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Fabrication of an Inorganic Nano-Zirconium Tungstovanadate Ion Exchange to be Utilized for Heavy Metal Decontamination

M.F. Elkady[1,2], E.M.EL-Sayed[2], H. A. Farag[3], A. A. Zaatout[3]
[1]Chemical and Petrochemical Engineering Department, Egypt-Japan University of Science and Technology, New Borg El-Arab City, Alexandria, Egypt.
[2]Fabrication Technology Department, Advanced Technology and New Materials Research Institute (ATNMRI), City for Scientific Research and Technology Applications, Previously "Mubarak City for Scientific Research and Technology Applications (MuCSAT)", Alexandria, Egypt.
[3] Chemical Engineering Department, Faculty of Engineering, Alexandria University, Alexandria, Egypt.
*Corresponding author: E-mail: maroelkady @yahoo.com
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Abstract: *An innovative heteropolyacid salt of ion exchanger, nano-zirconium tungstovanadate has been synthesized under varying conditions using sol–gel technique. The different synthesized ion exchange materials were compared based on both their ion exchange capacity (IEC) and their efficiency in separating lead ions from aqueous streams by conducting batch experiments with a batch factor of 50ml/g. Nano- zirconium tungstovanadate prepared from the reaction of 0.2 M zirconium oxychloride, 0.2M ammonium metavanadate and 0.1 M sodium tungstate in presence of 0.01 M HCl at room temperature was record the highest IEC value that equal to 1.5 mequiv/g. Structural characterization of this most proper ion exchanger was performed with powder X-ray diffraction (XRD), thermogravimetry (TGA), scanning electron microscopy (SEM) equipped with energy dispersive spectrometer (EDS) and with inductively coupled plasma optical emission spectrometry (ICP-OES). The X-ray spectrum of the prepared material suggested that of Zr (IV) tungstovanadate is crystalline in nature with average crystallite size between19 and 37 nm. The SEM result confirmed that the ion exchanger was produced in nano-scale with average particle diameter equal to 28 nm . Good thermal and chemical stabilities have also been observed for the prepared nano-zirconium tungstovanadate. On the basis of these results, the prepared nano-zirconium tungstovanadate is a promising cation exchanger for lead ion decontamination from the polluted water in view of the fact that lead ion removal rate was recorded up to 99.24 % within 3hours.*

Keywords: *nano-zirconium tungstovanadate; sol-gel technique; equilibrium isotherm; Lead ion separation.*

Introduction

The presence of heavy metals in the environment can be detrimental to all living organisms including humans. This pollution originates from discharge effluents from industries such as cement industries, electro plating, production of metal alloys, production of pigments for paints, mining, etc. The removal of toxic heavy metal contaminants from aqueous waste streams is currently one of the most important environmental issues being researched as their toxic nature, even at trace levels in natural waters, has been a public health problem (Gode. & Pehlivan, 2003). Although this issue has been studied for many years, effective treatment options are still limited. Chemical precipitation, adsorption, reverse osmosis and ion exchange processes are the most commonly techniques utilized for removing heavy metals ions from dilute aqueous streams (Shaidan, etal, 2012).. Lead is one of the most dangerous pollutants; even at low concentrations is extremely toxic, causing brain damage in children (Jang, etal, 2008). The ion exchange separation technique characterize over the other separation techniques by its simplicity, cheap and no energy consumable.

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Accordingly, the ion exchange process represents the most suitable technique for lead ion separation from polluted wastewaters. There are various types of ion exchange materials that are suitable to be utilized for the ion exchange process either from the organic or inorganic nature. Synthetic inorganic ion exchangers have gained much attention owing to their high selectivity for certain elements, good kinetics of sorption, good selectivity and specially their greater stability to heat, ionizing radiation doses and acidic to moderately alkaline medium compared with the organic ion exchangers. Most investigations have been concerned with the use of these materials in the separation and removal of heavy toxic metal ions from industrial wastewater (Gupta, etal, 2000). The heteropolyacid salts of polyvalent metals are of great interest because of their ion exchange character, as they are superior to single insoluble salts of these metals. It is possible to vary their compositions and change their selectivity to a particular ion. Thus the ion exchange behaviour, analytical application and synthesis of several zirconium based materials have been extensively studied. These inorganic ion exchangers were found to show relatively increased ion exchange capacity, selectivity and played a prominent role in water processing in the chemical and nuclear industries (Sharma, 2011; Shehaa & El-Khouly, 2013). In this regard an inorganic heteropoly acid salt of zirconium based compound will be synthetized in nano-scale using the sol gel preparation technique. This investigation will be deal with optimization of the different factors that affect the nano-zirconium tungstovanadate properties to attain nano powder ion exchanger with high IEC with high lead ion sorption affinity. Moreover, the influence of the different parameters affecting the lead ion sorption process onto the prepared cation exchanger will be monitored. Finally, the equilibrium lead ions sorption data will be modelled as an attempt to determine the sorption process mechanism.

Materials and Methods

Materials and reagents

Zirconium oxychloride [$ZrOCl_2.8H_2O$, Germany], ammonium metavanadate [India] and Sodium tungstate [$Na_2WO_4.2H_2O$, India] have been used as the raw precursors for nano-zirconium(IV) tungstovanadate synthesis. Various reaction solutions from these materials have been prepared in de-mineralized water (DMW) to be reacted. All other utilized materials/reagents were mainly of analytical grade.

