PRECONCENTRATION AND DETERMINATION OF TRACE AMOUNTS OF METAL IONS IN CAST IRON, GRANITE, AND WATER USING POLYURETHANE FOAM FUNCTIONALIZED WITH β-NAPHTHOL

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SUMMARY

Polyurethane foam functionalized with β-naphthol was prepared by covalently linking the reagent with the polyurethane foam matrix through $-N=N-$ groups. The reagent-bonded polyurethane foam (β-Nap-PUF) was characterized by use of elemental analysis, UV–visible and IR spectroscopy, thermal analysis (TGA), density, and stability. β-Nap-PUF was found to be very suitable for preconcentration and determination of nickel, copper, silver, and mercury ions in cast iron, granite, tap, and waste water. Various conditions affecting the adsorption of Ni^{2+}, Cu^{2+}, Ag^+, and Hg^{2+} on β-Nap-PUF were studied. Maximum adsorption of Ni^{2+}, Cu^{2+}, Ag^+, and Hg^{2+} on β-Nap-PUF was in the pH ranges 3–9, 4–10, 9–10, and 1–5, respectively. Extraction of these metal ions followed first-order rate equations and the average values of k_1, k_M, and $t_{1/2}$ at room temperature were calculated 0.17 min^{-1}, 4.68 $\mu mol\ g^{-1}\ min^{-1/2}$, and 5.08 min, respectively. Uptake of the metal ions on the β-Nap-PUF was determined as a function of metal ion concentration in solution and the results were analyzed in terms of the Freundlich, Langmuir, and Dubinin Radushkevich models. Measurement of variation of adsorption of the metal ions with temperature yielded average values of ΔH, ΔS, ΔG, and ΔE of −21.4 $kJ\ mol^{-1}$, −47.8 $J\ K^{-1}\ mol^{-1}$, −5.9 $kJ\ mol^{-1}$ and 9.1 $kJ\ mol^{-1}$, respectively. The capacities of β-Nap-PUF were 0.2, 0.2, 0.1 and 0.07 $mmol\ g^{-1}$ for Ni^{2+}, Cu^{2+}, Ag^+, and Hg^{2+}, respectively. Enrichment factors >50 were achieved and the relative standard deviation (RSD) was ~3.67. The mechanism of adsorption of the metal ion on to β-Nap-PUF is also discussed.

INTRODUCTION

The azo dyes are the largest group of organic reagents used for pre-concentration and determination of trace metal ions [1–7]. Methods using azo dyes are sensitive. Preconcentration of the trace metal ions is achieved by formation of neutral metal complexes then extraction with organic solvents or by using ion exchanger and chelating resins. Use of chelating agent-loaded polymers for preconcentration and separation of trace metal ions results in additional selectivity.

Polyurethane foam loaded with azo dye reagents has been widely exploited for extraction and preconcentration of trace metal ions from different media by batch and dynamic methods [8–11]. Although conventionally loaded polyurethane foam sometimes has excellent properties for preconcentration and separation of specific metal ions, leaching of the reagent from the loaded foam is a problem necessitating preparation of chelating resins in which the reagent is chemically bonded. There is, consequently, interest in developing chelating resins of good stability which have high capacity for metal ions and low analyte matrix effects that tolerate flexible working conditions. Important chelating matrices have recently been developed by attaching the reagent, the ligand, to a polymer matrix by covalent coupling by means of a spacer arm, usually the –N=N– group [12–17].

Many studies have recently shown that the functional groups of polyurethane foam are highly reactive toward diazotization by sodium nitrite and then azo coupling with 4-nitrophenyldiazonium tetrafluoroborate [18,19], 8-hydroxyquinoline [20], alizarin red s [21], and resorcinol [22]. This paper reports the development of an analytical method based on such techniques. A stable, chelate-forming resin matrix has been synthesized by covalent linking of β-naphthol to polyurethane foam; the product has been recycled many times without affecting its efficiency. The matrix has been investigated for separation, preconcentration, and determination of nickel, copper, silver and, mercury ions in cast iron, granite, tap and waste water.

MATERIAL AND METHODS

Reagents and Materials

All reagents were prepared from analytical reagent-grade chemicals and bidistilled water. Stock solutions containing 1 mg mL^{-1} nickel, copper,

silver, and mercury ions were prepared by dissolving 0.3112, 0.3928, 0.1575, and 0.1713 g $Ni(NO_3)_2$ (BDH), $CuSO_4 \cdot 5H_2O$ (Merck), $AgNO_3$ (Merck), and $Hg(NO_3)_2.H_2O$ (Merck) in water containing 1 mL of corresponding concentrated acid and diluting to 100 mL in a graduated flask [1]. β-Naphthol solution (1%) was prepared by dissolving 0.1 g reagent (Adwic) in 10 mL of 1 M NaOH. Commercial white sheets ($d \approx 20$ kg m^{-3}) of open-cell polyether-type polyurethane foam was used.

