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Talanta 65 (2005) 476–480
Talanta
www.elsevier.com/locate/talanta

Thermal modified Kaolinite as useful material for separation and preconcentration of trace amounts of manganese ions

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Received 12 May 2004; received in revised form 17 June 2004; accepted 28 June 2004
Available online 14 August 2004

Abstract

This work assesses for the first time the potential of natural Kaolinite as adsorptive material for preconcentration of metal traces. Manganese is quantitatively retained by 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (5-Br-PADAP) on thermal modified Kaolinite by column method in pH range of 8.5–10.0 at flow rate of 2 ml min^{-1}. Manganese was removed from column with 5.0 ml of H_2SO_4 4 mol l^{-1} and determined by flame atomic absorption spectrometric at 279.5 nm. In this case, 0.l μg of manganese can be concentrated from 800 ml of aqueous sample (where concentration is as low as 0.125 μg l^{-1}). Detection limit is 4.3 μg l^{-1} ($3\,\delta_{bl}$ m^{-1}) and analytical curve is linear in the 0.02–10 mg l^{-1} in final solution with correlation coefficient 0.9997 and relative standard deviation for eight replicate determination of 5 μg of manganese in final solution is 0.71%. The interference of a large number of anions and cations has been studied in detail to optimize the conditions and method was successfully applied for determination of manganese in complex materials.

Keywords: Manganese determination; Kaolinite; Solid-phase extraction; 5-Br-PADAP

1. Introduction

A large number of industries discharge metal-containing effluents into water resources without adequate treatment. Contamination of the environment by manganese is currently an area of concern. Although, manganese is an essential micronutrient, over-exposure causes poisonous effects such as memory impairment, disorientation, hallucinations speech disturbance, compulsive behavior and acute anxiety [1,2]. Manganese is present in many alloys and is found in a number of pharmaceutical, biological and environmental samples. The world health organization study group suggested occupational limits of manganese are 0.2 mg m^{-3} and 0.03 mg l^{-1} in air and water, respectively [1]. Very low concentrations of manganese are present in various complex samples. Therefore, it is important from analytical point of view to develop sensitive, selective and economical method for determination of the trace amounts of manganese [3–5].

The most technique available for preconcentration of metals from aqueous sample are solvent extraction and solid-phase extraction using various adsorbents such as activated carbon [6], adsorption resins [7], cellulose [8], microcrystalline naphthalene [9–11], Amberlite XAD-2 resins [12], octadecylsilica membrane disk [13] and synthetic Zeolites [14]. Some of these adsorbents may be fairly effective for preconcentration of metal ions, but their methods of preconcentration are lengthy and involve rigid control of conditions and they are commonly expensive. Kaolinite is a 1:1 aluminosilicate consisting of stacked pairs of tetrahedral silica sheets and octahedral alumina sheets. Each pair of sheet is bound together through common oxygen atoms and successive pairs are held together by hydrogen bonding between Si–OH and Al–OH groups. The resulting crystal has a silica face of SiO_2 tetrahedral, and alumina face carrying Al–OH groups and edges, which carry both Si–OH and Al–OH sites

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doi:10.1016/j.talanta.2004.06.027

[15]. Isomorphism substitution of Al^{3+} for Si^{4+} in the silica layer leaves that face with a small permanent negative charge, while the charge alumina face and on the edges is pH-dependent. Pure Kaolinite ($Al_2Si_2O_5(OH)_4$) is one of the more highly weathered clay minerals. The adsorptive properties of Kaolinite make its valuable both scientifically and commercially. Kaolinite has been utilized in removal of organic and metal ions from wastewater [16–20]. In present work, we have investigated for the first time potential of thermal modified Kaolinite as adsorptive materials for preconcentration of traces manganese. We have found, modified Kaolinite has advantages than other sorbents including, large surface area (because kaolinite is porous) and good chemical stability in different media. We have developed a flame atomic absorption spectrometry method for determination of trace amounts of manganese after adsorption onto thermal modified Kaolinite loaded with 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol and subsequent desorption with 5.0 ml of 4 mol l^{-1} H_2SO_4. The developed method is found to be sensitive and selective and has been employed for estimation of manganese in various complex samples.

