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Sonochemical synthesis of nano coordination polymer as sorbent for removal of uranyl (UO_2^{2+}) ions from aqueous solutions

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ABSTRACT

The nano particles of two-dimensional coordination polymer were synthesized by sonochemical method. The TEM image was shown that the particles of sorbent are in the nano scale. The sorbent was utilized as a unique filter for removal of uranyl ions by solid phase extraction method. For investigation of the sorption procedure, sorbent was immersed in trace level (ppm) of uranyl ions. By considering the solution of salt before and after extraction, removal of uranyl ions were confirmed by UV-Vis spectrophotometer.

Keywords: Sonochemistry, nano sorbent, Uranyl ions, Solid phase extraction

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INTRODUCTION

Uranium is a naturally radioactive metallic element which is chemically active at its pure form. Uranyl ions and its derivatives commonly found in the ground waters, Seawaters, waste waters and drinking waters. According to the World Health Organization (WHO), the maximum uranium concentration should be less than $15 \mu\text{gL}^{-1}$ in drinking waters [1]. However, uranium and its compounds are highly toxic and lead to kidney failure or even death. Therefore, different analytical methods, were utilized to detect even at low concentrations of uranyl ions, such as: Phytoremediation method [2-3], nanofiltration method [4] voltammetric determination [5], liquid extraction method [6] ion imprinted method [7] electrochemical detection [8]. One of the useful methods for removal of uranyl ions and its derivatives is solid phase extraction (SPE). The SPE method, because of its simplicity, ability to achieve higher enrichment factor and accessibility to selective sorbents can be used to improve the analytical detection limit, effective pre-concentration, and sensitivity of the method [9].

The major objective of many research have been concentrated on, new sorbents with high surface area, stable at a wide pH range, and low swelling behavior. So far, several selective sorbents for removal and extraction of uranyl ions from aqueous solutions have been utilized either by physical loading or chemical binding, such as: Terrestrial Plants [10], hydrogels [11], Ion imprinted polymer (IIP) materials [12], silica gel [13], nano-magnetic composite [14].

Metal organic frameworks (MOFs) can be applied as unique solid sorbent in extraction and removal of heavy and toxic metal ions. MOFs are a recently-identified as class of porous polymeric material (PCPs), which are composed of metal ions as connectors that are bridged by organic ligands. Coordination polymers are a branch of extended family of MOFs which have characteristic features. Because of the special structure of MOF and PCPs compounds, they have been used in a number of applications, such as; separation, sensors, switching materials and drug delivery [15-16]. The development of micro and nano coordination polymers synthesis has recently been reviewed [17]. Microwave and ultrasound assisted methods of synthesis, allow PCP nanocrystal preparation to be completed in timescales of several minutes [18-19]. Nevertheless, when using these methods, the size, shape and dimensionality of the nanocrystals cannot be accurately controlled.

In this research, the two-dimensional coordination polymer that was synthesized, utilized as a unique nano sorbent for solid phase extraction of uranyl ions.

EXPERIMENTAL

Reagents and physical measurement

$\text{Cd}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, 2-pyrazinecarboxylic acid (Hpzca), $\text{UO}_2(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ were purchased from Merck company. All solvent were of analytical grade and was used without further purification. Stock solution of uranyl ions was prepared by dissolving an appropriate amount of uranium acetate in deionized water and diluted with the buffer. Buffer solutions were prepared from $0.01 \text{ mmol mL}^{-1}$ sodium acetate-acetic acid. The stock solutions of the metal ions (10 ppm) were prepared by dissolving metal acetate in deionized water.

Infrared measurements (KBr pellets) were carried out on a Shimadzu FT-IR spectrometer. Elemental analyses were carried out on a Finningflash 1112 CHN elemental analyzer. A multiwave ultrasonic generator was used on UP-400-Hiescher for ultrasonic irradiation. X-ray powder diffraction (XRD) measurements were performed with a Philips X'pert diffractometer. The extraction of medicine was detected by Shimadzu-2550 UV-Vis spectrophotometer and the TEM images were obtained using a Philips CM120 instrument.