Synthesis of the Naphthol-Bonded Polyurethane Foam

Small cubes (0.5g, ~0.125 cm^3) of white polyurethane foam ($d = 20$ kg m^{-3}) were washed with distilled water then acetone and left to dry at room temperature. The cubes were then soaked in 50 mL 3 M HCl with stirring for 2 h. After cooling in an ice-bath $NaNO_2$ solution (0.5 M, 10 mL) was added drop by drop to the foam cubes with continuous stirring. β-Naphthol solution was then added to the foam, with stirring. The mixture was then kept for 2 h under refrigeration. The β-Nap-PUF material was then isolated by filtration, washed, in sequence, with 0.1 M HCl, distilled water, and acetone, then dried at room temperature.

Instrumentation

All spectrophotometric measurements were performed by use of either Spectronic 501 (Milton Roy) or UV-1601 (Shimadzu) spectrophotometers. Atomic absorption spectrophotometry (Solaar 969 AA Spectrometer) was used to determine Ni^{2+}, Cu^{2+}, Ag^+, and Hg^{2+} in real samples at 232.0, 324.8, 328.1 and 253.7 nm, respectively. pH was measured with a pH meter from Microcomputer pH-Vision. Glass columns approximately 15 cm long and 1.5 cm in diameter were used for chromatographic separation experiments.

General Procedures

Batch method

Preconcentration of Ni^{2+}, Cu^{2+}, Ag^+, and Hg^{2+} was performed by a batch technique at 25°C except where otherwise specified. β-Nap-PUF (0.2 g) was mixed with the metal ion solution (1.6 μg mL^{-1}, 25 mL) in a shaker thermostatted to the desired temperature and adjusted to the desired shaking speed. After a fixed time the solution was separated and the concentration of metal ions was determined spectrophotometrically [1]. The

distribution coefficients (K_d), percentage uptake (%E) were calculated by use of the equations:

$$K_d = \frac{C_0 - C}{C} \times \frac{V}{M} \tag{1}$$

$$\%E = \frac{C_0 - C}{C_0} \times 100 \tag{2}$$

where C_0 and C are the initial and final concentrations of metal ions in solution, respectively, V is the volume of solution, and M is the weight of the Nap-PUF.

Dynamic method

In dynamic experiments 1 g β-Nap-PUF was packed into a column (15 cm × 1.5 cm), by use of the vacuum method of foam packing [8], and test solutions were passed through the foam column at a flow rate of 3 mL min^{-1}. Stripping of the metal ions from the foam column was performed with eluting agent and the amounts of metal ions were determined spectrophotometrically [1].

RESULTS AND DISCUSSION

Characterization of the β-Naphthol Bonded Polyurethane Foam (β-Nap-PUF)

Terminal urethane (–NHCOO–) and isocyanate (–NCO) groups in white open-cell polyether-type polyurethane foam (d ≈ 20 kg m^{-3}) were readily hydrolyzed with 6 M HCl producing amino groups (–NH$_2$) distributed on the foam [8,20–22]. Polyurethane foam functionalized with β-naphthol (β-Nap-PUF) was then synthesized by diazotization of the white polyurethane foam by use of sodium nitrite then coupling with β-naphthol (C$_{10}$H$_7$OH; MW 144.17 g mol^{-1}). In this work reaction of the PUF with nitrite ion then coupling with naphthol, and the structure of the new polymeric extractor were confirmed and characterized by a variety of methods. Results from elemental analysis, UV–visible and IR spectroscopy, thermal analysis (TGA), density measurement, and determination of stability were studied carefully to characterize the β-Nap-PUF.

Elemental Analysis

The amount (%) of carbon, hydrogen and nitrogen in the β-Nap-PUF was increased and amount of oxygen reduced by hydrolysis of some of the isocyanate and urethane groups (with release of CO_2) and coupling to the naphthol. The results from elemental analysis suggested that an average of one naphthol moiety was present in the β-Nap-PUF per repeat unit of the polymer.

UV–Visible Spectrum of β-Nap-PUF

The UV–visible spectrum of β-Nap-PUF was compared with those of white PUF and the salt of diazotized PUF. That of the diazotized salt PUF had a new absorption band at 385 nm which shifted to 410 and 555 nm after coupling with β-naphthol. The red color of the β-Nap-PUF changed to brown in alkaline solution.

Infrared Spectrum of β-Nap-PUF

The infrared spectra of white PUF and β-Nap-PUF were acquired by use of the potassium bromide technique. It was found that the –NH absorption band of the urethane groups (–NHCOO–) was shifted from 3354.4 to 3381 cm^{-1} after washing with 3 M HCl and to 3473.7 cm^{-1} after coupling with β-naphthol and that the band at 2274.4 cm^{-1} characteristic of the isocyanate (–NCO) groups of the white foam had disappeared. Two additional bands characteristic of β-Nap-PUF appeared at 1726.7 and 1549.3 cm^{-1}.

Density of β-Nap-PUF

The densities of white PUF, the salt of diazotized PUF, and β-Nap-PUF were found to be 20, 37, and 64 kg m^{-3}, respectively. The much higher density of the β-Nap-PUF could be attributed to the bonding between the reagents and the PUF groups.

