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Mechanism of Cu(II), Cd(II) and Pb(II) ions sorption from aqueous solutions by macroporous poly(glycidyl methacrylate-*co*-ethylene glycol dimethacrylate)

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ABSTRACT

The mechanism of Cu(II), Cd(II) and Pb(II) ions sorption from aqueous solutions by macroporous poly(glycidyl methacrylate-*co*-ethylene glycol dimethacrylate) (PGME) functionalized by reaction of the pendant epoxy groups with diethylene triamine (PGME-deta) was studied using X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FTIR) analysis. Atomic force microscopy (AFM) and scanning energy-dispersive X-ray spectroscopy (SEM-EDX) were used for the determination of surface morphology of the copolymer particles. The sorption behavior of heavy metals Cu(II), Cd(II) and Pb(II) ions sorption was investigated in batch static experiments under non-competitive conditions at room temperature (298 K). The obtained results were fitted to pseudo-first order, pseudo-second order and intraparticle diffusion kinetic model. The kinetics studies showed that Cu(II), Cd(II) and Pb(II) sorption obeys the pseudo-second-order model under all investigated operating conditions with evident influence of pore diffusion.

1. Introduction

Heavy metals, especially lead, cadmium, mercury and arsenic due to their high degree of toxicity rank, pose the main threat to human health and the environment [1,2].

Copper (Cu) is an essential and beneficial element in human metabolism required for various biochemical and physiological functions, as a co-factor for oxidative stress-related enzymes (like catalase, superoxide dismutase, peroxidase, ferroxidases, monoamine oxidase, and dopamine β-monooxygenase), it is involved in hemoglobin formation, cross-linking of collagen, elastin, and hair keratin [3–5]. Nevertheless, short term Cu exposure may cause gastrointestinal distress, while long term exposure can cause liver or kidney damage [6].

Copper compounds are widely used in food additives, fungicides, algicides, fertilizers, insecticides, in electroplating, lithography, petroleum refining, coatings, etc. [7].

The main source of Cu in drinking water is the corrosion of household plumbing systems [8]. The U.S. Environmental Protection Agency (EPA) and the European Drinking Water Directive (DWD) set the maximum acceptable Cu concentrations in drinking water as 1.3 mg/L and 2.0 mg/L, respectively [8,9].

It is established that cadmium (Cd) and lead (Pb) have no biological functions and are considered as non-essential metals [9]. Even at low exposure levels cadmium can cause kidney damage effects, osteoporosis and bone fractures [1]. Nowadays, Cd is used in the production of re-chargeable nickel–cadmium batteries, PVC stabilizers, pigments, alloys, fertilizers, solar panels, as a barrier to control neutrons in nuclear fission, etc. [10–12].

The main sources of Cd in drinking water are corrosion of galvanized pipes, discharge from metal refineries, waste batteries and paints [8]. The U.S. Environmental Protection Agency (EPA) and the European Drinking Water Directive (DWD) set the maximum acceptable Cd concentration in drinking water as 0.005 mg/L [8,9].

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Lead (Pb) is a neurotoxin and causes headache, brain disorders, kidney problems and high blood pressure [8,13]. Lead has many different industrial, agricultural and domestic applications. Presently, Pb is used in the production of lead-acid batteries, ammunitions, metal products and as a radiation shield [1]. The main source of Pb in drinking water is the corrosion of household plumbing [8]. The maximum acceptable Pb concentration according to the European Drinking Water Directive (DWD) in drinking water is 0.01 mg/L [9].

Having it all in mind, the need was imposed for finding suitable and cost-effective physico-chemical methods for treating metal-containing industrial wastewaters, like adsorption, membrane filtration, and photocatalysis. Porous polymeric adsorbents consisting of crosslinked copolymer (solid support) and functional group (ligand) have potential application for the selective removal and/or recovery of metal ions from waste solutions. These sorbents are highly efficient, selective and cost-effective with possible reusability of the adsorbent [14–16]. Among them, the copolymers based on glycidyl methacrylate (GMA) becomes more attractive as sorbents of heavy and precious metals due to the fact that the epoxy group in GMA molecule can easily be transformed into the pyridine groups [17], urea and iminodiacetic [18], pyrazole [19], amines [20,21], etc. Gupta et al. studied the removal of Hg(II) and Pb(II) ions from aqueous solutions by GMA, styrene and *N*,*N*′-methylenebisacrylamide terpolymer functionalized with ethylenediamine (-en), diethylenetriamine (-deta) and tetraethylenepentamine (-tepa) [22]. Atia et al. used glycidyl methacrylate (GMA) and divinylbenzene copolymer functionalized with ethylenediamine to study the uptake behavior of Cu(II) and Pb(II) from their aqueous solutions [23]. Liu et al. investigated the selective removal of Cu(II) and Pb(II) ions from aqueous solutions by diethylenetriamine functionalized GMA and trimethylolpropane trimethacrylate copolymer functionalized with diethylenetriamine [24]. Also, Liu et al. investigated Cu(II) sorption by poly(glycidyl methacrylate) (PGMA) grafted with diethylenetriamine [25].