Synthesis of nano sorbent

To prepare nano-particles of coordination polymer, 15 mL of $\text{Cd}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (1 mmol) in MeOH was placed in high-density ultrasonic probe, operating at 25 kHz with a maximum power output of 400 W, then Hpzca (2 mmol) in 15 mL methanol was added dropwise to the solution. The precipitate was filtered off, washed with MeOH and ether several time and dried in air. Yield: 58.78%. Anal. Calc for $\text{C}_{20}\text{H}_{12}\text{Cd}_4\text{N}_8\text{O}_{10}$: C, 24.66; H, 1.24; N, 11.50. Found C, 22.90; H, 1.12; N, 11.01. IR (cm^{-1}) selected bands: 451(w), 549(w), 729 (m),

794 (m), 848(m), 1041(w), 1049(w), 1170(m), 1353(s), 1469(w), 1526(w), 1575(s), 1625(vs), 1652(vs), 3077(w), 3444 (b).

Solid phase extraction of uranyl ions

UO_2^{2+} ion (10 ppm) was dissolved in dionized water (10 ml), pH adjusted to 3-4 then the solution kept for 30 min in an ultrasonic bath. Nano coordination polymer as sorbent (100 mg) was added to the uranyl solution and was sonicated for 10 min again. The sample was centrifuged subsequently at 3000 rpm for 10 min. To confirm the absorption of uranyl ions, the solution before and after extraction were analyzed by UV-Vis spectrophotometer.

RESULTS AND DISCUSSION

Two-dimensional nano coordination polymer was synthesized by sonochemical method. The structure was characterized by CHN analysis, PXRD, FT-IR, and TEM image. The nano coordination structure was utilized as a sorbent for extraction of uranyl ions by solid phase extraction method (SPE). The extraction of uranyl ions was confirmed by UV-Vis spectrophotometer.

Characterization of nano sorbent

The nano Cd coordination polymer that we synthesized by sonochemical method, is isostructural with the single crystal according to the literature [20]. The FT-IR spectrum in Figure 1, the broad region between $3000\text{--}3500\text{ cm}^{-1}$ indicate O–H stretching vibration of the intermolecular hydrogen bonds between oxygen atom of carbonyl group and nitrogen atoms from pyrazine rings. The weak bands at 848 and 794 cm^{-1} shows the aromatic skeleton vibrations of the pyrazine rings. Some moderately and weak intense bands appeared in the $400\text{--}500\text{ cm}^{-1}$ region are assigned to new $\nu(M\text{--}N)$ and $\nu(M\text{--}O)$ ($M = \text{Cd}$) bands, which further suggest bond formation between the metal and N^- and O^- donors of the ligand. The IR spectra of sorbent displays a band at 1625 cm^{-1} which is attributed to the asymmetric stretching vibration of C=O group of pzca and the bands at 1384 and 1353 cm^{-1} refer to symmetric stretching vibration of carboxyl group, respectively. The separation [$\nu(\text{COO}^-) - \nu(\text{COO}^-)$] for nano sorbent (272 cm^{-1}) which is shorter than 200 cm^{-1} , indicating that the COO^- of pzca coordinated to Cd in a mono dentate mode. Therefore, the absence bands in the region $1690\text{--}1730\text{ cm}^{-1}$ indicating complete deprotonation of Hpzca molecule. These data showed that Cd, Coordinated to ligands through nitrogen and oxygen of heterocyclic.

