Removal of heavy metal ions from aqueous solution by multi-walled carbon nanotubes modified with 8-hydroxyquinoline: Kinetic study

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A B S T R A C T

Carbon nanotubes were modified with 8-hydroxyquinoline and used for the removal of Cu(II), Pb(II), Cd(II), and Zn(II) from aqueous solutions. Different instrumentation parameters and methods of development for determining metal ions from aqueous solutions using differential pulse anodic stripping voltammetry were studied. The adsorption of heavy metals from aqueous solution by the pristine and modified MWCNTs was studied kinetically using different kinetic models, and the results showed that the adsorption process best fitted the pseudo-second-order model and the Elovich model. The mechanism of adsorption was explored using the intra-particle diffusion model and the liquid-film model.

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1. Introduction

Aquatic pollution by heavy metals is considered one of the most important environmental problems, greatly threatening all life on earth, and mankind in particular. Humans have used heavy metals for thousands of years. Although, it has been known for a long time that heavy metals have adverse effects on human health, exposure to them continues and is increasing in the third-world countries, particularly those with limited water resources. Many technologies have been universally adapted to eliminate or lessen the concentration of heavy metals in aquatic environments. Among them, adsorption to solid adsorbent [1], chemical complexation [2], membrane filtration [3], reduction [4], ion exchange [5], precipitation [6], and alkali kneading [7], and/or flocculation [8], usually used for the removal of heavy metals from polluted water. Adsorption is considered the most practical method for removal of heavy metals due to the ability to recycle both metal ions and the solid adsorbent. The modification of carbon nanotubes is considered an important route for the enhancement of removal efficiency, selectivity, and sensitivity of heavy metals. The surfaces of multiwalled carbon nanotubes (MWCNTs) can be modified chemically through the formation of a chemical bond between the modifying species and MWCNTs' surfaces, or physically through the adsorption of the modifier to MWCNTs' surfaces [9]. There are many studies that focus on the modification of CNTs and their application for the removal of heavy metal ions from aqueous solution. Different chemically modified MWCNTs have been used to study the removal of cadmium [10], nickel and strontium [11], lead [12], europium [13], uranium [14], copper [15], zinc [16], and copper, zinc, cadmium, and nickel [17] ions from aqueous solutions.

8-Hydroxyquinoline (8-HQ), also known as 8-quinolinol or oxine, is a well-known monoprotic, bidentate chelating agent. It is a compound that contains an oxygen donor atom and a nitrogen donor atom that can both bind to metal atoms. 8-HQ was used previously in studies as a modifier for different solid adsorbents where it showed great enhancement for the removal of heavy metal ions from aqueous solutions [18–22]. In our previous study [23], multi-walled carbon nanotubes were physically modified through the immobilization of 8-HQ onto the CNT surfaces, and the modified CNTs were used for the removal of Cu(II), Pb(II), Cd(II), and Zn(II) from aqueous solutions. The adsorption parameters, such as the mass of MWCNTs, temperature, pH, ionic strength, metal-ion concentration, and competition among metal ions, were studied and optimized.

In this study, the effect of different instrumentation parameters was studied, as was a method of development for the determination of the Cu(II), Pb(II), Cd(II), and Zn(II) from aqueous solutions using differential pulse anodic stripping voltammetry (DPASV). The adsorption of heavy metals from an aqueous solution by the pristine and modified MWCNTs was studied kinetically using different kinetic models to understand and reveal the possible adsorption mechanism for efficient removal.

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2. Experimental

2.1. Materials

Multiwalled carbon nanotubes with diameters of 10–20 nm were obtained from Shenzhen Nanotech Port Co., Ltd. and used as received. Analytical-grade cadmium, lead, copper, and zinc nitrate (Fluka, Ion Standard Solution, 1000 mg/L) were employed to prepare stock solutions, each containing 100 mg/L of Cd(II), Pb(II), Cu(II), and Zn(II). The stock solutions were further diluted to the desired ion concentrations. All other chemicals were analytical grade and were obtained from Sigma–Aldrich. The experiments were performed using ultrapure water with resistivity not less than 18.2 MΩ cm obtained with a Millipore Milli-Q system (Billerica, USA).

The modification of CNTs was performed using 8-hydroxyquinoline (8-HQ) according to the method discussed previously [23], and can be summarized as follows: 10.0 g of MWCNTs were added to the saturated solution of 8-HQ and stirred for 2 days, then the solid MWCNTs were filtered through a 0.45-μm filter membrane and washed with deionized water to remove excess 8-HQ until the filtrate became colorless. The final product, 8-hydroxyquinoline MWCNTs (8-HQ-MWCNTs), was dried in an oven at 110 °C overnight.

All glassware used in this work was rinsed with 10% nitric acid (suprapure, 69%) to remove all impurities that might be present and to prevent further adsorption of heavy metals to the walls of the glassware.

2.2. Analytical measurements

The total metal-ion concentration was determined by voltammetric measurement using a Metrohm, 797 VA Computrace (Switzerland) with a three-electrode system, including hanging mercury as the working electrode, a platinum plate as the counter electrode, and Ag/AgCl (3.0 mol/L^{-1} KCl) as the reference electrode. The metal-ion determination was evaluated by differential pulse anodic stripping voltammetry (DPASV).

