Preparation of a novel cartridge column for solid phase extraction, used for separation of some heavy metal

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Abstract: This study included the removal of heavy metal ions by developing the solid-phase extraction method and preparing separation columns in order to isolate unwanted water pollutants. Single-use separator columns contain a modified extraction block consisting of (organic azo reagent 6-MBTAMP with chitosan) low the cost and this mass are saturated with the aforementioned organic reagent for the purpose of increasing the extraction surface area by increasing the effective aggregates. The modified extraction mass was characterization by means of the X-ray diffraction technique and several sharp crystal peaks appeared for us, and the highest of these peaks were equal to 38.81.

KEYWORD: Chitosan, XRD, SPE, 6-MBTAMP, azo compound, heavy metal

Introduction:
Chitosan is a substance mainly composed of Chitin, which is a natural poly saccharide polymer and is extracted from the external structure of shellfish, oysters and shellfish such as shrimp, which is like a magnet because it carries positive charges along its fibers and works to attract any negative charge and its capacity is twice its size, which gives a high capacity it is very absorbent and chitosan is non-toxic and has the ability to dissolve in acidic solutions. Figure(1): illustrate the preparation of chitosan in the following figure:
Extraction: is a chemical method of chemical separation methods, that aims to isolate and separate a certain substance from a group of substances and make it in one mixture, where special materials are used to extract the desired substance and isolate all other materials, and several factors must be taken into account to start the extraction process such as selectivity, solubility, financial cost, and laboratory safety. Isolating a compound from one phase to another by removing the concern, that is insoluble by treating it with a selective solvent for this substance. Liquid-liquid extraction and solid-phase extraction are two of the types of extraction, in which several factors must be available in order for the separation, efficiency to be high, including solubility, temperature, pH, mass and properties of the solute. Among the types of extraction are:

1-Liquid-liquid extraction The principle of work of this type of extraction is to isolate a compound from the solvent, as the solute particles distribute themselves between two immiscible solvents. Miscible, this technique is characterized by its simplicity as well as its applications that include trace and micro quantities of metal ions.

2-Solid phase extraction the resort to the solid phase extraction method is to avoid the difficulties that occur in liquid - liquid extraction because it is manual, tedious, slow and is limited to samples solutions that are not miscible with water.

As for the working principle of solid phase extraction, it depends on fractionation compounds between two phases, where by the material to be extracted is split by the solid phase between the liquid and solid phase so that this material has either an affinity towards the solid phase or a retention process due to the forces arising in the effective sites between the solid surface and the material.

This technique is based on the use of membranes or cylindrical injection columns called single-use cartridge, and the highest extraction efficiency can be obtained by testing the fixed phase with effective groups, as it provides an appropriate to retain the largest amount of material to be separated, and the most important characteristic of solid phase extraction is to reduce the extraction time It uses less solvents than it is in the liquid-liquid extraction method.

Figure (1): Chitin turns into chitosan by a process Alkaline de-acetylation.
and it is also characterized by the different types of bonds for the functional groups, which allows the extraction of multiple and different types of compounds. This method is based on the Van der Waals forces, the hydrogen bonding, bipolar interactions and electrostatic interactions. This work aimed to prepare a novel cartridge for SPE column used for extracted of some heavy metals such as Fe, Cr, Co and Cu.

**Experimental**

**Materials & Instrumentation:**

All the organic and inorganic chemicals used were of a high degree of purity according to the companies supplying them from Sigma-Aldrich, Merck, BDH, Fluka, Scharlau, CDH, and MOH Companies. Stock solutions were prepared by dissolving a required amount of chloride salt of each (Fe, Cu, Cr, and Co) solutions were prepared by dissolving a required amount of acetate salt in ammonium acetate buffer solutions, and then dilution of the stock solution in double distilled water with a concentration of (1000 mg L$^{-1}$) for all metallic ions, and these solutions were diluted daily to obtain working solutions.