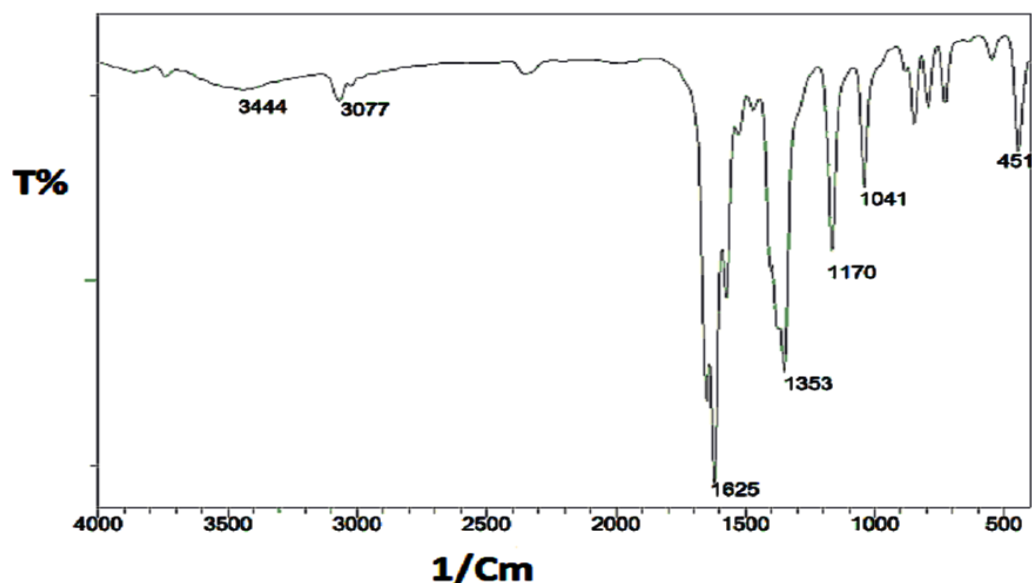


Figure 1: The FT-IR spectrum of nano sorbent

X-ray diffraction

Comparison between XRD patterns of bulk and nano structure of sorbent are shown in Figure 2. Considering to Figure 2, the acceptable matches were observed between the XRD pattern of nano and bulk structure. This indicates that the compound obtained by sonochemical process is iso-structure with bulk compound which is synthesized before. There is a significant broadening band in XRD pattern of nano size polymer, confirms the nanometer dimensions of particles of sorbent. Average crystallite size of nano-particles is estimated, using Scherer formula ($D=0.891 \lambda/\beta \text{ Cos}\theta$) which is in agreement with that observed from TEM image (Figure 3).

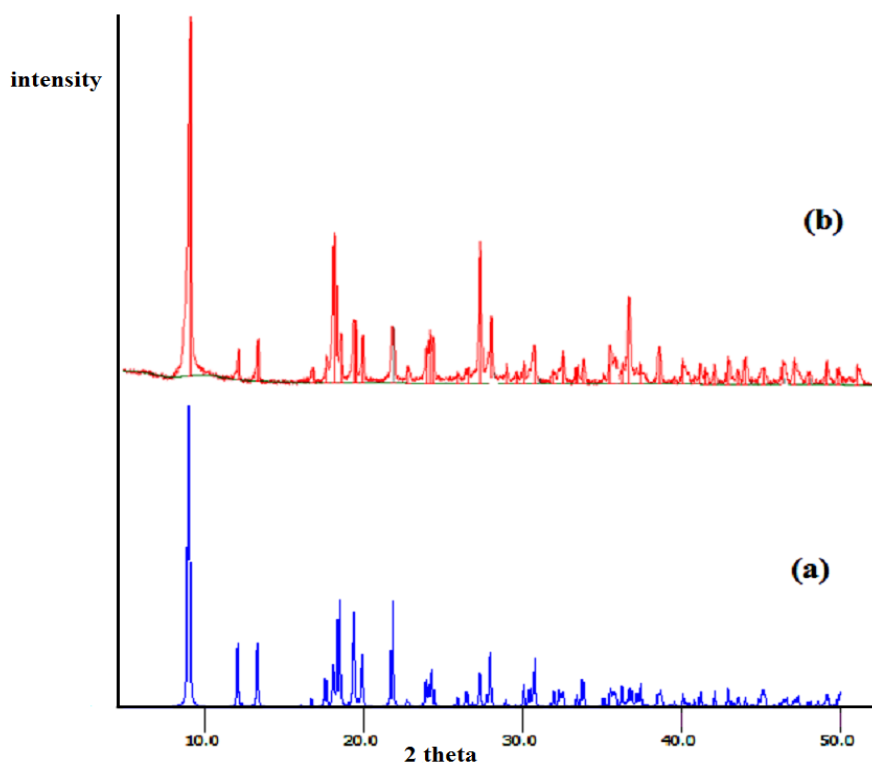


Figure 2: The PXRD pattern of bulk (Reference) (a), and nano sorbent (b).

