Electronic supplementary information

Graphene oxide-branched polyethylenimine foams for efficient removal of toxic cations from water

Dawid Pakulski, abc Włodzimierz Czepa,abc Samanta Witomska,abc Alessandro Aliprandi,a

Piotr Pawluć, c Violetta Patroniak,*b Artur Ciesielski* a and Paolo Samori* a

a Université de Strasbourg, CNRS, ISIS, 8 allée Gaspard Monge, 67000 Strasbourg, France
E-mail: ciesielski@unistra.fr; samori@unistra.fr

b Faculty of Chemistry, Adam Mickiewicz University, Umultowska 89b, 61614 Poznań, Poland
E-mail: violapat@amu.edu.pl

c Centre for Advanced Technologies, Adam Mickiewicz University, Umultowska 89c, 61614 Poznań, Poland.

Table of Contents

1. Experimental section S2
2. Experimental analysis S4
   2.1 FTIR analysis S4
   2.2 Raman analysis S4
   2.3 XRD analysis S5
   2.4 XPS analysis S5
   2.5 TGA analysis S8
   2.6 BET surface area analysis S8
3. Adsorption study S9
4. Comparison tables for Pb(II), Cd(II), Cu(II) S12
5. Kinetic study S14
   5.1 Kinetic study onto activated carbon S14
   5.2 Kinetic study onto GO-BPEI S16
6. Thermodynamic studies S17
7. Multicomponent sorption onto GO-BPEI S19
   7.1 Background electrolyte effect onto GO-BPEI S20
8. Additional adsorption experiments S20
9. Reusability of GO-BPEI composite S21
10. LC-MS measurements S22
11. References S23
1. Experimental section

Materials: Commercially available salts, i.e. Pb(NO$_3$)$_2$, Cd(NO$_3$)$_2 \times 4$H$_2$O and Cu(NO$_3$)$_2 \times 2$H$_2$O are purchased from Sigma Aldrich. Branched polyethyleneimine (BPEI) M.W. 50,000 - 100,000 is acquired from Alfa Aesar (CAS 9002-98-6). All the products are used without further purification. Salts solutions are prepared with MilliQ water. Graphene oxide (GO) 4 mg mL$^{-1}$ aqueous dispersion is acquired from Graphenea.

Synthesis of GO-BPEI: A batch of GO-BPEI is prepared as follows: a mixture of ethanol (100 mL) and GO (100 mL, 4 mg mL$^{-1}$) is sonicated for 30 min and then 100 mL of BPEI in ethanol (4 mg mL$^{-1}$) is added. The mixture is rigorously stirred overnight under reflux. The resulting powder is then filtered and washed several times with water/ethanol mixture (1:1 vol:vol) in order to remove the unreacted BPEI. The process is monitored with liquid chromatography–mass spectrometry (LC-MS). The washing procedure is repeated until no traces of BPEI are seen on LC-MS spectra (see Fig. S19 for details) taken on the filtrate. The GO-BPEI is then freeze-dried for 48 h under vacuum to obtain black solid foam-like material.

Fourier transform infrared spectroscopy: FTIR spectra were studied within the mid-IR range (400–4000 cm$^{-1}$) by using a Perkin Elmer Spectrometer (Spectrum Two) equipped with ATR Diamond. The adsorbent in the form of powder, earlier dried in a freeze dryer was studied at room temperature.

Raman spectroscopy: Raman spectra were recorded by a Renishaw microscope with a 100x objective, laser excitation wavelength of 532 nm and laser power of 0.05%. The silicon peak at 520.3 cm$^{-1}$ was took as reference for wavenumber calibration. The D, and G peaks were fitted with combined Gaussian and Lorentzian functions.

X-ray photoelectron spectroscopy: XPS analyses were carried out on a Thermo Scientific KAlpha X-ray photoelectron spectrometer with a basic chamber pressure of $\sim 10^{-9}$ mbar and an Al anode as the X-ray source (x-ray radiation of 1486 eV). Spot sizes of 400 µm were used.
and pass energies of 200.00 eV for wide energy scans and 10.00-20.00 eV for scans were used. ~5 mg of GO and GO-BPEI are attached to copper film.

Thermal gravimetric analysis: TGA decomposition curves are recorded in the range 25-500 °C operating under nitrogen atmosphere, with a thermal step of 10 °C/min on a Mettler Toledo TGA/SDTA851e system.

Determination of the surface area by the Brunauer–Emmett–Teller (BET) method: The specific surface area was measured using a Micromeritics ASAP 2050 surface area and porosity analyzer. Prior to the BET measurements, the samples were outgassed for 10 hours at 100 °C. Adsorption isotherms were calculated for nitrogen adsorption at 77 K and pressures up to 1 bar.

X-ray powder diffraction: is performed on a Bruker AXS D8 Advanced equipped with Cu anode with Kα radiation (λ = 1.5418 Å). Diffraction patterns were collected at room temperature in the scattered angular range between 6° and 60° with an angular resolution of 0.02° per step and a typical counting time 4 of 10 s per step.

