



## Polyethyleneimine cryogels for metal ions sorption

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### ABSTRACT

Polyethyleneimine (PEI) cryogels have been fabricated using poly(ethylene glycol) diglycidyl ether (DGE-PEG), 1,4-butanediol diglycidyl ether (DGE-1,4-BD), and glutaric aldehyde (GA) as cross-linking agents. The rate of PEI cross-linking changes in the order GA > DGE-1,4-BD > DGE-PEG. The established correlations between the modification degree, swelling, and static ion-exchange capacity revealed a tendency of diglycidyl ethers, especially DGE-1,4-BD, to graft as a side chain to PEI in alkaline media. Low reactivity of cross-linkers at temperatures below zero resulted in lower modification degree and higher sorption capacities of PEI cryogels in comparison with PEI cross-linked at room temperature. Due to the difference in mechanisms of sorption of metal cations and anions, PEI cryogels cross-linked with DGE-1,4-BD and DGE-PEG were the most efficient for sorption of Hg(II) as  $[\text{HgCl}_4]^{2-}$  complex and Cu(II) ions, respectively. The morphology of PEI cryogels depends on the type of the cross-linking agent, cross-linker/PEI molar ratio, and concentration of PEI solution; the pore volume of cryogels obtained under the same conditions decreased in the order GA > DGE-1,4-BD > DGE-PEG.

### 1. Introduction

Polyethyleneimine (PEI) is one of the most efficient commercially available polymers for sorption of dyes [1], metal ions [2–8], CO<sub>2</sub> [9,10] and fabrication of metal-containing catalysts [11]. PEI can be used in water-soluble forms in polymer-assisted ultrafiltration [4] or as a solid sorbent after cross-linking [1,6–8] or grafting to the surface of porous inorganic materials [12], other polymers [9,13], and bacterial biomass [2,3]. Despite high efficiency of PEI for metal ions recovery using ultrafiltration [4], it is expensive and time-consuming process with strict requirements to the molecular weight of the polymer to be used that significantly lowers the ultrafiltration competitiveness in comparison with sorption on solid PEI-based materials [14].

Due to the presence of primary, secondary, and tertiary amino groups PEI is soluble in water in a wide pH range. To obtain solid sorbents, PEI is usually cross-linked with epichlorohydrine [7,8], diglycidyl ethers [1] or glutaric aldehyde [6]. Cross-linking of water-soluble polymer can be considered as the simplest chemical modification resulting not only in reduction of solubility but in the introduction of new functional fragments, which can change the sorption capacity and affinity of the polymer to metal ions and other sorbates. The effect of the cross-linking agent on rigidity and spatial structure of the material

can be very significant [15], that leads, in some cases, to fabrication of polymeric sorbents with anomalously poor properties [16]. Thus, the right choice of the agent and conditions for cross-linking is a crucial step in the synthesis of highly efficient sorption materials.

Another problem in application of granulated polymeric sorbents is their poor kinetic characteristics. This can be improved via formation of highly porous structures using different templates [17]. One of the most promising and “green” approach to fabrication of highly porous polymers is cryogelation based on cross-linkage of the polymer in frozen solution, when the ice crystals play the role of porogeneous templates easily removable through thawing [18]. However, cryogelation sets additional requirements to the cross-linking agents. First, cross-linker must have sufficiently high reactivity at temperature below zero. Second, the cross-linkages shall be formed only after the homogeneous polymer/cross-linker solution is completely frozen.

At present, cryogels have found application mainly in biomedicine [19], while their potential for metal ions recovery and separation remains underestimated and has just started to become of urgency [17,20]. The dependences of cryogels sorption properties toward metal ions on the cross-linking conditions are only scarcely investigated. At the same time, poorly optimized conditions of cross-linkages result in fabrication of cryogels with very low sorption characteristics despite

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the presence of highly efficient complexing functionalities [21].