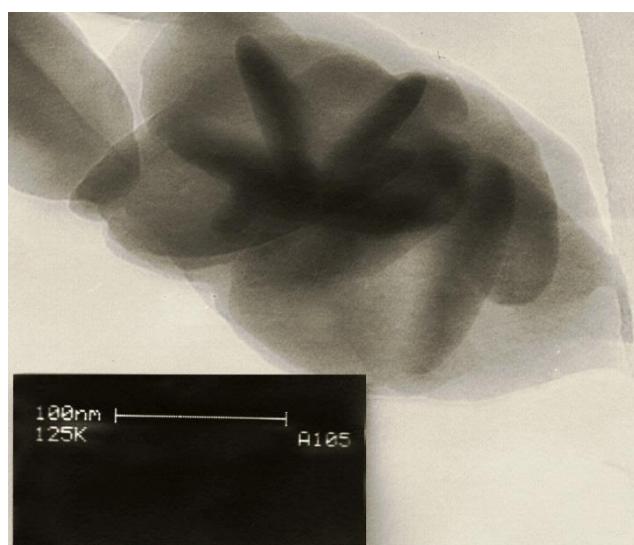


Figure 3: The TEM image of nano sorbent

Extraction analysis

The objective of this report is to develop a simple and sensitive UV-Vis spectrophotometry method for Separation of uranyl ions from aqueous solution. The utilized method in our extraction procedure is simple, sensitive and time consuming without using a lot of solvent can be applied for determination of each ions and molecules. Nano coordination polymer as a sorbent showed the highest efficiency in extraction of uranyl ions and UV-Vis spectrophotometry confirmed the results. In the extraction procedure, the nano sorbent was immersed into the sample solution and then uranyl ions travel from the donor phase to the solid phase. The absorption spectra was recorded. Using a UV-Vis spectrophotometer at a range of 350-500 nm [21-22]. The UV-Vis spectra of uranyl ions before and after extraction are shown in Figure 4.

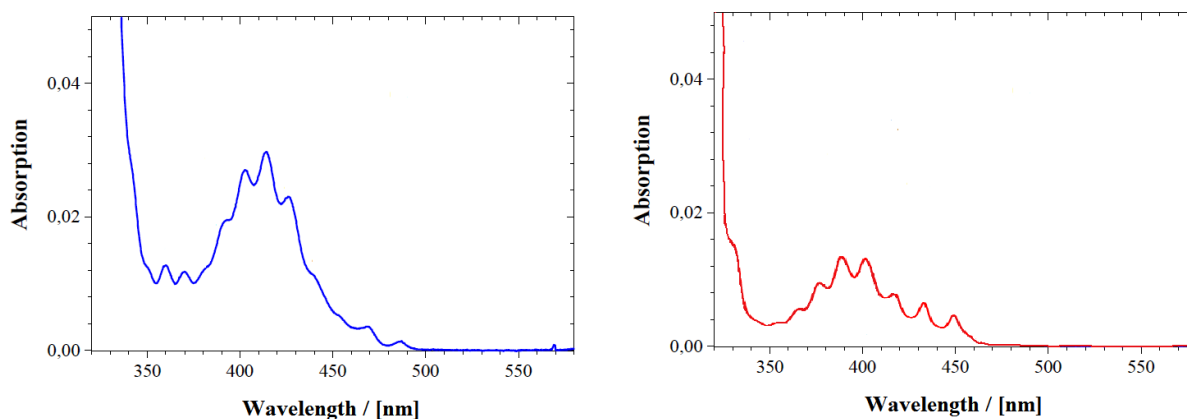


Figure 4: The UV-Vis spectrum of uranyl ions, before extraction (left), after extraction (right)

The golden and main role of this extraction is due to the structure of sorbent as a solid phase for removing of ions. This structure have two-dimensional channel pores (Figure 5) that results from connection between Cd atom and pyrazinecarboxylate molecules. By considering to the intramolecular hydrogen bond and other weak interactions, the structure converts to the three-dimensional supramolecular structure which has a lot of amount of pores (Figure 6). The presence of these channels and regular pores has resulted in efficiency extraction of uranyl ions. Another advantage of this study is to determine the trace amount of uranyl by simple and inexpensive method.

