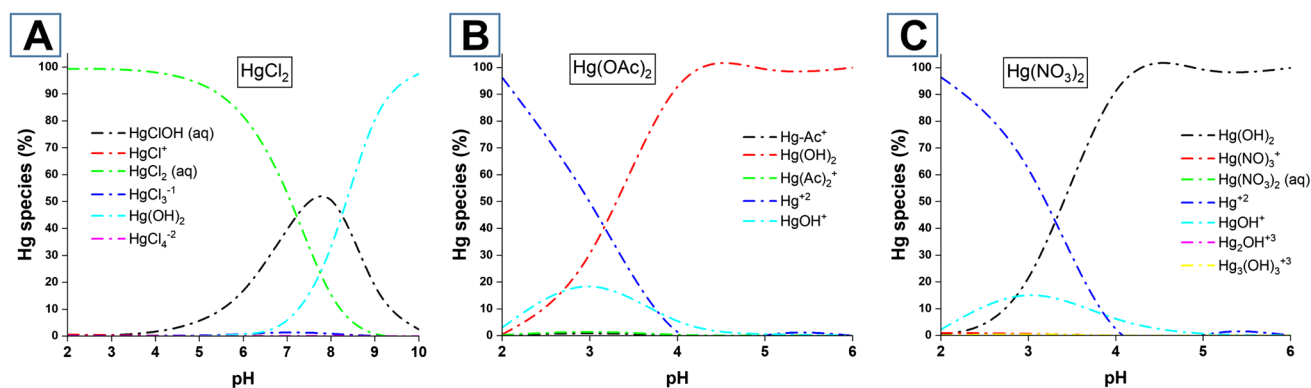


Fig. 3 Distribution of Hg species from **A** HgCl_2 , **B** $\text{Hg}(\text{OAc})_2$, and **C** $\text{Hg}(\text{NO}_3)_2$ as a function of pH modeled by Visual MINTEQ 3.1 software

to 800–1000 mg/L, just 10% difference in $q_{\max}$ values of the PEI/MXene (805 mg/g) and PEI/MXene@Ag (875 mg/g) were observed. Hence, a main factor of Hg uptake is MXene, but there is still improvement with the MXene modified with AgNPs. The adsorption isotherms (Fig. 4B) of Hg onto PEI, modified PEI/MXene, and PEI/MXene@Ag in solutions of $\text{Hg}(\text{OAc})_2$ at lower concentrations ($C_0 < 300$ mg/L) show a similar pattern than that for the removal from HgCl_2 solutions, where all Hg ions were removed by the composites. However, with the increase of initial Hg concentrations and using $\text{Hg}(\text{OAc})_2$ as starting salt, $q_{\max}$ reached 912 mg/g for PEI/MXene while it was 761 mg/g for PEI/MXene@Ag. Like for the study with HgCl_2 , MXene appears to have the key active sites for the removal of Hg.

The difference observed with the uptake of Hg with composites with or without Ag could be attributed to the speciation of Hg ions in solution, where positively charged Hg^{2+} and HgOH^+ are the main species (50 and 18.5%, respectively). It is already reported in the literature that O^- and F^- negatively charged functional endings of MXene may attract various positively charged ions [60]. For PEI/MXene@Ag, some negatively charged groups of MXene were occupied with Ag during the modification step, which in turn decreases

the removal capability of Hg cations. This observation also agrees with the removal performance of Hg from $\text{Hg}(\text{NO}_3)_2$ in solution (Fig. 4C), where 75% of Hg species are positively charged (60% for Hg^{2+} and 15% for HgOH^+). The increase of positively charged Hg ions content in solution increased the maximum removal capacity of composites, where PEI/MXene@Ag reached ~840 mg/g, while PEI/MXene was able to remove up to 1280 mg/g of Hg. The experiments with distinct Hg salts highlight that the charge of the adsorbate plays an important role in the removal performance of Hg(II) by MXene-containing adsorbents and are aligned with previously published work that used the oxygen-containing MXene for the removal of Hg from nitrate and chloride salts [61]. In this research, Hu et al. reported that their synthesized adsorbents reached the maximum removal capacity of 1057 mg/g from $\text{Hg}(\text{NO}_3)_2$ and 773 mg/g from HgCl_2 which supports the statement that MXene plays a significant role in adsorption performance [61]. In our recent experimental study of single-layered PEI/MXene@Ag composites for adsorption of Hg ions from water, ~98% removal efficiency was achieved with a maximum adsorption capacity of 156.2 mg/g [32]. However, the use of multi-layer MXene particles in current research increased the removal capacity of the composites possibly due to the

