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Synthesis and characterization of Nano Zirconia for use in Chromatographic $^{188}W/^{188}Re$

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ABSTRACT

The purpose of this dissertation can be represented as the synthesis of nano zirconia gel material via hydrothermal route under different preparation conditions, choosing the optimum gel material as indicated from the batch distribution studies of tungstate(VI)^{188}W to be characterized by different analytical tools (XRD,IR, FESEM, HRTEM, studying kinetics of ^{188}W (VI). Finally, preparation of $^{188}W/^{188}Re$ for chromatographic column generator. Specification of ^{188}Re eluates was used in the requirements of nuclear medicine applications.

Introduction

Rhenium-188 is an attractive radionuclide used for various therapeutic applications [1] due to its favorable nuclear properties and its convenient half-life ($t_{1/2}$ =17.01 h). ^{188}Re is a high energy β^--emitter (E_{max} = 2.118 MeV, 71.1%) accompanying a predominant (155 keV, 15.8 %) gamma-ray emission [2]. The total radiation dose of β^-- emission of ^{188}Re sufficient for effective penetration in solid tumors and destroy abnormal tissues [3]. In addition, the low-energy gamma (155 keV) emission enables imaging with gamma-ray cameras interesting for clinical use for therapy [4]. Specific activity of the desired radioisotope is an important parameter, where very high specific activity of carrier-free radioisotope is required for medical applications.^{188}W via further neutron sorption leads to limited specific activity. Production of a high specific activity ^{188}W requires relatively long irradiation periods (2-3 months) [5]. So, $^{188}W/^{188}Re$ generator that can easily use large amounts of low specific activity ^{188}W. Because of the limited sorption capacity of the sorbent material for ^{188}W ions, the size of the column matrix should be large or using nano material sorbent. Recently, the researchers use nanomaterial methods in preparation of sorbent matrix to increase its surface area that increase the radioisotope capacity on the sorption matrix, where ^{188}W specific activity raise hence^{188}Re eluate specific activity become suitable for Requirements of medicine applications. Nanotechnology is a field of science that involves the combination of chemistry, biology, physics and/or engineering for the production of new nano-scale material size in the range of 1 nm - 100 nm. There are various techniques for synthesis of nanoparticles such as chemical precipitation, sol-gel, microemulsions, sonochemical and hydrothermal syntheses. In this search we use hydrothermal method which defined as crystal growth under high temperature and pressure water conditions.

Materials and Methods

Chemical reagents

All chemical reagents used in this work were of AR grade. Distilled water was used for preparation of different solutions.

The following chemical reagents were used:

- Hydrochloric acid, 37 % HCl (MW = 36.46 g), are purchased from BDH.
- HNO_3 65 %, H_2O_2 30 % , NaOH are purchased from Merck.
- Urea, $CO(NH_2)_2$, Sodium tungstate dihydrate, $Na_2WO_4.2H_2O$, Zirconium oxychloride octahydrate, $ZrOCl_2.8H_2O$ are purchased from Sigma-Aldrich.

Instruments and equipment

Gamma-ray spectrometer, Analytical balance, FT-IR spectrometer, X-ray diffractometer, Scanning electron microscope (SEM), High resolution transmission microscope (TEM), Hydrothermal reactors.

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Radiotracer stock solution

Radio tungsten (including ^{188}W) was obtained by irradiation of sodium tungstate targets 0.1g $Na_2WO_4.2H_2O$ powder wrapped in aluminum foils placed in special aluminum cans which were sealed by welding for 12 h at a thermal neutron flux of 1×10^{14} n cm^{-2} s^{-1} and cooled for 90-120 days. The irradiated targets were separately dissolved in 5 ml of 5M NaOH with adding 0.5 ml of 30 % H_2O_2 at room temperature.

Preparation under hydrothermal conditions

Urea : zirconium molar ratio

0.5 M Zr(IV) solution was prepared by dissolving 32.23g $ZrOCl_2.8H_2O$ in 200 ml H_2O. In addition, 0.624, 0.75, 1, 2.5 M urea solutions were prepared by dissolving 4.50, 5.41, 7.21 and 18.02 g of urea in 50 ml H_2O for each case. Urea solutions were added dropwise with stirring to 50 ml fractions of 0.5 M Zr(IV) solution to obtain mixtures of urea : Zr molar ratios of 1.25 : 1, 1.5 : 1, 2 : 1 and 5 : 1, respectively.

