Comparative Study about Adsorption Behavior of Two New Chelating Resins Containing Amine and Alizarin Groups with Rhodium (III) Ions in Environmental Samples

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Expanded Abstract

Introduction
Rhodium metal is known for its stability in corrosive environments, physical beauty, and its unique properties. Rhodium is now widely used for alloying platinum in thermocouples, crucibles, evaporating dishes, weighing boats windings for high-temperature furnaces. It has been applied as a coating material because of the hardness and luster of its surface. Rhodium is present at about 0.001 mg. L-1 in crust of the earth. Because of its commercial importance, a wide variety of reagents have been proposed for pre-concentration of Rhodium before spectrophotometric determination. The interest in ligand immobilized solid phases like silica gel, organic polymer or copolymers, cellulose and polyurethane foam. The solid phase extraction of metal ions present at micro/trace level in environmental samples, high purity materials, biological samples and other complex matrices, makes analytical techniques possible, such as flame atomic absorption spectrometry (FAAS) and inductive couple plasma Atomic Emission Spectroscopy (ICP-AES). Solid phase extraction is preferable over ion exchange and solvent extraction due to its advantages like selectivity. This is by controlling the pH, reusability, high pre-concentration factors, durability, versatility and metal loading capacity. Adsorption of metal ions is widely used in the removal of contaminants from wastewaters. Amberlite XAD resins are widely used for modification with chelating materials due to its proper physical and chemical properties such as porosity, high surface area, durability and purity. The aim of the present study were to use two new chelating resins prepared by coupling Amberlite XAD-2 with Diethylenetriamine (DETA) and Alizarin prepared by chemically bonding as an adsorbent of Rhodium

Materials and Methods
All the solutions were prepared in deionized water using analytical grade reagents acetic acid, sodium acetate, sodium hydrogen phosphate, sodium dihydrogen phosphate, rhodium chloride, tin (II) chloride, hydrochloric acid, sulfuric acid, nitric acid, sodium nitrite, sodium hydroxide, DETA, Alizarin red S and iodide-starch paper. Amberlite XAD-2 resin (surface area 330 m2/g, pore diameter 9 nm and bead size 20-60 mesh) was obtained from Flucka (Germany). The stock solution (500 mg L-1) of Rh (III) were prepared by dissolving appropriate amounts of RhCl3.H2O, in deionized water. 10
mL of 0.1 mol L-1 acetic acid - acetate buffer (pH 3-6.5), and 0.01 mol L-1 phosphate buffer (pH 6.5-9) were used to adjust the pH of the solutions, wherever suitable.

Amberlite XAD-2 beads (5 g) were treated with 10 mL of concentrated HNO3 and 25 mL of concentrated H2SO4 and the mixture was stirred at 60°C for 1 h on an oil bath. Thereafter, the reaction mixture was poured into an ice water mixture. The nitrated resin was filtered, washed repeatedly with water until it is free from acid. It was treated with a reducing mixture of 40 g of SnCl2, 45 mL of concentrated HCl and 50 mL of ethanol. The mixture was refluxed for 12 h at 90°C. The solid precipitate was filtered and washed with water and 2 mol L-1 NaOH which released amino resin (RNH2) from (RNH3)2 SnCl6 (R= resin matrix). The amino was first washed with 2 mol L-1 HCl and finally with distilled water to remove the excess HCl. It was suspended in an ice-water mixture (350 mL) and treated with 1 mol L-1 HCl and 1 mol L-1 NaNO2 (added in small aliquots of 1 mL) until the reaction mixture showed a permanent dark blue color with starch-iodide paper. The diazotized resin was filtered, washed with ice-cold water and reacted with alizarin red S 0.03 mol in 30 mL 2 mol L-1 HCl, respectively. The reaction mixture was stirred at 0-3°C for 24 h. Thereafter, the resulting colored beads were filtered, washed with water and air dried in air.

Five grams of Amberlite XAD-2 beads were acidified with 10 mL of concentrated HNO3 and 25 mL of concentrated H2SO4 and the resulting mixture was stirred at 60°C for 1 h. After that, the reaction mixture was poured into an ice water mixture. The nitrated Amberlite resin was filtered and washed repeatedly with distilled water until it is free from acid. Next, it was treated with a reducing mixture of 40 g of SnCl2, 45 mL of concentrated HCl and 50 mL of ethanol. The mixture was refluxed for 12 h at 90°C. The solid precipitate was filtered and washed with water and 2 mol L-1 NaOH which released amino resin (RNH2) from (RNH3)2 SnCl6 (R= resin matrix). The amino resin was first washed with 2 mol L-1 HCl and finally with distilled water to remove the excess HCl. It was suspended in an ice-water mixture (350 mL) and treated with 1 mol L-1 HCl and 1 mol L-1 NaNO2 (added in small aliquots of 1 mL) until the reaction mixture showed a permanent dark blue color with starch-iodide paper. The diazotized resin was filtered, washed with ice-cold water and react with DETA, 0.03 mol in 30 mL 1 mol L-1 of HCl, respectively. The reaction mixture was stirred at 5°C for 24 h afterward; the resulting colored beads were filtered, washed with water and air dried in room temperature.