Synthesis of ion exchange material using Sol-gel technique

The sol–gel technique represents one of the fastest growing fields of contemporary chemistry. The attractive feature of this technology is the fact that sol–gel materials can be obtained as bulks, thin films (on various supports) and (nano) powders. Thus, Different samples from zirconium tungstovanadate cation exchanger will be prepared using the sol-gel technique. Zirconium (IV) tungstovanadate was synthesized through the addition of 50 ml ammonium metavanadate and 50 ml sodium tungstate into 150 ml zirconium oxy chloride solution in different molar ratios in presence of HCl gradually with continuous stirring in order to get a stable product with good ion exchange properties. After the addition was complete a fine yellow precipitate powder was appeared. The reaction mixture was diluted to 1 L and allowed to settle for 24 h for complete digestion (Abd El-Latif & El-Kady, 2008). The supernatant liquid was decanted and gels were filtered by suction and the excess acid was washed thoroughly with hot water. The washed precipitate was then dried by gentle heating at 40 ºC. Then the product is grounded and immersed in 1 M nitric acid for 1 day with gentle stirring in order to transform the ion exchanger to its hydrogen form. In order to optimize the preparation conditions of zirconium(IV) tungstovanadate using sol gel technique, the effect of hydrochloric acid concentration (0 –0.5 M), gelation temperature (25–80 ºC) and molar ratio of the reactants were studied. The different prepared samples from the ion exchanger will be screened on the basis of Na^+ ion exchange capacity and lead ions separation affinity, and then the best sample will be selected to be fully characterized and utilized for optimizing the ion exchange process conditions.

Chemical characterization of the prepared nano-zirconium tungstovanadate ion exchangers

Ion-exchange capacity (IEC)

To determine the ion-exchange capacity, which generally taken as a measure of the hydrogen ion liberation by neutral salt, The ion exchange capacities of different prepared ion exchangers were determined by acid ‑ base titration (Roy,2004).]. The weighted sample of the ion exchanger in its H^+ form were soaked in 50 mL of 1 M NaCl solution for at least 12 h with shaking at ambient temperature to exchange protons with sodium ions. The ion exchanged was titrated against a standard solution of 0.1M NaOH using phenolphthalein as indicator. The ion exchange capacity (IEC) was calculated using the following equation:

$$\text{IEC (mequiv/g)} = V_{NaOH} * \frac{C_{NaoH}}{W_d} \qquad (1)$$

Where; V_{NaOH}, C_{NaOH} and W_d are the volume of NaOH consumed in titration, the concentration of NaOH solution, and the weight of the dry sample, respectively.

Ion Exchange Capacity for Different Metal Ions:

The ion exchange capacity of prepared nano zirconium tungstovanadate for alkali and alkaline earth metal ions was determined by equilibrating 0.25 g of the exchanger with 50 ml from 2 M solution of different metal salts. The liberated acid was measured by titration with standard alkali solution.

Thermal effect on IEC

The effect of temperature on the ion exchange capacity of the most efficient prepared nano-zirconium tungstovanadate was determined by heating a 0.5 g from the ion exchange material at various temperatures in muffle furnace for 1 h. The Na^+ ion exchange capacity after cooling the samples at room temperature was determined as mentioned in the ion exchange capacity technique (Inamuddin, etal, 2007).

Chemical stability

The extent of dissolution of the material in common mineral acids (HCl, HNO_3 and H_2SO_4), bases (NaOH and KOH) and organic solvents (acetone, benzene, diethyl ether, heptane, acetic acid and alcohol) was studied. 0.5 g of ion exchanger was equilibrated with 20 ml of the solution of interest for 24 h at room temperature; the remaining amount of material was filtered and washed by DMW. After removal of the remaining excess solvents, the sample w dried in oven at 40±5 ºC. The changes in color, weight and the ion exchange capacity of the remaining material were observed.

Physical characterization of the differed prepared zirconium(IV) tungstovanadate ion exchangers

X-ray diffraction (XRD)

X-ray diffraction pattern of the best prepared ion-exchange material was recorded by X-ray diffractometer with Cu Ka radiation beam (l = 0.154060 nm) to determine the structure of the ion exchanger material. Where the finely powdered sample of the ion exchanger was packed into a flat aluminium holder, and the X-ray source was a rotating anode operating at 30 kV and 30 mA with a copper target. Data were collected between 10º and 80º in 2θ.

Thermal analysis (TGA)

The measurements of the thermal analysis of the best prepared sample were carried out using thermal gravimetric analysis (TGA) with a heating rate 20 ºC/min under flow of N_2 to avoid thermal oxidation of the powder samples, starting from ambient condition up to 700 ºC.

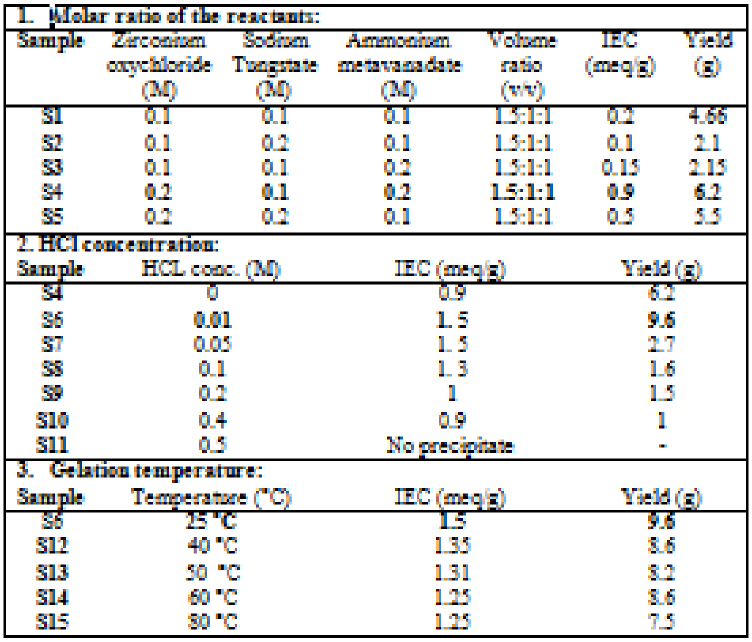
Infrared spectroscopy (FTIR)

The I.R. spectrum of the best prepared ion exchanger was examined. The disc technique using KBr as a matrix was found to be suitable. In this concern, the ion exchanger was thoroughly mixed with KBr and the mixture was ground and then pressed with a special press to give a disc of standard diameter. The I.R. spectrum was scanned through a wave length range of 600 – 4000 cm^{-1}.

Scanning electron microscope (SEM)

The grounded prepared sample was scanned to identify their structure and estimate the particle diameter at different magnifications.

