Chemical Engineering Journal 270 (2015) 9–21

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Synthesis, characterization of PMDA/TMSPEDA hybrid nano-composite and its applications as an adsorbent for the removal of bivalent heavy metals ions

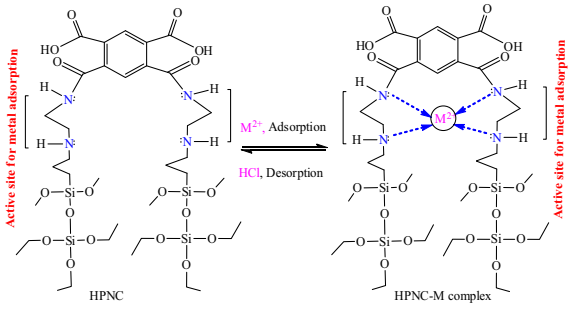
Ibrahim Hotan Alsohaimi [a], Saikh Mohammad Wabaidur [a], Mahendra Kumar [b], Moonis Ali Khan [a,*], Zeid Abdullah Alothman [a], Mohammad Abulhassan Abdalla [a]

[a] Chemistry Department, College of Science, King Saud University, Riyadh 11451, Saudi Arabia
[b] School of Biotechnology, Dublin City University, Dublin 9, Ireland

HIGHLIGHTS

- HPNC was synthesized by ring opening polymerization and sol–gel reaction.
- Hydrated radius and electronegativity played significant role in metal adsorption.
- Metal ions interaction with –NH active sites was a possible adsorption mechanism.
- Elution was maximum (Pb(II) 94.13% > Zn(II) 93.59% > Cd(II) 84.15%) with 0.1 M HCl.
- 28.99% and 16.96% loss in Pb(II) adsorption and recovery after four consecutive cycles.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 17 December 2014
Received in revised form 2 February 2015
Accepted 3 February 2015
Available online 10 February 2015

Keywords:
HPNC
Heavy metals
Exothermic
Freundlich isotherm
Pseudo-second-order model

ABSTRACT

Novel PMDA/TMSPEDA hybrid polymeric nano-composite (HPNC) was synthesized by ring opening polymerization and sol–gel reaction. TGA analysis showed thermally stable polymeric material. FT-IR analysis revealed co-ordinate bonding between amine groups (present on HPNC) and bivalent metal ions as a possible adsorption mechanism. Adsorption studies showed maximum uptake of Pb(II) (49.72 mg/g) on HPNC followed by Cd(II) (45.22 mg/g), and Zn(II) (41.75 mg/g) at pH 7. Thermodynamically, the process was exothermic. Freundlich and pseudo-second-order kinetics model were the best fitted models to the experimental data. Kinetics studies showed better performance of HPNC for Cd(II) at lower concentration while Pb(II) adsorption was highly favorable at higher concentration. Rapid adsorption kinetics was observed for Pb(II) with equilibration time at various concentrations varied between 10 and 30 min. Desorption studies showed maximum metal elution [Pb(II) (94.13%) > Zn(II) (93.59%) > Cd(II) (84.15%)] with 0.1 M HCl. Regeneration studies showed 28.99% and 16.96% loss in Pb(II) adsorption and recovery after four consecutive cycles, respectively. The findings of present study showed potentiality of HPNC as an effective and economically feasible adsorbent for Pb(II).

* Corresponding author.
E-mail addresses: moonisalikhan@gmail.com, mokhan@ksu.edu.sa (M.A. Khan).

http://dx.doi.org/10.1016/j.cej.2015.02.008
1385-8947/

1. Introduction

Effluents discharged from mining, electroplating, metal finishing, welding, and alloy manufacturing industries provide a major route for heavy metals to ecosystem. Toxicity, persistency, and bioaccumulation tendency make heavy metals a serious threat to both humans and environmental health. Heavy metals can easily enter the food chain through numerous pathways. Many of them above permissible levels are highly toxic or carcinogenic. Therefore, stringent regulations have been imposed world over for removing or minimizing heavy metals to permissible limits. Heavy metals such as cadmium [Cd(II)], and lead [Pb(II)] have no essential biological functions but these metals could be extremely toxic to living organisms. Furthermore, zinc [Zn(II)] is an essential element for human health, but it could be toxic when present in excessive concentrations.

Treatment techniques such as ion-exchange [1], chemical precipitation, chemical oxidation or reduction, electrochemical treatment, evaporation, flocculation [2], membrane filtration [3], and reverse osmosis [4] have been used to remove or to minimize heavy metal ions concentration in industrial wastewater and municipal water supplies. High capita, incomplete heavy metal ions removal, low selectivity, high energy requirements, and generation of toxic slurry are the major flaws of these processes [5]. Adsorption, another treatment technique, considered effective and economical for treating both industrial effluents and potable water. Effectiveness even to remove trace amount of heavy metal ions present in aqueous phase is the major merit of adsorption process [5]. In addition, it is an important process to understand the accumulation of heavy metal ions at solid-solution interfaces [6]. Clay minerals [7], plant wastes [8,9], carbon nano-tubes [10], activated carbon [11], nano-graphite encapsulated alginate beads [12], and lignite [13] have been widely investigated adsorbents for the removal of heavy metal ions from aqueous solution and wastewater.