Effect of Solvent on Leaching of the Reagents from β-Nap-PUF

The chemical stability of β-Nap-PUF was studied by attempting to leach the reagent from β-Nap-PUF with different solvents, in batch mode. β-Nap-PUF cubes (0.2 g) were mixed with 25 mL of the solvent tested in a 100 mL flask and shaken for 30 min. β-Naphthol was not detected in the solvents by use of $FeCl_3$ or CH_2O/H_2SO_4. These results show β-Nap-PUF has good chemical stability in the presence of distilled H_2O, 6 M H_2SO_4, 6 M HCl, 6 M NaOH, ethanol, isopropanol, amyl alcohol, diethyl ether, pe-

troleum ether, tributyl phosphate, chloroform, carbon tetrachloride, and acetonitrile. In the presence of dichloromethane and tetrahydofuran, however, the PUF matrix swelled substantially.

Capacity of β-Nap-PUF for Metal Ions

The capacity of the β-Nap-PUF calculated for Ni^{2+}, Cu^{2+}, Ag^{+}, and Hg^{2+} using the batch technique were 0.19, 0.22, 0.10, and 0.07 mmol g^{-1}, respectively, i.e. the capacity sequence was in the order $Cu^{2+} > Ni^{2+} > Ag^{+} > Hg^{2+}$. These results showed that adsorption capacity for these metal ions depends on ionic size, the structure of the complexing agent, and steric hindrance. The amount of the reagent on the PUF matrix is 0.139 mmol g^{-1} and the corresponding molar ratios (M:β-Nap-PUF) for these ions are 2:2.7, 2:3.1, 2:1.4, and 2:1 for Ni^{2+}, Cu^{2+}, Ag^{+}, and Hg^{2+}, respectively. When the sorption capacity of β-Nap-PUF was compared with Amberlite XAD-2 functionalized with different reagents [12–17] it was found the capacity of β-Nap-PUF was better or comparable for most metal ions.

Thermal Analysis

Thermogravimetric analysis (TGA) of white PUF reveals thermal decomposition beginning at 172ºC, weight loss of 1.7, 38.3, 52.8, and 7.2%

Table I

The characteristics of white, diazotized, and β-naphthol-derivatized polyurethane foam

Property	White foam	Salt of diazotized PUF	β-Nap-PUF
Density (kg m^{-3})	20	37	64
Color	White	Pale yellow	Orange–red
UV–visible spectra			
λ_{max} (nm)	280	385	410, 555
IR spectra			
v –NH (cm^{-1})	3354.4	3381	3473.7
v –NCO (cm^{-1})	2290	Disappear	Disappear
v –N=N– (cm^{-1})	Nil	1660.5	1726.7, 1549.3
Elemental analysis			
C, H, N%	66.53, 8.66, 6.89	70.81, 11.55, 9.35	61.92, 10.11, 8.16
TGA			
Weight losses (%) at 233, 337, 400, and >400°C	1.68, 38.39, 52.88, 7.05		3.65, 41.35, 43.50, 11.55
Endothermic peak (°C)	322.6, 374.7		271.7, 344.7

occurring at 233, 337, 396, and >400°C, respectively, and three endothermic peaks at 315.6, 322.6 and 374.7°C. TGA of β-Nap-PUF showed thermal decomposition beginning at 188.4°C, weight loss of 3.7, 41.4, 43.5, and 11.6% occurring at 233, 337, 400, and >400°C, respectively, and two endothermic peaks at 271.7 and 344.7°C. These curves showed that the reagent had reacted with the foam matrix. β-Nap-PUF has good thermal stability compared with other chelating resins. Also, the β-Nap-PUF was stable for several months if stored in a polyethylene bag. These results show that β-Nap-PUF has good characteristics compared with unloaded and loaded PUF [8–11].

The characteristics of white PUF, the salt of diazotized PUF, and β-Nap-PUF are summarized in Table I. The reaction pathway proposed for hydrolysis of urethane and isocyanate groups on white polyurethane foam and reaction of amino ($-NH_2$) groups on the foam to produce β-Nap-PUF is represented schematically in Fig. 1.
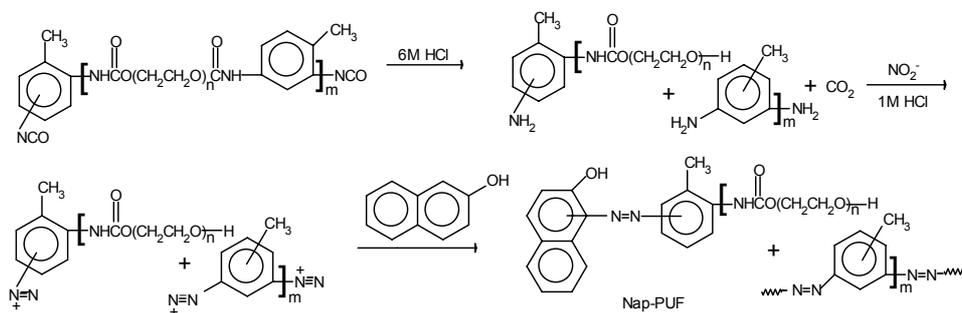