The mean diameter of the grains was determined from the SEM pictures by measuring at least 5 crystals for each formulation using the software Image tool.



1. Molar ratio of the reactants:

Sample	Zirconium oxychloride (M)	Sodium Tungstate (M)	Ammonium metavanadate (M)	Volume ratio (v/v)	IEC (meq/g)	Yield (g)
S1	0.1	0.1	0.1	1.5:1:1	0.2	4.66
S2	0.1	0.2	0.1	1.5:1:1	0.1	2.1
S3	0.1	0.1	0.2	1.5:1:1	0.15	2.15
S4	0.2	0.1	0.2	1.5:1:1	0.9	6.2
S5	0.2	0.2	0.1	1.5:1:1	0.5	5.5

2. HCl concentration:

Sample	HCL conc. (M)	IEC (meq/g)	Yield (g)
S4	0	0.9	6.2
S6	0.01	1. 5	9.6
S7	0.05	1. 5	2.7
S8	0.1	1. 3	1.6
S9	0.2	1	1.5
S10	0.4	0.9	1
S11	0.5	No precipitate	-

3. Gelation temperature:

Sample	Temperature (°C)	IEC (meq/g)	Yield (g)
S6	25 °C	1.5	9.6
S12	40 °C	1.35	8.6
S13	50 °C	1.31	8.2
S14	60 °C	1.25	8.6
S15	80 °C	1.25	7.5

Lead ion sorption affinity

The ion exchange efficiency of the prepared samples toward lead ions was tested. The ion exchange efficiency was determined by equilibrating 0.25 g of the prepared cation exchange sample of zirconium(IV) tungstovanadate in H^+ form with 100 ml of 50 ppm lead ion solution for 3 h with continuous shaking.

The removal efficiency is expressed as:

$$\eta = \frac{(Ci-Ce)}{Ci} * 100 \qquad (1)$$

Where, C_i is the initial metal ion concentration (ppm) and C_e is the concentration of metal ions (ppm) at equilibrium.

Batch procedure for ion exchange technique:

The experiments were conducted in batch mode using synthesized wastewater which was prepared initially, where lead chloride ($PbCl_2.5H_2O$) was dissolved in distilled water to obtain the required waste solution concentration that contaminated with lead ions. 0.25 g ion exchange material was shacked with 100 ml of a metal solution in different stopper graduated glass bottles. The bottles were shaken for different time intervals using shaking incubator. These experiments were carried out to validate the effect of contact time (0-4 hr), waste solution pH (2–12), waste solution temperature (25–80 °C), mixing speed (0–400 rpm), initial concentration of the synthesis waste solution (5–1000 ppm), and the amount of ion exchanger (0.1 –5 g) on the ion exchange process using the most proper synthetized ion exchanger.

The experiments carried out through mixing a certain amount of ion exchanger in the H^+ form in a vial with the test solution (typically 100 ml) spiked with waste solution. The samples were mixed in shaking incubator till the solid/ solution system obtained equilibrium after 3 h. Then the different phases are separated using centrifugation at 6000 rpm for 10min. The residual lead ion concentration in the solution was analyzed using inductive coupled plasma mass spectrophotometer (ICP-AES, USA). All experiments were carried out in duplicate and mean values are presented. The lead ion measurements onto the ICP equipment were repeated three times to obtain an accurate lead ion concentration. The percentage error in the measurement of lead ion concentration is ±0.1. The mean lead concentration values in the remaining waste solution were obtained and used for calculation the percentage ions removal onto the prepared nano-cation exchange sample as mentioned before from equation (2). The sorption capacity of the prepared material was calculated using following formula:

$$q_e = \frac{(Co - Ce)V}{m} \quad (2)$$

where; qe (mg/g) is the equilibrium adsorption capacity, C_o and C_e (mg/L) are the initial and equilibrium concentration of lead ions in solution, V (L) is the solution volume, and m(g) is the amount of the cation exchanger.

Equilibrium Isotherm modelling for the ion exchange process

Sorption isotherms are basic requirements for designing any sorption system. The sorption isotherm is fundamental in the understanding of sorption processes since equilibrium studies the capacity of the synthesized nano- zirconium(IV) tungstovanadate and indicate the affinity of the prepared material toward lead ions. This isotherm provides a relationship between the concentration of lead ion in the waste solution and the amount of ions sorbed onto the ion exchange material when the two phases were at a fixed temperature at equilibrium. The Langmuir and Freundlich equilibrium isotherms models were examined to fit the experimental data. The sorption data obtained for equilibrium conditions have been analyzed using the linear forms of these kinds of isotherms.

Results and Discussion

Different factors that affecting the preparation process are optimized to attain heteropoly acid cation exchanger of nano-zirconium tungstovanadate that characterized by its high IEC and prepared in nano-scale. The various synthetized samples of this innovative cation exchanger that produced using sol-gel technique under varying conditions are investigated in table (1). It was obvious from this table that sample S6 recorded the highest production yield and the maximum ion exchange capacity. In contrast to sample S2 that attains the minimum IEC. The efficiency of these prepared samples for heavy metal sorption was tested toward lead ion removal and the results are investigated in figure (1). These results have been used to confirm the ion-exchange capacities values that have been calculated previously for each prepared ion exchange sample (table 1).

