Journal of the Taiwan Institute of Chemical Engineers 70 (2017) 382–390

Contents lists available at ScienceDirect

Journal of the Taiwan Institute of Chemical Engineers

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

Substitution influence of halo polyurethane foam on the removal of bismuth, cobalt, iron and molybdenum ions from environmental samples

E.A. Moawed*, M.A. El-Hagrasy, N.E.M. Embaby

Chemistry Department, Faculty of Science, Damietta University, Damietta, Egypt

ARTICLE INFO

Article history:
Received 8 June 2016
Revised 4 October 2016
Accepted 19 October 2016
Available online 15 November 2016

Keywords:
Halo polyurethane foam
Bismuth
Cobalt
Iron
Molybdenum

ABSTRACT

Polyurethane foam was modified by the addition of halogen atoms and amino groups into the foam matrix in order to increase its polarity for the sorption of ionic species. The halo-modified sorbents (X-PUFs, $X =$ Cl, Br or I) were characterized using FTIR, UV/Vis and Raman spectroscopy, EA, XRD and SEM. The average values of pH_{ZCP}, maximum value of ΔpH (pH 9) and bulk DC conductivity for X-PUFs are 3.8, −1.9 and 2.6×10^{-5} Ω^{-1} cm^{-1}, respectively. The activity of the surface functional groups of X-PUFs were evaluated by the extraction of Bi(III), Co(II), Fe(III) and Mo(III) ions and extraction conditions including pH, shaking time, flow rate, temperature and initial metal concentration were optimized. Maximum extraction of those ions was achieved as their thiocyanate complexes in acidic medium (pH 1–3, 5–6 and 1.5–2 mol L^{-1} H_2SO_4) within 1–30 min. A perfect isotherm curve with almost zero intercept (0.008), good correlation coefficient R^2 (0.973) was obtained. The values of LOD, LOQ and RSD ($n = 6$) for the determination of Bi(III), Co(II), Fe(III) and Mo(III) ions are 2 ng L^{-1}, 7 ng L^{-1} and 0.75%, respectively. The sorption capacities of the tested metal ions onto Cl-PUF, Br-PUF and I-PUF are 0.16, 0.14 and 0.14 mmol g^{-1}, respectively. The accuracy of the procedure was verified by the analysis of food, ground water and pharmaceutical samples with recovery and average RSD values of 99–100% and 2.39%, respectively.

1. Introduction

Flexible polyurethane foam (PUF) is a copolymer consisting of low molecular weight polyols [polyether, $(CH_2CH_2O)_n$], which are linked through urethane groups (NHCOO) [1–3]. PUF was reported as an efficient–low cost sorbent [4–7]. It is an excellent material due to its cellular structure and in addition it has excellent thermal stability and solvent resistance [8–11]. PUF was applied in its native form, immobilized, incorporated or coupled with chelating ligands for the preconcentration and/ or separation of trace metal ions [12–16]. The high density of PUF/ligand is inconvenient and results in low sorption capacity of PUF and decreases its extraction rate of metal ions. To overcome this problem, PUF has been modified by increasing the matrix polarity *via* the addition of new chelating groups without increasing the density of PUF. Halo-modified PUF (X-PUFs, X = Cl, Br or I) sorbents were prepared according to Sand Meyer reaction [17,18] and their structure was identified then applied for the removal of Bi(III), Co(II), Fe(III) and Mo(III) ions.

Some trace elements including bismuth, cobalt, iron, and molybdenum are very important due to their physical and chemical properties, which have led to their wide application in different life areas. They are considered as essential micronutrients with a variety of biochemical functions in all living organisms and also are important as micronutrients for plants [19–22]. Cobalt and iron play a key functional role in the synthesize of hemoglobin, myoglobin and contribute to the prevention of pernicious anemia and production of red blood cells [23–27]. Molybdenum is used for the treatment of domestic animals disease, and has been linked epidemiologically to human disorders [28,29]. Bismuth is used in pharmaceutical preparations due to its antiseptic, astringent, diuretic properties and also used as antiulcer and antibacterial this is in addition to its application in cosmetic products like pigments in eye shadow, lipsticks and hair dyes [30–33]. Direct determination of those elements in different environmental samples is to some extent a problem because of the high concentration of interfering matrix components. Separation and recovery procedures of those elements, to eliminate such interference prior to their detection are necessary.