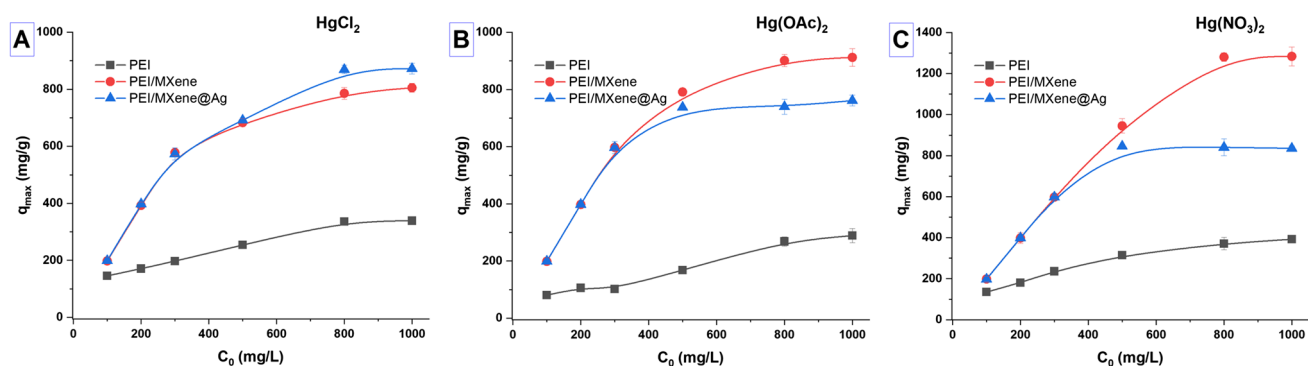


Fig. 4 Isotherms of Hg removal from different salts **A** HgCl_2 , **B** $\text{Hg}(\text{OAc})_2$, and **C** $\text{Hg}(\text{NO}_3)_2$ by MXene composites and bare cryogel ($\text{Hg } C_0$ 100–1000 mg/L, $V=20$ mL, pH 3, mass of adsorbent = 10 mg)

increased number of available functional groups in both the MXene and in the polymer carrier. Exceptional removal capacities exceeding 5400 mg of Hg per g of single-layer MXene nanosheets were reported by Shahzad et al. [62], study that attributed the high removal capacity of Hg to the attraction an interaction between Hg(II) and OH groups, which led to sorption-electrochemical reduction [48].

Langmuir and Freundlich's models were fitted to adsorption isotherms to explain the adsorption behavior (Table 1). The adsorption of Hg from HgCl₂ and Hg(NO₃)₃ by PEI, PEI/MXene, and PEI/MXene@Ag fit better a Langmuir model (R^2 values are in the range 0.9065–0.9925). The obtained model results propose that a monolayer adsorption on homogeneous sites of samples is predominant for these adsorbents. Nevertheless, the Langmuir model presented low R^2 0.7122 for the pristine PEI. The Freundlich model, on the other hand, does not fit the sorption of most of the samples under study, and the corresponding R^2 is showing low values (Table 1). However, for adsorption isotherms conducted with PEI and PEI/MXene using Hg(NO₃)₂, it had a good fit with the experimental values, demonstrating a possible multi-layer adsorption behavior on heterogeneous sites. A recent study on PEI-grafted carbon nanofibers for remediation of Hg²⁺ from solution reached an adsorption capacity of 19.2 mg/g, and it adjusted to a Langmuir model of isotherm [63]. Another study of a PEI composite (starch/PEI surface modified with mesoporous silica) by Yang et al. [64] achieved 97.9% removal of Hg with a capacity of 244.9 mg/g in 150 min and also had a good fit to the Langmuir model.

Table 1 Calculated parameters of Langmuir and Freundlich isotherm models

Model	Hg salt	Units	PEI	PEI/MXene	PEI/MXene@Ag
Langmuir	HgCl ₂	q_m , mg/g	416.7	714.3	769.2
		K_L , L/mg	0.0056	0.4	0.9285
		R^2	0.9065	0.9925	0.9848
	Hg(OAc) ₂	q_m , mg/g	227.3	1111.1	769.2
		K_L , L/mg	0.0081	0.4285	1.3
		R^2	0.7122	0.8773	0.9846
	Hg(NO ₃) ₂	q_m , mg/g	476.2	1250	909.1
		K_L , L/mg	0.0054	0.5714	0.1571
		R^2	0.9991	0.9228	0.9425
Freundlich	HgCl ₂	n	0.2952	0.1859	0.1729
		K_F	47.8	269.6	308.2
		R^2	0.8870	0.8492	0.8940
	Hg(OAc) ₂	n	0.5622	0.16	0.1326
		K_F	7.16	359.5	362.4
		R^2	0.8553	0.7206	0.7209
	Hg(NO ₃) ₂	n	0.3539	0.178	0.0898
		K_F	37.56	488.2	511.2
		R^2	0.9838	0.9178	0.7846

3.2.3 Kinetics

The kinetics studies of Hg adsorption using PEI, PEI/MXene, and PEI/MXene@Ag composites from three different Hg aqueous solutions (HgCl₂, Hg(OAc)₂, and Hg(NO₃)₂) at pH 3 were effective and fast. Most of the removal was < 10 h (Fig. 5A–C). Regarding the solutions spiked with HgCl₂, > 50% of Hg²⁺ was removed in 5 h by the three sorbents, wherein the maximum Hg removal was reached with PEI/MXene (99%) and PEI/MXene@Ag (99%) within 48 h. In contrast, pristine PEI had an average removal of ~60% from that same starting salt within 48 h. Similar adsorption kinetic profiles were observed from Hg(NO₃)₂ solution, with the composites presenting the highest removal (99%) within 48 h. In contrast, the pristine PEI removed around 62% within 48 h under the same conditions. The removal performance of Hg by PEI, PEI/MXene, and PEI/MXene@Ag from Hg(OAc)₂ solution was similar to that from HgCl₂, wherein the half-fraction was removed within initial 5 h, while the remaining adsorption was reached in 48 h, achieving 99% Hg removal with PEI/MXene and PEI/MXene@Ag. The maximum adsorption of Hg from Hg(OAc)₂ by PEI was similar in magnitude to that from the salts HgCl₂ and Hg(NO₃)₂; it reached ~70% removal within 48 h. Such removal was lower than what was achieved with an adsorbent made of graphene oxide and PEI (GOPEI) [21]. The adsorption of Hg²⁺ from natural waters under conditions close to real environmental concentrations (50 µg/L) had the highest removal efficiency of 91% [21].