1. Molar ratio of the reactants:						
Sample	**Zirconium oxychloride (M)**	**Sodium Tungstate (M)**	**Ammonium metavanadate (M)**	**Volume ratio (v/v)**	**IEC (meq/g)**	**Yield (g)**
S1	0.1	0.1	0.1	1.5:1:1	0.2	4.66
S2	0.1	0.2	0.1	1.5:1:1	0.1	2.1
S3	0.1	0.1	0.2	1.5:1:1	0.15	2.15
S4	**0.2**	**0.1**	**0.2**	**1.5:1:1**	**0.9**	**6.2**
S5	0.2	0.2	0.1	1.5:1:1	0.5	5.5
2. HCl concentration:						
Sample	**HCL conc. (M)**		**IEC (meq/g)**			**Yield (g)**
S4	0		0.9			6.2
S6	**0.01**		**1. 5**			**9.6**
S7	0.05		1. 5			2.7
S8	0.1		1. 3			1.6
S9	0.2		1			1.5
S10	0.4		0.9			1
S11	0.5		No precipitate			-
3. Gelation temperature:						
Sample	**Temperature (°C)**		**IEC (meq/g)**			**Yield (g)**
S6	25 °C		1.5			9.6
S12	40 °C		1.35			8.6
S13	50 °C		1.31			8.2
S14	60 °C		1.25			8.6
S15	80 °C		1.25			7.5

Table1: Effect of synthesis parameters on the ion-exchange capacity (IEC) of zirconium tungstovanadate

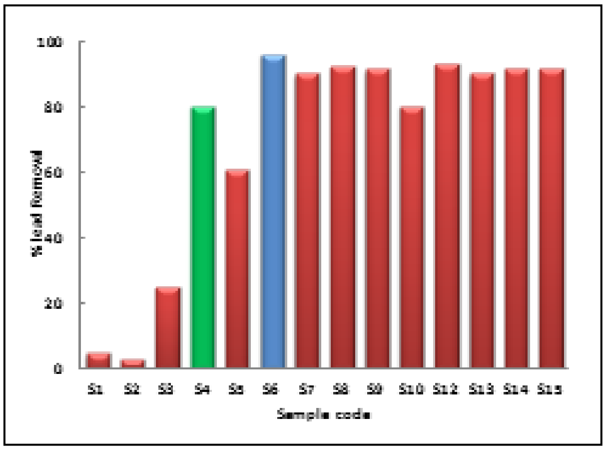


Figure (1): % lead ion sorption using the different prepared samples produced from sol–gel technique.

Effect of reactants molar ratio:

The reactants molar ratio affected the ion-exchange capacity of the prepared materials as seen in table (1). It was obvious that the increment in zirconium and vanadate concentration in the reaction mixture enhance the ion-exchange capacity of the prepared material compared with the increase in tungstate ion concentration that has no effect on the IEC for the prepared material. The EDX and ICP analysis of sample S4 that represent the most proper cation exchanger prepared sample investigate its chemical composition and tabulated in table (2). It is clear from this table that the ratio of anionic part represented by vanadate and tungstate ions in the ion exchanger is higher than that of cationic part represented by zirconium ions, this result confirm that the anionic part in the prepared ion exchange material is the responsible for the ion exchange process inside the ion exchanger rather than the cationic part (Nabi, etal, 2007). Accordingly, this prepared ion, exchanger characterized by its high ion exchange value, where, the replacement H^+ ion inside the ion exchanger is associated with the anionic groups rather than cationic one.

Table 2: The molar composition of the prepared Zr (IV) tungstovanadate

Sample	Preparation molar ratio (Zr:V:W)	EDX analysis (Zr:V:W)	ICP analysis (Zr:V:W)
S4	(2:2:1)	(2: 1.8: 0.6)	(2: 1.7: 0.6)
S5	(2:1:2)	(2: 1: 0.4)	(2: 1.1: 0.5)

The sorption efficiency of the prepared materials was tested toward lead ions removal from synthetic wastewater. Sample S4 which has the highest IEC achieved the highest lead percentage removal compared to the other prepared samples as indicated in figure (1). This may be returned to that sample S4 has the highest number of H+ ions that represent the possible replacement sites inside its structure and that can be exchanged by lead ions. Consequently, on the basis of higher production yield, ion exchange capacity, and higher affinity for lead ions sorption compared to others prepared samples, so the reactant molar ratio that produce sample S4 was utilized to optimize the remaining preparation parameters.

Effect of hydrochloric acid concentration

Various samples of zirconium tungstovanadate ion exchanger were prepared using the predetermined optimum conditions of 0.2 M ZrOCl2, 0.2 M ammonium metavanadate and 0.1M sodium tungstate at different hydrochloric acid concentrations. The ion exchange capacities of the different prepared samples were tabulated in table (1). It was evident from this table that the ion exchange capacity of the produced ion exchangers affected by HCl concentration present in the preparation media. The highest IEC value was recorded using 0.01M HCl (sample S6), this may be due to the presence of HCl contributed in increasing the replacement hydrogen ions that present inside the produced ion exchangers structure, which are the main responsible for the exchange process inside the ion exchanger. While, further increment in acid morality than 0.01M was decline the ion exchange capacity of the prepared material until 0.5 M, when no precipitate has been formed. This may be due to the increase in the acid concentration in the reaction media dissolve some of the formed ion exchanger until 0.5 M, all produced exchanger powder materials has been dissolved immediately as formed (Abd El-Latif, etal, 2008).

The results obtained from testing the ion exchange efficiency of the prepared materials toward lead ions sorption are given in figure (1), which indicated that sample S6 attained the highest % lead sorption compared to the others. This may be returned to its relatively high contents of replacement hydrogen ions which are responsible for the exchange process compared with the remaining prepared ion exchangers. Finally, preparation parameters that produce sample S6 which achieved the highest lead ions % sorption capacity and recorded the largest IEC has been selected to optimize the remaining preparation conditions.

Effect of gelation temperature:

The effect of gelation temperature was determined using 0.2 M ZrOCl2, 0.2 M ammonium metavanadate and 0.1 M sodium tungstate in presence of 0.01M HCl at different temperatures. Table (1) investigated that the IEC of the prepared materials decreases with increasing gelation temperature. Where, the increment in the reaction temperature evaporates water from the reaction media that decreases the presence possibility of replacement hydrogen ions inside the exchanger which are responsible for the exchange process, accordingly decreases their IEC. So, the achievement of the sol-gel production process at mild temperatures is favourable to produce ion exchange material with high IEC. Finally, after studying the preparation parameters using sol-gel technique, sample S6 that record the highest IEC (1.5 meq/g), the best production yield and the highest lead percentage removal which produced from the reaction of 0.2 M ZrOCl2, 0.01 M HCl, 0.1 M sodium tungstate and 0.2 M ammonium metavanadate at 25 ºC was selected as the most proper prepared ion exchange sample produced from sol-gel technique to be fully characterized.