Fig. 1

Schematic representation of the synthesis and structure of polyurethane foam derivatized with β-naphthol

Optimum Conditions for Preconcentration and Determination of Ni^{2+}, Cu^{2+}, Ag^+, and Hg^{2+}

Effect of pH

The effect of pH on the adsorption of Ni^{2+}, Cu^{2+}, Ag^+, and Hg^{2+} by β-Nap-PUF was studied using batch technique. Uptake (%) was plotted against pH as shown in Fig. 2. Maximum adsorption of Ni^{2+}, Cu^{2+}, Ag^+, and Hg^{2+} by β-Nap-PUF was observed in the pH ranges 3–9, 4–10, 9–10 and 1–5, respectively. Values of the separation factors (α) for the metal ions
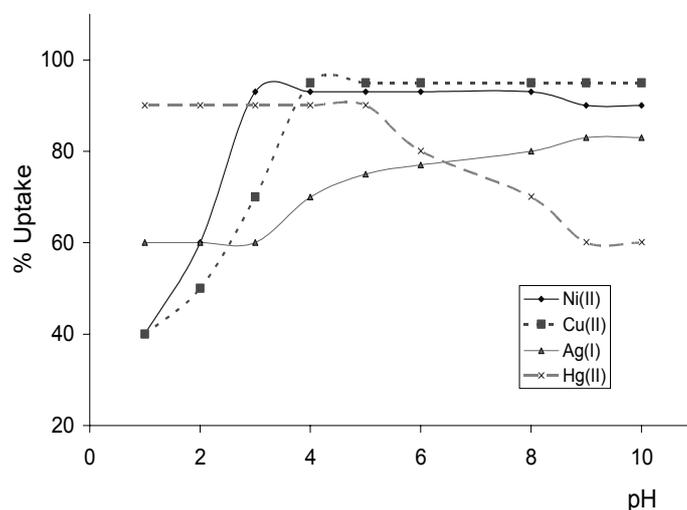
Fig. 2

Effect of pH on the adsorption of Ni^{2+}, Cu^{2+}, Ag^+, and Hg^{2+} by β-Nap-PUF

are summarized in Table II. The selectivity sequence is $Hg^{2+} > Ag^+ \approx Ni^{2+} > Cu^{2+}$ in the pH range 1–3, and $Ni^{2+} \approx Cu^{2+} > Ag^+ > Hg^{2+}$ in the pH range 6–12. The distribution coefficients for adsorption of Ni^{2+} and Cu^{2+} increase with increasing pH ($\log K_d = \text{constant} + n\text{pH}$). These results show that control of the pH can be used to enhance the selectivity for separation of these metal ions by use of β-Nap-PUF.

Table II

Effect of pH on separation factor (α) and selectivity for adsorption of metals by β-Nap-PUF

pH	Separation factor (α)					
	Ni/Cu	Ni/Ag	Ni/Hg	Cu/Ag	Cu/Hg	Ag/Hg
2	1.2	1.0	0.7	0.8	0.6	0.7
4	1.0	1.3	1.0	1.4	1.1	0.8
6	1.0	1.2	1.2	1.3	1.2	0.9
8	1.0	1.2	1.3	1.2	1.4	1.1
10	0.9	1.1	1.5	1.1	1.6	1.4

Kinetic Study

The effect of shaking time on extraction of Ni^{2+}, Cu^{2+}, Ag^+, and Hg^{2+} by β-Nap-PUF was measured by the batch technique. The time required

for equilibration of adsorption for Ni^{2+}, Cu^{2+}, Ag$^+$, and Hg^{2+} ions was from 5 to 15 min (Fig. 3). This rapid extraction was because of application of the batch technique, which was relatively fast and efficient compared with other resins.
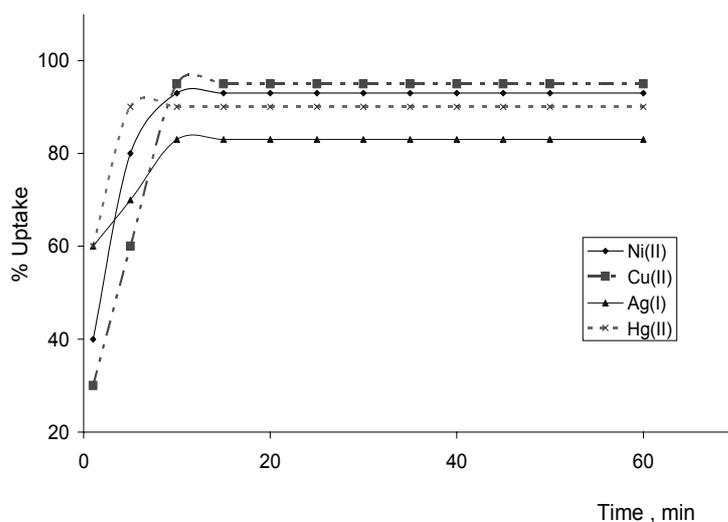

Fig. 3

Effect of shaking time on extraction of Ni^{2+}, Cu^{2+}, Ag$^+$, and Hg^{2+} by β-Nap-PUF