The only example of PEI cryogel reported up to now was obtained via cross-linkage with glycerol diglycidyl ether and used for separation of organic dyes [1] or design of metal-containing hybrid catalysts [11]. The effect of cross-linking conditions and the reagent type on sorption properties of PEI cryogels toward metal ions has not been investigated. Taking into account a limited commercial availability of glycerol diglycidyl ether in comparison with diglycidyl ethers of glycols, and the necessity to understand correlations between structure of the cross-linkers and sorption properties of the obtained materials, it is of high interest to investigate fabrication of highly porous PEI sorbents using the cryogelation approach and commercially available and affordable reagents.

This work was aimed to investigating the effect of the type of cross-linking agent and reaction conditions on composition of PEI cryogels, their swelling, morphology and sorption properties toward transition metal ions.

## 2. Experimental

### 2.1. Materials

Branched polyethylenimine (PEI) with the average molecular weight of 25 kDa was purchased from “AlfaAesar” as 50% solution in water. According to  $^1\text{H}$  NMR spectroscopy data the molar ratio between primary, secondary, and tertiary groups of PEI was 1:1:1. Cross-linking agents – poly(ethylene glycol) diglycidyl ether, average  $M_n$  500 (DGE-PEG), 1,4-Butanediol diglycidyl ether (DGE-1,4-BD) and glutaric aldehyde (GA) were purchased from Sigma–Aldrich. Other reagents – HCl, NaOH, metal salts were of analytical grade.

### 2.2. Cross-linking PEI and fabricating PEI cryogels

The calculated amounts of the cross-linking agents (at molar ratios to the repeating PEI unit of 1:1 and 1:2) were added dropwise under constant stirring to the diluted PEI solution of concentrations of 5 or 10%. pH of the PEI solution was pre-adjusted with 10M HCl solution. The synthesis conditions are summarized in Table 1. The mixtures were divided into two portions, one was left for cross-linking at room

**Table 1**  
Cross-linking conditions and characteristics of PEI cross-linked at 23 °C (1–8) and under cryogelation conditions at –20 °C (1c–8c).

Sample code	C(PEI), pH	CL:PEI molar ratio	C/N	MD	SIEC, mmol/g
Cross-linking with DGE-1,4-BD					
1	10%	1:1	8.9 ± 0.2	0.69 ± 0.01	2.2 ± 0.1
1c	pH 10		7.0 ± 0.1	0.49 ± 0.01	2.5 ± 0.1
2	10%	1:1	8.0 ± 0.6	0.59 ± 0.06	2.3 ± 0.1
2c	pH 4.4		5.4 ± 0.6	0.32 ± 0.06	1.9 ± 0.6
3	10%	1:2	3.3 ± 0.1	0.12 ± 0.01	7.9 ± 0.7
3c	pH 8.8		5.2 ± 0.1	0.29 ± 0.01	4.6 ± 0.2
4c	5%	1:1	5.6 ± 0.1	0.34 ± 0.01	3.4 ± 0.2
	pH 8.8				
Cross-linking with DGE-1,4-PEG					
5	10%	1:1	9.8 ± 0.6	0.33 ± 0.03	2.2 ± 0.2
5c	pH 8.8		7.2 ± 0.7	0.22 ± 0.03	3.6 ± 0.2
6	10%	1:2	5.6 ± 0.1	0.15 ± 0.01	2.4 ± 0.1
6c	pH 8.8		6.9 ± 0.4	0.21 ± 0.02	3.1 ± 0.9
7	5%	1:1	11.5 ± 0.1	0.41 ± 0.01	2.5 ± 0.1
7c	pH 8.7		7.8 ± 0.1	0.25 ± 0.01	5.8 ± 0.2
Cross-linking with GA					
8	10%	1:1	4.2 ± 0.1	0.40 ± 0.03	5.3 ± 0.1
8c	pH 4.6		4.3 ± 0.1	0.43 ± 0.03	5.2 ± 0.1

\* C(PEI)-PEI concentration, CL:PEI molar ratio – cross-linker/PEI molar ratio, C/N – carbon/nitrogen atomic ratio, MD – modification degree, SIEC – static ion exchange capacity ( $\text{H}^+$  ions).

temperature (23 °C), another was placed into plastic tubes of the inner diameter of 4 mm and kept in a freezer at –20 °C until cross-linked. When GA was used as a cross-linker, the solution was pre-cooled down to –1 °C using ice/NaCl bath to avoid cross-linking before freezing. The cross-linked PEI was immersed into 0.1 M NaOH solution for 24 h to remove all soluble material, then thoroughly washed with distilled water; PEI cryogels were cut to the cylinders with length 4–5 mm. Cross-linked PEI and cryogels were dried in the vacuum oven at 50 °C and stored in the desiccator. The yield of the materials was > 95% as calculated with respect to PEI introduced to the cross-linking reaction.

