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This paper should be cited as follows:

Elkady, M. and Shokry, H. (2016). **"Nano-tube Zirconium Tungesto-vanadate as Cation Exchanger for Lead Decontamination from Polluted Wastewater",** Athens: ATINER'S Conference Paper Series, No: **CHE2016-2031.**

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URL Conference Papers Series: www.atiner.gr/papers.htm

ISSN: 2241-2891
02/11/2016

Nano-tube Zirconium Tungesto-vanadate as Cation Exchanger for Lead Decontamination from Polluted Wastewater

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Abstract

A unique zirconium tungesto-vanadate cation exchange material was architecture at the nanotube morphological structure using microwave technique in presence of poly vinyl alcohol as stabilizing agent. The prepared cation exchanger was characterized using different physical and chemical techniques. The material characterized by its high surface area is equivalent to 640 m^2/g. The material assigned as an efficient cation exchanger, where, it possess 4.8 meq/g ion exchange capacity. The X-ray diffraction pattern explored its pure crystalline structure. Scanning electron microscope identifies the average aspect ratio of the architecture zirconium tungesto-vanadate nano-tubes as 6.5. The efficiency of the prepared material for lead ions sorption from aqueous solutions was examined using a batch technique. The material poses 97.2% lead ion decontamination within 90 minutes.

Keywords: Cation exchanger; Lead ions, Nanotube architecture, Zirconium tungsto-vanadate.

Acknowledgments: This work was supported by the Egyptian Science and Technology Development fund (STDF) (Grant no. 5546).

Introduction

Reliable access to clean and healthy water is considered one of the most essential human goals, and remains a major global challenge for the 21st century. Heavy metals are widely distributed in the environment as a result of numerous industrial processes such as battery manufacturing, acid metal plating and finishing, painting, dying, leather tanning, lead smelting and metal- finishing industries [1]. The concentration of these metals in waste water may therefore rise to a level that can be hazardous to live stock. Lead is of particular interest because of its toxicity and its widespread presence in the environment [2]. The released Lead ions into the environment may be accumulated in food chain and exist in nature. Lead can cause the severe health hazard even in the trace concentration due to non-biodegradability. For instance, lead is extremely toxic and can damage to the nervous system, kidney, organ, and reproductive system [3]. Moreover it is toxic to human via interaction with the sulfhydryl group of proteins, resulting in disruption of the metabolism and biological activities of many proteins and it also impairs hemoglobin synthesis [3]. The treatment processes for lead ions from wastewater must be selected to remove the existing form of lead. In general, lead is precipitated or otherwise attached to an insoluble form through adsorption or ion exchange. The precipitation process is usually not sufficient to reduce lead concentration to the level required by water quality standard. Recently, it was verified that both adsorption and ion exchange processes represent the most effectiveness techniques for lead decontamination from polluted water and wastewater [4]. Zirconium-based ion exchangers have received attention because of their excellent ion exchange behavior and some important chemical applications in the field of ion exchange and solid state electrochemistry. Accordingly, various hetero-polyacid salts based on zirconium (IV) have been reported as cation exchange materials. Among these hetero-polyacid salts, zirconium tungesto-vanadate nanoparticles as novel material establish its effectiveness for cationic ions decontamination [5, 6]. Accordingly, the goal of this dissertation is to assess the lead decontamination efficiency of novel zirconium tungesto-vanadate fabricated in nano-tube morphological structure using microwave technology.

Materials and Methods

Preparation of Nano-tube Zirconium Tungesto-vanadate

One molar solution from zirconium oxy chloride was mixed with two different solutions from 8 ml ammonium metavanadate and 8 ml sodium tungestate in same molarity in presence of 0.1M high molecular weight poly vinyl alcohol (Mwt= 72000) as a stabilizing agent. This reaction mixture was poured into 100 ml stainless steel closed pressurized vessel and heated at 60ºC in the microwave for 1hour under the reactant vapor pressure. After

completeness the reaction period, the fine yellow precipitate was separated, washed and dried.

Characterization of Prepared Cation Exchange Material

In order to establish the cation exchange capacity of the prepared nano-tube matrix, it was chemically equilibrated with 2M NaCl solution for 48 hours. The resulting solution was titrated against the NaOH solution to determine the amount of exchanged hydrogen ions liberated from the cation exchange matrix. The crystalline structure of the prepared zirconium tungesto-vanadate was elucidated from X-ray diffracted between 2θ range 10-80°C using Schimadzu-7000 diffractometer. Scanning electron microscope (SEM) was defined the material morphological structure after gold sputtering using JEOL JSM 6360LA. The material average surface area was estimated by nitrogen adsorption using Beckman Coulter AS3100, USA.