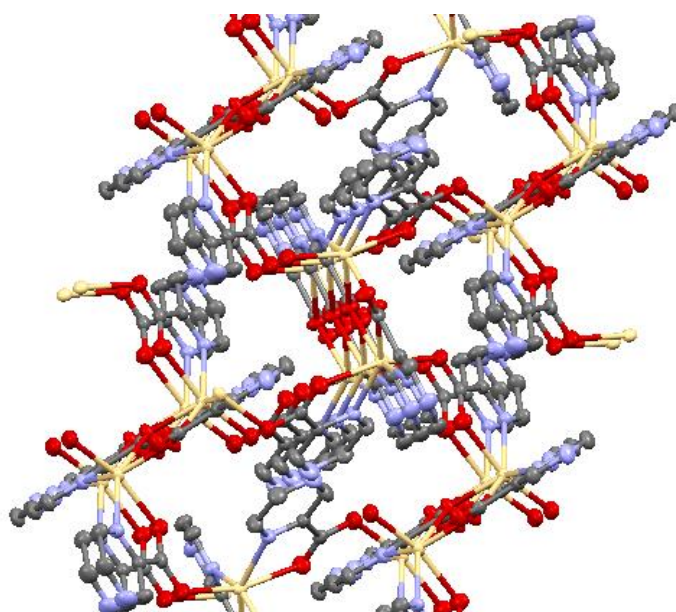


Figure 5: The channel pores of nano sorbent.

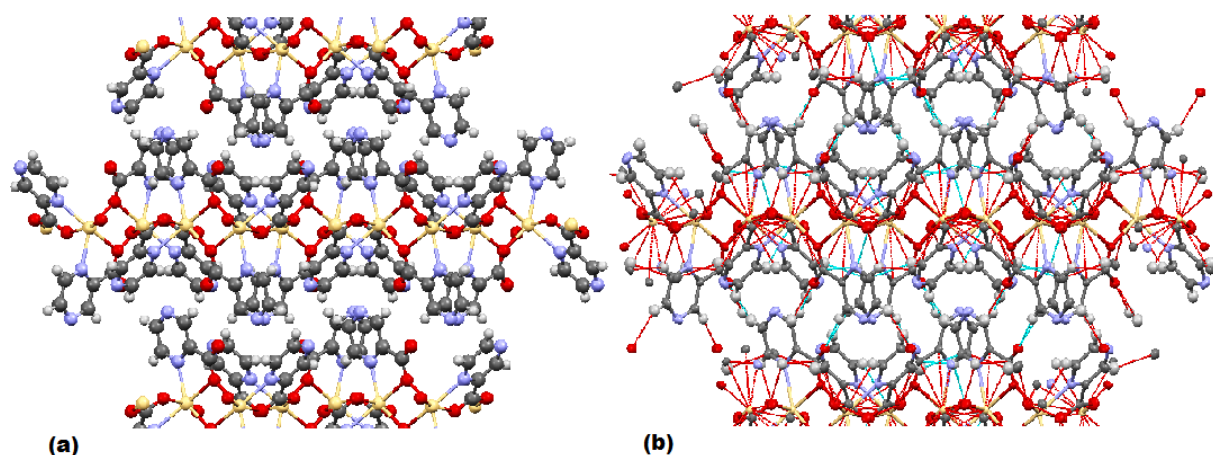


Figure 6: The structure of nano sorbent, Two-dimensional structure (a), three-dimensional structure (b).

CONCLUSION

In this paper we describe a simple synthetic sonochemical preparation of nano sorbent (coordination polymer). This synthesis method has some advantages such as: it takes places in shorter reaction times, better yields, and the producing compounds at nano-size. The structures similarities of nano and the reference compound was confirmed by the PXRD method. This two-dimensional structure nano sorbent was utilized as a unique sorbent for solid phase extraction of uranyl ions from aqueous solution. Monitoring and determination of trace amount of removed uranyl ions was performed by UV-Vis spectrophotometer. This study has also some advantages: such as, using time consuming and simplicity of synthesis and extraction method, inexpensive instrument, and observance of principles of green chemistry.

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