Drying temperature

ZrO_2 gel was synthesized as the optimum urea: Zr molar ratio, and dried at 50, 100, 200, 250, 300, 350, 400 and 500 °C.

Hydrothermal reaction temperature

The gel was prepared at hydrothermal temperature 100, 150 and 200°C for 24 h.

Batch distribution studies

Batch equilibration of 10 ml of tungstate (VI)-^{188}W solution 10^{-4} M with 0.1g zirconia gel under different conditions was conducted to calculate the distribution coefficient of tungstate.

Batch distribution studies with hydrothermal route zirconia gel

Distribution coefficient of tungstate (VI)-^{188}W was studied at previous optimum condition.

Characterization of zirconia gels

The optimum zirconia gel synthesized via hydrothermal routes were characterized by (XRD, IR, FESEM, HRTEM).

Kinetic studies

Kinetic studies were carried out for tungstate (VI)-^{188}W batch sorption from chloride solution on the optimum zirconia gel to determine the most suitable kinetic model that the sorption process obeys **[6].**

Preparation and performance of $^{188}W/^{188}Re$ generators

Performance studies of $^{188}W/^{188}Re$ chromatographic column generator based on gel included elution yield, elution profiles at the optimum pH-value.

Results and Discussion

Fig. 1 shows neutron activation scheme of ^{186}W isotope, through which ^{188}W is produced **[7]**.

Gel synthesis via hydrothermal route

The hydrothermal synthesis via rapid temperature rise gives a suitable reaction zone for nanoparticle synthesis.

Batch distribution studies

Distribution coefficient, k_d, of tungstate(VI)-^{188}W between 10 ml aqueous solution and 0.1 g of zirconia gel was determined as a function of some parameters; urea: Zr molar ratio at Cl^- and NO_3^- media, pH-value of ^{188}W solution 10^{-4}M, gel drying temperature and hydrothermal reaction temperature. All of those parameters were studied for zirconia gel synthesized via hydrothermal route at optimum pH and medium obtained using in chromatographic column applications for studying uptake of ^{188}W and performance studies of $^{188}W/^{188}Re$ generators.

Distribution coefficient, k_d, can be defined as:

$$k_d = \frac{C_0 - C_e}{C_e} \times \frac{m}{V} \quad (\text{ml/g}) \qquad (1)$$

Where,

C_0: initial count rate of ^{188}W in solution (before batch contact with gel material).

C_e: count rate of ^{188}W in solution at equilibrium (after batch contact with gel material).

m: mass of gel material (0.1 g).

V: volume of ^{188}W solution (10 ml).

Effect of urea: zirconium molar ratio at NO_3^- and Cl^- media

Distribution coefficient of 10^{-4} M tungstate (VI)- ^{188}W was studied as a function of urea : zirconium concentration at pH 1.5 (using NO_3^- and Cl^- media), hydrothermal reaction at 100°C and dried at 100°C, According to **Fig. 2** k_d -values decreased with increasing urea : zirconia molar ratio . The highest k_d -value was achieved with Cl^- medium at urea: zirconium molar ratio of 1.25.

Effect of equilibrium pH at different urea:zirconium molar ratios at media (NO_3^- and Cl^-)

Fig. 3 shows that equilibrium pH increased, k_d-values decreased. The highest k_d -value was achieved with Cl^- medium at (pH =1.5) and urea: zr molar ratio of (1.25).

Effect of drying temperature

Fig. 4 shows studying k_d-values of tungstate(VI)^{188}W against drying temperature. The highest k_d -value for the hydrothermal route-zirconia gel was obtained at 350 °C.

Effect of hydrothermal reaction temperature

According to **Fig. 5**, under previous optimum conditions, k_d -values of tungstate (VI)^{188}W increased at hydrothermal reaction temperature from 100 to 150 °C then drastically decreased with further. increase of the hydrothermal reaction temperature to 200 °c.

Characterization of the optimum zirconia gel materials

From the aforementioned studies **Fig. 2, 3, 4** and **5**, it was clear that the optimum gel material conditions of tungstate(VI)-^{188}W were urea : zr molar ratio of (1.25), (pH =1.5)at cl^- media hydrothermal reaction temperature at 150 °C and dried at 350 °C.