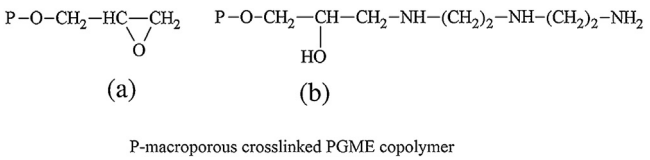
Previously, we found amino-functionalized PGME suitable for removal of cations and oxyanions from aqueous solutions, like Cu(II), Mn(II), Cd(II), Zn(II) and Pb(II) ions [21], Cr(VI) ions [26,27], Rh(III), Au(III) and Pt(IV) ions [28], Tc(VII) [29].

In order to elucidate mechanism of Cu(II), Cd(II) and Pb(II) ions sorption and the surface interactions, the Fourier transform infrared spectroscopy (FTIR) analysis and X-ray photoelectron spectroscopy (XPS) were used. The surface morphology of the copolymer samples before and after metal ions sorption was investigated by scanning energy-dispersive X-ray spectroscopy (SEM-EDX) and atomic force microscopy (AFM). Kinetic data were analyzed using chemical-reaction and particle-diffusion models (pseudo-first order, pseudo-second order and intraparticle diffusion model) in order to determine the nature of sorption kinetics and the rate limiting step for Cu(II), Cd(II) and Pb(II) ions sorption by PGME-deta samples.

2. Experimental

2.1. Materials

Glycidyl methacrylate, GMA (Merck, Germany), ethylene glycol dimethacrylate, EGDMA (Fluka, Buchs, Switzerland), cyclohexanol (Sigma Aldrich, Germany), dodecanol (Merck, Germany) and diethylene triamine (Merck, Germany) were analytical grade products and used as received. Initiator 2,2′-azobisisobutyronitrile, AIBN (Sigma Aldrich, Germany) was purified by recrystallization in methanol before use. Poly(*N*-vinyl pyrrolidone) (PVP) (Kollidone 90, M_w = 3,60,000 g/mol, BASF, Germany) was used as stabilizer. Toluene and ethanol were supplied by Zorka Pharma (Šabac, Serbia). Metal solutions were prepared from reagent grade $CuCl_2$, $CdCl_2$ and $Pb(NO_3)_2$ (Sigma-Aldrich), using deionized water (Milli-Q Millipore, 18 MΩ cm^{-1} conductivity).



Scheme 1. Chemical structure of PGME-10/12 (a) and PGME-10/12-deta (b).

2.2. PGME preparation and functionalization with diethylene triamine

Macroporous crosslinked PGME copolymer (with 40 mass% of crosslinker, EGDMA) was prepared by radical suspension copolymerization in the presence of inert component (90 mass% of cyclohexanol and 10 mass% dodecanol) as described previously [30]. The resulting crosslinked beads were sieved, purified by Soxhlet extraction with ethanol and designated as PGME-10/12. The particles with average particle diameter of 150–300 μm were additionaly functionalized with diethylene triamine as described elsewhere [31]. The amino-functionalized sample was filtered, washed with ethanol, dried, and labeled as PGME-10/12-deta. The chemical structure of PGME-10/12 and PGME-10/12-deta is schematically presented in Scheme 1.

The relevant porosity parameters for the macroporous amino-functionalized sample PGME-10/12-deta, i.e. specific surface area, S_{Hg} (53 $m^2 g^{-1}$), specific pore volume, V_s (0.63 $cm^3 g^{-1}$), and pore diameter which corresponds to half of pore volume, $D_{V/2}$ (59 nm), were published previously. Amino group concentration, C_{AG}, calculated from the elemental analysis was 5.01 mmol g^{-1} [31].

2.3. Characterization metods

Infrared spectra were taken in attenuated total reflection (ATR) mode using a Nicolet 380 FTIR spectrometer equipped with a Smart Orbit™ ATR attachment containing a single-reflection diamond crystal in the range 4000–400 cm^{-1}. The angle of incidence was 45°. Typically, 32 scans were performed for each spectrum at a resolution of 4 cm^{-1}.

Concentrations of Cu(II), Cd(II) and Pb(II) were determined by inductively coupled plasma optical emission spectrometry ICP-OES (Thermo iCAP 6500 ICP OES). Standard statistical methods were applied to calculate the mean values and standard deviations for each set of data. All experiments were repeated in triplicate or more if necessary. Relative standard deviations were less than or equal to 5%.

The scanning electron microscopy SEM analysis was performed with JEOL JSM-6610 LV (Tokyo, Japan), at a working distance of ca. 14 mm and an accelerating voltage of 20 kV instrument using W filament as an electron source. Air-dried membrane samples were fractured after cooling in liquid nitrogen and coated with a thin gold film by sputter-deposition. The SEM-EDX (energy-dispersive X-ray spectroscopy) analysis was performed to identify the type of atoms present in the functionalized copolymers at a depth of up to approximately1000 nm from the surface.

Samples were analyzed with an XPS instrument TFA XPS Physical Electronics Inc. (Chanhassen, MN, USA). The base pressure in the chamber was about 6×10^{-8} Pa. The samples were excited with X-rays over a 400-μm spot area with a monochromatic Al $K\alpha_{1,2}$ radiation at 1486.6 eV. The photoelectrons were detected with a hemispherical analyzer positioned at an angle of 45° with respect to the normal to the sample surface. Survey-scan spectra were made at a pass energy of 187.85 eV and 0.4 eV energy step. High