Results and Discussion

The experimental FTIR spectrum of alizarin red S loaded on Amberlite XAD-2 is compared with that of free Amberlite XAD-2. There are two additional bands at 1638 and 3432 cm⁻¹ which appear to originate due to modification of N=N and O-H, and the experimental FTIR spectrum of DETA, loaded Amberlite XAD-2 is compared with that of free Amberlite XAD-2. There are two additional bands at 1629 and 3418 cm⁻¹ which appear to originate due to modification of N=N and O-H, respectively.

For XAD-2 DETA the optimum pH value and the sorption capacity have been found 7, and 13.4 mg g⁻¹, and for XAD-2-Alizarin 8.4, and 12.1 mg g⁻¹, respectively.

The kinetics of sorption was studied by batch method for Amberlite XAD-2–DETA. 0.05g resin was shaken with 50mL of solution containing 0.3 μg mL⁻¹ of Rh(III) with different equilibration times (10, 30, 45, 90, 180, 300 min) under optimum conditions. Five milliliters of the solution was withdrawn at predetermined intervals for analysis (using recommended batch method). The concentration of Rhodium ion in the supernatant solution was determined by FAAS. The sorption is a function of time for Rh (III). The time taken for the sorption of 27.38 % of the metal ion for XAD-2–DETA was found to be 10.0 min, which indicates a very good approachability of Rh (III) towards chelating sites on resin.

Alizarin red S-Amberlite XAD-2 (0.1g) was shaken with 50 mL of solution containing 300 μg mL⁻¹ of Rh (III) for different times (10, 30, 45, 90, 180 and 300 min) under optimum pH. After taking out the sorbent, the concentration of Rhodium ions in the solution was determined with (FAAS) using recommended batch method. The sorption is a function of contact time for all the metal ions.

Less than 10 min of shaking was required for about 22.8% sorption. The profile of Rhodium uptake on this sorbent reflects good accessibility of the chelating sites in the Alizarin red S-Amberlite XAD-2.
Kinetic adsorption data were analyzed by the adsorption time of Rh (III) on modified resin by four isotherm models Langmuir, Freundlich, Temkin, and Redlich-peterson. The results showed that the obtained Langmuir type-2 isotherm was the best fit in linear equations (R2= 0.9995, RL = 0.7720, qm = 22.8908 mg g⁻¹, Ka = 0.0591 L mg⁻¹) for XAD-2 DETA, and (R2= 0.9983, RL = 0.717, qm = 19.04 mg g⁻¹, Ka = 0.079 L mg⁻¹) for XAD-2-Alizarin. In order to evaluate the selectivity of the pre-concentration system, the effects of some metal ions (20 mg.L⁻¹) on the sorption behavior of Rh ion (concentration 20 mg.L⁻¹) was investigated.

Conclusion
Two new resins were synthesized by coupling of Amberlite XAD-2 with DETA and Alizarin red S. The synthesis of the resin is simple and economical. The resin has a good potential for enrichment of trace amount of Rh (III) from large sample volumes. The Rh (III) adsorption was due to immobilized ligand- metal ion interactions. The resins also present the advantage of high adsorption capacity, good reusability and high chemical stability. The sorption/desorption of metal ion takes place in moderate time, making the analytical procedure reasonably fast. Finally, the different isotherms were tested for their ability to correlate with the experimental results by comparing theoretical plots of each isotherm with the experimental data for the adsorption of rhodium ions on DETA-Amberlite XAD-2 and Alizarin red s at 293 K. The amount of rhodium adsorbed per unit mass of DETA-Amberlite XAD-2 and Alizarin red s, qe, is plotted against the concentration of rhodium remaining in the solution, Ce, and the good fit of the Freundlich and Langmuir isotherms were not the same even when the coefficient of determinations was high for both isotherms. Our results have demonstrated the applicability of the presented procedure for Rh (III) determination in real samples and environmental studies with high recovery.

Keywords: alizarin, Amberlite XAD-2, Diethylenetriamine, isotherm study, Rhodium, solid phase extraction.