Scanning Electron Microscopy (SEM): characterization is carried out using an FEI Quanta 250 FEG instrument with energy-dispersive X-ray (EDX) analyses. The accelerating voltage was 5 keV incident beam energy. SEM samples were prepared by mounted on carbon conductive tabs followed by gold coating.

Adsorption experiments: The adsorption experiments are carried out by mixing 5 mg of adsorbate, i.e. GO, BPEI, or GO-BPEI, and 100 mL of Pb(II), Cd(II) or Cu(II) aqueous solutions at the desired concentration and pH. After addition of GO-BPEI foam into the salt solution with NaNO\textsubscript{3} the pH is adjusted with HNO\textsubscript{3} (0.1 M) and KOH (0.1 M). The suspensions are then rigorously stirred for 12 h to achieve the adsorption equilibrium and subsequently filtered through polytetrafluoroethylene (PTFE) membranes (0.22 μm). The concentration of metal ions is determined using flame atomic absorption spectrometry (F-AAS) with deuterium arc background correction, equipped with a hollow cathode lamp.
(Varian 280FS). An air–acetylene burner is used. The wavelengths (spectral band pass) are 217.0 nm (0.5 nm), 324.8 nm (0.5 nm), 228.8 nm (0.5 nm) and for Pb(II), Cu(II), and Cd(II), respectively. The nebulizer flow rate is set to 5.0 mL min$^{-1}$. The adsorption capacity variation upon GO-BPEI foam regeneration is defined as: $(q_e/q_{max})\times100$.

2. Experimental analysis

2.1 FTIR analysis

![Figure S1.](image)

**Figure S1.** Fourier transform infrared spectroscopy (FTIR) spectra of unfunctionalized GO, neat BPEI, and GO-BPEI foam

2.2 Raman analysis

The GO-BPEI was further characterized by Raman spectroscopy a non-destructive technique used to study the structural changes of graphene oxide based materials. As shown on Figure S2 the Raman spectrum of GO displays two prominent peaks around 1350 cm$^{-1}$ (D band) and at 1600 cm$^{-1}$ (G band), correspond to sp$^3$ hybrid orbital and sp$^2$-hybridized carbon atoms from the aromatic regions of GO.$^1$ Typically, chemical modification of graphene-derived materials is often characterized by the changes in the ratio of the D and G bands areas. In fact, $I_D/I_G$ is commonly used to quantify the disorder level in graphene. After the functionalization of GO with BPEI the $I_D/I_G$ intensity ratio increases from 1.00 to 1.30, and is attributed to the increase of the sp$^3$ carbon atoms after functionalization, and is consistent with other reports.$^2$ Moreover the G band shifts to a lower wavenumber, reaching 1589 cm$^{-1}$ for the
GO-BPEI, which is consistent with the observed effect of the functionalization of graphitic materials. The results indicate that BPEI was effectively grafted onto the surfaces of the graphene oxide through nucleophilic reaction between the amine groups of BPEI and the epoxy and carboxyl groups of GO.\textsuperscript{3}

**Figure S2.** Raman spectra of GO and GO-BPEI composite.

### 2.3 XRD analysis

**Figure S3.** Wide-angle X-ray scattering patterns powder of GO (black) and GO-BPEI (red).

### 2.4 XPS analysis

X-ray photoelectron spectroscopy (XPS) is then used to study the chemical composition of hybrid material by identifying the relevant chemical elements present in both GO and GO-BPEI. In the wide energy spectrum of pristine GO, only two peaks at 286.7 eV and 532.3 eV are found, and are attributed to C1s and O1s, respectively (see Fig. S4a). In contrast, the
appearance of the N1s peak is observed in the wide energy spectrum of GO-BPEI (see Fig. S4b).

![Figure S4. XPS wide energy spectra of GO (a) and GO-BPEI (b).](image)

The C1s XPS spectrum of the neat GO (Fig. S5a) shows two main peaks at 284.6 eV (C-C) and 286.8 eV (C-O) and one smaller peak at 288.3 eV, which is ascribed to C=O bonds. Compared to GO, the C1s spectrum of the GO-BPEI hybrid material (Fig. S5b) appears differently and has four peaks, including sharp peaks at 284.6 eV and 285.7 eV and broader peaks at 286.2 eV and 287.9 eV which can be assigned to C-C, C-N, C-O and C=O bonds, respectively. While similar O1s spectra are observed for GO and GO-BPEI (Fig. S5c and S5d), successful functionalization of GO with BPEI is particularly evidenced in the N1s spectra.

The high-resolution N1s spectrum of GO sample does not show any nitrogen signal (Fig. S5e). Conversely, clear signal is observed in GO-BPEI samples (Fig. S5f), and it can be deconvoluted into three peaks, i.e. at 398.8 eV, 399.5 eV and 401.0 eV, which can be ascribed to primary, secondary/tertiary and quaternary amines, respectively.
Figure S5. X-ray Photoelectron Spectroscopy (XPS) characterization. High-resolution C1s, O1s and N1s spectra of (a,c,e) neat graphene oxide (GO), and (b,d,f) graphene oxide cross-linked with polyethylenimine (GO-BPEI). Experimental data are shown as red dots, and the individual deconvoluted components as coloured lines.