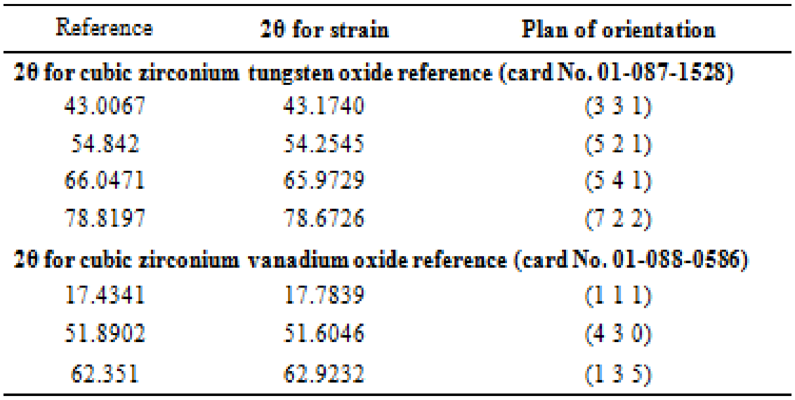
Chemical characterization:

The best prepared sample was chemically characterized in terms of its chemical composition, in addition to its chemical and thermal stabilities.

Thermal effects on ion exchange capacity:

Ion-exchange capacity of the prepared material was affected by heating. On heating at different temperatures for 1 h, the mass, physical appearance and ion-exchange capacity of the best prepared Zr(IV) tungstovanadate was changed as given in Table (3). One interesting property of nano-Zr (IV) tungstovanadate distinguishes by its thermal stability as the heating temperature incremented up to 700 ◦C.

Table 3: Effect of temperature on the ion-exchange capacity of Zr (IV) tungstovanadate on heating time for 1 h.



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)

Chemical stability of cation exchanger:

Results showing the extent of dissolution of the prepared materials in different solutions are given in table (4). It is clear from that the prepared zirconium tungstovanadate exchangers is quite stable in water, organic solvents, alkalies and fairly stable in acids of low concentration and bases whereas it is less stable in strong acids. This solubility experiments showed that the prepared material is highly chemically stable.

Table 4: Solubility of Zr(IV) tungstovanadate in various solvents (0.5 g of the material was initially taken for the treatment).

Heating temperature (°C)	Appearance	IEC for Na^+ ion (mequiv.g^{-1})	% loss in IEC
50	yellow	1.5	0
100	yellow	1.45	3
200	yellow	1.39	7
400	yellow	1.25	16.7
500	Dark yellow	1.15	23
600	Dark yellow	1.0	33
700	Greenish yellow	0.92	38.7

Physical characterization:

The X-ray diffraction pattern of the best prepared sample (S6) is shown in Figure (6). The X-ray diffraction spectrum shows a number of peaks at different 2θ values. The relatively sharp peaks intensities of these signals suggested that the nature of the prepared nano-Zr(IV) tungstovanadate is crystalline. The different intense peaks presented in the sample 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 cation exchange sample produced (Table 5). It was clear from the table that the produced sample represents a mixture of zirconium tungsten oxide and zirconium vanadium oxide with cubic crystal configurations.

Figure (2): X-ray curve for Zirconium tungstovanadate.

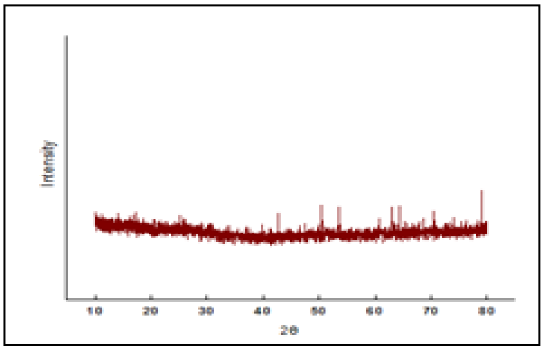
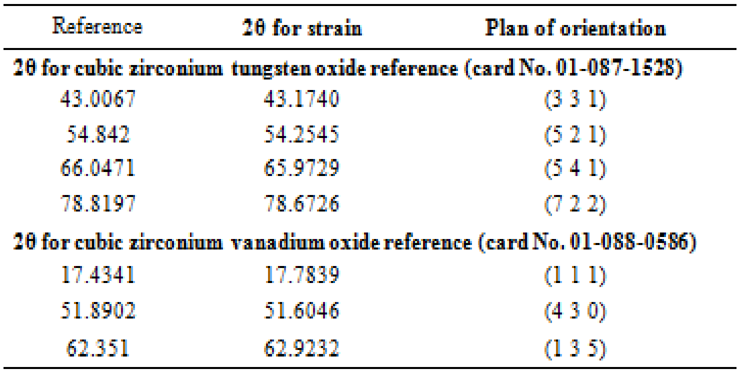


Table (5): X-ray peak values for two reference phases.



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51.8902	51.6046	(4 3 0)
62.351	62.9232	(1 3 5)

According to the TGA analysis given in figure (3), patterns of the prepared zirconium tungstovanadate sample show two main weight losses or degradation regions. The first weight loss region that terminated around 140 ºC may be due to the free external water molecules removal (Yavari, etal, 2009). While, the second gradual loss in the samples weight that began from temperatures above 370 ºC is due to the removal of interstitial water molecules by condensation of exchangeable hydroxyl groups(–OH) from the material, which is characteristic of synthetic inorganic ion exchangers. Above 450 ºC there is no significant degradation, which means that no structural changes can occur for the materials. This suggests that the prepared the ion exchanger is stable up to 800 ºC.