Batch Technique for Cationic Pollutants Decontamination using Prepared Cation Exchange Material

Firstly, the selectivity of the prepared nano-zirconium tungesto-vanadate was tested toward different cations of lead, cadmium and copper using batch mixing technique. Lead ions were proofed as the most selective metal to be decontaminated onto the prepared zirconium tungesto-vanadate cation exchange material. For all experiments, 0.2g from the prepared matrix was mixed with 80ml from 10ppm synthetic polluted wastewater with different cationic metals in a 100ml closed vial. The vial was shacked using orbital shaker at 400rpm for 3 hours. For lead metal only 1ml sample was withdrawn each 15min to be measured using Atomic Spectrophotometer. The remaining metal concentrations at the different contact time were determined and the decontamination efficiency of the prepared cation exchange material toward cationic metal ions was calculated.

Results and Discussion

Properties of Prepared Nano-zirconium Tungesto-vanadate

In order to assign and define the prepared yellow powder material produced from the microwave technology in presence of PVA as stabilizing agent and under the reactants pressure, XRD pattern of the material was considered. Figure 1 investigated both the physical appearance and the XRD pattern of the prepared matrix. It was indicated that the prepared material has a crystalline structure, where the pattern investigates various peaks with high intensities. The different intense characteristic peaks that are present in the pattern were compared with that in the two references of zirconium oxide phases (Card No. 01-087-1528) and (No. 01-088-0586) in order to determine the plane orientation of the prepared cation exchange material. The comparison identified that the prepared sample is composed from

zirconium tungsten oxide and zirconium vanadium oxide mixture with cubic crystal configurations as evident from Table 1. It was clear from this table that the sample represents a mixture of zirconium tungsten oxide and zirconium vanadium with cubic crystal configurations [7].