### 2.3. Methods

Elemental compositions of PEI and cross-linked materials were determined in triplicates using the EuroEA3000 CHNS analyzer (Eurovector, Italy). The degree of modification (MD) of PEI with the cross-linking agent was calculated using the following formula:

$$MD = (C/N_{\text{sorb}} - C/N_{\text{PEI}})/n$$

where  $C/N_{\text{sorb}}$  and  $C/N_{\text{PEI}}$  – the atomic ratios carbon/nitrogen in cross-linked PEI and original PEI, respectively;  $n$  – the number of carbon atoms in cross-linking fragment.

Swelling of the cross-linked PEI and cryogels was determined from the difference in weights of swollen for 24 h in distilled water and dry material.

The static ion-exchange capacity (SIEC) was determined for the cross-linked PEI and cryogels via addition of excess amounts of HCl and back titration of the solution with NaOH after 24 h of equilibration.

Structure of the freeze-dried PEI cryogels was investigated by the means of scanning electron microscopy (SEM) on a device Carl Zeiss Crossbeam 1540-XB (Germany) with field emission cathode (FE-SEM) under accelerating voltage 2 kV.

The sorption of Cu(II) ions in the form of  $\text{Cu}(\text{NO}_3)_2$  was studied from 1 M  $\text{NH}_4\text{NO}_3$  solution, pH 5.3 and distilled water (without pH adjustment). The sorption of Cu(II), Ni(II), and Co(II) ions from solutions of sulfate salts was studied in distilled water without pH adjustment. The sorption of Hg(II) ions was studied from solution of  $\text{Hg}(\text{NO}_3)_2$  and  $\text{HgCl}_2$  in 0.001 M  $\text{HNO}_3$  and 0.1 M NaCl/0.001 M HCl, respectively. The solid:liquid ratio in sorption experiments was set to 1:1000, the contact time was 24 h at 23 °C. The kinetics of Cu(II) sorption on cross-linked PEI and cryogel was investigated in 1 M  $\text{NH}_4\text{NO}_3$  solution, pH 5.3 at solid:liquid ratio 1:250, and initial Cu(II) concentration of 34 mg/L. The adsorbed amounts were calculated using the difference in initial and equilibrium concentrations of the metal ions in the solutions determined by the atomic absorption spectrometry (AAS) using a Solaar M6 (Thermo, USA) device. To regenerate PEI cryogel after sorption of Cu(II) ions from solution containing 20 ppm copper, 1 ml of 0.1 M  $\text{HNO}_3$  solution was added to 5 mg of the cryogel and left for 1 h. The equilibrium copper concentration was determined by AAS. The mercury concentration was determined using a HVG-1 Hydride Vapor Generator and an AA-6200 atomic absorption spectrometer (Shimadzu, Japan). At least three replicates were made to assure the results reproducibility. The sorption isotherms were fitted using the Langmuir equation, affinity coefficient ( $K_{\text{affinity}}$ ) was calculated as  $K_L \cdot Q_{\text{max}}$  [22], where  $Q_{\text{max}}$  – the maximal sorption capacity,  $K_L$  – the Langmuir constant.

Distribution coefficients ( $K_D$ ) were calculated as follows:

$$K_D = C_{\text{sorbent}}/C_{\text{solution}}$$

where  $C_{\text{sorbent}}$  – metal content is sorbent phase,  $C_{\text{solution}}$  – metal content in solution.

## 3. Results and discussion

### 3.1. Synthesis and characterization of cross-linked PEI and PEI cryogels

Thanks to the solubility of PEI in a wide pH range, it can be cross-

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