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# A new low-cost polymeric adsorbents with polyamine chelating groups for efficient removal of heavy metal ions from water solutions

Michał Cegłowski[a,*], Błażej Gierczyk[a], Marcin Frankowski[a], Łukasz Popenda[b]

[a] Faculty of Chemistry, Adam Mickiewicz University in Poznan, Umultowska 89b, 61-614 Poznań, Poland
[b] NanoBioMedical Centre, Adam Mickiewicz University in Poznań, Umultowska 85, 61-614 Poznan, Poland

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ABSTRACT

Two new low-cost polymeric adsorbents have been obtained in a simple reaction of diethylenetriamine (DETA) or pentaethylenehexamine (PEHA) with 1,3,5-tris(6-isocyanatohexyl)-1,3,5-triazinane-2,4,6-trione (HDI-IC). The reagents used for the synthesis are inexpensive and are produced yearly in high quantities to be applied in various industrial processes. The resulting HDI-IC-DETA and HDI-IC-PEHA polymers possess ethyleneamine chains of various lengths therefore they are capable of forming polyamine chelating complexes with heavy metal ions. The composition, properties and morphology of the two polymers were investigated by Fourier transform infrared spectroscopy, elemental analysis, thermogravimetric analysis, solid state nuclear magnetic resonance, and scanning electron microscopy. The influence of parameters such as pH, initial concentration, contact time, and temperature on the adsorption of $Cd^{2+}$, $Co^{2+}$, $Cr^{3+}$, $Cu^{2+}$, and $Ni^{2+}$ ions was investigated. The adsorption isotherm data were well fitted by Langmuir model, whereas the adsorption kinetics followed the pseudo-second-order kinetic model. The values of maximum amount of ions adsorbed, calculated using the Langmuir model for adsorption of $Cd^{2+}$, $Co^{2+}$, $Cr^{3+}$, and $Cu^{2+}$ ions on HDI-IC-PEHA polymer, were at least twice higher than those calculated for HDI-IC-DETA polymer. The findings reported indicate that HDI-IC-DETA and HDI-IC-PEHA polymers are excellent adsorbents for efficient removal of heavy metal ions from aqueous solutions.

## 1. Introduction

Pollution with heavy metal ions is a serious environmental problem in view of their toxicity, persistence and non-biodegradable nature. The release of heavy metal ions caused by extensive industrialization and indiscriminate disposal, results in contamination of aquatic ecosystems, atmosphere and soil. These ions tend to accumulate in the biosphere and enter living organisms through the alimentary chain which results in their circulation in the environment [1]. As a result, the presence of heavy metal ions in the ecosystem is a major and long-term environmental hazard. Many of these ions pose a serious threat to human health even at very low concentrations. Some of them like iron, cobalt, zinc, and copper are required in human diet in small quantities, however their presence at higher concentration leads to toxic effects. The removal of heavy metal ions from the environment has therefore received much attention in recent years and is considered as an important subject of environmental chemistry [2].

Various techniques such as adsorption, ion exchange, dialysis precipitation and extraction have been applied to remove excess heavy metal ions from water solutions. Among these techniques adsorption has received much attention due to high environmental friendliness and low cost of adsorbents production [3, 4]. The additional benefit of using adsorption is the possibility to easily remove adsorbent from a purified solution which significantly reduces the overall cost of purification process. Moreover, usually under appropriate conditions the adsorbed pollutant can be desorbed which allows the adsorbent reuse.

The adsorption properties of particular adsorbent are closely related to its specific surface area, internal structure and presence of accessible functional groups. These factors affect the types of interaction that are taking place between adsorbate and adsorbent and ultimately control the effectiveness of adsorption process. As a result, numerous materials with various adsorption properties can be obtained to meet specific needs. Among the commonly synthesized adsorbents one can find functional polymers [5–12], activated carbon [13–16], zeolites [17–19], modified silica [20–25] and metal oxides [26–28]. Functional polymers have received much interest due to their vast surface area, perfect skeleton strength and the fact that their basic physicochemical properties such as pore size distribution or internal surface area can be adjusted by varying the polymerization conditions [29]. The possibility to introduce various functional groups into the polymeric matrices

* Corresponding author.
*E-mail address:* ceglowski.m@gmail.com (M. Cegłowski).

