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Modified Natural Zeolites as Sorbents for Separation and Preconcentration of Traces Amount of Metal Ions

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This work assesses the potentialities of natural zeolites as useful adsorptive material for separation and preconcentration of trace amounts of metal ions. Natural analcime and natrolite zeolites were modified by benzyldimethyltetradecylamonium chloride solution at 110 ºC for 12 h and then was saturated with 2-(5-bromo-2-pyridylazo)-5-diethylamino-phenol (5-Br-PADAP) as useful reagent for preconcentration of trace metal ions. A column contains modified zeolite as useful adsorbent was used for solid-phase extraction of trace lead and cadmium ions. Different parameters that necessary for solid-phase extraction were examined in this work and zeolites were known useful adsorbents for solid-phase extraction and preconcentration of traces metal ions.

Key Words: Zeolites, Analcime, Natrolite, Solid-Phase extraction, Preconcentration.

INTRODUCTION

Cleanup of analytical samples prior to determination of various metal ions has been a long standing problem in chemical analysis. This sample pretreatment has two main goals. One is to separate the target metal ions from large amounts of salt, organic material, dirt or other sample substances that would interfere in analytical measurement step. A second goal is to preconcentrate the metal ions to be determined to a point where their analytical determination of facilitated. For many years liquid-liquid extraction has been a popular method for sample pretreatment. But such difficult, includes the frequent formation of emulsions that are slow to break up, impurities introduced by liquid organic solvents, the need to concentrate the organic extract and air-and water pollution problems stemming from the use of substantial quantities of organic solvent. The use of solid-phase extraction an attractive way to avoid many of difficulties associated with liquid-liquid extraction. Uptake of metal ions by solid phase extraction (SPE) column or membrane tends to be more complete than liquid-liquid extraction because multiple equilibria occur in column method. In some instances no organic solvent at all are used in SPE of metal ions[1]. Properties of good SPE materials are: (i) porous, large surface area[2],

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(ii) reversible adsorption[3], (iii) pure, low leachable[4], (iv) good chemical stability[3], (v) good surface contact with sample solution[5-7], (vi) high-percentage recoveries[1].

Zeolites in narrow definition are porous crystalline aluminosilicates having a uniform pore structure frameworks comprising $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ tetrahedral units. T atoms (Si, Al) are joined by an oxygen bridge. Thus resulting in the general framework formula $(AlO_2)_x (SiO_2)_{n-x}$, where n is the number of tetrahedral per unit cell and $x < n/2$. Since aluminum is trivalent, every AlO_2 unit carries a negative charge, which is compensated by a positive charge associated with a cation[8,9]. Due to unique structural zeolites and modified zeolites have been utilized for pollution control of heavy metal ions[10], organic pollutants[11], catalyst applications[12], separation processes[13], solid-phase ion exchange[14] and ion selective electrode[15,16].

For solid-phase extraction various adsorbents such as, activated carbon[17], adsorption resins[18], bonded-phase silica[19], chelating resins[20], organic materials (such as naphthalene)[21] were used. In the present work we studied the analytical potential of natural modified analcime and natrolite of zeolites as sorbent materials for solid-phase extraction and preconcentration of trace metal ions.

EXPERIMENTAL

Natural analcime and natural zeolites were collected from Torfeh, Shahr Babak and Hejin, Sarcheshmeh, area, Kerman region in Iran[22]. The zeolites were sieved to obtain a particle size between 30-50 µm and then were washed with distilled water to remove suspended material, then nitric acid (2 M) was added to zeolites. The modification of zeolites were performed as follows: benzyldimethyltetradecyl ammonium chloride was dissolved in water to obtain a solution of 0.0001 M. This solution was added to zeolites and the mixture was heated at 110 °C for 12 h while stirred then dried in an oven and stored in calcium chloride desiccator until used.

