Removal of Pb(II), Cu(II) and Cd(II) ions from aqueous solution using polyazomethineamides: Equilibrium and kinetic approach

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ABSTRACT

The removal of Pb(II), Cu(II) and Cd(II) ions onto polyazomethineamides (PAMA) has been investigated using batch adsorption techniques. The extent of adsorption was investigated as a function of pH, adsorbent dose, contact time and initial metal ion concentration. The metal ion removal was pH-dependent and reached maximum at pH 6.0. Experimental data were analysed by Langmuir, Freundlich, Redlich-Peterson and Temkin adsorption isotherms. The characteristic parameters for each isotherms and related correlation coefficients have been determined using MATLAB 7.1. The maximum adsorption capacities of PAMA for Pb(II), Cu(II) and Cd(II) ions were calculated from the Langmuir isotherm 452.1, 470.7 and 462.3 mg/g respectively. Pseudo-first-order, pseudo-second-order, Elovich kinetic and intraparticle diffusion models were used to fit the experimental data. Kinetic parameters, rate constants, equilibrium sorption capacities and related correlation coefficients, for each kinetic model were calculated and discussed. The kinetic studies showed that the pseudo-second-order rate equation was better described by the adsorption process. The FT-IR spectra of the adsorbent indicated that the amide, amide carbonyl and azomethine groups were major binding sites with the metal ions. The adsorption of PAMA for heavy metal is selective, and the adsorption capacity is in the order of Cu(II) > Cd(II) > Pb(II).

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1. Introduction

Heavy metal pollution has become a serious problem with the rapid increase of global industrial activities. The pollution of water by toxic heavy metals is considered as a threat due to their immense toxicity and their non-biodegradability. These heavy metal ions can be accumulated through the food chain even at lower concentration, leading to a threat to aquatic life as well as to animal, plant life and human health. Toxic heavy metals are mainly derived from lead, mercury, cadmium, chromium, copper, arsenic species, etc. owing to the capability of these species to severe health threat [1–5]. There is a continuous need for new separation techniques which selectively remove the metal ions from dilute wastewaters and industrial process streams.

Several methods have been widely applied for the removal of heavy metal ions such as precipitation, ion exchange, reduction, electrochemical treatment, reverse osmosis, solvent extraction, membrane filtration, etc. [6]. Most of these methods are not widely acceptable owing to their high cost, low efficiency, disposal of sludge, and inapplicability to a wide range of pollutants. On the other hand, adsorption process is well recognized as one of the most effective methods for the removal of heavy metals from their matrices. Adsorption is mainly based on the utilization of solid adsorbents from organic, inorganic or biological nature [6–8]. Nowadays, among the various solid adsorbents, chelating resins are widely used in the removal of metal ions due to their high adsorption capacities and selectivity [9–13]. Regeneration and reusability of the sorbent material must also be considered when assessing the efficiency and feasibility of a treatment process. If the sorbent can be regenerated through desorption cycle (dissolution in adequate eluent, e.g., strong acid) without destruction, the process will become more lucrative. The successive regeneration of sorbents decreases their efficiency, therefore limiting the number of cycles. After that they may be considered as wastes and need to be further disposed.

The objective of the present work was to synthesize, characterize and evaluate the potential of polyazomethineamides (PAMA) for the adsorption of heavy metal ions such as Pb(II), Cu(II) and Cd(II) ions from aqueous solutions. The effect of various experimental parameters such as solution pH, adsorbent dose, contact time and initial metal ion concentration has been investigated.

2. Experimental

2.1. Chemicals and reagents

2-Aminoterephthalic acid (Aldrich), terephthalaldehyde (Aldrich), diaminodiphenylether, triphenylphosphate (Fluka), and ammoniumthiocyanate (Fluka) chemicals were procured from India and Japan. Dimethylformamide (DMF) (Himedia), pyridine (Qualigens), N-methylpyrolidene (NMP) (Rambacks) ethanol (Merck) and distilled water were received from the Makalakshmi chemicals and purified using standard process. $Pb(NO_3)_2$, $CuSO_4 \cdot 5H_2O$ and $3CdSO_4 \cdot 8H_2O$ salts were procured form Aldrich-Sigma Chemical, India. All the chemicals and reagents used for experiments and analysis were of analytical grade.

2.2. Metal solutions

The various concentrations of metal solutions were prepared by dissolving $Pb(NO_3)_2$, $CuSO_4 \cdot 5H_2O$ and $3CdSO_4 \cdot 8H_2O$ in appropriate amount of distilled water. Desired test solutions of heavy metal ions were prepared using appropriate subsequent dilutions of the stock solution. The range in concentrations of heavy metal ions prepared from experimental solution varies from 100 to 500 mg/L. Before mixing the adsorbent, the pH of each test solution was adjusted to the required value with 0.1 M NaOH or 0.1 M HCl.