IR spectroscopy:

Fig. 6 shows IR spectra of nano gel, respectively. Bands appearing at 1634 cm^{-1} may be attributed to the bending modes of -OH groups on the surface of gel materials, whereas the broad bands at 3405 cm^{-1} may be attributed to H-O-H stretching modes which generated from intermolecular hydrogen bonds formed between -OH groups attached to Zr^{4+} ions **[8]**. The band at 1372 cm^{-1} may be assigned to the adsorbed non-bridging -OH groups**.** The strong band at 767 cm^{-1}, in addition to bands at 511 and 587 cm^{-1} (weak band) may be ascribed to vibrations of Zr-O bonds of monoclinic phase of nano zirconia **[9].** The weak band at 743 cm^{-1} may be an indication to the minor contribution monoclinic phase.

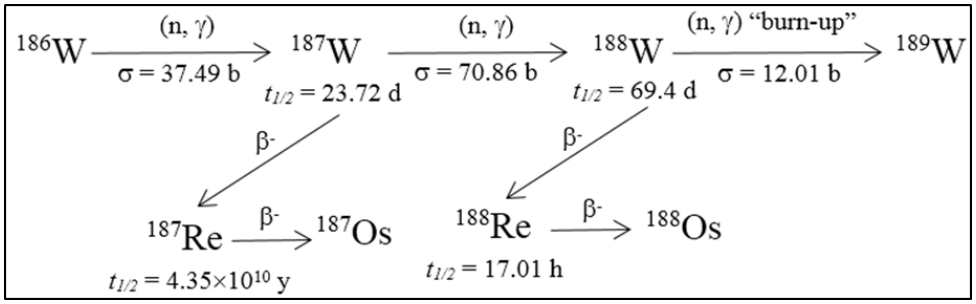


Fig. 1: Neutron activation schemes of ^{186}W.

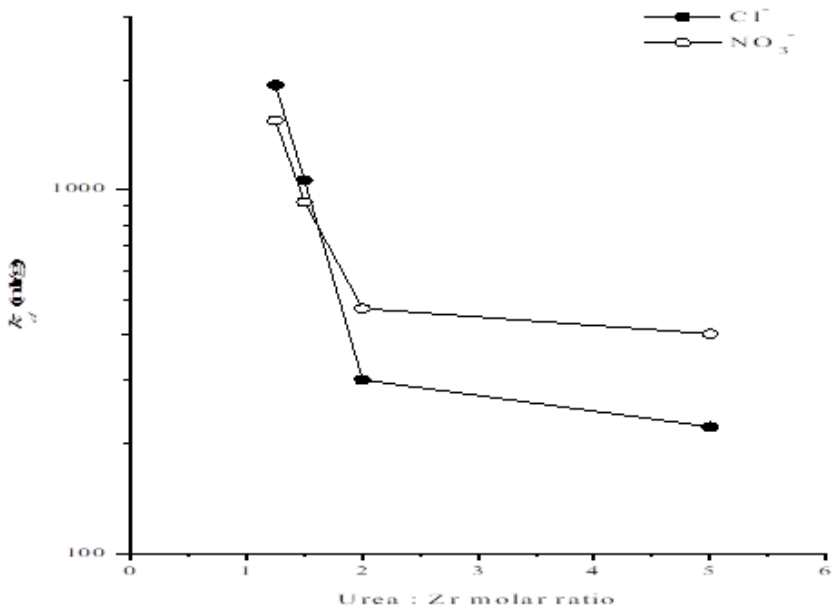


Fig. 2: Effect of urea: zirconium molar ratio on distribution coefficient of ^{188}W (using NO_3^- and Cl^- media).