The rate of extraction of Ni^{2+}, Cu^{2+}, Ag$^+$, and Hg^{2+} by β-Nap-PUF has been measured by the batch technique in separate experiments. The kinetic data were treated in accordance with a mass action process, which assumes that the metal ions adsorbed on the foam in accordance with a first-order reaction and that the time-dependence was given by the Lagergren equation in the form:

$$\log (q_e - q_t) = \log q_e - k_1 t/2.303$$

A plot of $\log (q_e - q_t)$ against t results in a straight line relationship which indicates that the process is first-order with regard to the concentration of each adsorbed metal ion. The rate constants for adsorption (k_1), calculated from the slope, are 0.16, 0.09, 0.11, and 0.3 min^{-1} for Ni^{2+}, Cu^{2+}, Ag$^+$, and Hg^{2+}, respectively. The half life of adsorption ($t_{1/2}$), the rate constant for desorption (k_{-1}) and the overall rate constant (k') at room temperature can be calculated by use of the equations:

$$t_{1/2} = 0.693/k_1, \quad K_c = k_1/k_{-1}, \quad \text{and} \quad k' = k_1 + k_{-1}$$

where K_c is the equilibrium constant. Calculated values of $t_{1/2}$, k_1, k_{-1} and k' are summarized in Table III. The average values of the rate constant for desorption (k_{-1}) and overall rate constant (k') at room temperatures were calculated as 0.02 and 0.18 min^{-1}, respectively (Table III). Also, the average value of the half-life for adsorption ($t_{1/2}$) is 5.08 min. These results show that the rate of adsorption of these metal ions during separation with β-Nap-PUF is relatively fast and efficient compared with the other resins.

Table III

Kinetic data for adsorption and desorption of metal ions by β-Nap-PUF

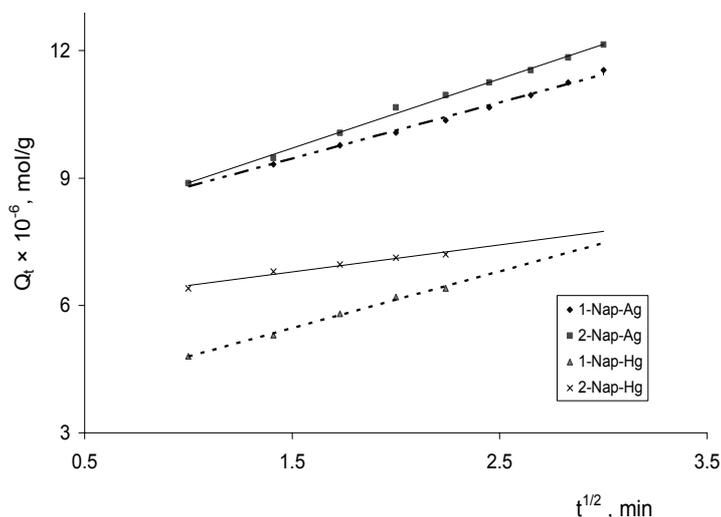| Metal ion	Rate constant for interparticle transport, K_M (μmol g^{-1} min$^{-1/2}$)	Rate constant for adsorption, k_1 (min^{-1})	Rate constant for desorption, k_{-1} (min^{-1})	Overall rate constant, k' (min^{-1})	Half-life for adsorption, $t_{1/2}$ (min)
Ni^{2+}	8.4	0.16	0.012	0.17	4.3
Cu^{2+}	7.4	0.09	0.005	0.10	7.4
Ag$^+$	1.6	0.11	0.022	0.13	6.3
Hg^{2+}	1.3	0.30	0.033	0.33	2.3

Fig. 4

Plots of $Q_t \times 10^{-6}$ against $t_{1/2}$ for adsorption of the metal ions on β-Nap-PUF

The Morris–Weber equation ($Q_t = k_M \sqrt{t}$) was used to study the mechanism particle diffusion for adsorption of these metal ions, where Q_t is the amount of metal ions adsorbed at time t and k_M is the rate constant for interparticle transport ($\mu mol\ g^{-1}\ min^{-1/2}$). The data obtained show that the rate of diffusion is rapid – k_M values were 8.4, 7.4, 1.6, and 1.3 $\mu mol\ g^{-1}\ min^{-1/2}$ for adsorption of Ni^{2+}, Cu^{2+}, Ag^+, and Hg^+, respectively, by β-Nap-PUF (Fig. 4). The rate constant sequence for interparticle transport was $Ni^{2+} > Cu^{2+} > Ag^+ > Hg^{2+}$; the different rate constants for these metal ions can be attributed to their different ionic sizes. Also, the half-life ($t_{1/2}$) for adsorption of these ions by β-Nap-PUF was in the order $Hg^{2+} > Ni^{2+} > Ag^+ > Cu^{2+}$. These results show that the rate constant for adsorption depends mainly on the reaction between the metal ion and the chelating groups of β-Nap-PUF.