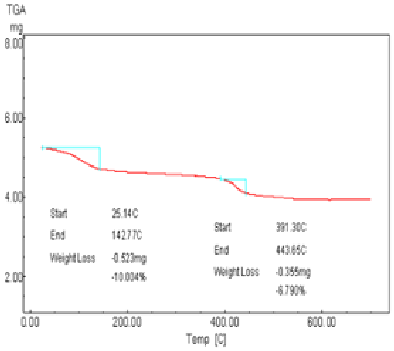
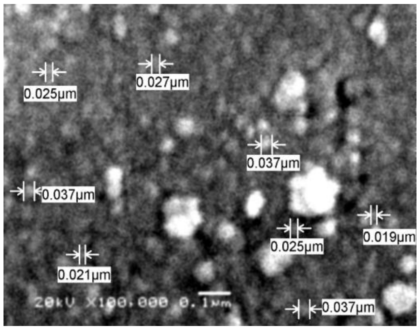
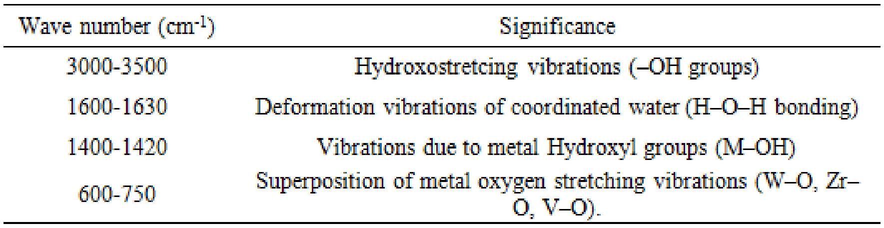


Figure (3): TGA curve for nano-Zirconium tungstovanadate.

Morphological characterization of the prepared cation exchanger zirconium tungstovanadate was performed using SEM. Figure (4) indicates that the selected optimum prepared sample shows average particle size diameter equal to 0.028 nm. Thus, all the prepared materials particle size produced in the nano-range.

Figure 4: SEM micrograph of prepared Zirconium tungstovanadate.





Wave number (cm^{-1})	Significance
3000-3500	Hydroxostretcing vibrations (–OH groups)
1600-1630	Deformation vibrations of coordinated water (H–O–H bonding)
1400-1420	Vibrations due to metal Hydroxyl groups (M–OH)
600-750	Superposition of metal oxygen stretching vibrations (W–O, Zr–O, V–O).

The FTIR spectra of the selected cation exchange zirconium tungstovanadate sample showed in figure (5). The analysis of its absorption peaks investigated in table (6). The appearance of the peaks has been designated accordingly (Miller & Wilkins, 1952). This analysis assign the presence of structural H-OH that is responsible mainly for the exchangeable H+ ion inside the prepared nano-cation exchange sample. Moreover, it was confirmed from the characteristics peaks analysis that the materials composed mainly from a mixture of zirconium tungsten oxide and zirconium vanadium oxide as stated previously at XRD section.

Figure (5):FTIR spectra of Zr(IV) tungstovanadate cation exchanger.

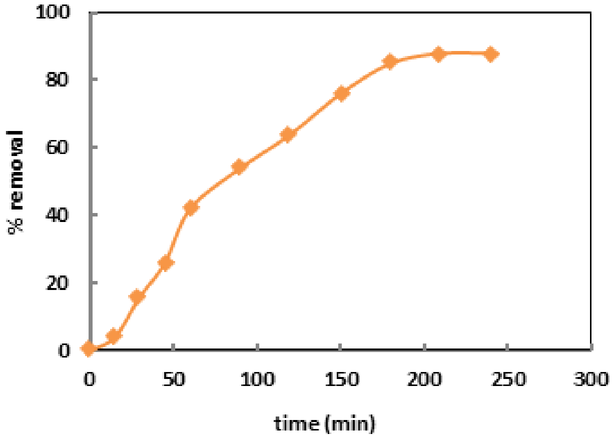


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Table (6): Details of IR spectrum of nano-zirconium tungstovanadate

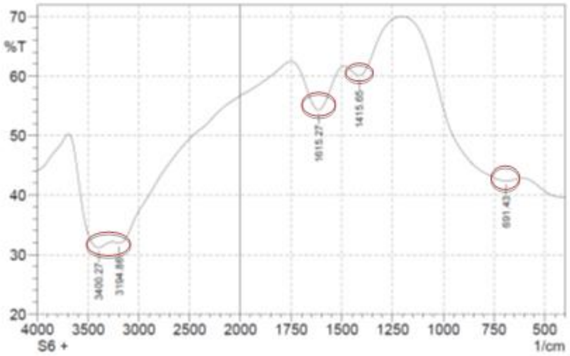
Wave number (cm^{-1})	Significance
3000-3500	Hydroxostretcing vibrations (–OH groups)
1600-1630	Deformation vibrations of coordinated water (H–O–H bonding)
1400-1420	Vibrations due to metal Hydroxyl groups (M–OH)
600-750	Superposition of metal oxygen stretching vibrations (W–O, Zr–O, V–O).

Batch experiments for lead ion separation:

Effect of contact time

The effect of contact time on the lead ions sorption onto nano-zirconium tungstovanadate was investigated in Figure (6). This figure elucidated that the percentage lead removal increases with contact time and attains equilibrium within 3 hr, this effect has arisen from the fact that heavy metal-zirconium tungstovanadate interaction is a dynamic process and the amount of metal uptake is a function of time (Ho & McKay, 2000). Thus, 3 hr is chosen as the reaction time required for equilibrium achievement for the lead ion sorption process.

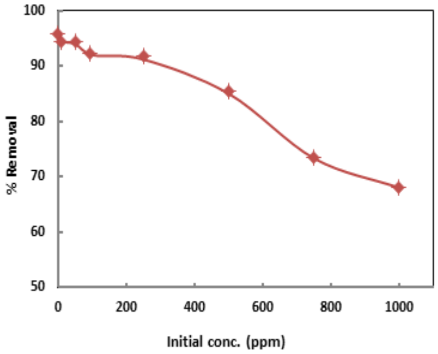
Figure (6): Effect of contact time on the sorption of pb^{2+} by zirconium tungstovanadate (initial lead conc. = 500 ppm; resin dose = 0.25 g; solution volume, 100 ml, temperature = 25±2 °C; Agitation speed = 200 rpm; pH = 7).