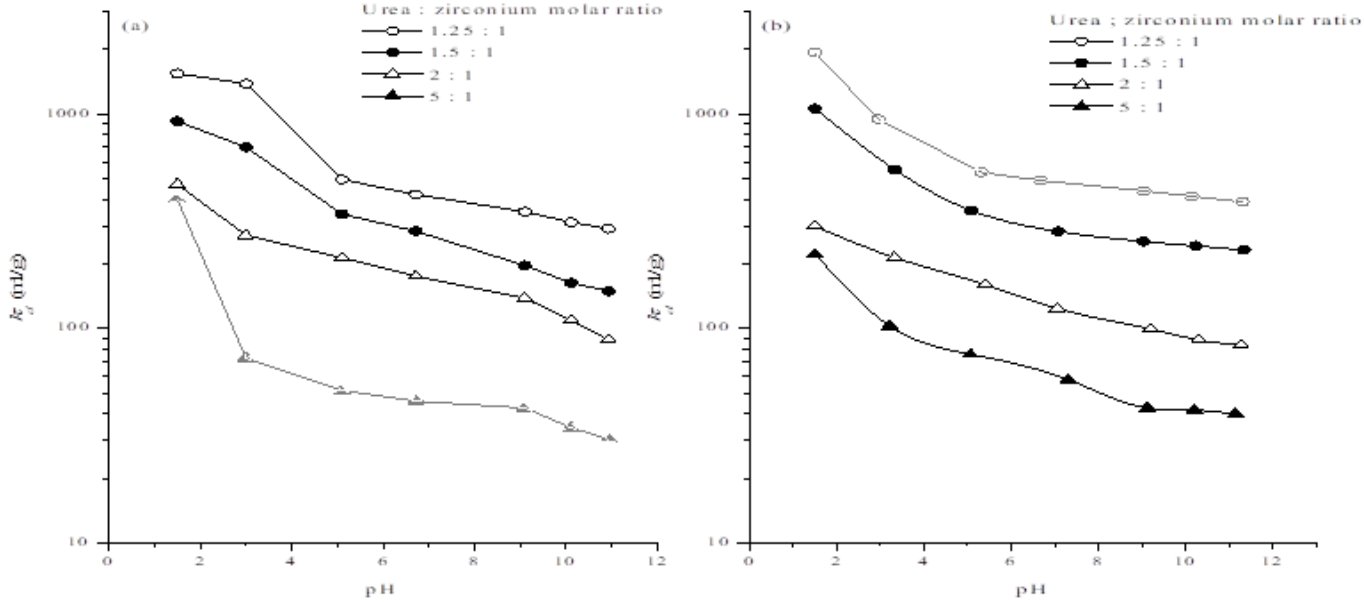


Fig. 3: Effect of equilibrium pH of using (a) NO_3^- and (b) Cl^- media.

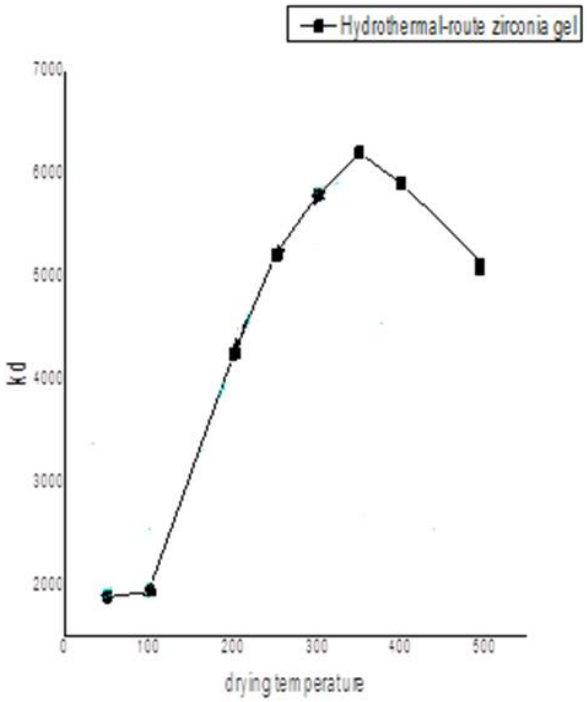


Fig. 4: Effect of drying temperature via hydrothermal through time of 24 h.