In order to confirm the chemical nature of adsorption of metal ions on GO-BPEI, XPS wide range energy spectra were performed before and after metal ions sorption (Fig. S6) and confirms the presence of metal ions after the adsorption cycle.

Figure S6. The XPS spectra recorded before and after metal ions adsorption on GO-BPEI.
2.5 TGA analysis

Figure S7. Thermal decomposition of GO, BPEI and GO-BPEI.

2.6 BET surface area analysis

Figure S8. Pore volume dV/dD plots for mesoporous GO-BPEI composite.

Figure S9. BET adsorption-desorption isotherms of the GO-BPEI composite.
Table S1. Specific surface area calculated from the nitrogen adsorption isotherm using the BET method. Pore volume obtained from Barret–Joyner–Halenda (BJH) desorption cumulative volume of pores and GO and GO-BPEI results obtained from BJH desorption average pore diameter.

<table>
<thead>
<tr>
<th></th>
<th>BET surface area (m² g⁻¹)</th>
<th>Pore volume (cm³ g⁻¹)</th>
<th>Average pore size (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GO</td>
<td>14 ± 1.6</td>
<td>0.09 ± 0.01</td>
<td>123 ± 14</td>
</tr>
<tr>
<td>GO-BPEI</td>
<td>220 ± 17</td>
<td>1.5 ± 0.2</td>
<td>131 ± 15</td>
</tr>
</tbody>
</table>

3. Adsorption study

Among various adsorption isotherm models Freundlich and Langmuir are most commonly used for describing the sorption of metal ions on both 2D and 3D carbon-based adsorbents⁸⁻¹², and in this work are applied to gain insights into the adsorption mechanism of metal ions on GO-BPEI. Freundlich¹³ (Equation S1) and Langmuir¹⁴, ¹⁵ (Equation S2) isotherm models are expressed as:

\[
q_e = K_F C_e^{1/n} \quad \text{(Equation S1)}, \quad q_e = \frac{q_{\text{max}} K_L C_e}{1 + (K_L C_e)} \quad \text{(Equation S2)}
\]

where \(K_F\) (mg⁻¹ Lⁿ g⁻¹) and \(n\) are Freundlich constants related to the adsorption capacity and the adsorption intensity, \(q_{\text{max}}\) is the maximum amount of metal ions adsorbed per unit weight of adsorbent (mg g⁻¹), \(K_L\) represents the enthalpy of adsorption (L mg⁻¹). Isotherm parameters are acquired by fitting GO-BPEI adsorption equilibrium data to the isotherm models and are listed in Table S2 (Parameters for control samples, i.e. GO and BPEI are reported in Table S3).

Table S2. Parameters for Freundlich and Langmuir adsorption isotherm models. The parameters for adsorption models of Cu(II), Cd(II) and Pb(II) metal ions sorption on GO-BPEI foam.

<table>
<thead>
<tr>
<th></th>
<th>Freundlich</th>
<th>Langmuir</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>n</td>
<td>(K_F)</td>
</tr>
<tr>
<td>Cu (II)</td>
<td>2.7 ± 0.3</td>
<td>151 ± 15</td>
</tr>
<tr>
<td>Cd (II)</td>
<td>2.6 ± 0.3</td>
<td>258 ± 26</td>
</tr>
<tr>
<td>Pb (II)</td>
<td>2.9 ± 0.2</td>
<td>525 ± 34</td>
</tr>
</tbody>
</table>
It should be noted the \( n \) values calculated from the Freundlich model are found to fall in the range between 2 and 3, indicating good adsorption of metal ions onto GO-BPEI foam.\(^{16}\) Noteworthy, the adsorption isotherms for GO-BPEI as well as for the control samples are fitted better by the Langmuir model than by the Freundlich model, suggesting that sorption of metal ions onto GO, BPEI and GO-BPEI foam is not exceeding the monolayer coverage.

**Table S3.** Parameters for Freundlich and Langmuir adsorption isotherms models of Cu(II), Cd(II) and Pb(II) sorption on neat GO and BPEI.

<table>
<thead>
<tr>
<th></th>
<th>Freundlich</th>
<th>Langmuir</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( n )</td>
<td>( K_T )</td>
</tr>
<tr>
<td>GO</td>
<td>Cu (II)</td>
<td>3.3 ± 0.3</td>
</tr>
<tr>
<td></td>
<td>Cd (II)</td>
<td>3.0 ± 0.2</td>
</tr>
<tr>
<td></td>
<td>Pb (II)</td>
<td>4.7 ± 0.6</td>
</tr>
<tr>
<td>BPEI</td>
<td>Cu (II)</td>
<td>3.3 ± 0.2</td>
</tr>
<tr>
<td></td>
<td>Cd (II)</td>
<td>3.1 ± 0.2</td>
</tr>
<tr>
<td></td>
<td>Pb (II)</td>
<td>2.7 ± 0.3</td>
</tr>
</tbody>
</table>