Figure 1. *Physical Appearance and XRD Pattern of Zirconium Tungesto-vanadate*

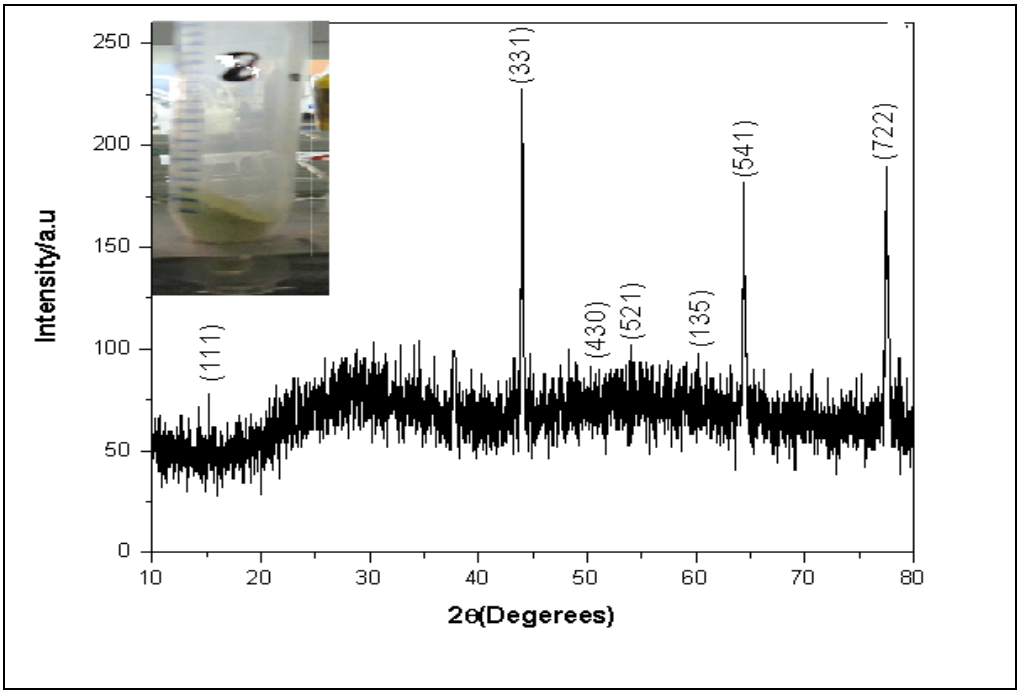


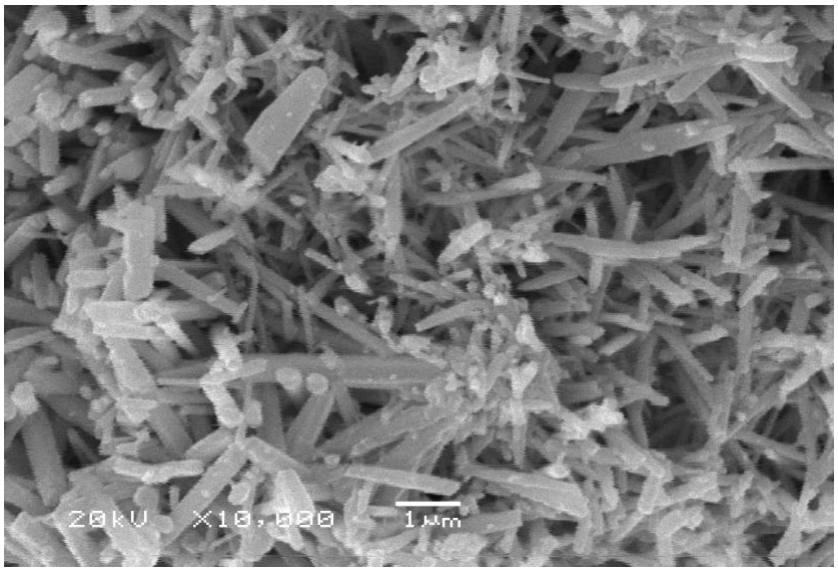
Table 1. *Orientation Planes of Prepared Zirconium Tungesto-vanadate*

Reference	2θ for strain	Plan of orientation
2θ for cubic zirconium tungsten oxide reference (card No. 01-087-1528)		
43.0067	43.1740	(3 3 1)
54.842	54.2545	(5 2 1)
66.0471	65.9729	(5 4 1)
78.8197	78.6726	(7 2 2)
2θ for cubic zirconium vanadium oxide reference (card No. 01-088-0586)		
17.4341	17.7839	(1 1 1)
51.8902	51.6046	(4 3 0)
62.351	62.9232	(1 3 5)

The morphological structure of the prepared zirconium tungesto-vanadate matrix was examining using Scanning electron microscope (SEM). It was evident from Figure 2 that the prepared material has nano-tube morphological structure with an average aspect ratio of 6.5. This morphological structure gives prediction about the high surface area of the prepared matrix that was measured as 640 m^2/g. With respect to the

characteristics surface area of the microwave produced zirconium tungesto-vanadate, it was considered as an efficient cation exchange material. The chemically measured cation exchange capacity of the liberated hydrogen ion from the prepared material that was titrated against sodium hydroxide solution was equivalent to 4.8 meq/g.

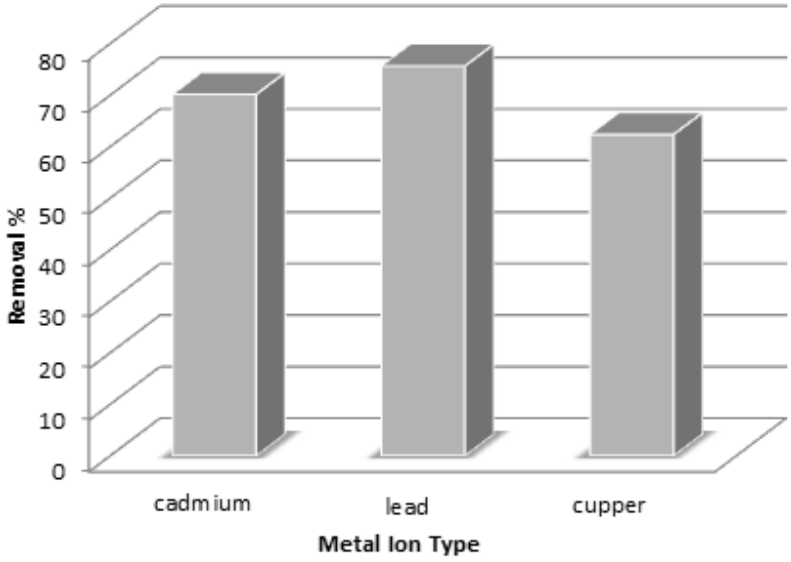
Figure 2. *Scanning Eletron Microscope (SEM) of Zirconium Tungesto-vanadate*



Cation Exchange Performance of Synthetized Nano-zirconium Tungesto-vanadate

In order to evaluate the performance of the prepared nano-zirconium tungesto-vanadate toward the cationic pollutants, its sorption efficiency toward different cations such as copper, lead and cadmium was tested using a batch technique. It was designated from Figure 3 that the material selectivity toward cationic pollutants follows the sequence lead > cadmium > copper. Where, the material poses higher lead removal efficiency that is equivalent to 72% at the specific treatment conditions. Accordingly, this metal ion was considered the most selective ion to be decontaminated from aqueous waste water using the prepared nano-zirconium tungesto-vanadate cation exchange material.