In this study, we aimed to modify the surface of the PUF by the addition of halogen (Cl, Br or I) atoms and amino groups to the PUF matrix to improve its polarity and increase its sorption capac-

* Corresponding author. Fax: +20572403868.
E-mail address: eamoawed@yahoo.com (E.A. Moawed).

http://dx.doi.org/10.1016/j.jtice.2016.10.037
1876-1070/

ity towards ionic species. The structure of the modified sorbents Cl-PUF, Br-PUF and I-PUF were confirmed by FTIR, Raman, and UV–Vis spectroscopy, elemental analysis (EA), XRD and SEM. The efficiency of the developed sorbents was then tested for the extraction of Bi(III), Co(II), Fe(III) and Mo(III) ions. Factors affecting the removal of the tested ions from different matrices by X-PUFs prior to their spectrophotometric determination were investigated and optimized. In addition, equilibrium, kinetic and thermodynamic studies were performed and their parameters were estimated. The equilibrium, kinetic and thermodynamic models for the sorption of Bi(III), Co(II), Fe(III) and Mo(III) onto X-PUFs was studied. The accuracy of the procedure was verified by the analysis of the new sorbents (X-PUFs) were then applied for the removal and the recovery of Bi(III), Co(II), Fe(III) and Mo(III) ions in various samples.

2. Materials and methods

2.1. Pretreatment of polyurethane foam

Commercial PUF sheets ($d = 12\ kg\ m^{-3}$) were supplied from Foamex Company for foam production, Damietta, Egypt. PUF cubic plugs, with almost similar dimensions ($0.125\ cm^3$), were obtained by slicing the sheets with a slicer. To produce the maximum amount of primary amino groups, the PUF cubes were refluxed in 250 mL of HCl ($2\ mol\ L^{-1}$) for 6 h. Then PUF cubes were washed with distilled water followed by ethanol and dried in a desiccator.

2.2. Preparation of X-PUFs

X-PUFs sorbents were prepared by refluxing PUF with HCl to produce the highest number of amino groups, then diazotized by the addition of a solution of $NaNO_2$. According to Sand Meyer reaction, the substitution of an aromatic amino group is possible via the preparation of its diazonium salt and subsequent replacement with a nucleophile *e.g.,* Cl^-, Br^- or I^- by the addition of CuCl, CuBr or KI solution [17,18].

5 g of dry acid–treated PUF cubes were kept in HCl ($0.1\ mol\ L^{-1}$) in an ice bath. Then the PUF was diazotized by the drop-wise addition and vigorous stirring of 250 mL of $NaNO_2$ ($1\ mol\ L^{-1}$) to the cold acidic solution containing PUF to form PUF$-N_3{}^+Cl^-$ salt. Azo groups were replaced by halogen atoms to produce X-PUFs, a solution of $0.5\ mol\ L^{-1}$ CuCl, CuBr or KI was added to the previous solution at 7°C. The X-PUFs material was separated, washed with distilled H_2O then soaked in $1\ mol\ L^{-1}$ HCl (24 h) at room temperature to produce (–NH_2) groups. Finally, the X-PUFs sorbent was washed with distilled water followed by C_2H_5OH and finally air-dried. The color of the PUF changed from white to orange, yellow and brown after the substitution with halogen atoms (Supl-1).

2.3. Preparation of metal ions solutions

Stock solutions ($1\ mg\ mL^{-1}$) of Bi(III), Co(II), Fe(III), and Mo(III) were prepared by dissolving appropriate amounts of $Bi(NO_3)_3\ 5H_2O$ (Carlo Erba, Italy), $CoSO_4\ 7H_2O$ (Adwic, Egypt), $Fe_2(SO_4)_3$ (Riedel-deHaen, Germany), and $(NH_4)_6Mo_7O_{24}\ 4H_2O$ (Adwic, Egypt) in one liter of distilled water containing 1 mL H_2SO_4 acid [34].