X-ray diffraction was performed on Shimadzu model XRD-6000 spectroscopy.

**Methods:**

1. **preparation of the extraction column:**

   Includes the stage of saturation of the base material with the organic reagent (6-MBTAMP). The purpose of this process is to increase the efficiency of chitosan in removing contaminants and thus be more effective in removing heavy metals.

   Preparation of the extraction column The preparation process begins based on the previous study. This process begins with taking a specific weight of 0.5 g of chitosan, then adding to its 25ml of organic reagent solution (6-MBTAMP) by dissolving a weight of 0.03% using absolute ethanol as a solvent for the organic reagent, and then leaving the mixture for 12 hours in continuous stirring in order to complete the saturation process, and after the end of this period of time, the mixture is filtered and purified, the sediment is washed several times with distilled water and dried at a temperature not exceeding 60 °C by means of an electric drying oven.

2. **Solid phase extraction procedure:**

   After preparing the modified extraction block (impregnated with the organic reagent 6-MBTAMP) and drying it well to be ready to be placed in the extraction column, then the environmental solutions are prepared by preparing the stock solution at a concentration of $10^{-2}$ by dissolving it with the buffer solution and then adjusting the acidity function of each selected metal ion during this study and after In order to prepare a series of dilute solutions ranging from $10^{-3}$ to $5*10^{-7}$ by taking 1ml of the mother solution and diluting it to the required concentration during work and preparing these solutions immediately and on a daily basis. After that, we prepare the extraction block to place it in the separation column and choose short single-use separating columns. In order to make the extraction mass acceptable and regular, a polymeric bond must be placed in order to hold the molecules together inside the extraction column and this material is known as polyvinyl alcohol. The latter is prepared by taking a weight of 1 g, dissolved in 10ml of hot distilled water, and after dissolving it, a
thick gelatinous solution is formed and very small drops are added from the inspirational solution to the extraction mass in order to coat the inner part of the separation column. The column is filled with a modified chitosan filling by taking a weight of 0.5g of it inside the column and pressed until it takes the shape of the circular column, then the acidic function of the extraction block is neutralized by passing a buffer solution whose acidity is equal to pH = 6 and after the extraction process, the output solutions are collected and their concentration measured using an Visible-ultraviolet spectrophotometer.

Result and discussion:

X-ray diffraction

Conducting X-ray diffraction spectroscopy of the modified extraction mass in its solid state (organic reagent + chitosan) in order to find out the crystal structure and study the atomic arrangement and determine the granular crystal size and the interval between atomic levels of the prepared extraction mass where the spectroscopy was performed to measure the X-ray diffraction. The measurement process was within the angular range of the scanning process 2θ = 10-100 degree, by using the Cu-Kα spectrum beam as an X-ray generator with a wavelength of 1.54056 Å, and it was operated at a current of 30.0 mA and a voltage value equal to 40.0 KV, and this was within the standard operating conditions for conducting the scanning process. Spectrophotometry for XRD of modified extraction block, where we note that the extraction block has a poly crystalline structure, and these systems by their nature have different sizes, random distribution and irregular crystalline ratio (i.e. irregularity in the crystal structure). The X-ray diffraction spectrum showed many different peaks of different intensities, while several sharp peaks indicated the crystal structure of the compound 6-MBTAMP, and the highest of these peaks had a value equal to 38.81, where these peaks at the angular range were equal to, and the corresponding have d-spacing values. In succession, where these peaks represented the preferred orientation, the height of these peaks indicates (the intensity at which these peaks appeared depends on the arrangement of the crystals, the properties of the crystal lattice and the crystal planes).

The appearance of sharp and high-intensity peaks in the modified extraction mass particles indicates the presence of crystalline levels and a crystalline structure that are of a homogeneous nature (high crystalline nature). On the contrary, the peaks that appeared with low and low strength and broad in the X-ray diffraction spectrum return to the crystal structure less homogeneous in nature (low crystalline nature).