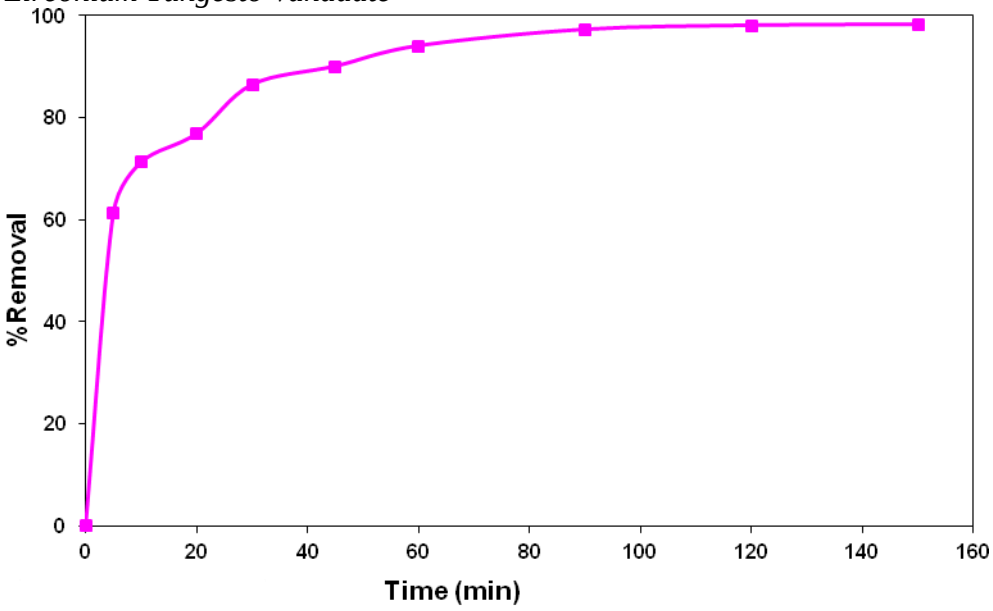
Figure 3. *Cation Exchange Performance of Prepared Zirconium Tungesto-vanadate toward Different Cationic Metals*



Kinetic Profile of Lead Ions Decontamination onto the Prepared Nano-zirconium Tungesto-vanadate

In regard to the comparatively high selectivity of lead ions to be sorbed onto the prepared nano-zirconium tungesto-vanadate matrix, the influence of contact time on the sorption process was examined. It was indicated from Figure 4 that the percentage of lead removal was enhanced as the contact time between the liquid solution and solid matrix improved. Moreover, it can observe that the lead decontamination process is rapid initially, where; large fraction of the total lead amounts was removed within the first few minutes [6]. The linear increment in the lead ions removal period was terminated with the plateau removal period. At this plateau period the amount of adsorbed lead ions onto nano-zirconium tungesto-vanadate was in a state of dynamic equilibrium with the amount of dye desorbed from the nano-material. This behavior may be returned to the availability of a large surface area of nano-zirconium tungesto-vanadate at the beginning of process that was suitable for ion exchange process until it reached to the equilibrium state [8]. The time required to attain the equilibrium state was termed as equilibrium time and the amount of lead adsorption at the equilibrium time reflected the maximum lead adsorption capacity of the prepared nano-zirconium tungesto-vanadate under these particular conditions. The results showed that the equilibrium state for lead sorption process was attained at 90 min.

Figure 4. *Kinetic Profile of Lead Sorption Process onto Prepared Zirconium Tungesto-vanadate*



Conclusions

Nano-tube zirconium tungesto-vanadate cation exchange material was successfully prepared using microwave technology in the presence of poly vinyl alcohol as a stabilizing agent and under reactants vapor pressure. The examination of the material crystalline structure was verifying that prepared material composed from mixture of zirconium tungsten oxide and zirconium vanadium oxide with cubic crystal configurations. The material poses high surface area respecting to its morphological structure that reflected on its performance for cationic metal ions decontamination from wastewater. The prepared material has high lead ions decontamination efficiency compared with both copper and cadmium. The kinetic profile of the most selective cationic pollutants implies the rapid sorption of lead ions onto nano-zirconium tungesto-vanadate that attain its equilibrium state within 90minutes. So, the prepared nano-tube zirconium tungesto-vanadate represents an efficient cation exchange material toward most cationic pollutants presence in waste water.

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