2.3. Preparation of polymer adsorbent

The dicarboxylic acid monomer containing azomethine groups was synthesized by condensing 0.22 mol of terephthalaldehyde with 0.25 mol of p-amino benzoic acid in DMF with pyridine as a catalyst at 140 °C for 3 h. The resulting dicarboxylic acid monomer (1) was precipitated in water and recrystallized from DMF/water solution, filtered and dried. Polyazomethineamides were synthesized using phosphorylation technique using NMP as a solvent and triphenylphosphite and $CaCl_2$ as condensing agent. Dicarboxylic acid monomer (1) and simple diamine or diamine containing phenylthiourea were taken in equimolar quantities along with triphenylphosphite and $CaCl_2$ in NMP in round bottomed flask and stirred using magnetic pellet at 140 °C for 6 h. The resulting viscous liquid was poured into methanol. Precipitated polyamides were filtered, washed with 5% HCl, 5% Na_2CO_3, distilled water and ethanol, and dried in vacuum. The solid polyazomethine amides were powdered and used for the adsorbent.

2.4. Analytical method

The concentration of heavy metal ions in the solutions before and after equilibrium was determined by AA6300 Atomic absorption spectrometer (Shimadzu, Japan). The pH of solution was measured with a Hanna pH meter using a combined glass electrode. Fourier Transform Infrared Spectrometer analysis was used to identify the different chemical functional groups present in the adsorbent and also to determine the functional groups which are reasonable for the metal binding with the adsorbent. The analysis was carried out using KBr and the spectral range varies from 4000 to 450 cm^{-1}. The surface morphologies of the solids were analysed using a Leo Gemini 1530 scanning electron microscopy at an accelerating voltage of 15 kV and with the working distance of 10 μm for PAMA.

2.5. Adsorption studies

Batch adsorption experiments were carried out by shaking the flasks at 200 rpm for a constant period of time using a horizontal bench shaker (Orbitek-Teqip-ACT/EQ/454). Following a systematic process, the removal of heavy metal ions from aqueous solutions by the use of PAMA in a batch system was studied in the present work. The data obtained in batch studies were used to calculate the percentage removal of heavy metal ions by using the following mass balance relationship:

$$\% \text{ heavy metal ions removal} = \left(\frac{C_o - C_e}{C_o} \right) \times 100 \qquad (1)$$

where, C_o and C_e are the initial and equilibrium concentration (mg/L) of the metal solutions respectively.

2.5.1. Effect of solution pH on adsorption

The effect of pH on the adsorption of PAMA was investigated using a 50 mL of 300 mg/L metal ion solution in the pH range between 2.0 and 10.0 at 30 °C. The samples were then agitated in a horizontal bench shaker at 200 rpm at a different solution pH for 60 min and then filtered through Whatman 42 filter paper. The filtrate was analysed using AA6300 Atomic absorption spectrometer. Each determination was repeated thrice and the result obtained was their average values.

2.5.2. Effect of adsorbent dosage

Batch adsorption experiments were carried out at a different adsorbent dosage of PAMA from 20 to 100 mg for a 50 ml of 300 ppm of metal ion solution at 6.0 pH, for contact time of 60 min at a room temperature of 30 °C. The samples were filtered and the filtrates were analysed as mentioned above.

2.5.3. Effect of contact time

Batch adsorption experiments were carried out at different contact time (10 to 100 min) for an initial concentration of 300 mg/L of metal ion solution at pH 6.0, the PAMA dose concentration is 50 mg in 50 ml of metal ion solution in 250 ml conical flask at 30 °C. Flasks were agitated on the shaker for 60 min to ensure that the equilibrium is attained. The mixture was then filtered and the concentration of metal ion in the filtrates was measured.

2.5.4. Effect of metal ion concentration

Batch adsorption experiments were carried out by contacting 50 mg of PAMA with 50 mL of metal ion solution of different initial concentration (100 to 500 mg/L) at a pH value of 6.0 at 30 °C. A series of such conical flasks were shaken for 60 min at a speed of 200 rpm. The samples were filtered and the filtrates were analysed as mentioned above.

2.6. Adsorption isotherms

Batch adsorption experiments were conducted using 250 mL conical flasks at 30 °C. 50 mg of adsorbent was added to each conical flask which consists of 50 mL metal ion solution of various initial concentrations. All flasks were shaken at 200 rpm in the horizontal bench shaker for 60 min. After filtration, the metal ion concentration in the filtrate solution was analyzed using AA6300 Atomic absorption spectrometer. The amount of metal adsorbed q_e (mg/g) was determined by using the following mass balance relationship:

$$q_e = \frac{(C_o - C_e)V}{m} \qquad (2)$$

where V is the volume of the solution (L); and m is the mass (g) of the adsorbent.

2.7. Adsorption kinetics

Kinetic studies were conducted using a 250 mL conical flask at 30 °C. The experiment was conducted using 50 mL of metal ion