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allows their use as adsorbents that can effectively trap many organic and inorganic pollutants. Moreover, the exhausted adsorbents can be regenerated under mild conditions usually by treatment with acidic or alkaline solution [30].

A good heavy metal ion adsorbent designed for large-scale application, besides showing adequate adsorption properties, must be inexpensive in preparation. The main drawback of activated carbons and many functional polymers is their high production cost, caused by the necessity of altering their structure by introduction of functional groups or complexing units [31]. In recent years, the search for low-cost adsorbent for heavy metal ions has become a very important research focus. Various materials such as agricultural wastes, industrial by-products and wastes of natural substances have been studied as adsorbents of heavy metal ions [30]. For instance, pecan shell-based granular activated carbons pretreated with HCl were used for removal of metal ions ($Cu^{2+}$, $Pb^{2+}$, $Zn^{2+}$) from water solutions [32]. Rice husk treated with $K_2HPO_4$ was used for removal and recovery of $Cd^{2+}$ from wastewater [33]. Hydrous titanium oxide obtained by $TiCl_4$ hydrolysis was used for purification of industrial waste contaminated with chromium (VI) [34]. Clay sorbent treated with hydrochloric acid was used for removal of nickel, copper, and zinc ions from wastewater [35].

In this study, a simple reaction of polyamines, particularly diethylenetriamine (DETA) and pentaethylenehexamine (PEHA), with 1,3,5-tris(6-isocyanatohexyl)-1,3,5-triazinane-2,4,6-trione (HDI-IC) was used to obtain two polymeric adsorbents. The obtained polymers can be regarded as low-cost adsorbents of heavy metal ions, as the reagents used for their synthesis are inexpensive and are produced yearly in high quantities to be applied in various industrial processes [36–38]. Moreover, most low-cost adsorbents need some additional pretreatment before they can be applied in adsorption of heavy metal ions, therefore a reaction that takes only 2 h can be regarded as low time-consuming process. The materials obtained were characterized and their adsorption properties towards $Cd^{2+}$, $Co^{2+}$, $Cr^{3+}$, $Cu^{2+}$, and $Ni^{2+}$ ions were tested. The influence of factors affecting the adsorption of these ions such as pH, concentration, contact time, and temperature was investigated. The polymeric adsorbents obtained were applied for the removal of heavy metal ions from real wastewater samples.

## 2. Experimental

### 2.1. Materials and chemicals

Diethylenetriamine, pentaethylenehexamine, ethylenediaminetetraacetic acid disodium salt (EDTA), acetonitrile, ethyl acetate, metal perchlorates: $Cd(ClO_4)_2 \times 6H_2O$, $Co(ClO_4)_2 \times 6H_2O$, $Cr(ClO_4)_3 \times 6H_2O$, $Cu(ClO_4)_2 \times 6H_2O$, and $Ni(ClO_4)_2 \times 6H_2O$ were obtained from Sigma-Aldrich (St. Louis, MO, USA) and were used without further purification. 1,3,5-tris(6-isocyanatohexyl)-1,3,5-triazinane-2,4,6-trione (HDI-IC) was obtained from Covestro (Leverkusen, Germany). Wastewater samples were obtained from PRESSEKO (Bolechowo near/Poznan, Poland) company.