Kinetics models, pseudo-first order and pseudo-second order, were fitted to explain the removal dynamics under the study experimental conditions (presented in Table 2). The modeling results demonstrate that the rate-limiting mechanism of Hg removal in all studied samples is most probably chemisorption, based on the correlation coefficients (R) achieved. The latter hypothesis fits well with all sorbents PEI, PEI/MXene, and PEI/MXene@Ag as the removal process in all of them is attributed to chemical sorption involving interaction with superficial functional groups in all of them, in addition to Hg-Ag reactions in the case of PEI/MXene@Ag. The modeling results here are in agreement with the recent studies by Gou et al. [65] on PEI based polymer sponge developed by a cryopolymerization and PEI-modified carboxymethylcellulose beads by Yoo et al. [66].

3.3 Removal of Hg ions from ultrapure and tap water with the derivatized PEI materials and commercial adsorbents

To evaluate the performance of Hg removal, the sorption of the new material PEI and its modifications (PEI/MXene and PEI/MXene@Ag samples) was compared with that from commercially available adsorbents, e.g., ion-exchange resin (IER), zeolite (ZEO), and activated carbon (AC). This was

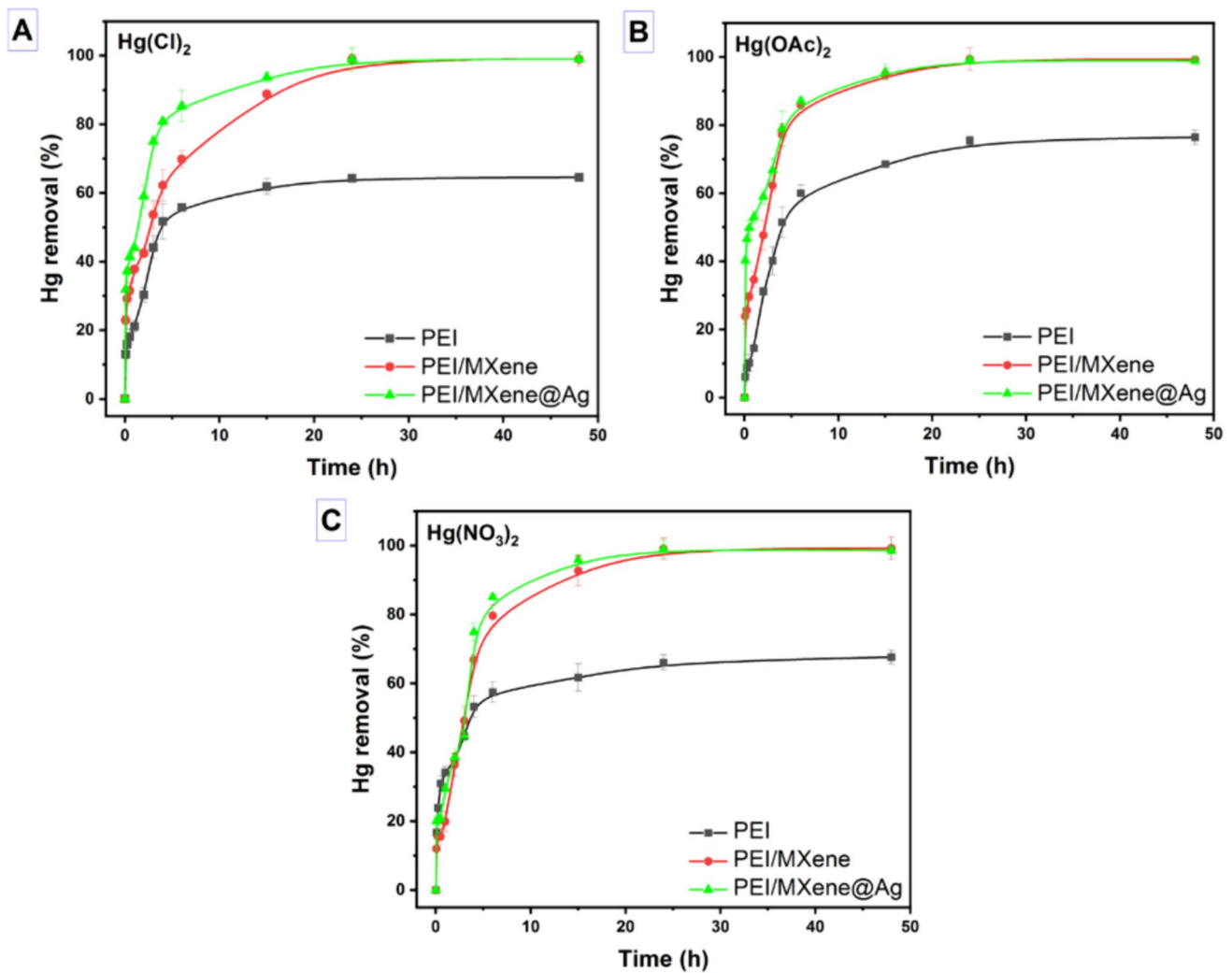


Fig. 5 Kinetics of Hg removal from different salts **A** HgCl_2 , **B** $\text{Hg}(\text{OAc})_2$, and **C** $\text{Hg}(\text{NO}_3)_2$ by MXene composites and bare PEI cryogel

Table 2 Parameters of pseudo-first and pseudo-second-order models calculated for Hg removal by PEI, PEI/MXene, and PEI/MXene@Ag samples