Modified zeolite (1 g) was added to a funnel tipped glass tube (80 mm × 10 mm) and 5 mL 0.02 % of solution 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (5-Br-PADAP) in ethanol was passed from column. An aliquot solution contains 0.03-600 and 0.1-300 µg of lead and cadmium respectively, was passed from column. After passing the solution, lead and cadmium in this solution were determined by anodic stripping differential pulse voltammetry. The adsorbed lead and cadmium were eluted by 5 mL of nitric acid 2 M then lead and cadmium were determined by anodic stripping differential pulse voltammetry. Different parameters are necessary in solid-phase extraction such as, flow rate of sample and eluted solution, breakthrough volume, pH effects and selectivity was studied.

RESULTS AND DISCUSSION

Porous, large surface area: Zeolites are porous aluminosilicates have uniform pore structure, the diameter of the channels and cavities varies according to the structure from 0.3 to 1.3 nm, the highest values of the internal surface area and pore volume, respectively, 800 m^2/g and 0.35 cm^3/g. From this point, zeolites can be applied for solid-phase extraction.

Reversible adsorption, successful SPE has two major requirements: (i) a high, reproducible percentage of the analytical solutes must be taken up by solid extraction and (ii) the solutes must be easily and completely eluted from the solid particles. This section was studied for the solid particles. This section was studied for natural zeolites and natural modified zeolites after saturated with 5-Br-PADAP. Both, natural zeolites and natural modified zeolites adsorbed 5-Br-PADAP, but modified zeolites capacity was higher. It is noticed that the saturated adsorbents with 5-Br-PADAP reagent, especially modified zeolites can be taken up, a high reproducible percentage of analytical solutes and adsorbed solutes can be easily and completely eluted from adsorbent by organic solvent and inorganic solvents especially acids solution. In this work, nitric acid (2 M) has been applied for elution of lead and cadmium ions.

Pure, low leach able impurities: The solid particle need to be as free as possible of impurities that might be leached from the solid during elution of retained sample constituents. For purification of particles of zeolites accomplished by washing with nitric acid solution, for removal the leaching impurities if probably exit it the zeolites.

Good chemical and thermal stability: An acidic or basic sample solution or eluting solution is needed in some applications. Solid phase extraction minicolumn can be placed in convenient heater that is attached to gas chromatograph and analytes thermally desorbed directly into the chromatograph. This mode of operation requires the use of solid particles with good thermal stability. Solid particles need to be stable in the organic solvents used in the elution step as well as in the aqueous sample. Zeolites have high temperature stability and stable in organic solvents. For investigation of acidic and basic sample solution, it is well known that mineral zeolites decomposed when treated with strong acids, where as in the pH range *ca*. 1-10 that is necessary for solid-phase extraction, zeolites are stable. Therefore, from this point zeolites can be applied for solid-phase extraction. In this investigation, it is observed that natural analcime and natrolite zeolites can be applied as adsorbent particles for solid phase extraction.

Good surface contact with sample solution: Zeolites have porous crystal and they are hydrophilic surface but benzyldimethyltetradecylamonium cation make the surface hydrophobic and ethanol was passed from column for activating solvent must be used to obtain better surface contact with the aqueous solution being extracted.

Good recoveries: Recoveries of metal ions were investigated and it is found that the recovery was high than 99 % for modified zeolites.

For solid-phase extraction and preconcentration of lead and cadmium ions, modified analcime and natural zeolites have been used and a preconcentration factor of 200 and 140 were obtained, respectively. In this case, 0.3 µg of lead can be concentrated from a 1000 mL of solution with passing through column of modified analcime zeolite and 0.1 µg cadmium can be concentrated from a 700 mL of solution with passing through column modified natural zeolite.

Conclusion

The present work suggests that the zeolites can be used as useful adsorbent material for separation and preconcentration of trace metal ions that have main advantage than other sorbents such as: (1) natural zeolites is very cheap, (2) the preparation of extractor system is simple and fast, and (3) good preconcentration factor can be achieved.

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