2.4. Apparatus

All absorbance measurements were monitored by V-630 UV–Vis Spectrophotometer from Jasco, Japan. IR spectra were recorded by a Shimadzu FTIR-8400 Fourier transform infrared spectrophotometer. The pH measurements were carried out using a pH meter from Jenway 3510 pH-m (Staffordshire ST15 OSA, UK). The bulk conductivity was measured using Keithley, 6517B Electrometer- high resistance meter.

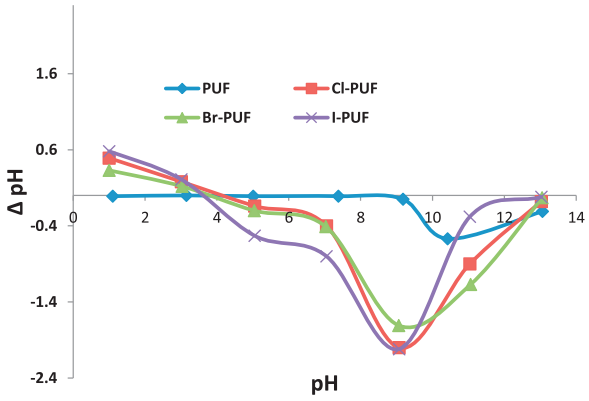

Fig. 1. pH_{ZPC} of PUF and X-PUFs.

2.5. Batch adsorption experiments

Extraction of the investigated ions were carried out by batch technique at room temperature by agitating 0.1 g X-PUFs sorbent with 25 mL of Bi, Co, Fe and Mo solutions of known pH and concentration. After shaking for 1 h, the solution samples were filtered and both the concentration of the remaining and the recovered ions from X-PUFs were spectrophotometrically estimated [34]. The percentage of metal ions and the capacity of the X-PUFs sorbents were calculated by $\%E = ((C_o - C)/C_o) \times 100$ and $Q = C_oEV/m$ where C and Co are the final and initial concentrations of Bi, Co, Fe and Mo ions in solution and V (L) is the volume of the solution and m (g) is the mass of the X-PUFs.

2.6. Fixed bed column adsorption studies

For dynamic experiments, 1.0 g of X-PUFs was packed into a glass column (30-cm long and 1.0 cm in diameter; $L = 7 - 8$ cm). Into the X-PUFs columns, volumes of 25 mL of Bi, Co, Fe and Mo solutions were passed through the column with a flow rate of $2\ mL\ min^{-1}$; then the effluates were collected then analyzed spectrophotometrically [34]. Also, the sorbed metal ions were recovered from the X-PUFs columns by using H_2SO_4, HCl, KCl or NH_4OH solutions then the eluates were collected and determined spectrophotometrically.

2.7. Conductivity measurement

Conductivity of X-PUFs (0.2 g) compressed disks ($p = 5$ tons/cm^2 at room temperature) was investigated. Each disk has a thickness (L) of 2–3 mm with a diameter of 8 mm. The conductivity was calculated from $\sigma = L/RA$ equation where A is the area (m^2) of the electrode touch and R is the resistance value of the sorbent disk unit (Ω).

3. Results and discussion

3.1. Characterization of the X-PUFs

The surface-charge at different pH values and pH of zero charge point (pH_{ZPC}) of X-PUFs were estimated. The values of pH_{ZPC} for Cl-PPUF, Br-PUF and I-PUF are 4.1, 3.9 and 3.5, respectively (Fig. 1), which are less than that of the PUF (8.9). The sequence of the pH_{ZPC} values is in the order of Cl-PPUF > Br-PUF > I-PUF, this order is in agreement with that of the pK_a values of m-chloroaniline, m-bromoaniline and m-iodoaniline (3.98, 3.89 and 3.81) [35,36]. Based on the values of pH_{ZCP}, the surfaces of the X-PUFs would be positively charged at pH values lower than 4.1 due to the protonation of the surface functional groups in acidic medium. Over a