Hg salt	Sample	Pseudo-first order				Pseudo-second order		
		q_{exp} , mg/g	q_{eq} , mg/g	K_1 , min^{-1}	R^2	q_{eq} , mg/g	K_2 , min^{-1}	R^2
HgCl_2	PEI	129.1	95.3	2.47×10^{-6}	0.9758	134.0	10.3×10^{-5}	0.9916
	PEI/MXene	198.0	140.9	1.54×10^{-6}	0.9881	202.0	5.38×10^{-5}	0.9809
	PEI/MXene@Ag	197.9	108.7	0.11×10^{-6}	0.9033	200.8	11.1×10^{-5}	0.9963
$\text{Hg}(\text{OAc})_2$	PEI	152.8	132.5	1.98×10^{-6}	0.9722	163.7	4.12×10^{-5}	0.9739
	PEI/MXene	198.4	145.2	2.35×10^{-6}	0.9322	206.2	6.67×10^{-5}	0.9914
	PEI/MXene@Ag	197.8	117.2	0.23×10^{-6}	0.9381	201.6	0.11×10^{-5}	0.9956
$\text{Hg}(\text{NO}_3)_2$	PEI	132.3	94.6	2.82×10^{-6}	0.9344	134.4	15.0×10^{-5}	0.9988
	PEI/MXene	198.4	198.4	2.86×10^{-6}	0.9632	209.2	3.64×10^{-5}	0.9924
	PEI/MXene@Ag	197.2	165.2	2.78×10^{-6}	0.9655	205.3	4.94×10^{-5}	0.9936

done with Hg^{2+} from three different counter ions as it is well known that these can affect Hg sorption [67]. The adsorption characteristics were further assessed in ultrapure water and tap water (Fig. 6A, B). According to the findings, from Hg spiked in ultrapure water, PEI showed a comparable or slightly higher removal (between 8 and 27%) than the commercial adsorbents, where the Hg removal for IER and Zeo was $< 10\%$. The sorption was indeed affected by the nature of the counter-ion. The modified PEI composites displayed a substantially improved removal that ranged from 55 to 95% in all three counter-ion solutions of Hg^{2+} . In contrast, the removal capacity of Hg in solution (pH 3) with the commercial adsorbents was $< 30\%$ in tap water using three different Hg-solutions (HgCl_2 , $\text{Hg}(\text{OAc})_2$, $\text{Hg}(\text{NO}_3)_2$) and 10 mg Hg/L as initial concentration. There were comparable values of Hg adsorption with all the salts used. PEI presented an adsorption value of 10–20%, while the modified PEI/MXene and PEI/MXene@Ag had higher removal (45–87%). The different adsorption behavior of PEI/MXene and PEI/MXene@Ag samples was in agreement with the speciation studies of various Hg salts used: it was dependent on the surface charge of the sorbent and the active surface area of MXene involved in attracting more Hg^{2+} from the solution to enhance the adsorption performance. Similar studies on Hg^{2+} removal from water using natural and synthetic zeolites were performed by Inglezakis et al. [68] and Tauanov et al. [69]. They emphasized a crucial role of impregnating sorbents with Ag^+ , Ag, and Ag_2O nanoparticles to enhance Hg removal [68]. Further research on the influence of Cl^- and NO_3^- counter ions on Hg^{2+} uptake concluded that the adsorption of Hg^{2+} from solution using silver-modified zeolites depended on the pH, the initial concentration of Hg, and the counter ions present (acetate, chloride, or nitrate) [68, 69].

Here, we add that the adsorption of Hg is also affected by surface charge with the PEI/MXene@Ag composites. The modified PEI/MXene and PEI/MXene@Ag demonstrated a significant improvement (3–9 times better) over commercial adsorbents (IER, zeolites, AC), and this can be because of the availability of the abundant number of available functional groups (e.g., OH) and the interaction of Ag with Hg.

To further understand the Hg adsorption mechanisms onto PEI composites from real water matrices, adsorption profiles of the prepared composites and commercial adsorbents were compared. This was carried out by treating spiked tap water spiked with Hg from salts with different counter ions. In addition, the concentrations of other cations were quantified (before and after the removal of Hg) in water. The initial Hg^{2+} aqueous solution mainly contained > 10 mg/L of Hg, high concentrations of the following metal ions $\text{Na} \geq \text{Ca} > \text{Mg} > \text{K}$, and a trace amount of Ba, Fe, and Zn (see results in Table 3). Post-adsorption measurements demonstrated that metal ions changed in the IER and Zeo samples, which may be because of ion exchange that can take place with these adsorbents. The water tested with commercial AC had an increase of Ca^{2+} after Hg adsorption, most probably related to ion exchange of the Ca ions from the surface of AC. It was confirmed by EDX analysis that bare AC has $> 4\%$ in mass of Ca^{2+} (Supplementary Figure S5). The same statement could be applied for Fe ions in AC, where the initial Fe content in the AC of $1.21 \pm 0.002\%$ could be leached into the solution. The increase of the iron content in water samples after the Hg removal was observed for all Hg salt solutions after the AC treatment. Other metals such as Na^+ , Mg^{2+} , and K^+ decreased their concentration in real water samples after interactions with adsorbent. This is possibly due to the non-selectivity of the composites