All experimental parameters used during GO-BPEI uptake measurements, i.e. initial concentration \( C_0 = 0.1 \text{ g L}^{-1} \), adsorbent concentration \( C_{AC} = 0.05 \text{ g L}^{-1} \), temperature \( T = 25 ^\circ\text{C} \), pH=5, stirring speed = 200 rpm, are used to perform the adsorption experiments on activated carbon (AC). The maximum adsorption capacity and adsorption kinetics of commercially available AC are studied. Similarly, to the case of GO-BPEI, the pH of the solutions of salts are adjusted with HNO\(_3\) (0.1 M) and KOH (0.1 M) and filtered through polytetrafluoroethylene (PTFE) membranes (0.22 \( \mu \text{m} \)). Subsequently, AC is added into the salt solution and pH was re-adjusted. In particular, the amount of metal ions captured by AC (mg g\(^{-1}\)) is calculated from the difference between the initial \( (C_0; \text{ mg L}^{-1}) \) and the equilibrium \( (C_e; \text{ mg L}^{-1}) \) concentration by using Eq. 1 presented in manuscript. As in the case of metal ion adsorption on GO-BPEI, the adsorption of Pb\(^{2+}\), Cd\(^{2+}\) and Cu\(^{2+}\) on AC is strongly dependent
on the pH in range from 2 to 10 (Figure S10). The uptake capacity of metal ions by AC increases considerably at pH 5, reaching its maximum, then slowly decreasing at higher pH values. The maximum uptake capacities are achieved at pH = 5 and are estimated with Freundlich (Eq. S1) and Langmuir (Eq. S2) isotherm models (Figure S11) to simulate and understand the adsorption mechanism of metal ions on AC. The values of maximum adsorption capacity of Pb(II), Cd(II) and Cu(II) ions on AC are 141, 87 and 56 mg g\(^{-1}\), respectively. Noteworthy, the adsorption isotherms for AC as well as for the control samples are fitted better by the Langmuir model than by the Freundlich model (see Figure S11), suggesting that sorption of metal ions onto AC is not exciding monolayer coverage. Isotherm parameters are acquired by fitting AC adsorption equilibrium data to the isotherm models and are listed in Table S4.

**Figure S10.** The influence of pH on the maximum adsorption capacity \(q_{\text{max}}\) by activated carbon (AC).

**Figure S11.** Adsorption isotherms on activated carbon for Pb(II), Cd(II), Cu(II) ions at pH = 5 (\(C_{\text{AC}} = 0.05\) g L\(^{-1}\), \(T = 25^\circ\)C, stirring speed = 200 rpm, \(t = 6\) h). The experimental adsorption data are fitted with Langmuir (solid lines) and Freundlich (dashed lines) models.
Table S4. Parameters for Freundlich and Langmuir adsorption isotherms models of Cu(II), Cd(II) and Pb(II) sorption on activated carbon (AC).

<table>
<thead>
<tr>
<th></th>
<th>Freundlich</th>
<th></th>
<th>Langmuir</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>n</td>
<td>K_F</td>
<td>R^2</td>
<td>q_max</td>
<td>K_L [x10^-2]</td>
</tr>
<tr>
<td>Cu (II)</td>
<td>3.1 ± 0.3</td>
<td>10.1 ± 1.3</td>
<td>0.901</td>
<td>56 ± 1.4</td>
<td>5.1 ± 0.5</td>
</tr>
<tr>
<td>Cd (II)</td>
<td>2.7 ± 0.3</td>
<td>12.7 ± 1.5</td>
<td>0.879</td>
<td>87 ± 1.9</td>
<td>3.7 ± 0.3</td>
</tr>
<tr>
<td>Pb (II)</td>
<td>2.8 ± 0.3</td>
<td>20.8 ± 1.9</td>
<td>0.915</td>
<td>141 ± 2.7</td>
<td>3.9 ± 0.3</td>
</tr>
</tbody>
</table>

4. Comparison tables for Pb(II), Cd(II), Cu(II)

Table S5. Maximum adsorption capacities of chemically modified GO used as sorbents in Pb(II) removal process.

