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Modified Bentonite as Sorbent for Removal of Tl^+ and Bi^{3+} from Water Samples

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In present work, modified bentonite sorbent is used for removal of Tl^+ and Bi^{3+} from water samples at trace levels. Modification of bentonite was established with Pd^{2+} and TiO_2 in the solution and solid state. The results showed that TiO_2 is proved to be better modifier.

Key Words: Removal, Modified bentonite, Sorbents.

INTRODUCTION

Recently, bismuth has been used in medicines for the treatment of helicobactor pylori-induced gastritis. However, a number of toxic effects in humans have been attributed to bismuth compounds such as, nephropathy, osteoarthropathy, hepatitis and neuropathology[1]. As the use of bismuth in medicine increase, it has spread in the environment and the exposure of organisms to bismuth has increased[2].

Thallium is a rare element in the earth's crust. Both the element and its compounds are extremely toxic *i.e.*, skin-contact, ingestion and inhalation are all dangerous. The determination of thallium in environmental samples is of interest because of the high toxicity of its compounds. Due to new concerns regarding the toxicity of thallium, there are growing needs for improved analytical methods for monitoring this metal[3].

Toxicity of metals has received considerable attention in recent years because industrial effluents frequently contain metals that can have adverse effects on human health and the environment[4,5]. Bentonite is the commercial natural clay mineral. The main component of which is montmorillonite, a 2:1 di octahedral smectite. Montmorillonite possesses a two dimensional crystalline structure based on staked layers of tetrahedral, octahedral and tetrahedral connected to each other by oxygen bridges. Whereas tetrahedral are made of silicon, octahedral are mainly made of aluminum and magnesium, which is described as octahedral substitution

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(of Mg for Al). This substitution provides a net negative charge to the montmorillonite, which is distributed over the complete oxygen framework and balanced by exchangeable cations. These cations, mainly Na^+ and Ca^{2+}, are localized within the interlayer space and their ratio can vary significantly from one deposit to another. The particular affinity of proteins for bentonites is based on the commonly high specific surface areas associated with swelling and cation-exchange properties of the latter[6]. In present studies, the potentials of bentonite and modified bentonite are investigted for removal of Ti^+ and Bi^{3+}.

EXPERIMENTAL

Voltammetric measurements were taken with a Metrohm 757 VA computrace, with a three electrode system consisting of a hanging mercury drop electrode (HMDE) as the working electrode, an Ag/AgCl reference electrode and platinum counter electrode. A funnel tipped glass tube (80 × 10 mm) was used as a column for preconcentration. The glassware and column, was kept overnight in a 5 % nitric acid solution. A Beckman pH meter was used for pH measurements.

All Chemicals used were of analytical reagent grades. Bismuth(III) nitrate was dissolved in a minimum volume of concentrated nitric acid and then diluted to 1000 mL with distilled water in a standard flask and standardized by known methods[7]. A standard thallium solution was prepared from thallium(I) nitrate in a minimum volume of concentrated nitric acid and then diluted to 1000 mL with distilled water in a standard flask and standardized by known methods[7]. Bentonite was collected from Bardsir area, Kerman Region in Iran.

Preparation and modification of the bentonite: After purification of bentonite[8], It was sieved to obtain a particle size of < 150 µm (200 mesh) and nitric acid 5 mol L^{-1} was added to bentonite for removal of the cation from bentonite, especially these ions if exit in the bentonite. The modification of bentonite was performed as follows: 10 mL of Pd^{2+} solution (0. 01 mol L^{-1}) was added to 10 g of bentonite and the mixture was heated at 80°C for 12 h while being stirred. Then the adsorbent in this form was dried at 110ºC in an oven and was stored in calcium chloride desiccators until use. For modification of bentonite with TiO_2, 1 g of this matter was added to 50 g of bentonite in solid state and then mixture with stirrer, then this mixture was heated in 900ºC for 0.5 h then sorbent in this form was stored in $CaCl_2$ desiccators until use.