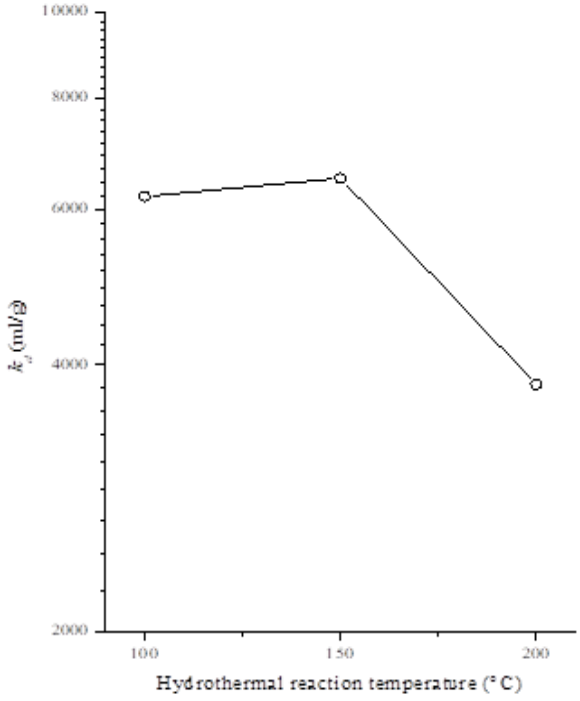


Fig. 5: Effect of hydrothermal reaction temperature on distribution coefficient of ^{188}W.

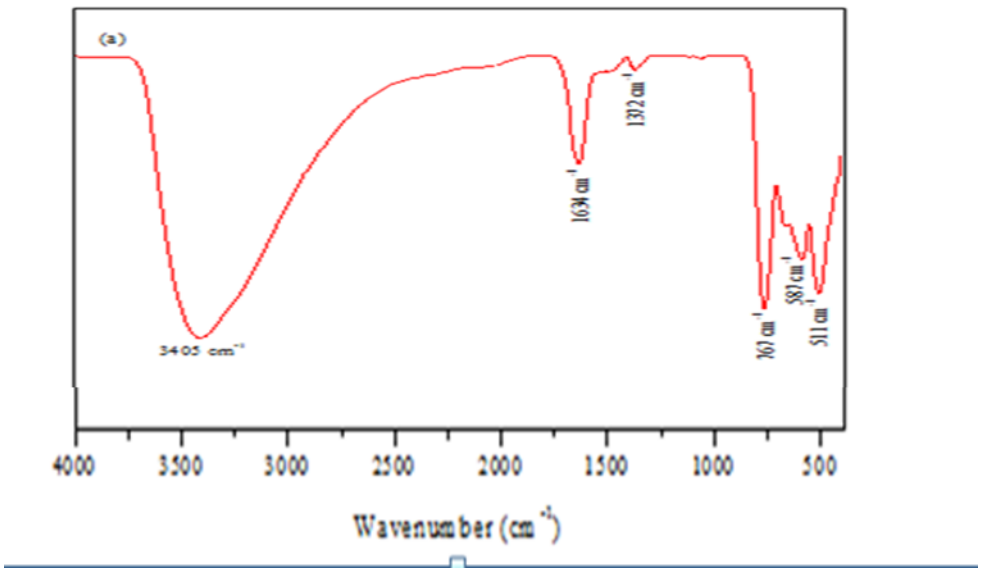


Fig. 6: FT-IR spectra of ZrO_2 gel synthesized via hydrothermal route.

X-ray diffraction

Fig. 7 represents the XRD pattern of the hydrothermal route-ZrO2 gel indicates a high crystallinity and characteristic of monoclinic phase [10].

The crystallite size of gel was found to be 42.27 nm indicates a lower Crystallinity, monoclinic-ZrO_2 phase, other peaks and shoulders may be related to other intermediate phases.

SEM analysis (Scanning electron microscopy)

Fig. 8 shows SEM image of the hydrothermal route-nano ZrO_2 gel at different magnifications (2000χ), which indicates irregular aggregations with indefinite morphology.

HRTEM (High-resolution transmission electron microscopy)

Fig. 9 shows HRTEM image of nano zirconia gel where gel particles look like blackberries; oval shape and appears to be an aggregate of many smaller particles (100 and 70 nm, respectively) and crystallite size as determined from XRD (42 nm, respectively), proves particle aggregation.