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>q_max (mg g^-1)</th>
<th>Conditions</th>
<th>Isotherm</th>
<th>Kinetic model</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>GO-BPEI</td>
<td>3390</td>
<td>pH 5, T 298 K</td>
<td>Langmuir</td>
<td>PSO</td>
<td>This work</td>
</tr>
<tr>
<td>FGO</td>
<td>1850</td>
<td>pH 6, T 333 K</td>
<td>Langmuir</td>
<td>-</td>
<td>9</td>
</tr>
<tr>
<td>GO</td>
<td>1119</td>
<td>pH 5, T 298 K</td>
<td>Langmuir</td>
<td>PSO</td>
<td>19</td>
</tr>
<tr>
<td>RGO/PAM</td>
<td>1000</td>
<td>pH 6, T 298 K</td>
<td>Langmuir</td>
<td>PSO</td>
<td>20</td>
</tr>
<tr>
<td>PYK-GO</td>
<td>888</td>
<td>pH 7, 298 K</td>
<td>Langmuir</td>
<td>-</td>
<td>21</td>
</tr>
<tr>
<td>HPA-GO</td>
<td>820</td>
<td>pH 5.9, T 318 K</td>
<td>Langmuir</td>
<td>PSO</td>
<td>22</td>
</tr>
<tr>
<td>PAM-g-graphene</td>
<td>820</td>
<td>pH 6, T 288 K</td>
<td>Langmuir</td>
<td>PSO</td>
<td>23</td>
</tr>
<tr>
<td>FGO2</td>
<td>758</td>
<td>pH 5.5, T 333 K</td>
<td>Langmuir</td>
<td>PSO</td>
<td>24</td>
</tr>
<tr>
<td>MnFe_2O_4/GO</td>
<td>673</td>
<td>pH 5, T 298 K</td>
<td>Langmuir</td>
<td>PSO</td>
<td>25</td>
</tr>
<tr>
<td>GO/Iron Oxide</td>
<td>588</td>
<td>pH 5, T 303 K</td>
<td>Langmuir</td>
<td>-</td>
<td>26</td>
</tr>
</tbody>
</table>

Table S6. Maximum adsorption capacities of chemically modified GO used as sorbents in Cu(II) removal process.

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>q_max (mg g^-1)</th>
<th>Conditions</th>
<th>Isotherm</th>
<th>Kinetic model</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adsorbents</td>
<td>$q_{\text{max}}$ (mg g$^{-1}$)</td>
<td>Conditions</td>
<td>Isotherm</td>
<td>Kinetic model</td>
<td>Ref.</td>
</tr>
<tr>
<td>--------------</td>
<td>--------------------------------</td>
<td>----------------</td>
<td>---------------</td>
<td>---------------</td>
<td>--------</td>
</tr>
<tr>
<td>GO-BPEI</td>
<td>2051</td>
<td>pH 5, 298 K</td>
<td>Langmuir</td>
<td>PSO</td>
<td>This work</td>
</tr>
<tr>
<td>Trp/GO</td>
<td>588</td>
<td>pH 5, T 293 K</td>
<td>Langmuir</td>
<td>PSO</td>
<td>27</td>
</tr>
<tr>
<td>Chitosan/GO</td>
<td>425</td>
<td>pH 5, T 293 K</td>
<td>Langmuir</td>
<td>PSO</td>
<td>28</td>
</tr>
<tr>
<td></td>
<td>424</td>
<td>pH 6, T 318 K</td>
<td>Redlich-Peterson</td>
<td>DE</td>
<td>29</td>
</tr>
<tr>
<td></td>
<td>203</td>
<td>pH 5, RT</td>
<td>Freundlich</td>
<td>-</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>162</td>
<td>pH 5.5, 303K</td>
<td>Langmuir</td>
<td>PSO</td>
<td>31</td>
</tr>
<tr>
<td>PAH/GO</td>
<td>349</td>
<td>pH 6, T 293 K</td>
<td>Langmuir</td>
<td>PSO</td>
<td>32</td>
</tr>
<tr>
<td>EDTA/MGO</td>
<td>301</td>
<td>pH 5, T 298 K</td>
<td>Langmuir</td>
<td>PSO</td>
<td>33</td>
</tr>
<tr>
<td>GO</td>
<td>294</td>
<td>pH 5, T 298 K</td>
<td>Langmuir</td>
<td>PSO</td>
<td>19</td>
</tr>
<tr>
<td>PAA/GO</td>
<td>228</td>
<td>pH 5, T 293 K</td>
<td>-</td>
<td>-</td>
<td>12</td>
</tr>
<tr>
<td>PAA-HB/GO</td>
<td>210</td>
<td>pH 5, RT</td>
<td>-</td>
<td>-</td>
<td>12</td>
</tr>
</tbody>
</table>

**Table S7.** Maximum adsorption capacities of chemically modified GO used as sorbents in Cd(II) removal process.
5. Kinetic study

5.1 Kinetic study onto activated carbon

The kinetics of an adsorption process are studied using the pseudo-first (Eq. S3) and pseudo-second (Eq. S4) order rate adsorption kinetic models. In particular, the amount of metal ions adsorbed by GO-BPEI and AC (mg g\(^{-1}\)) as a function of time are calculated by applying Eq. S5. These models are expressed as:

\[
\ln (q_e - q_t) = lnq_e + k_1t \quad \text{(Eq. S3)}
\]

\[
\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{t}{q_e} \quad \text{(Eq. S4)}
\]

\[
q_t = \frac{(C_0 - C_t)V}{m_{adsorbent}} \quad \text{(Eq. S5)}
\]

Where \(q_e\) = equilibrium adsorption capacity, \(q_t\) = adsorption capacity at a given time, \(k_1\) = rate constant (1/min), \(k_2\) = rate constant [g/min*mg], \(t\) = time (min), \(C_t\) = concentration of free metal ions at given time [mg/l], \(C_e\) = equilibrium concentration of free metal ions [mg/l], \(V\) = volume [l] ; \(m\) = mass [g].