The use of polymeric (inorganic–organic) hybrid materials as an adsorbent is regarded as one of the most effective methods for the abatement of heavy metal ions from aqueous phase, as these materials have a tendency to bound heavy metal ions via co-ordinate and electrostatic interactions [14]. On other hand, structural flexibility, mechanical stability, and potential applications in harsh environmental conditions are some of the major merits of these polymeric materials. Research is going on to synthesize and test the applicability of the hybrid polymeric adsorbents for removing heavy metals from aqueous solutions [15–19]. Several novel routes to synthesize these adsorbents have already been proposed by various research groups. Pan et al. [15] developed a polymer-based hybrid adsorbent (HFO-001) for an efficient removal of heavy metals from contaminated waters. Ge et al. [16] synthesized and modified an iron oxide derived magnetic nanoparticles for the removal of divalent heavy metal ions from aqueous solution. Iesan et al. [17] synthesized hybrid adsorbents by *in situ* encapsulation of hydrated ferric oxide in the porous structure of a strong base anion exchange resins based on the styrene divinyl benzene copolymer and investigated their adsorptive performance for arsenic removal from drinking water [17]. Liu et al. [18] synthesized a series of zwitterionic hybrid adsorbents by ring-opening polymerization of pyromellitic acid dianhydride and N-[3-(trimethoxysilyl)propyl] ethylene diamine or phenylaminomethyltrimethoxysilane for heavy metal ions removal from aqueous phase. The zwitterionic inorganic–organic hybrids adsorbents were synthesized by Dong et al. [19], and their suitability was tested in Cu(II) removal.

Considering the merits of aforementioned polymeric adsorbents for heavy metal ions removal from aqueous phase, here in, we have synthesized thermally stable novel hybrid polymeric nanocomposite (HPNC) by ring opening polymerization and sol–gel reaction. Moreover, the applicability of the adsorbent for the removal of divalent heavy metal ions [Cd(II), Pb(II), and Zn(II)] from aqueous phase was studied. Kinetics, thermodynamics, and isotherms studies were carried out to evaluate the adsorptive potential of synthesized HPNC. The economic feasibility of HPNC was estimated by desorption and regeneration studies.

2. Experimental

2.1. Chemicals and reagents

Pyromellitic acid dianhydride, PMDA, purity: ⩾97%; *N*-(3-(trimethoxysilyl) propyl ethylene diamine, TMSPEDA, ⩾97%; *N*,*N*-dimethylformamide anhydrous, DMF, purity: ⩾99.8%; and tetraethyl orthosilicate, TEOS, purity: ⩾99.99% were purchased from Aldrich (Sigma–Aldrich Inc., St. Louis, MO, USA). Heavy metal stock solutions (1000 mg/L) were prepared by using their nitrate and chloride salts (BDH Chemical, England). The other chemical and reagents used were of analytical reagent grade.

2.2. Preparation of HPNC

The HPNC was synthesized using TMSPEDA and PMDA monomers by ring opening polymerization and sol–gel reaction at pH 2.0 (Scheme 1). A typical procedure to synthesize HPNC was as follows: 5 g PMDA was dissolved in a round bottom flask containing 30 mL DMF, under continuous stirring condition for an hour at room temperature (30 °C). Then, 3.5 g TMSPEDA in 10 mL DMF was slowly added (drop wise) to the solution. The presence of polar (hydrophilic) aprotic solvent DMF facilitates reaction between TMSPEDA and PMDA that followed polar mechanisms, such as S_N2 reactions. Subsequently, the reaction mixture was stirred for 2 h at 30 °C to complete ring opening reaction. Thereafter, 20 wt% TEOS to the total weight of TMSPEDA and PMDA monomers was added and subsequently, pH of the resulting mixture solution was adjusted to 2 by adding few drops of 4 M HCl solution. The resulting mixture was then stirred for 12 h at 30 °C to hydrolyze the alkoxy groups on the adsorbent. Furthermore, *in situ* thermal crosslinking of the adsorbent in solution was conducted by raising the temperature up to 80 °C for 4 h. A pale yellow solution was obtained which was precipitated in deionized water. The resulting precipitate was separated by vacuum filtration and dried in a vacuum oven at 60 °C for 12 h to obtain hybrid polymeric nano composite (HPNC). Furthermore, the solubility of the synthesized HPNC was tested in tetrahydrofuran (THF), dimethylformamide (DMF), *N*,*N*-dimethylacetamide (DMAc), dimethyl sulfoxide (DMSO), *N*-methyl-2-pyrrolidone (NMP), ethylacetate (EOAc), dichloromethane (DCM), toluene, methanol, and ethanol. In addition; the solubility of HPNC was also checked in aqueous solutions of varied pH in range 2–10. The synthesize HPNC was insoluble in the aforementioned solvents and aqueous solutions of varied pH.

2.3. Characterization of adsorbent

The infra-red spectra of HPNC before and after heavy metal ions adsorption were recorded by employing Fourier transform infrared (FT-IR; Nicolet 6700 FTIR Thermo Scientific) spectrometer using KBr pellet method. The spectra were recorded in 4000–400 cm^{-1} region with 32 scans. The thermal stability of synthesized adsorbent was investigated by thermo gravimetric (TGA; Mettler Toledo TGA/SDTA851 with Starc software) analyzer in temperature range 20–700 °C, under N_2 flow at a heating rate of 10 °C/min. The crystallinity of HPNC was investigated by X-ray diffractometer (XRD;