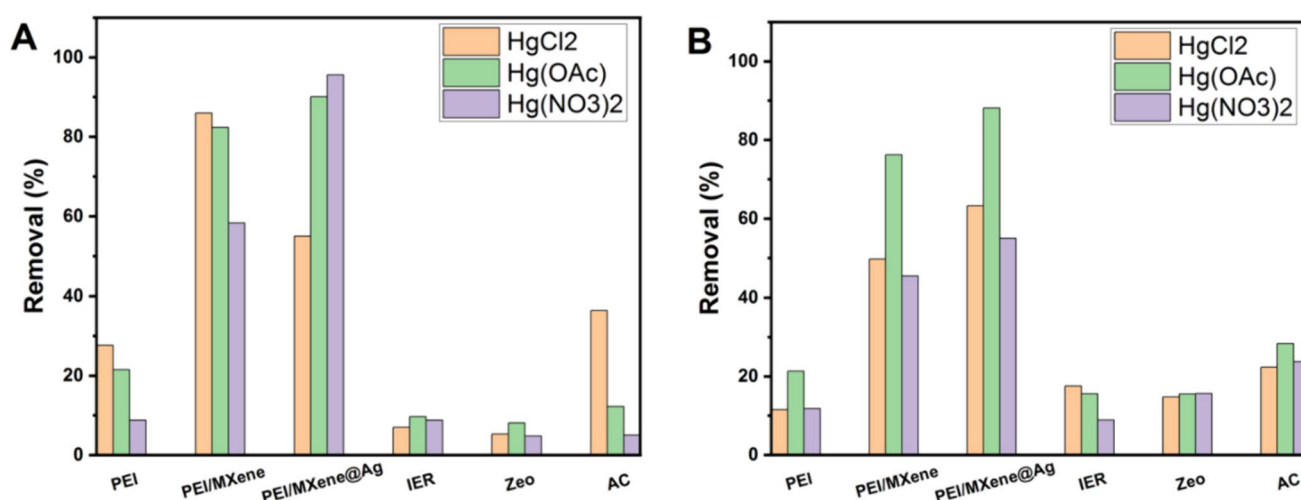


Fig. 6 Removal of Hg from different salts from **A** ultrapure water and **B** tap water with synthesized and commercial adsorbents. IER refers to H^+ -form ion-exchange resin, Zeo refers to NaY synthetic

zeolites, and AC corresponds to activated carbon. The material mass was 10 mg; volume of solution, 50 mL; concentration of Hg ions, 10 mg/L; pH 3

Table 3 Cations content in tap water after Hg removal with a range of materials

Water matrix	Material	Cations, mg/L							
		Hg ²⁺	Ba ²⁺	Ca ²⁺	Fe ²⁺	K ⁺	Mg ²⁺	Na ⁺	Zn ²⁺
Tap water + HgCl ₂	PEI	9.66	0.28	67.5	0.07	4.81	21.4	70.4	0.95
	PEI/MXene	5.49	0.28	68.0	0.07	4.85	21.6	71.1	0.97
	PEI/MXene@Ag	4.01	0.28	68.9	0.06	4.71	21.5	69.7	0.95
	IER	9.01	0.17	57.5	0.05	4.79	20.4	71.1	0.88
	Zeo	9.31	0.23	68.9	0.10	5.53	22.0	73.5	0.97
	AC	8.48	0.32	71.8	0.28	4.88	22.7	71.4	0.98
	Blank	10.7	0.28	69.6	0.07	4.85	22.3	73.1	1.01
Tap water + Hg(OAc) ₂	PEI	8.52	0.27	65.2	0.07	4.58	20.7	7.8	0.85
	PEI/MXene	2.57	0.27	66.5	0.10	4.58	20.7	67.1	0.92
	PEI/MXene@Ag	1.29	0.27	65.6	0.06	4.56	20.8	67.5	0.83
	IER	9.14	0.17	56.3	0.05	4.50	19.4	66.9	0.76
	Zeo	9.15	0.20	6.8	0.09	5.04	21.3	70.1	0.84
	AC	7.76	0.29	71.3	0.24	4.71	22.5	68.7	0.85
	Blank	10.1	0.27	66.2	0.06	4.50	20.6	66.1	0.83
Tap water + Hg(NO ₃) ₂	PEI	10.02	0.28	69.0	0.04	4.85	21.8	72.7	0.85
	PEI/MXene	6.19	0.29	69.8	0.04	4.92	22.1	71.5	0.86
	PEI/MXene@Ag	5.11	0.28	69.0	0.04	4.91	21.9	71.7	0.86
	IER	10.35	0.19	57.9	0.02	4.75	20.2	72.0	0.78
	Zeo	9.58	0.25	69.8	0.09	6.02	22.0	74.4	0.86
	AC	8.66	0.34	74.7	0.45	4.94	23.6	74.2	0.87
	Blank	11.1	0.28	69.5	0.04	4.82	22.1	71.9	0.84

Abbreviations: *IER*, commercial ion-exchange resin; *Zeo*, commercial zeolite; *AC*, commercial activated carbon; *blank*, tap water (50 mL) spiked with 10 mg/L of corresponding Hg salt without adsorbent, calculated standard deviation for all measured concentrations $\leq 4.5\%$

when uptaking Hg. In contrast, the MXene-modified samples showed comparatively higher adsorption of Hg species across the studied counter ions of Hg²⁺ in solution, demonstrating a degree of selectivity for the removal of Hg regardless of the counter ion present.

3.4 Analysis of breakthrough parameters in filtration studies

The effectiveness of monolithic adsorbents in fixed-bed columns can be evaluated by assessing the breakthrough curves presented in Fig. 7. These were achieved under flow rates, expressed with liquid hourly space velocity (LHSV), of 0.42, 0.94, and 1.37 h⁻¹ for PEI, PEI/MXene, and PEI/MXene@Ag; these are comparable to the conditions in water treatment plants [70]. The breakthrough from unmodified PEI cryogel reached saturation faster (~ 1 h) than its composites. The PEI/MXene filtration media reached saturation after 82 min, while PEI/MXene@Ag was fully loaded with Hg ions from 100 min. All the three sorbents tested sorbed Hg very fast given the concentrations of Hg < limit of detection (0.01 mg/L) at the start of the water filtration. The fast saturation of the PEI cryogel indicates that the number of active sites on the polymer adsorb is limited, while MXene

