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Equilibrium and Kinetic studies on Pb^{2+}, Cd^{2+}, Cu^{2+} and Ni^{2+} Adsorption from aqueous solution by Resin 2, 2'–(Ethylenedithio)diethanol Immobilized Amberlite XAD-16 (EDTDE-AXAD-16) with Chlorosulphonic acid

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ABSTRACT

The present study aims to investigate the adsorption behavior of Pb^{2+}, Cd^{2+}, Cu^{2+} and Ni^{2+} ions from aqueous solution onto modified Amberlite XAD-16 functionalized using 2, 2'– (Ethylenedithio) diethanol with chlorosulphonic acid. The batch equilibrium method was used for studying the metal sorption. It has been observed that the Pb(II) ion is highly adsorbed compared to other metal ions and the adsorption capacity was found to be in the sequence $Pb^{2+} > Cd^{2+} > Ni^{2+} > Cu^{2+}$ and the preference of this sorbent for a metal may be explained on the basis of electronegativity of the metal ions and on the basis of hard - soft Lewis acids and bases concept. Adsorption kinetics was explained based on pseudo-first-order and pseudo-second order models. The data showed that the sorption of metal (II) ions on the chelating resin perfectly fit a pseudo-second-order model.

1. Introduction

Contamination of aqueous environment by toxic heavy metals is a major threat to human beings. It is recognized as a priority issue in environmental protection. Metal ions such as copper, lead, mercury, cadmium, cobalt, nickel, iron; and so on represent an environmental concern when present in uncontrolled or high concentrations. For example, elevated copper concentrations are frequently associated with leaching from antifouling paints and pressure-treated dick pilings, discharge from power and desalination plants and run off from land-based sources [1–5]. Also copper, nickel, cobalt, lead, iron and other heavy elements are present in the acidic manganese chloride solution resulting from the preparation of battery grade MnO_2 directly from manganese ore [6–8]. Due to their persistence in the environment and their relatively rapid uptake and accumulation in living organisms, heavy metal ions are polluting water sources and posing a long-term risk to both humans and the eco-system. Therefore, the determination of trace concentrations of metal ions in man-made and natural water sources is essential in order to keep a check on the various eco-systems. Hence, this requires frequent analysis of trace metal ions in environmental as well as bio-fluid samples in order to sustain and preserve the eco-systems. The determination process is not simple because the metal ions are surrounded and encapsulated by a variety of complex matrix species [9].

Various methods have been employed for the trace determination of metal ions in different samples including flame atomic absorption spectrometry (FAAS) [10,11], electrothermal atomic absorption spectrometry (ETAAS) [12], inductively coupled plasma optical emission spectrometry (ICP-OES) [13], inductive couple plasma atomic emission spectroscopy (ICP-AES) [14], inductively coupled plasma mass spectroscopy (ICP-MS) [15] and stripping voltammetry [16]. However, the direct determination of metal ions by these instruments still faces challenges posed by the low concentration and the associated complex matrices. Usually, a preconcentration step, as well as separation step, is required prior to metal analysis by these instruments [17]. For this purpose, numerous separation and preconcentration procedures have been developed for trace metal ion determination in various matrices [18].

Accordingly, there is a need for an extraction technique which could selectively extract the analytes of interest. This has paved the way for the development of solid phase extraction (SPE) techniques. (SPE) technique is thus recognized as the fast and reliable approach for quantitative metal ion extraction and pre-concentration [19–21]. Moreover, modified resins bridge the gap between solvent extraction and ion exchange. They combine not only the advantages of resin ion exchange

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for processing dilute solutions with specific properties of the extractants, but also a high distribution ratio and selectivity characteristic of the extractants dissolved in a liquid organic phase with the simplicity of equipment and operation characteristics of solid ion-exchange technology [22].

Various solid phases including Chelex 100 [23], silica gel [24–26], Amberlite XAD resins [27–35], polyurethane foam [35] and activated carbon [36] have been used for the solid-phase extraction of traces of heavy metals in environmental samples prior to their instrumental analysis. Many chelating sorbents have been developed, of which the XAD-based chelating resins have proved themselves as an efficient preconcentrating and clean-up sorbents [37].

Advantage of using Amberlite XAD series over other supports lies in the fact that they have good physical properties such as their porosity, uniform pore size distribution, high surface area as chemical homogeneous non-ionic structure and good adsorbent properties for great amounts of uncharged compounds. Amberlite XAD-16 has an edge over the most commonly used XAD-2 and XAD-4 resins due to the high surface area in comparison to the XAD-2 and XAD-4 resins [38].

Chemical modification of Amberlite XAD-16, modified with organic moieties via chemical route has gained appreciable interest [38–46]. The modification of Amberlite is a method used to enhance the performance where it converts the Amberlite into a functionally substituted polymer, which improves its metal uptake and ion selectivity. Commercially available resins of the Amberlite have been found to be very promising as a support for designing chelating resins due to their good physical properties such as their porosity, uniform pore size distribution, high surface area, chemical homogeneous non-ionic structure, and good adsorbent properties for great amounts of uncharged compounds. The most widely used matrix materials for immobilization of ligands are Amberlite XAD-2, XAD-4, and XAD-16. Amberlite XAD-16 upon ligand immobilization gave chelating resins of better sorption capacities than the others due to its higher surface area of 800 m^2/g and a pore size of 200 Å. Besides, it also offers a high chemical stability that favors its further modification both chemically as well superficially [38].