Adsorption Isotherm

Uptake of Ni^{2+}, Cu^{2+}, Ag^+, and Hg^{2+} by β-Nap-PUF as a function of metal ion concentration in aqueous solution was determined by using a batch technique. The isotherms obtained showed there was a good linear relationship over a relatively wide range of tested ion concentrations (Fig. 5). Plots of adsorption capacity of β-Nap-PUF against concentration of metal ions had an almost zero intercept (0.0017). Regression analysis of the adsorption isotherm plot revealed the correlation was good, $r = 0.998$
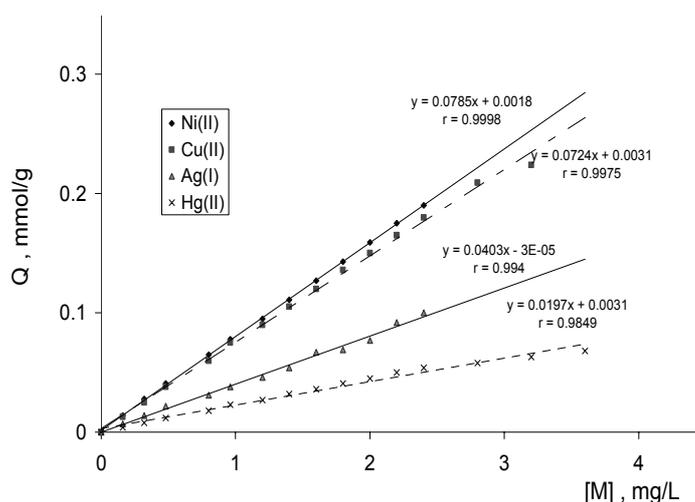

Fig. 5

Isotherms for adsorption of Ni^{2+}, Cu^{2+}, Ag^+, and Hg^{2+} by β-Nap-PUF

(Table IV). The sensitivity sequence was in order $Ni^{2+} \approx Cu^{2+} > Ag^+ > Hg^{2+}$; average values for the detection limit were 0.44, 0.44, 0.51, and 0.52 ng mL^{-1}, respectively.

Table IV

Characteristics of the isotherms for adsorption of metal ions by β-Nap-PUF

Metal ion	Least squares equation		Correlation coefficient, r	LOD	LOQ
	Intercept × 10^{-3}	Slope × 10^{-2}			
Ni^{2+}	1.8 ± 0.18	7.9 ± 0.56	0.999	6.84×10^{-5}	2.28×10^{-4}
Cu^{2+}	3.1 ± 0.21	7.2 ± 0.20	0.997	8.75×10^{-5}	2.92×10^{-4}
Ag^+	0.03 ± 0.19	4.0 ± 1.09	0.994	1.43×10^{-4}	4.45×10^{-4}
Hg^{2+}	3.1 ± 0.05	2.0 ± 0.47	0.985	7.50×10^{-5}	2.50×10^{-4}

Plots of experimental q_c and ε^2 data according to Dubinin–Radushkevich model ($\ln q_c = \ln k_{dr} - \beta\varepsilon^2$ where $\varepsilon = RT \ln (1 + 1/q_c)$, β is constant related to the energy of the transfer of the solute from the bulk solution to the solid adsorbent, and ε^2 is the Polanyi potential) were indicative of linear relationships. The values of β computed from the slopes for adsorption of Ni^{2+}, Cu^{2+}, Ag^+, and Hg^{2+} were -5.6×10^{-3}, -5.2×10^{-3}, -6.9×10^{-3}, and -6.0×10^{-3} kJ^2 mol^{-2}, respectively. The value of the sorption energy, (activation energy, E), can be correlated with β ($E = 1/\sqrt{(-2\beta)}$). The values of E were found to be 9.05, 9.71, 8.47, and 9.13 kJ mol^{-1} for Ni^{2+}, Cu^{2+}, Ag^+, and Hg^{2+}, respectively, indicating that extraction of the metal ions by β-Nap-PUF occurs by chemisorption and that the rate of sorption is relatively rapid.

Thermodynamic Investigations

The dependence on temperature of adsorption of Ni^{2+}, Cu^{2+}, Ag^+, and Hg^{2+} by β-Nap-PUF was evaluated by use of the equations $\Delta G = -RT \ln K_c$ and $\Delta G = \Delta H - T\Delta S$, where ΔH, ΔS, ΔG and T are the enthalpy, entropy, Gibbs free energy, and absolute temperature, respectively. R is the gas constant (8.314 J mol^{-1}) and K_c is the equilibrium constant. Plots of log K_c against $1/T$ give the numerical values of ΔH and ΔS from slope and intercept, respectively. The values of ΔG, ΔH, and ΔS at room temperature for adsorption of Ni^{2+}, Cu^{2+}, Ag^+, and Hg^{2+} are given in Table V. The average value of (ΔG) is -5.87 kJ mol^{-1}. The negative values of ΔG are indicative of the spontaneous nature of the adsorption process. The values of ΔH for adsorption of Ni^{2+}, Cu^{2+}, Ag^+, and Hg^{2+} by β-Nap-PUF were found to be

−0.15, −0.14, −26.8, and −52.7, respectively. The negative values of ΔH indicate the chemisorption process is exothermic.