Preparation of column: 1 g of modified bentonite was added to a funnel tipped glass tube and 5 mL distilled water passed from the column. Afterward it was washed with water. All experiments were done in a funnel tipped glass tube (80 × 10 mm) as a column.

Procedures for the sorption of these ions by column: An aliquot of the solution containing 750 µg of each these ions was taken in a 100 mL beaker and it was added to it 5 mL of buffer solution with pH 2.5, then diluted to 30 mL with distilled water. This solution was passed through the column at a flow rate of 5 mL min^{-1}. After passing this solution, the column was washed with 5 mL of distilled water. The adsorbed ions on the column were eluted with 5 mL of 4 mol L^{-1} nitric-acid, at a flow rate of 2 mL min^{-1}. The effluent was collected in a 5 mL volumetric flask and these ions were determined by anodic stripping voltammetry.

RESULTS AND DISCUSSION

Preliminary studies with bentonite and modified bentonite: 750 µg of Tl^+ and Bi^{3+} ions with 750 µg of the other cations were used in this investigation. The results showed recovery for Tl^+ and Bi^{3+} ions less than 50 %. Therefore, the bentonite without modification was not suitable for separation of these ions. Therefore, reagents were added to bentonite and then modified bentonite was studied for separation.

Reaction conditions: The sorption of these ions on the column found to be a maximum in the pH range of 3.5-5.5 (Fig. 1). In subsequent studies, the pH was maintained at *ca.* 4.5. The flow rate of sample solution varied from 1-6 mL min^{-1}. It was found that a flow rate of 1-5 mL min^{-1} did not affect adsorption. A flow rate of 5 mL min^{-1} was recommended in all experiments.

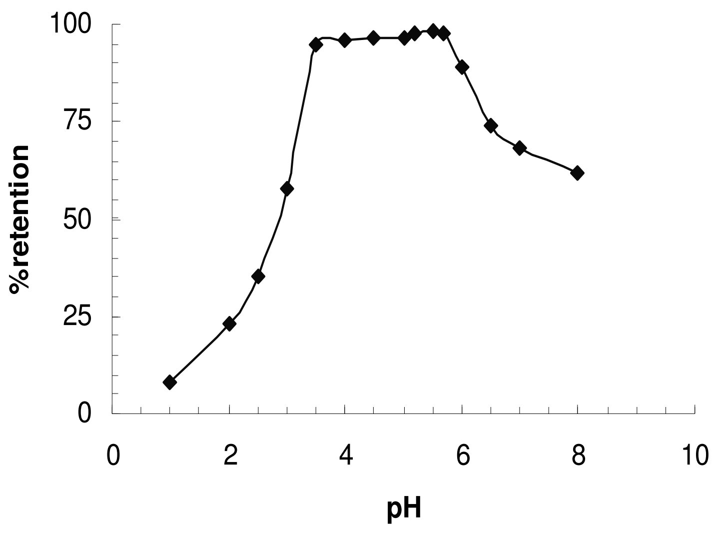

Fig. 1.

Sorption capacity of modified for Tl^{+} and Bi^{3+} ions: The sorption capacity of modified natural bentonite for Tl^{+} and Bi^{3+} ions was evaluated. In this case, the column containing 1.0 g of modified natural bentonite was used and different volume of 1000 mg L^{-1} these ions solution was passed through the column. Each time, the solution after passing the column, was determined these ions. The modified natural bentonite has a sorption capacity of 4.85 mg these ions per gram of modified natural bentonite.

Conclusion

In this study, a suitable method for separation bismuth and thallium has been developed. The results were shown that bentonite alone not suitable. Therefore we have modified bentonite and were cleared modification could be suit and modified bentonite could be used for removal of these ions from wastewater. The main advantages of this procedure are: (I) natural bentonite is cheap (II) the preparation of the extractor system is simple and fast.

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