The absorption behaviour of the metal ions AC as a function of time is portrayed in Fig. S12. The calculated kinetic parameters for adsorption of Cu(II), Cd(II) and Pb(II) ions on AC at pH 5 are listed in Table S8. The \(q_e\) values calculated from the pseudo-first and pseudo-second-order kinetic models are close to experimental \(q_e\) values, yet, the latter model seems to give better results. In particular, the calculated \(q_e\) values of the Cu(II), Cd(II) and Pb(II) adsorption acquired using the pseudo-second-order kinetic model amount to 46, 61 and 111 mg g\(^{-1}\), which are closer to the experimental \(q_e\) values of 45, 65 and 113 mg g\(^{-1}\), respectively. Moreover, the analysis of the fitting parameters reveals that the experimental data is fitted better with the pseudo-second-order kinetic model as evidenced by the correlation coefficients. The data of the pseudo-second-order kinetic model indicate that the adsorption of
Cu(II), Cd(II) and Pb(II) ions on AC is controlled by an adsorption process involving the strong surface complexation of metal ions with the oxygen containing groups of AC.

Figure S12. Time dependent heavy metal ions sorption on activated carbon (AC) (a) \(C_0 = 0.1 \text{ g L}^{-1}, C_{AC} = 0.05 \text{ g L}^{-1}, T = 25 \text{ °C}, \text{stirring speed} = 200 \text{ rpm}, t = 3h, \text{pH} = 5\). The kinetic plots obtained pseudo-first (b) and pseudo-second (c) order model reactions.

Table S8. Coordination kinetic rate constants and unit adsorption capacity of activated carbon (AC) towards Cu(II), Cd(II), Pb(II).

<table>
<thead>
<tr>
<th></th>
<th>Pseudo-first order kinetics</th>
<th>Pseudo-second order kinetics</th>
<th>(q_e) (exp)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(q_e)</td>
<td>(k_1 \times 10^{-2})</td>
<td>(R^2)</td>
</tr>
<tr>
<td>Cu(II)</td>
<td>28 ± 1</td>
<td>1.8 ± 0.1</td>
<td>0.867</td>
</tr>
<tr>
<td>Cd(II)</td>
<td>48 ± 2</td>
<td>2.4 ± 0.2</td>
<td>0.932</td>
</tr>
<tr>
<td>Pb(II)</td>
<td>86 ± 6</td>
<td>2.9 ± 0.2</td>
<td>0.916</td>
</tr>
</tbody>
</table>
5.2 Kinetic study onto GO-BPEI

The calculated kinetic parameters for adsorption of Cu(II), Cd(II) and Pb(II) ions on GO-BPEI foam at pH 5 are listed in Table S9 and graphically presented on Fig. S13. The $q_e$ values calculated from the pseudo-first and pseudo-second-order kinetic models are close to experimental $q_e$ values, yet, the latter model seems to give better results. In particular, the calculated $q_e$ values of the Cu(II), Cd(II) and Pb(II) adsorption acquired using the pseudo-second-order kinetic model amount to 763, 1186 and 1612 mg/g, which are closer to the experimental $q_e$ values of 757, 1171 and 1592 mg/g, respectively. Moreover, the analysis of the fitting parameters reveals that the experimental data is fitted better with the pseudo-second-order kinetic model as evidenced by the correlation coefficients. The data of the pseudo-second-order kinetic model indicate that the adsorption of Cu(II), Cd(II) and Pb(II) ions on GO-BPEI foam is controlled by the strong surface complexation of metal ions with the oxygen-and the nitrogen-containing groups of GO-BPEI.

Table S9 Coordination kinetic rate constants and unit adsorption capacity of GO-BPEI towards Cu(II), Cd(II), Pb(II).

<table>
<thead>
<tr>
<th></th>
<th>Pseudo-first order kinetics</th>
<th>Pseudo-second order kinetics</th>
<th>$q_e$ (exp)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$q_e$</td>
<td>$k_1$ [x10^{-3}]</td>
<td>R$^2$</td>
</tr>
<tr>
<td>Cu(II)</td>
<td>727±18</td>
<td>8.3±0.3</td>
<td>0.982</td>
</tr>
<tr>
<td>Cd(II)</td>
<td>1085 ± 30</td>
<td>9.1 ± 0.6</td>
<td>0.952</td>
</tr>
<tr>
<td>Pb(II)</td>
<td>1465 ± 37</td>
<td>13 ± 1</td>
<td>0.979</td>
</tr>
</tbody>
</table>
Figure S13. Time dependent heavy metal ions sorption on GO-BPEI foam (a) \( C_0 = 0.1 \text{ g L}^{-1}, C_{GO-BPEI} = 0.05 \text{ g L}^{-1} \), \( T = 25 \degree\text{C}, \) stirring speed = 200 rpm, \( t = 8\text{h}, \) pH = 5). The kinetic plots obtained pseudo-first (b) and pseudo-second (c) order model reactions.