Table V

Thermodynamic data and capacity for adsorption of metal ions by β-Nap-PUF

Metal ion	Gibbs free energy, ΔG (kJ mol^{-1})	Enthalpy, ΔH (kJ mol^{-1})	Entropy, ΔS (J K^{-1} mol)	Activation energy, ΔE (kJ mol^{-1})	Capacity, Q (mmol g^{-1})
Ni^{2+}	−6.62	−0.15	21	9.05	0.190
Cu^{2+}	−7.53	−0.14	24	9.71	0.223
Ag$^+$	−4.17	−26.8	−76	8.47	0.099
Hg^{2+}	−5.14	−52.7	−160	9.13	0.068

These results show that the different numerical values for the enthalpy of adsorption of Ni^{2+}, Cu^{2+}, Ag$^+$, and Hg^{2+} by β-Nap-PUF depend on the type of the chelating group on β-Nap-PUF reacting with the metal ion and dehydration of water molecules from the hydrated shells of the adsorbed species. The negative value of the entropy of adsorption for Ag$^+$ and Hg^{2+} may be indicative of the more rapid adsorption of these metal ions by β-Nap-PUF. The positive entropy of adsorption of Ni^{2+} and Cu^{2+} is indicative of liberation of water molecules from the hydrated zone of the adsorbed species. The low activation energy of adsorption compared with the enthalpy is indicative of strong attraction during the adsorption/uptake process, even under normal conditions.

Effect of Sample Flow Rate

Adsorption of the metal ions on a β-Nap-PUF column was studied at different solution flow rates. For each metal ion solutions (100 mL) containing 40 μg of the ion were passed through the column at a flow rate varying from 1 to 7 mL min^{-1}. The metal ions were then eluted with 0.1 M HNO$_3$. It was found that the optimum flow rate was 2 mL min^{-1}. Uptake decreased from 95 to 90% when the flow rate was increased from 2 to 7 mL min^{-1}.

Preconcentration of Metal Ions from Different Volumes

To study the performance of β-Nap-PUF columns for preconcentration of Ag$^+$ and Hg^{2+}, each element (50 mg) in different volumes of sam-

ple (25–100 mL) was passed through a column at 2 mL min^{-1}. Elution of the metal ions from the columns resulted in recoveries of 80–98% (average RSD% ~3.67). Uptake of the metal ions decreased with increasing sample volume. These results show that these metal ions can be concentrated effectively from large volumes of dilute aqueous solutions by use of β-Nap-PUF columns.

Effect of Foreign Ions

The effect of different metal ions (40 µg mL^{-1}) on the adsorption behavior of Ni^{2+}, Cu^{2+}, Ag^{+}, and Hg^{2+} ions (1.6 µg mL^{-1}) on β-Nap-PUF was studied using a batch technique. The data obtained revealed that Na^{+}, K^{+}, Mg^{2+}, Ca^{2+}, and Ba^{2+} ions do not affect adsorption of the metal ions whereas Zn^{2+}, Cd^{2+}, Fe^{3+}, and Al^{3+} ions cause slight interference (reducing adsorption by 1–3%). Fe^{2+} and Co^{2+} reduce the adsorption of the tested metal ions by 10–40%. Besides controlling the pH of the adsorption medium, use of a masking agent, e.g. tartaric acid, citrate, or phosphate ions, masks several common ions and minimizes their interfering effect.

ANALYTICAL APPLICATIONS

Validation of this procedure for preconcentration and determination of Ni^{2+} and Cu^{2+} in certified reference samples of cast iron, hematite iron, and granite was investigated. The validity and accuracy of the method were also investigated for selective separation and determination of Ag^{+} and Hg^{2+} from two samples of tap water from Cairo city and industrial wastewater from a fertilizers and chemicals company.

Determination of Nickel and Copper Ions in Cast and Hematite Iron

High silicon and phosphorus cast iron reference sample (British Chemical Standard, B.C.S. No. 206/3), which contain 0.068% nickel and 0.1% copper (equivalent to 0.68 and 1.0 mg Ni and Cu per gram iron, respectively) were determined by use of β-Nap-PUF after suitable dissolution. The results obtained showed average values from 1 g cast iron were 0.6 and 1.0 mg Ni^{2+} and Cu^{2+}, respectively. Analysis of nickel and copper in hematite iron reference sample (B.C.S. No. 236/3), which contains 2.1 and 0.7 mg of nickel and copper per gram iron, gave an average values of 1.8 and 0.5 mg g^{-1} of Ni^{2+} and Cu^{2+}, respectively. When these results were compared with those obtained by using atomic absorption spectrometry (AAS) the data were in good agreement (Table VI).