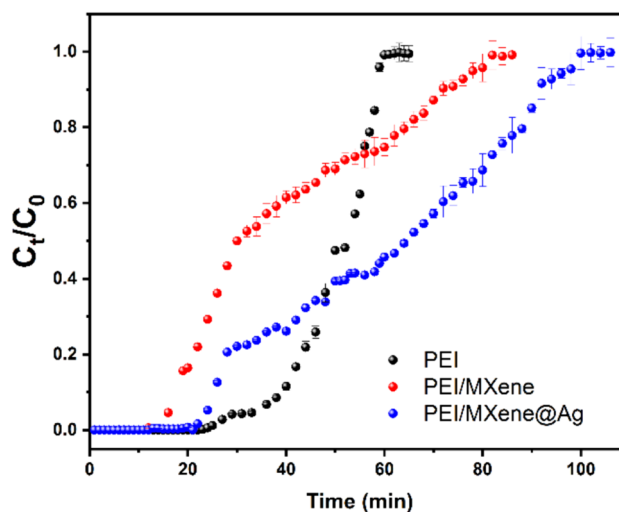


Fig. 7 Breakthrough curves showing the adsorption of Hg ions by PEI, PEI/MXene, and PEI/MXene@Ag sample

composites took longer to reach saturation and removed more Hg ions, mainly due to MXenes which were estimated to adsorbed up to 5473 mg of Hg/g of MXene [62]. The assessment of the breakthrough curves from Hg removal from water samples is in Table 4. The breakthrough time (t_b)

for PEI was 33 min, 16 min for PEI/MXene, and 24 min for PEI/MXene@Ag composite. The exhaustion time t_s reached 58, 78, and 98 min, respectively. The maximum removal capacity $q_{\max}$ was estimated at 52, 63, and 114 mg/g of Hg ions for PEI, PEI/MXene, and PEI/MXene@Ag, respectively. The increasing trend of $q_{\max}$ by composites corresponds to the results of isotherm studies.

The breakthrough experiment results were analyzed by applying the Thomas, Adam-Bohart, and Yoon-Nelson adsorption models [48–50]. The parameters from these models extracted from the filtration experiments are presented in Table 5. According to the Thomas model, k_{TH} values for PEI and PEI/MXene@Ag are almost similar (0.0032 and 0.0039 mL/mg/min), while the PEI/MXene had > 2 increase in k_{TH} value. The values of q_0 also follow the same trend, where the PEI and PEI/MXene@Ag reached 120.6 and 173.8 mg/g of Hg removal, respectively, while PEI/MXene reached only 76.4 mg/g. However, the R^2 value for PEI/MXene was found to be close to 1 (0.9925) while the rest of the sorbents had lower R^2 values. In this regard, it can be concluded that the removal

of Hg ions by PEI/MXene sample fits well the Thomas model, while for PEI and PEI/MXene@Ag, the external and internal diffusion was a limiting step.

The Adam-Bohart model predicts a linear relationship between adsorbent bed depth and time required for the breakthrough. According to the obtained results, k_{AB} rate coefficient for PEI/MXene was the highest (0.022 mL/mg/min), followed by PEI/MXene@Ag and PEI cryogel. The N_0 , values which are the maximum adsorption capacity of the materials per unit of fixed-bed volume, took place following the order PEI > PEI/MXene > PEI/MXene@Ag. The values of the constant rate (k_{YN}), time needed for 50% breakthrough (τ), and q_0 estimated from the slope and intercept of the Yoon-Nelson plot, are collected in Table 5. The k_{YN} values were 0.2511 min⁻¹ for PEI, 0.0584 min⁻¹ for PEI/MXene, and 0.0438 min⁻¹ for PEI/MXene@Ag. The experimental data were also found to be well fitted with the Yoon-Nelson model with correlation coefficients in the range 0.9151–0.9833. This means that the study modifications of PEI reduced the speed of Hg uptake, possibly because the active sites are not immediately used.

Table 4 Parameters of breakthrough curves analysis for applied adsorbents

Parameter	Description	Unit	PEI	PEI/MXene	PEI/MXene@Ag
M	Mass of the sample	mg	14	15	16
Z	Total depth of the sample	mm	6	6	6
Q	Flow-through rate	mL/min	2.5	4	5
t_b	Breakthrough time	min	33	16	24
t_s	Exhaustion time	min	58	78	98
q_{total}	Total amount of mercury	mg	728.9	941.8	1820.8
$q_{\max}$	Maximum removal capacity of mercury	mg/g	52.1	62.8	113.8
MTZ	Mass transfer zone	mm	2.6	4.8	4.5
$R\%$	Removal percentage	%	73.5	44.9	56.3
V_s	Total effluent volume	mL	82.5	64.0	120.0
V_b	Breakthrough volume	mL	145	312	490

Table 5 Calculated model parameters for the flow-through experiments

Model	Unit	PEI	PEI/MXene	PEI/MXene@Ag
Thomas	k_{TH} (mL/mg/min)	0.0032	0.0081	0.0039
	Q_0 (mg/g)	120.6	76.4	173.8
	R^2	0.7907	0.9925	0.9406
Adam-Bohart	k_{AB} (mL/mg/min)	0.02246	0.00207	0.00359
	N_0 (mg/L)	83.66	74.82	70.95
	R^2	0.9262	0.9702	0.9906
Yoon-Nelson	k_{YN} (min ⁻¹)	0.2511	0.0584	0.0438
	τ (min)	16.5	8	12
	q_0 (mg/g)	11.6	2.1	2.7
	R^2	0.9151	0.9438	0.9833