2.3. Adsorption experiments

Kinetic experiments were carried out to establish the effect of time and temperature on the adsorption process and to identify the adsorption rate. The experimental procedures are described as follows: (1) a series of solutions containing different metal-ion concentrations was prepared in 250 ml conical flasks, (2) the pH of the solution was adjusted, (3) the ionic strength was adjusted using a potassium-nitrate solution, (4) 125.0 mg of MWCNTs were added into the solution, (5) the solution was stirred on a magnetic stirrer at 400 rpm to homogeneously disperse the MWCNTs in solution for a certain period of time at room temperature, (6) stirring was briefly interrupted at predetermined time intervals, and 10.0 mL of supernatant was pipetted from the conical flask and filtered through a 0.45 μm membrane filter. The residual metal-ion concentrations in the aqueous solution were then determined by DPASV. Except when the pH effect was studied, all experiments were carried out at an initial pH of 7.0.

The adsorbed metals ions were calculated as follows

$$q = \frac{(C_0 - C_t)V}{m} \tag{1}$$

where q is the amount of metals ions adsorbed by the MWCNTs (mg/g), C_0 is the initial metal-ion concentration (mg/L), C_t is the final metal-ion concentration after a certain period of time (mg/L), V is the initial solution (L), and m is the MWCNT dose (g).

Adsorption of metal ions on the walls of the glass flasks and the filter paper was determined by running a blank experiment without MWCNTs and was found to be negligible. All measurements were repeated three times and the reported value is the average value. The experimental uncertainties, including instrumental errors, were measured and were mostly ±5% of the reported values.

3. Results and discussion

3.1. Optimization of the instrumental parameters

The DPASV method is based on electrochemical reduction of metal ions at the hanging mercury drop electrode (HDME) by depositing the metals on the mercury-drop surface with subsequent anodic stripping by scanning the potential in anodic direction to allow electro-oxidation of the deposited metals at a characteristic potential of each metal. Conditions for deposition and stripping steps of DPASV were investigated. It is well known that in stripping analysis, the application of suitable deposition potential is very important to achieve the best sensitivity and sensibility. Fig. 1 shows the dependence of the peak current on the deposition potential. The deposition potential range varied from 0.2 to −1.5 V. The reduction peak of Cu(II) was recorded around −0.01 V, Pb(II) at −0.42 V, Cd(II) at −0.59 V, and Zn(II) at −1.00 V vs. the Ag/AgCl reference electrode. It is clear that peak current decreased gradually when the deposition potential became more positive. Also, when deposition potentials more negative than −1.23 V were employed, insignificant variation on the response was observed for Cu(II), Pb(II) and Cd(II); however, a significant decrease in the Zn(II) peak was observed. Thus, the deposition potential of −1.23 V was chosen as the best value due to the highest and uniform peak current of the Cu(II), Pb(II), Cd(II), and Zn(II). Fig. 2 shows the dependence of the peak current of the Cu(II), Pb(II), Cd(II), and Zn(II) on potential scan rate. When the potential was scanned from 0.005 to 0.01 V/s, an insignificant variation on the peak current was observed for Zn(II); however, the peak current of Pb(II), Cd(II), and Zn(II) at 0.005 V/s was the highest. Thus, the potential scan rate of 0.005 V/s was chosen due to the smoothest and highest peak current. Fig. 3 shows the peak current of Cu(II), Pb(II), Cd(II), and Zn(II) at different deposition times obtained by DPASV. It is clear from the figure that the peak currents of Cu(II), Pb(II), Cd(II), and Zn(II) are linearly proportional to the deposition time, as the peak currents increased with increasing the deposition time. The peak currents of Pb(II) and Zn(II) did not change significantly up to 300 s. The deposition time of 30 s was chosen to avoid the saturation
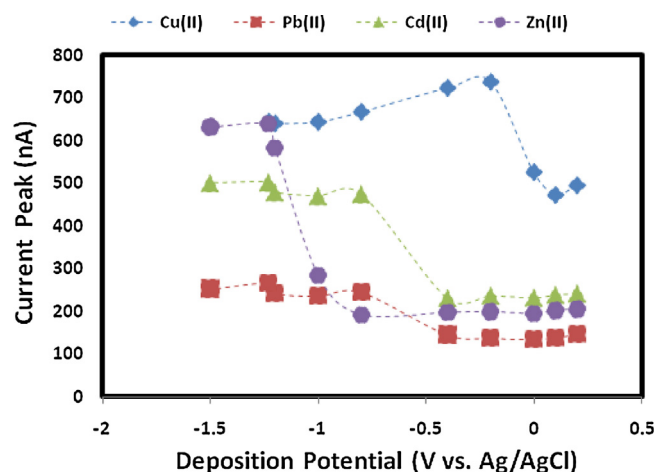

Fig. 1. The dependence of peaks current of the Cu(II), Pb(II), Cd(II) and Zn(II) on the deposition potential. The experiment was performed in 1 mg/L of each analyte at pH 0 with deposition time of 30 s and scan rate of 0.005 V/s.