Effect of ion exchanger dose

The exchanger amount is an essential parameter to obtain the quantitative uptake of metal ion. Different amount of the ion exchanger were tested in the range of (0.1 – 5 g) and equilibrated for 3 h at an initial lead concentration of 500 ppm, all experiments were carried out at the same stirring speed, 200 rpm. The lead ion removal results are given in Figure (7). It is apparent that sorption of lead ions was increased as the utilized cation exchange amount improved. This result was expected because for a fixed initial metal concentration, increasing adsorbent amount provides greater surface area and sorption sites for metal ions uptake that by its role enhance the metal ion removal (Ho, 2000; Alyüz, & Veli, 2009). It is readily understood that the number of available sorption sites increases by increasing the cation exchanger amount. From figure (7) it was investigated that the optimum cation exchanger dosage is 2gm that recorded percentage lead ion removal greater than 97%.

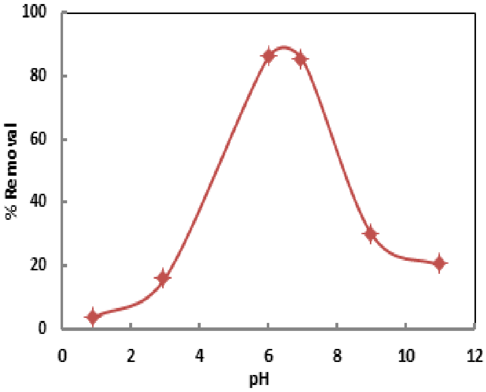
Figure (7): Effect of cation exchange dosage on the sorption of Pb^{2+} ions (initial lead concentration = 500 ppm; solution volume = 100 ml, temperature = 25±2 ◦C; Agitation speed = 200 rpm; pH = 7).



Effect of waste-solution pH

Hydronium ion concentration is an important parameter affecting the ion-exchange process. This is partly because hydrogen ions themselves are strongly competing adsorbate. In order to investigate the effect of pH on lead removal using the prepared nano-zirconium, experiments were performed in the pH range (1–11). As seen from Figure (9) optimal uptake of Pb^{2+} was occurred at pH range of 6-7. At high pH values, decrease in removal efficiency achieved by nano-zirconium tungstovanadate can be described with formation of $Pb(OH)_2$ during reaction of Pb^{2+} ions with OH^-. In this state, hydrolysis accompanied by precipitation of metal hydroxides may occur (Alyüz, & Veli, 2009). However, at low pH values, the decrease in lead ion removal may be returned to the competition of H^+ ions with Pb^{2+} in the ion exchange process onto the prepared cation exchanger.

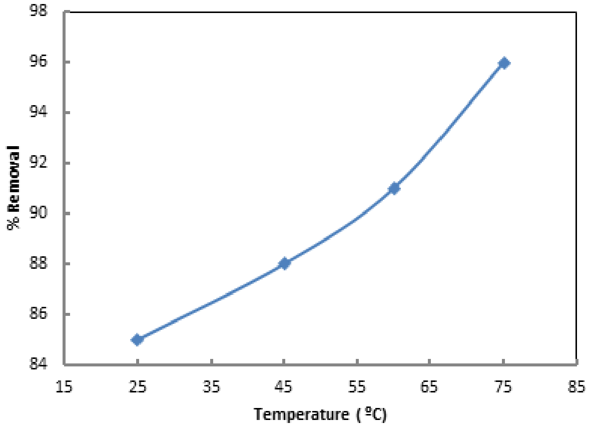
Figure (9): Effect of initial solution pH on the ion exchange of Pb^{2+} ions (exchanger dosage = 0.25 g; solution volume =100 ml, temperature = 25±1 ◦C; Agitation speed = 200 rpm; initial lead conc. = 500 ppm).



Effect of solution temperature:

The effect of temperature on the ion exchange process is important not only because it affects the rate and extent of sorption but also due to the fact that temperature dependence of sorption provides information about possible sorbate–sorbent interaction (Naseem& Tahir, 2001). In the temperature range of 25–80 °C, the percentage removal of the prepared inorganic ion exchanger for the lead ions was determined. From figure (10) it is clear that lead ions removal from the aqueous solution increases with raising temperature. It may be returned to that higher temperatures activate the lead ions for enhancing sorption at the coordinating sites of nano-cation exchanger. Also, it is mentioned that cations move faster when temperature increases. Potential explanations for this are that specific or electrostatic interactions become weaker and the ions become smaller, since solvation is reduced (Gode, & Pehlivan, 2005). This result indicates that the ion exchange process is an endothermic process onto the prepared nano-zirconium tungstovanadate.

Figure10: Effect of solution temperature on lead removal at equilibrium using the prepared cation exchanger (initial lead conc. = 500 ppm, ion exchanger dosage = 0.25 g, agitation time = 3 h, agitation speed = 200 rpm, solution volume = 100 ml, and pH=7).



Equilibrium isotherm modelling:

Results obtained for lead ions sorption using the prepared nano-zirconium tungstovanadate were analyzed with well-known adsorption models, Langmuir and Freundlich.