The aim of the present study was to develop a solid phase matrix by coating Amberlite XAD-16 with a suitable ligand that offers high sorption capacity for preconcentration of some metals simultaneously in aqueous solution and determination by ICP-AES that offers fast multi-elemental analysis. In the present work, Amberlite XAD-16 functionalized using 2, 2'– (Ethylenedithio)diethanol with chlorosulphonic acid has been evaluated for the preconcentration and separation of trace metal ions, Pb(II), Cu(II), Cd(II) and Ni(II). The effect of various parameters such as shaking time, adsorption dose on metal ion sorption has been reported. Adsorption equilibrium and kinetics had been studied under the optimum adsorption conditions. The Langmuir, Freundlich, Temkin, Dubinin - Radushkevich isotherms, Flory-Huggins isotherm models and Elovich equilibrium model were applied to evaluate the adsorption properties in the batch experiments. In addition, the pseudo-first-order, pseudo-second-order, intra-particle diffusion model, liquid particle diffusion model and Elovich kinetic models were also applied to examine the kinetics of the adsorption process.

2. Experimental

2.1. Materials and solvents.

All chemicals used in this work were of analytical grade from Merck (Darmstadt, Germany). Commercially available Amberlite XAD-16 was obtained from Aldrich and was thoroughly washed with 4.0 M HNO_3, 1.0 M NaOH, and double-distilled water successively and well dried before use. 2,2'–(Ethylenedithio)diethanol and chlorosulfonic acid, $Cd(NO_3)_2 \cdot 4H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$, and $Pb(NO_3)_2$, were purchased from Aldrich and used without further purification. Working metal ion solutions 0.1 M of Cd^{2+}, Ni^{2+}, Cu^{2+}, and Pb^{2+} were prepared by dissolving the metal nitrate salt in acidified double distilled water. The glassware used was soaked in 10 % HNO_3 over night before use and cleaned repeatedly with double distilled water.

2.2. Physical measurements.

The concentration of the metal ions was determined by an inductively coupled plasma optical emission spectrometer (ICP-OES Varian Vista-MPX ICP-OES system, axial ICP system), and the wavelength used for the analysis of Cd^{2+}, Ni^{2+}, Cu^{2+}, and Pb^{2+} was in the range of (200 to 700) nm. The instrument was calibrated by using ICP standards (Inorganic Ventures) for all metals that were analyzed. The process of calibration needs 5 min, and the correlation coefficient of the calibration curves was confirmed to be greater than 0.995. A few drops of 1 % HNO_3 were added to all standard samples to avoid any matrix interference.

2.3. Synthesis of the chelating resins.

2.3.1. Synthesis of chlorosulfonated polystyrene [PS-SO_2Cl]. [47]

To a swelled AmberliteXAD-16 (5 g) in $CHCl_3$ (50 mL) for 2 h, $ClSO_3H$ (50 mL)in $CHCl_3$ (50 mL) was added, and the mixture was stirred for 24 h at room temperature and then filtered off and washed thoroughly with dry CH_2Cl_2 followed by drying in a vacuum at 60 °C for 72 h.

2.3.2. Synthesis of the chelating resins H_2L. [47]

The dryPS-SO_2Cl (5.0 g) was treated with 2,2'–(Ethylenedithio)diethanol (3.98 g) in acetone (20 mL). The reaction mixture was refluxed for48 h. The product was filtered off and washed with acetone (3× 15 mL) and diethyl ether (3 × 15 mL) followed by drying in vacuum at 60 °C for 24 h.

2.4. Effect of adsorbent dose on metal ion sorption

Different amounts of resin varying from 0.1 to 0.5g/100 mL of solution with 50 mg/L concentration of Pb^{2+}, Cd^{2+}, Cu^{2+}, or Ni^{2+} in closed bottle flasks have been shaked for 180 min.

2.5. Effect of shaking time on the metal sorption.

The metal sorption capacity was determined in triplicate at an initial pH 6 for Cu^{2+} and Ni^{2+}, and 7.0 for Cd^{2+} and Pb^{2+}, which determined as the optimum pH values for the metal ions. To 50 mL of solution of the metal ion (0.002 M) in a stoppered glass bottle 50 mg of resin H_2L was added. The whole system was shaken at a constant shaking rate of 200 rpm at (25 ± 1) °C at appropriate intervals in the range of 5 to180 min and then filtered off. An appropriate volume of each solution of the filtrate of the metal ion was determined by ICP-OES.

2.6. Batch kinetic studies

The beads of the resin (250 mg) were equilibrated with a 100 mL of the solutions containing Pb^{2+}, Cd^{2+}, Cu^{2+}, or $Ni^{2+}$with $C_0 = 50$, 75, 100, 125, 150, 200 or 250 mg/L at an ambient temperature 25°C, shaking speed 200 rpm. The aqueous samples were taken at preset time intervals 5- 180 min. The concentrations of metal ions were measured by ICP-OES. The metal uptake (amount of adsorption) at time t, q_t (mg/g), was calculated by using Eq. (1):

$$q_t = (C_0 - C_t)\, V/m \qquad (1)$$