### 2.2. Instruments

A Shimadzu ICPE-9820 Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) with the mini-torch technology was used for determination of $Cd^{2+}$, $Co^{2+}$, $Cr^{3+}$, $Cu^{2+}$, and $Ni^{2+}$ ions concentrations. Each measurement was performed in 3 replications, and the % RSD did not exceed 5%. The FTIR spectra of the resins were recorded on a Bruker IFS 66s spectrometer (Billerica, MA, USA) using KBr pellets (about 1.5 mg of sample in 200 mg of KBr). $^{13}C$ and $^{15}N$ CP-MAS NMR spectra were recorded on an Agilent DD2 spectrometer (Santa Clara, CA, USA) equipped with Wide Bore Triple Resonance T3 MAS XY{1H-19F}, 4 mm probehead, using standard cross polarization sequence (*tancpx*) with $^{1}H$ decoupling, operating at frequencies 100.66 and 40.58 MHz, respectively. The following parameters were used: sample rotation – 8000 Hz, relaxation delay – 7 s, acquisition time – 0.05 s, cross-polarization contact time – 0.9 ms. The spectra were referred to the methylene signal of external glycine (43.30 ppm for $^{13}C$ and −347.60 ppm for $^{15}N$, respectively). Elemental analyses were carried out on a Vario EL III Element Analyzer (Hanau, Germany). Thermal data were obtained by using a Setaram Setsys 1200 (Caluire, France). The thermal stability of the resin was investigated by thermogravimetric analysis in air stream at a heating rate of 5 °C $min^{-1}$. The pH measurements were performed using Elmetron CP-505 apparatus (Zabrze, Poland) equipped with a combined pH electrode. Scanning electron microscopy (SEM) images were obtained on a Hitachi Scanning Electron Microscope SU3500 (Tokyo, Japan).

### 2.3. Synthesis of polymeric adsorbents

A portion of 10 g of HDI-IC (0.02 mol) was dissolved in ethyl acetate or acetonitrile (100 mL) and 0.03 mol of the corresponding amine (3.1 g of DETA or 7.0 g PEHA) was added upon vigorous stirring. The mixtures obtained were mixed for 1 h and the precipitated resin was filtered off, washed with ethyl acetate or acetonitrile, dried at room temperature, grounded using mortar and pestle, and sieved using a 30-mesh sieve.

### 2.4. Adsorption experiments

The adsorption of $Cd^{2+}$, $Co^{2+}$, $Cr^{3+}$, $Cu^{2+}$, and $Ni^{2+}$ ions on HDI-IC-DETA and HDI-IC-PEHA polymers was examined using batch experiments. The relations between the adsorption properties and the pH of the solution were studied in the pH range from 2 to 6. The pH of the solutions was adjusted with buffers containing KCl/HCl (pH 2) and acetic acid/sodium acetate (pH 3–6). To prepare each sample 10 mL of buffered solution was used with the initial metal ion concentration equal to 1 mM. To each solution 10 mg of HDI-IC-DETA or HDI-IC-PEHA polymers were added and the obtained mixture was stirred for 24 h at room temperature. The exact concentration of metal ions before and after adsorption was measured by ICP-OES.

To prepare adsorption isotherms, a series of samples containing 10 mg of HDI-IC-DETA or HDI-IC-PEHA polymers were equilibrated with 10 mL buffered (pH = 6) solutions containing various concentrations (0.1–20 mM) of $Cd^{2+}$, $Co^{2+}$, $Cr^{3+}$, $Cu^{2+}$, or $Ni^{2+}$ ions. The solution was shaken at room temperature for 24 h. The starting ($C_0$; mg $L^{-1}$) and equilibrium ($C_{eq}$; mg $L^{-1}$) concentrations of metal ions were measured by ICP-OES. The amount of metal ions adsorbed ($q_e$; mg $g^{-1}$) after equilibration was calculated using the following equation:

$$q_{eq} = \frac{(C_0 - C_{eq})V}{m} \quad (1)$$

where m is the mass of the polymer (g) and V is the volume of the solution (L).

For the adsorption kinetic studies, 50 mg of HDI-IC-DETA or HDI-IC-PEHA polymers were stirred at room temperature in 50 mL of buffered (pH = 6) metal ion solution with the initial concentration of 1 mM. The metal ion concentration was measured at preset time intervals using ICP-OES by withdrawing samples (200 μL) from the release medium. The amount of adsorbed metal ions at time t (h), $q_t$ (mg $g^{-1}$) was calculated from:

$$q_t = \frac{(C_0 - C_t)V}{m} \quad (2)$$

where $m$ is the mass of the polymer (g), $C_0$ (mg $g^{-1}$) is the initial concentration, $C_t$ (mg $g^{-1}$) is the concentration at time t, and V is the volume of the solution (L).

Thermodynamic studies were performed for a set of samples containing 10 mg of HDI-IC-DETA or HDI-IC-PEHA polymers and 10 mL of buffered (pH = 6) metal ion solution at the initial concentration of 1 mM. The samples were shaken at 296 ± 1 K, 303 ± 1 K, 313 ± 1 K,