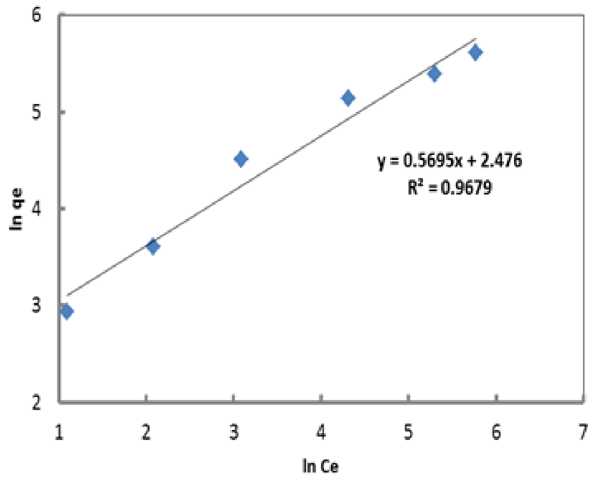
Langmuir model:

The Langmuir isotherm is a commonly applied model for adsorption on a completely homogenous surface with negligible interaction between adsorbed molecules (Gode & Pehlivan, 2005). The model assumes uniform adsorption energies onto the surface and maximum adsorption depends on saturation level of monolayer. Langmuir model can be represented with the following linear equation:

[1] $$\frac{Ce}{qe} = \frac{1}{kqm} + \frac{Ce}{qm} \qquad (3)$$
[2]

Where; q_e represents the mass of adsorbed lead per unit cation exchanger (mg/g), q_m is the monolayer capacity, k is the equilibrium constant and C_e is the equilibrium concentration of the solution (mg/L). Plot of C_e/q_e versus C_e should indicate a straight line of slope $1/q_m$ and an intercept of $1/q_m k$. Figure (11) illustrate the linear plot of Langmuir equation for lead ions removal at various initial ion concentrations onto the synthesized nano-zirconium tungestovanadate ion exchanger. From the correlation coefficient (R^2) value given in table (7), which is considered as a measure of the goodness of fit of experimental data on the isotherm's model, It was clear that the Langmuir equation represents the sorption process of lead ions at the prepared nano zirconium tungstovanadate ion exchanger very well. The applicability of this model gives predication that the main mechanism for lead ions separation using the synthesized material may be takes place through the ion exchange process as mono-layer at the ion exchange material. The Langmuir parameters for lead ions removal, q_m and k, were calculated from the slope and intercept of these figures and tabulated in Table (7). The results relevant that the prepared ion exchange sample has maximum monolayer sorption capacity equals to 250 mg/g for lead ions. So, the prepared nano-material distinguishes by its high lead ion sorption capacity. Accordingly, it is suitable to be utilized for industrial wastewater treatment processes.

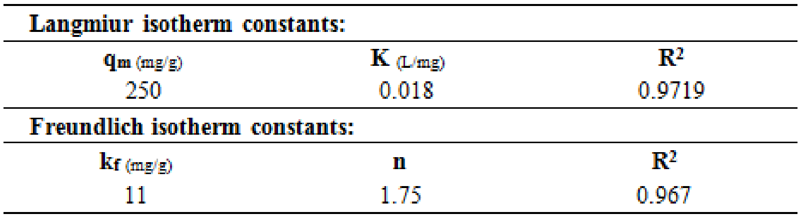
Figure 11: Langmuir adsorption isotherm for lead sorption using nano-zirconium tungstovanadate.



Freundlich model:

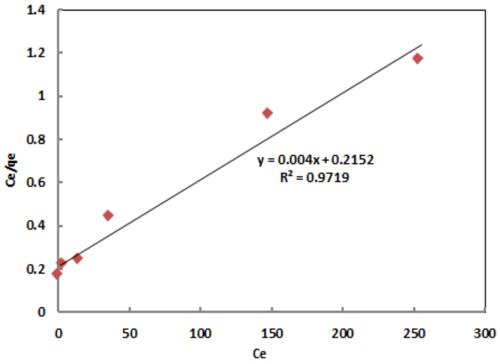
The Freundlich model is known as earliest empirical equation and is shown to be consistent with exponential distribution of active centers, characteristic of heterogeneous surfaces (Ho, 2005). Freundlich equation is: $\text{Log } q_e = \log k_f + \frac{1}{n} \log C_e$ (4)

Where; K_f and *n* represent adsorption capacity and intensity, respectively. K_f is an important constant used as relative measure for sorption efficiency of metal ions. The magnitude of the *n* acts *as* an indication of the sorption favourability. Values of *n* larger than 1 show the favorable nature of adsorption (Veliev, etal, 2006). The plot of ln q_e against ln C_e for lead ions sorption data on the prepared nano-cation exchanger is fitting well to the Freundlich isotherm (Figure 12). Where, the correlation coefficient value that equal to 0.967 is high enough for equation fitting. Accordingly, the lead ion sorption onto the prepared nano-cation exchanger may be described by both Langmuir and Freundlich isotherm models. However, the Langmuir applicability for the lead sorption process is much higher than the Freundlich applicability according to the models correlation coefficient values. This is give prediction that the adsorption phenomena have some degree of contribution beside the ion exchange mechanism in lead ions separation. The intercept of the straight line is roughly an indicator of the adsorption capacity, $K_{F,}$ and the slope, n, is an indication of adsorption effectiveness. The n value (n>1) tabulated at Table (7) confirm the favourability nature of lead ion sorption on the prepared nano-materials.



Langmuir isotherm constants:		
q_m (mg/g)	**K** (L/mg)	**R^2**
250	0.018	0.9719
Freundlich isotherm constants:		
k_f (mg/g)	**n**	**R^2**
11	1.75	0.967

Table (7): Isotherm parameters calculated for lead ions sorption using nano-zirconium tungstovanadate.



Conclusion:

New nano- zirconium (IV) tungstovanadate ion exchange material was synthesized successfully using sol-gel technique, characterized and its analytical application for lead separation was explored. The optimum preparation conditions which produce the most proper ion exchange material that characterized by its high IEC and lead ion sorption capacity was 0.2 M $ZrOCl_2$, 0.01 M HCl, 0.1 M sodium tungstate and 0.2 M ammonium metavanadate at 25 ºC. This sample recorded the highest IEC value equal to1.5 meq/g compared with the other sol-gel prepared samples. The XRD spectrum of this best ion exchange sample identified as S6 indicated that it has crystalline structure. Moreover the SEM imaging confirmed that it was produced in nano-structure. The material is fairly stable in inorganic acids, bases and organic solvents. The promising feature of the material is its affinity for Pb^{2+}ions, which is one of the most toxic metal ions present in environment. By studying the applicability of Langmiur and Freundlich equilibrium isotherm, it was clear that the sorption of lead ions by the prepared zirconium tungstovanadate ion exchanger seemed to involve adsorption phenomenon in addition to the ion exchange process.

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