The size of the nanoparticles is calculated by knowing the angle of incidence and the peak width of one of the peaks of the diffraction pattern.

Table (1): The values of diffraction angles, crystal size, relative intensity, width of peaks at mid-height, in addition to values lattice strain

| No | peak position (FWHM) | size nm | crystallite | retint.% | lattice strain |
|----|----------------------|---------|-------------|----------|----------------|

4
| Compound | no. | d.spacing | Intensity | rel.int.% | peak position 20 |
|----------|-----|-----------|-----------|-----------|-----------------|
| d= 6-MBTAMP | 1 | 4.56 | 1788 | 100% | 19.42 |
| 2 | 9.33 | 603 | %34 | 9.46 |
| 3 | 4.21 | 531 | %30 | 21.11 |
| 4 | 3.84 | 261 | %15 | 23.10 |
| 5 | 2.31 | 92 | 5% | 38.81 |
| 6 | 1.23 | 135 | 8% | 77.40 |

Table (2): The values of the angles, diffraction, spacing, and intersectionality of the modified extraction block

Method evaluation

After completing this study, we can evaluate the used analytical method by determining the accuracy, control and sensitivity of this method by calculating the percentage of relative and percentage deviation, standard deviation and percentage removal, as well as calculating the detection limit and finally calculating the quantitative limit for solutions of different concentrations ranging from $1\times10^{-4}$ to $1\times10^{-5}$ for each metal ion of the selected ions.
Cr, Cu, Co, Fe, taking into account the acidic function of each of them, and this is shown in the table below:

**Table (3): Analytical values to estimate the concentrations of the metal elements selected**

| Parameters | Fe(III) | Cu(III) | Cr(II) | Co(III) |
|------------|---------|---------|--------|---------|
| % RSD      | 0.203   | 0.14    | 0.265  | 0.123   |
| LOD        | 0.77    | 0.79    | 2.167  | 4.284   |
| LOQ        | 0.231   | 2.634   | 0.95   | 1.285   |
| S.D        | 0.06    | 0.0429  | 0.026  | 0.044   |
| X²         | 2.077   | 2.993   | 2.948  | 1.479   |
| Slope      | 0.0596  | 0.0594  | 0.015  | 0.0108  |
| R²         | 0.9957  | 0.9946  | 0.9973 | 0.9945  |
| % R        | 95      | 99      | 91.66  | 99      |

**Conclusion**

The X-ray diffraction (XRD) results of the new prepared azo reagent 6-MBTAMP with a crystalline nature and a nanoparticle modifier were shown. The use of chitosan prepared from shrimp shells used for solid phase extraction (SPE) technology, because it is a low-cost to be extracted surface and that the heavy metals present in water samples can be estimated and their concentration calculated. Chitosan contains very acceptable physical, chemical and diagnostic properties, which gives it great advantages. It can start to enter all fields and has wide applications due to its advanced and very high porosity capacity. The ease of performing the modification procedure on the surface of chitosan by introducing the new azo dye by the method of saturation or impregnation, and this was shown by the applied results (azo detector + chitosan), as the results of X-ray diffraction (XRD) showed us that the modified extraction mass was characterized by a Nanoscale arrangement of its particles capable of absorbing heavy metals with high concentrations, the environmental analysis of the extraction mass showed us the removal of pollutants in a large and remarkable way, as well as the high sensitivity that was clear to us through this method, as this can be applied to the modified extraction mass in the spectral estimation process of the selected elements in this study. The ease of carrying out the separation process demonstrated by the environmental analytical application using the solid phase extraction method (SPE) is attributed to the polymeric bonding material (PVA) as a binding agent for the modified extraction block, while the prepared extraction mass increased as an advantage in removing heavy element contaminants than it is in the use of cellulose fibers and activated charcoal.

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