6. Thermodynamic studies

In order to fully understand the nature of adsorption the thermodynamic parameters such as standard Gibbs free energy change \( (\Delta G^\circ) \), the enthalpy change \( (\Delta H^\circ) \) and entropy change \( (\Delta S^\circ) \) have been calculated using equilibrium constants changing as a function of temperature. The free energy changes of the sorption reaction are given by the following equation:

\[
\Delta G^\circ = -RT \ln K_d \quad (\text{Eq. S6})
\]

where \( R \) is the ideal gas constant \((8.314 \text{ J mol}^{-1}\text{K}^{-1})\), \( T \) is the absolute temperature \((\text{K})\) and \( K_d \) is the distribution coefficient.

The distribution coefficient \( (K_d) \) was defined as the following equation:

\[
K_d = \frac{q_e}{C_e} \quad (\text{Eq. S7})
\]

In this equation, \( q_e \) (mg g\(^{-1}\)) is the amount of metal in adsorbent, \( C_e \) (mg L\(^{-1}\)) is the amount of metal in solution and the values of \( K_d \) was obtained by plotting \( \ln(q_e/C_e) \) against \( C_e \) and extrapolating to zero \( C_e \).

The values of \( \Delta H^\circ \) and \( \Delta S^\circ \) can be calculated by the Van’t Hoff equation (Eq. S8) and can be determined from intercept and slope by plotting the values of \( \ln K_d \) vs. \( 1/T \) (Fig. S14).
\[
\ln K_d = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \quad \text{(Eq. S8)}
\]

Figure S14. The linear curve of \( \ln K_d \) vs \( 1/T \) for \( \text{Pb}^{2+}, \text{Cd}^{2+}, \text{Cu}^{2+} \) adsorption calculate to determine thermodynamic parameters.

The thermodynamic parameters from the fitting line such as Gibbs free energy change (\( G^\circ \)), the enthalpy change (\( \Delta H^\circ \)), the entropy change (\( \Delta S^\circ \)) and correlation coefficient (\( R^2 \)) are listed in Table S10.

<table>
<thead>
<tr>
<th>Metal ions</th>
<th>T (K)</th>
<th>( \ln K_d )</th>
<th>( \Delta G^\circ ) (KJ mol(^{-1}))</th>
<th>( \Delta H^\circ ) (KJ mol(^{-1}))</th>
<th>( \Delta S^\circ ) (KJ mol(^{-1}) K(^{-1}))</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Pb}^{2+} )</td>
<td>298</td>
<td>5.12</td>
<td>-12.69</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>308</td>
<td>4.72</td>
<td>-12.09</td>
<td>-27.26</td>
<td>49.01</td>
<td>0.994</td>
</tr>
<tr>
<td></td>
<td>318</td>
<td>4.43</td>
<td>-11.72</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{Cd}^{2+} )</td>
<td>298</td>
<td>2.95</td>
<td>-7.32</td>
<td>-25.34</td>
<td>60.59</td>
<td>0.990</td>
</tr>
<tr>
<td></td>
<td>308</td>
<td>2.57</td>
<td>-6.58</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>318</td>
<td>2.31</td>
<td>-6.12</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{Cu}^{2+} )</td>
<td>298</td>
<td>1.01</td>
<td>-2.50</td>
<td>-16.51</td>
<td>46.92</td>
<td>0.989</td>
</tr>
<tr>
<td></td>
<td>308</td>
<td>0.83</td>
<td>-2.12</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>318</td>
<td>0.59</td>
<td>-1.56</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The distribution ratio (\( K_d \)) of \( \text{Pb(II)}, \text{Cd(II)}, \text{Cu(II)} \) onto GO–BPEI composite are decreased with the increase in temperature, implying that the adsorption process is exothermic. The negative values of \( \Delta G^\circ \) at various temperatures indicated the spontaneous nature of the
adsorption process. The decreasing in ΔG° values with increasing temperature shows a decrease in feasibility of sorption at higher temperature. However, the low negative values ΔG° measured in temperature 318K (-11.72, -6.12 and -1.56 kJ.mol⁻¹, respectively for Pb²⁺, Cd²⁺, Cu²⁺) ascertains the favourability of the adsorption process. Furthermore, the more negative value of ΔG° for Pb(II) than that of Cd(II) and Cu(II) implies the GO-BPEI composite favours the adsorption of Pb(II) more than Cd(II) and Cu(II).

The negative value of ΔH° confirms the exothermic nature of the adsorption process as confirmed by the fact that as the temperature rises from 298 to 318K. This result also supports the suggestion that the adsorption capacity of adsorbent decreases with increasing temperature.

The positive values of ΔS° (49.01, 60.59 and 46.92 for Pb(II), Cd(II) and Cu(II), respectively) confirm the increment randomness in the system solid/solution interface during the adsorption process which can be reflected by the affinity of the GO-BPEI for heavy metal cations and suggested some conformational changes in GO-BPEI. This might be also attributed to the substitution of water hydration molecules for metal ions by chelating group.