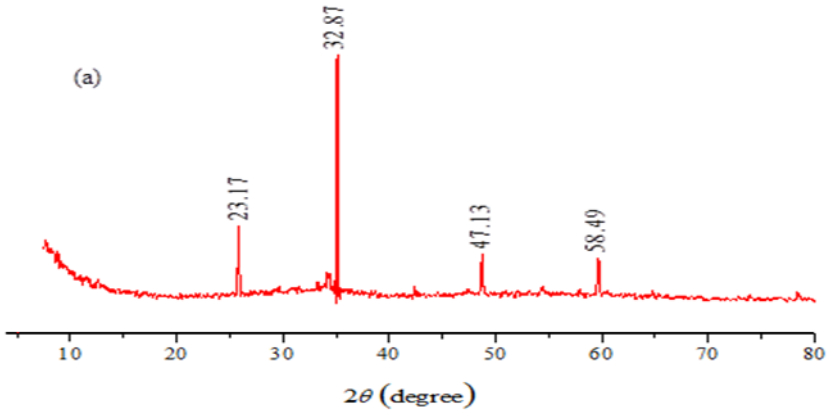


Fig. 7: XRD patterns of (a) nano ZrO_2 gel synthesized via hydrothermal route.

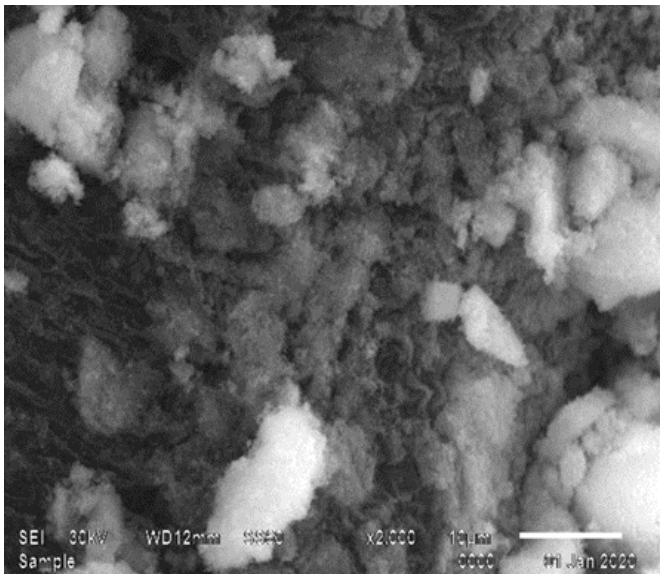


Fig. 8: SEM images of nano ZrO_2 gel synthesized via hydrothermal route with different magnifications; 2000 χ.

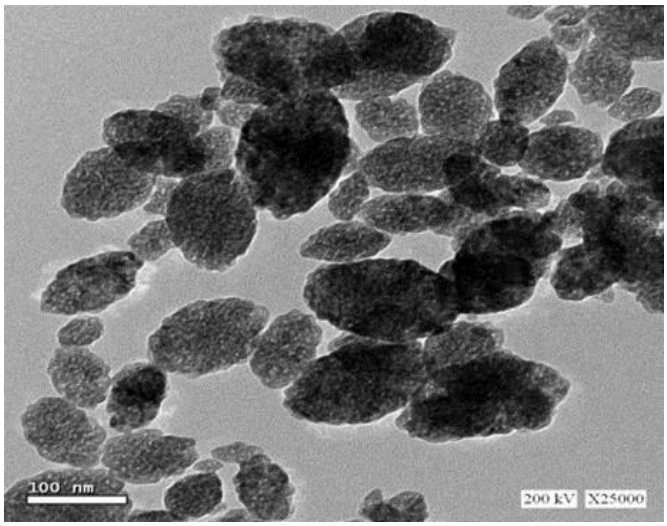


Fig: 9: HRTEM images of nano ZrO_2 gel synthesized via hydrothermal gel.

Kinetic modeling studies

Uptake of tungstate(VI)-^{188}W on gel was studied as a function of time. Uptake was calculated according to the following equation:

$$Uptake = \frac{C_0 - C_e}{C_0} \times 100 \quad (\%) \qquad (2)$$

Where,

C_0: initial count rate of ^{188}W in solution (before contact with gel material).

C_e: equilibrium count rate of ^{188}W (after contact with gel material).

Fig. 10 shows uptake-time profiles of 0.01 M tungstate(VI)-^{188}W, Cl^- solution at equilibrium pH 1.5, on 0.1 g of gel, by batch contact method for 26 h at different temperatures [25, 40 and 60] °C. In the first time periods (5-30 min), uptake rate increased rapidly and then increased slowly. Increasing temperature accompanied by uptake increased which indicating an endothermic sorption process. Uptake values were found to be 44.2, 48.3 and 56.9 % at [25, 40 and 60] °C after 24 h batch contact time, equilibrium was attained. The sorption rate follows the pseudo second-order kinetic model at all of the studied sorption temperatures [25, 40 and 60]°C . The pseudo second-order kinetic model (PSO) can be represented by the following equation [6]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (3)$$

Where,

t: sorption time (h).

q_t: sorption capacity at time t.

q_e: sorption capacity at equilibrium.

k_2: pseudo second-order rate constant (g/mg h).