Table VI

Determination of Ni^{2+} and Cu^{2+} in cast iron, hematite iron, and granite certified reference samples

Sample	Metal ion	Certified content (mg g^{-1})	AAS (mg g^{-1})	Resin (mg g^{-1})
Cast iron, B.C.S No. 206/3	Ni^{2+}	0.68	0.61	0.60
	Cu^{2+}	1.0	1.0	1.0
Hematite iron, B.C.S No. 236/3	Ni^{2+}	2.1	1.9	1.8
	Cu^{2+}	0.7	0.5	0.5
Granite sample, USGS, G-2	Cu^{2+}	0.011	0.011	0.011

Determination of Copper Ions in Granite

The copper content of granite reference sample, G2 (US Geological Survey Certificate of Analysis, USGS) was determined. Granite (0.5 g) was digested with 5 mL conc. HNO_3 and 20 mL HF until a solid residue remained. After cooling to room temperature the residue was dissolved in 25 mL 5 M HCl and diluted with distilled water. The pH of the solution was adjusted and the dynamic procedure was applied. The copper concentration was found to be 10.9 μg g^{-1} granite by use of β-Nap-PUF (Table VI). These results are in good agreement with the value of obtained by AAS measurement (10.9 μg g^{-1}) and with the certified content of the reference sample (11.0 μg g^{-1}).

Determination of Silver and Mercury Ions in Tap Water

Ag^+ and Hg^{2+} ions in certified reference tap water samples (Central Organization Greater Cairo of Water Supply 'COGCWR' certified ISO 9001/2000) were determined by use of the column method; the results

Table VII

Collection and determination of Ag^+ and Hg^{2+} in tap and waste water using β-Nap-PUF

Water matrix	Metal ions	Spiked (μg)	Found (μg)	Recovery (%)
Tap water	Ag^+	10	10	100
	Hg^{2+}	10	9.8	98
Wastewater	Ag^+	10	7.8	78
	Hg^{2+}	10	8	80
	$Ag^+ + Hg^{2+}$	5 + 5	3.9 + 3.95	78 + 79
	$Ag^+ + Hg^{2+}$	12.5 + 12.5	9.6 + 9.8	77 + 78

obtained are shown in Table VII. Silver and mercury were not detected in tap water in Cairo City. Hg^{2+} was detected (2 μg L^{-1}) in a river water sample. These results were in agreement with values obtained by use of AAS in the central laboratory of COGCWR. Analysis of 100 mL tap water spiked with 10 μg of Ag^+ or Hg^{2+} showed that average recovery of Ag^+ and Hg^{2+} was 100% and 98%, respectively (Table VII).

Collection of Metal Ions from Wastewater Using β-Nap-PUF

Use of β-Nap-PUF was tested for collection of metal ions from wastewater of a fertilizers and chemicals company. The wastewater sample (100 mL) was first filtered through filter paper and then spiked with 5–25 μg Ag^+ or Hg^{2+} and the pH was adjusted. The solutions were then passed through columns at 2 mL min^{-1}. The metals were eluted from the columns with 5 mL 1 M HNO_3. The results given in Table VII show the suitability of β-Nap-PUF for water analysis and for removal of metal ions from industrial wastewater.

ADSORPTION MECHANISM

The average value of the activation energy (ΔE) for adsorption of Ni^{2+}, Cu^{2+}, Ag^+, and Hg^{2+} by β-Nap-PUF was 9.1 kJ mol^{-1}, indicating that the metal ions were extracted on to β-Nap-PUF as a result of a chemisorption type interaction. Also, the molar ratios (M:β-Nap-PUF) for these ions were 2:3, 2:3, 2:1.4, and 2:1 for Ni^{2+}, Cu^{2+}, Ag^+, and Hg^{2+}, respectively. The rate constant order for interparticle transport was $Ni^{2+} > Cu^{2+} > Ag^+ > Hg^{2+}$; the different rate constants for adsorption of these metal ions by β-Nap-PUF may be attributed to their different ionic sizes. Values for the half-life of adsorption ($t_{1/2}$) were in the order $Hg^{2+} > Ni^{2+} > Ag^+ > Cu^{2+}$, showing that irrespective of ionic size adsorption depends on the reaction between the chelating groups of β-Nap-PUF and the metal ion. Finally this sorption was found to be exothermic, and the surface structure of β-Nap-PUF was heterogeneous. From these findings it can reasonably be suggested that adsorption of the metal ions by β-Nap-PUF proceeds via a chelation mechanism.

CONCLUSION

This paper deals with the preparation of a new polymeric extractor based on covalent coupling of β-naphthol to polyurethane foam by means

of an azo group. This new extractor was used to preconcentrate and determine Ni^{2+}, Cu^{2+}, Ag^+, and Hg^{2+} from tap and waste water, and granite, cast iron, and hematite iron certified reference samples. Characterization of the β-Nap-PUF indicates that the new resin is denser than the white foam from which it is made as a result of cross linkage because of additional bonds between the reagent and groups on the polyurethane foam matrix. Experiments show the reagent is not washed from the resin. The kinetics of adsorption of the tested metal ions on to β-Nap-PUF follow a first-order rate equation. Negative values of ΔG are indicative of the spontaneous nature of adsorption of the metal ions. Negative values of ΔH for adsorption of the metal ions indicate the reaction is exothermic. Our study indicates the new resin is suitable for extraction, determination, and removal of Ag^+ and Hg^{2+} in wastewater.

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