3.5 Removal mechanism

For the understanding of Hg removal mechanisms with the PEI/MXene@Ag composite, examining the Hg uptake mechanisms with 2D MXene and 3D cryogels separately is necessary. In this context, understanding the removal mechanisms for each material individually and collectively will lead to a comprehensive understanding of the Hg adsorption process. Surface functional groups of the composites (before and after Hg adsorption) were examined using XPS (Supplementary, Figure S3 and S8). New characteristic peaks of Hg appeared post-adsorption in all materials, confirming the removal of Hg ions from aqueous solution. For instance, the Hg 4f spectrum exhibited two peaks, $4f_{7/2}$ and $4f_{5/2}$, at binding energies of 100.5 eV and 104.6 eV, respectively, with a ~ 4.1 eV separation, indicating different oxidation states of Hg. Relatively weak doublet peaks at 101.6 eV and 105.5 eV correspond to Hg(II) $4f_{7/2}$ and Hg(II) $4f_{5/2}$, respectively. These findings are in agreement with earlier work [29], where the removal of Hg(II) from aqueous environments occurred via adsorption combined with catalytic reduction. HgClOH preferably interacts with open positive $\{001\}$ -Ti due to strong O-Ti atom interactions, leading to immediate homolytic cleavage, forming $\bullet\text{OH}$ and $\bullet\text{HgCl}$ radicals [29]. Both doublets are separated by ~ 4.1 eV between Hg $4f_{7/2}$ and Hg $4f_{5/2}$ peaks. Based on the proposed mechanism, the contribution of the catalytic reduction reaction to maximum removal capacity outweighs adsorption, demonstrating the significance of this new removal mechanism [29]. Moreover, Ti 2p spectra analysis also indicates the adsorption process of Hg ions, evident from the energy peak shift from 463.3 to 458.4 eV. This shift can be explained by the adsorption of Hg(II) on the MXene surface. In the case of interaction of Ag with Hg in PEI/MXene@Ag composite, it was found that silver before the interaction with Hg has doublet peak for $3d_{5/2}$ and $3d_{3/2}$ binding energy values of 367.3 and 373.3 eV while after the formation of AgHg amalgam, the Ag peaks shifted for the higher region (Supplementary, Figure S8). Moreover, the spectrum of the Hg 4f after AgHg formation shows two peaks at the binding energy values of 100.5 and 104.6 eV for $4f_{7/2}$ and $4f_{5/2}$, with the difference between peaks of 4.1 eV which indicate the presence of Hg in the Hg^0 state. These observations strongly match with the literature data and suggest the formation of AgHg amalgam [71].

The XRD characterization of the materials post-sorption was also carried out to understand mechanisms of Hg(II) removal from the three Hg salt solutions. Figure 8A presents XRD data for the PEI/MXene@Ag composite after sorption for Hg chloride, which is characterized by Hg_2Cl_2 peaks at $2\theta = 21.4$, 28.2 , and 32.8° , which confirms the reduction of HgCl_2 to Hg_2Cl_2 . In this case, peaks are observed at 2θ

32.3° , 52.9° , 54.8° , 57.4° , and 67.4° which can be attributed to Ag_2Hg_3 and the cubic phase of AgCl phases [61, 72]. The X-ray diffraction pattern demonstrates the reduction of Hg(II) to Hg^0 due to the formation of bonds with reactive atoms of silver nanoparticles, which also confirms the proposed mechanism, where the contribution of the catalytic reduction outweighs adsorption of Hg chloride, demonstrating the significance of this new removal mechanism. On the other hand, the removal mechanism of $\text{Hg}(\text{NO}_3)_2$ and $\text{Hg}(\text{OAc})_2$ solutions using PEI/MXene@Ag composite was found to have significant differences compared to HgCl_2 . Thus, the XRD spectra after the adsorption of solutions of Hg(II) from nitrate and acetate salts show a characteristic peak at 37.4° , indicating the formation of HgO (Fig. 8C). However, this peak is not observed for studies including HgCl_2 , which also confirms the proposed removal mechanism involving reduction. At the same time, the X-ray diffraction patterns for PEI/MXene@Ag after the adsorption of Hg from solutions of Hg(II) nitrate and Hg(II) acetate have similar peaks, for example, at 2θ 32.8° , 40.3° , 43.8° , 52.9° , 57.4° , and 67.4° which refer to Ag_2Hg_3 and the cubic phase of the AgCl phase. The formation of such compounds occurs regardless of the type of salt, which is confirmed by several studies and indicates the high reactivity of Ag nanoparticles. However, there is a difference in the X-ray diffraction patterns for pure PEI cryogel (Fig. 8B and C, black line). In this regard, for $\text{Hg}(\text{NO}_3)_2$ and $\text{Hg}(\text{OAc})_2$, the mechanism of adsorption of Hg ions is electrostatic interaction and surface complexation, which is consistent with many works [28, 73].

Thus, the adsorption mechanisms of heavy metal ions on MXene-based adsorbents may differ depending on the adsorbent used and surface charge of the heavy metal ion being removed. These mechanisms can take several forms, primarily including electrostatic interactions, ion exchange, surface complexation, and catalytic reduction. Further research into the mechanisms of adsorption of Hg when in the presence of other heavy metal ions onto MXene will be key to the effective use of this material in water treatment and other applications. Future work will also need to include a variety of water matrices although the sorbent will not be used in environmental remediation soon. This is because nano-enabled water purification devices, like this one, will also need some sustainable considerations regarding their life cycle before their use in the real scenario; these are impacts of the extraction of the precursors of the material, manufacturing, use, and end-of-life [74].