7. Multicomponent sorption onto GO-BPEI

![Figure S15. a) Single and multicomponent (binary and ternary) sorption of Pb(II), Cu(II), Cd(II) on GO-BPEI expressed in mmol g⁻¹ (initial amount of each metal: 17 mmol per 1 g of GO-BPEI, pH=5). b) The comparative amounts of adsorbed Pb(II), Cu(II), Cd(II) ions expressed as a mole percentage.](image)
7.1 Background electrolyte effect onto GO-BPEI

Figure S16. The effect of background electrolyte concentration on the adsorption Pb$^{2+}$, Cd$^{2+}$ and Cu$^{2+}$ ions by GO-BPEI composite.

8. Additional adsorption experiments.

We have performed additional experiments by substituting the MiliQ water with the tap water, which contains alkali metal ions e.g. Na(I), K(I), Mg(II) Ca(II) at the concentration of 16 mg/L, 7 mg L$^{-1}$ 10 mg L$^{-1}$ and 75 mg L$^{-1}$, respectively, and the results of competitive sorption experiments of binary and ternary solutions in tap water at equimolar ratios Pb(II)/Cu(II), Pb(II)/Cd(II), Cu(II)/Cd(II), and Pb(II)/Cu(II)/Cd(II) on the GO-BPEI are nearly identical with those obtained for MiliQ water experiments.(Fig. S17) The single adsorption tests were carried out for Pb(II), Cd(II), Cd(II) metal ions in the presence of tap water. Obtained results have been showed below.
Figure S17. The effect of environmental conditions on the adsorption Pb$^{2+}$, Cd$^{2+}$ and Cu$^{2+}$ ions by GO-BPEI composite.

Noteworthy, in our initial experiments we didn’t observe any significantly decreasing of $q_{max}$ value in the presence of the background electrolyte (NaNO$_3$) of the of Pb(II), Cd(II), Cu(II) adsorption on BPEI-GO at different concentrations (see Fig. S16 in ESI), which further demonstrates that monovalent non-toxic metal ions don’t affect on adsorption study.

9. Reusability of GO-BPEI composite

For practical application, the adsorbent regeneration is indispensable. Thus, the adsorbent material needs to combine a high adsorption capacity with good desorption characteristics. Such combinations would considerably enhance the efficiency of the adsorbent and possibly allow its use in real life applications. To study the reversible adsorption of heavy metal ions onto the GO-BPEI foam, the composite is repeatedly immersed in the aqueous solutions of heavy metal ions and treated with 0.1 M solution of either ethylenediaminetetraacetic acid (EDTA) or nitric acid. The adsorbent is washed several times with MiliQ water, freeze-dried overnight and used as adsorbent in subsequent adsorption cycles. The adsorption experiments are then carried out by mixing GO-BPEI and Pb(II), Cd(II) and Cu(II) aqueous solutions at pH = 5. Noteworthy, the use of EDTA for regeneration of GO-based adsorbents has some drawbacks. While EDTA has a high affinity for metal ions, as reflected in its high complexation constants for Cu(II) (18.8), Pb(II) (18.1) and Cd(II) (16.5), it can also interact with GO through strong electrostatic forces and block its binding sites.$^{17, 18}$ Such characteristics of EDTA may affect the reusability of GO-BPEI foam in the long term. As illustrated in Figure S18 a high decrease in the adsorption capacity is monitored for GO-BPEI treated with EDTA. In particular, the adsorption capacity decreases over ten cycles by 28% for Cu, 55% for Pb and 72% for Cd ions. On the other hand, HNO$_3$ treatment allows reaching high regeneration efficiency. The overall decrease in adsorption capacity is found smaller than in the EDTA treated foam, and it amounts to 45% for Cu, 20% for Pb and 33% for Cd ions.
Noteworthy, the decrease in the adsorption capacity after tenth cycle is most likely related to the decrease in the number of GO-BPEI coordination pockets and therefore in the decrease of the binding sites after each regeneration step. As a consequence of the strong acidic environment the decomposition of GO-BPEI can take place, and in particular hydrolysis of amide bonds may occur.

Figure S18. Adsorption capacity as a function of GO-BPEI foam regeneration cycle is defined as \((q_e/q_{max})\times100\).

\((C_0 = 0.1 \text{ g L}^{-1}, \ C_{GO,BPEI,BPEI-GO} = 0.05 \text{ g L}^{-1}, \ \text{at pH} = 5, \ T = 25 \degree \text{C}, \ \text{stirring speed} = 200 \ \text{rpm, t} = 12 \ \text{h}).\)

10. LC-MS measurements

To provide further evidence on the covalent cross-linking of BPEI to the GO surface LC-MS of post-reaction filtrate are performed. Filtered powder was washed with water/ethanol mixture and liquid chromatography mass spectra are performed and presented in Figure S19. Due to the removal of unreacted BPEI upon washing the foam with water/ethanol mixture (1:1 vol:vol), a disappearance of the peaks caused by abundance of ionic fragments of BPEI is visible in Figure S19a-e. As shown washing the precipitate with 50 ml of water/ethanol mixture results in complete removal of unreacted BPEI traces.
11. References