2. Experimental

2.1. Apparatus

A Varian model SpectrAA 220 flame atomic absorption spectrometer was used in following conditions: wavelength, 279.5 nm; lamp current, 5.0 mA; slit width, 0.2 nm; acetylene flow, 1.5 l min^{-1}; air flow as oxidant, 3.5 l min^{-1}.

A Beckman pH meter was employed for pH measurement. A funnel-tipped glass tube (80 × 10 mm) was used as column for preconcentration. All glassware and columns were washed with mixture of concentrated hydrochloric acid and concentrated nitric acid (1:1) before use.

2.2. Reagents

All chemical materials were analytical reagent grade. Manganese (II) sulfate monohydrate from Aldrich was dissolved in double distilled water, diluted to 1000 ml in a standard volumetric flask, and standardized by known method [21]. Buffer solution with pH 8.5–10.0 was prepared by mixing an appropriate ratio 0.5 mol l^{-1} ammonia and ammonium acetate. A 0.02% solution of 5-Br-PADAP in ethanol was prepared. Solution of various metals was used to study the interference of ions. Natural Kaolinite was collected from Rayen area, Kerman region in Iran.

2.3. Preparation of thermal modified Kaolinite

After purification of Kaolinite, it was heated to 850 °C and then was sieved to obtain a particle size <45 μm (350 mesh). Then, sulfuric acid 5 mol l^{-1} was added to it for removal of the cation exit in Kaolinite, especially manganese ion for 24 h, finally Kaolinite was washed with distilled water until pH was neutralized. Adsorbent was dried at 110 °C in an oven and stored in calcium chloride desiccators until used.

2.4. Preparation of column loaded with 5-Br-PADAP

One gram of thermal modified Kaolinite was treated with an ethanol:sulfuric acid:water (2:1:1) solution overnight, then Kaolinite was washed with distilled water. The Kaolinite was saturated with 5-Br-PADAP reagent by passing 2 ml of 0.02% 5-Br-PADAP solution in ethanol at flow rate of 0.5 ml min^{-1}. Afterward it was washed with water until excess reagent was eliminated from Kaolinite. Passing a buffer solution must precondition before sample load the column. Then column could be used repeatedly for eight times at least.

2.5. Procedure for the sorption of manganese by column

An aliquot of the solution containing 0.1–50 μg of manganese was taken in a 100 ml beaker and it was added to it 5.0 ml of buffer solution with pH 9.0, then diluted to 50 ml with distilled water. This solution was passed through the column at a flow rate of 2 ml min^{-1}. After passing this solution, the column was washed with 5 ml of distilled water. The adsorbed manganese on the column was eluted with 5 ml of 4 mol l^{-1} sulfuric acid, at a flow rate 1.0 ml min^{-1}. The eluent was collected in a 5.0 ml volumetric flask and manganese was determined by flame atomic absorption spectrometry.

3. Results and discussion

3.1. Reaction conditions

The reaction conditions were investigated with 5.0 μg of manganese. The sorption of manganese on the column was found to be a maximum in the pH range of 8.5–10.0 (Fig. 1). In

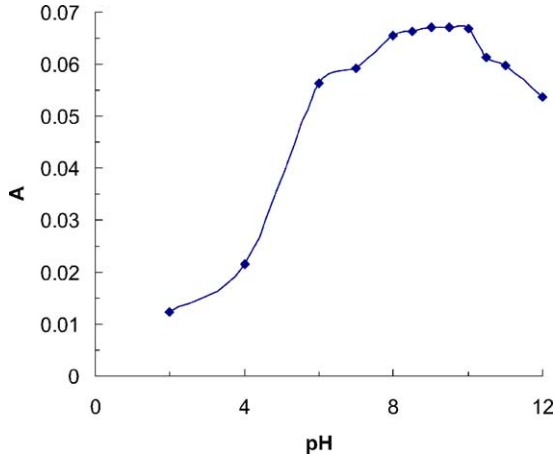

Fig. 1. Effect of pH on adsorption of manganese. Conditions: Mn, 5.0 μg; flow rate of sample, 2 ml min^{-1} and eluent solution, 5.0 ml H_2SO_4 of 4 mol l^{-1} with flow rate 1 ml min^{-1}. Instrumental setting: wavelength, 279.5 nm; lamp current, 5.0 mA; slit width, 0.2 nm; acetylene flow, 1.5 l min^{-1} and air flow as oxidant, 3.5 l min^{-1}.