4 Conclusion

The composite made of PEI cryogel modified by $\text{Ti}_3\text{C}_2\text{T}_x$ MXene with AgNPs has been prepared, and it presents high efficiency for removing Hg from aqueous solutions

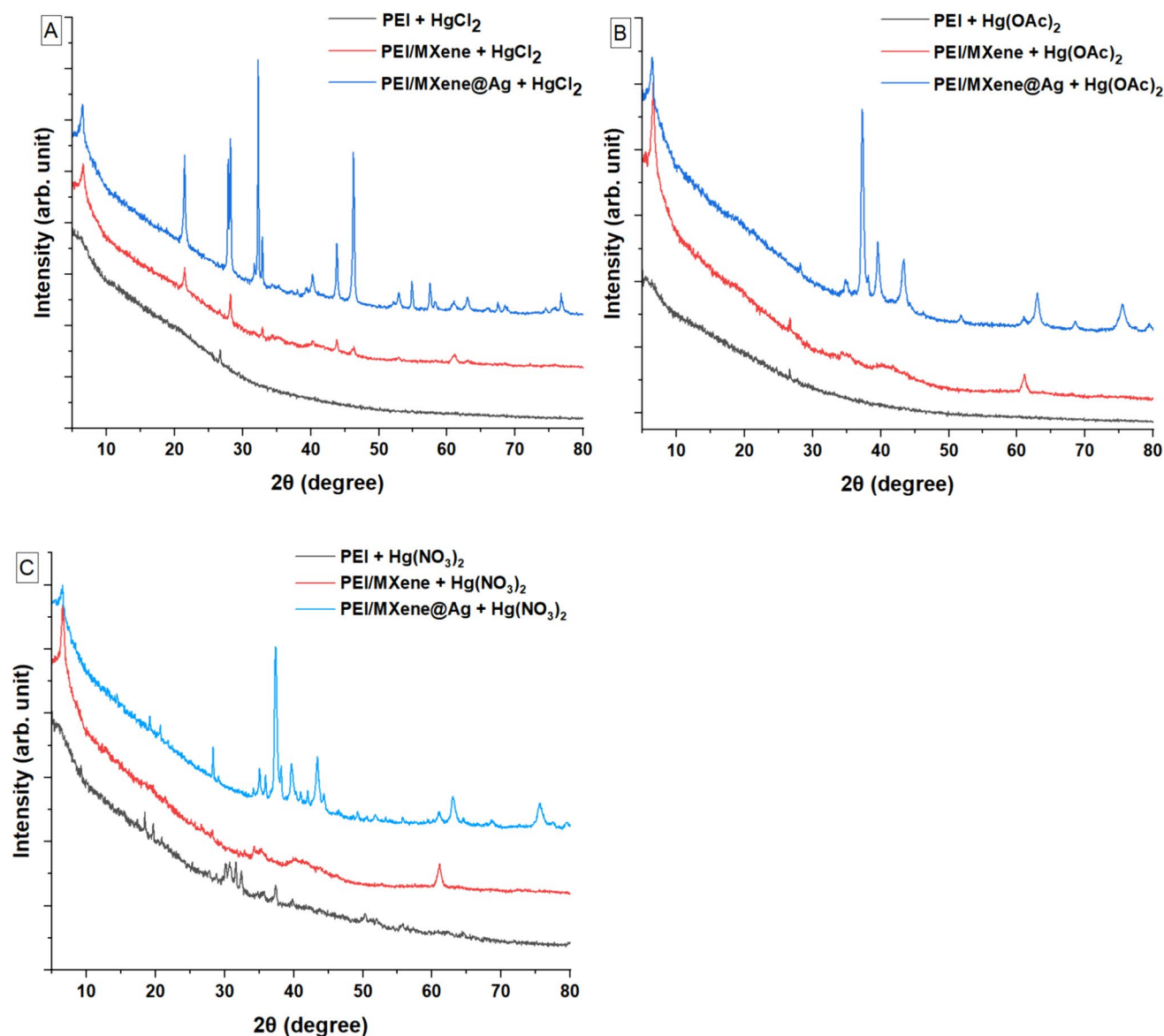


Fig. 8 XRD pattern of samples after Hg removal from **A** HgCl_2 , **B** $\text{Hg}(\text{OAc})_2$, and **C** $\text{Hg}(\text{NO}_3)_2$ solutions

at pH 3. The use of three different Hg salts, namely HgCl_2 , $\text{Hg}(\text{OAc})_2$, and $\text{Hg}(\text{NO}_3)_2$, gave an opportunity to evaluate the effect of co-existing anions and surface charge of Hg species to identify the mechanism of adsorption. Bare PEI cryogel enabled reaching the maximum removal capacity of Hg: 340 mg Hg/g by bare PEI when the source of Hg was HgCl_2 , while MXene modification increased the removal twofolds. The use of $\text{Hg}(\text{OAc})_2$ and $\text{Hg}(\text{NO}_3)_2$ resulted in the formation of positively charged Hg^{2+} species, which in turn increased Hg removal capabilities. The q_{max} for PEI/MXene reached 912 mg/g and ~840 mg/g from $\text{Hg}(\text{OAc})_2$ and $\text{Hg}(\text{NO}_3)_2$ salts, respectively, while PEI/MXene@Ag sorbed 761 mg Hg/g and 1280 mg Hg/g

from these same salts. Hence, Ag was not essential for boosting Hg removal. The analysis of PEI/MXene@Ag composite and individual MXene and cryogels unveils diverse Hg removal mechanisms: confirmation of effective Hg(II) adsorption with catalytic reduction, evident through distinct Hg peaks in XPS, emphasizing varied pathways for heavy metal ion adsorption contingent upon the adsorbent and metal type. These results can serve as a starting point for further research and development in the field of materials and technologies for water decontamination, contributing to the improvement of the environment and ensuring the safety of water resources for future generations.

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Author contribution Chingis Daulbayev wrote the main manuscript text and did some characterization; Armanbek Nursharip performed experiments; Zhandos Tauanov wrote some part of the manuscript text and revised the draft; Rosa Busquets revised the manuscript; Alzhan Baimenov did experiments conceptualization, general management, and manuscript revision.

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Data availability No datasets were generated or analysed during the current study.

Declarations

Competing interests The authors declare no competing interests.

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