By plotting t/q_t against t the straight-line obtained, according the following equation q_e and k_2, calculated through slope, s_{PSO} and intercept, i_{PSO} values obtained from **Fig. 10**

$$q_e = \frac{1}{s_{PSO}} \qquad (4)$$

$$k_2 = \frac{1}{i_{PSO} q_e^2} \qquad (5)$$

According to **Fig. 10**, using Equations (3) and (4), the calculated q_e values of gel were found to be 81.6, 89.0 and 105.9 mg/g at 25, 40 and 60 °C, respectively, showing a high agreement with the corresponding experimentally determined q_t values calculated from equation (3), which found to be 81.3, 88.8 and 104.7 mg/g. Agreement of q_t & q_e values and R^2 values ≅ 1, so the sorption rate of tungstate(VI)-^{188}W follows the pseudo second-order kinetic model **Table 1**.

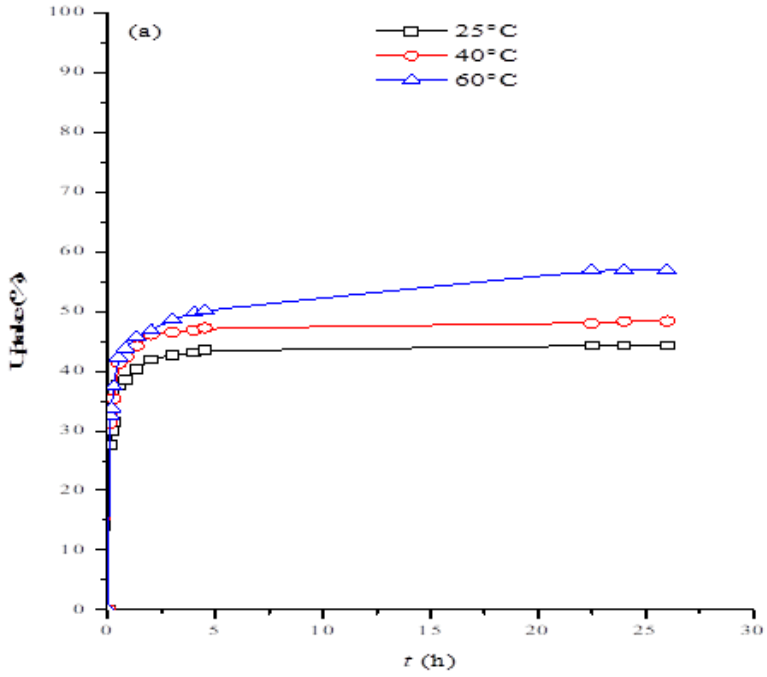


Fig. 10: Batch uptake of 0.01 M tungstate(VI)-^{188}W as a function of contact time with nano ZrO_2 gel synthesized via hydrothermal route at [25, 40 and 60]°C.

Table 1: Kinetic modeling and activation energy data for sorption of tungstate(VI)-^{188}W on nano ZrO_2 gel

Temp.	Slope	Intercept	R^2	q_e (calculated; 1/slope), mg/g	q_e (experimental), mg/g	k_2, g/mg h
25 °C	0.01225	0.00127	0.99999	81.6	81.3	0.118
40 °C	0.01124	0.00115	0.99998	89.0	88.8	0.110
60°C	0.00945	0.00307	0.99959	105.9	104.7	0.029

$^{188}W/^{188}Re$ chromatographic column generators based on nano ZrO_2 gel

Gel column was loaded with 25 ml of 1×10^{-2} M tungstate (VI)^{188}W. After loading, Column was then periodically eluted (≥ 72 h) 40 times along 60 days by passing 10 ml of 0.9 % NaCl solution. Typical elution profiles of gel at different flow rates of 0.5, 1 and 2 ml/min for the eluted ^{188}Re activity were represented in **Fig. 11**.

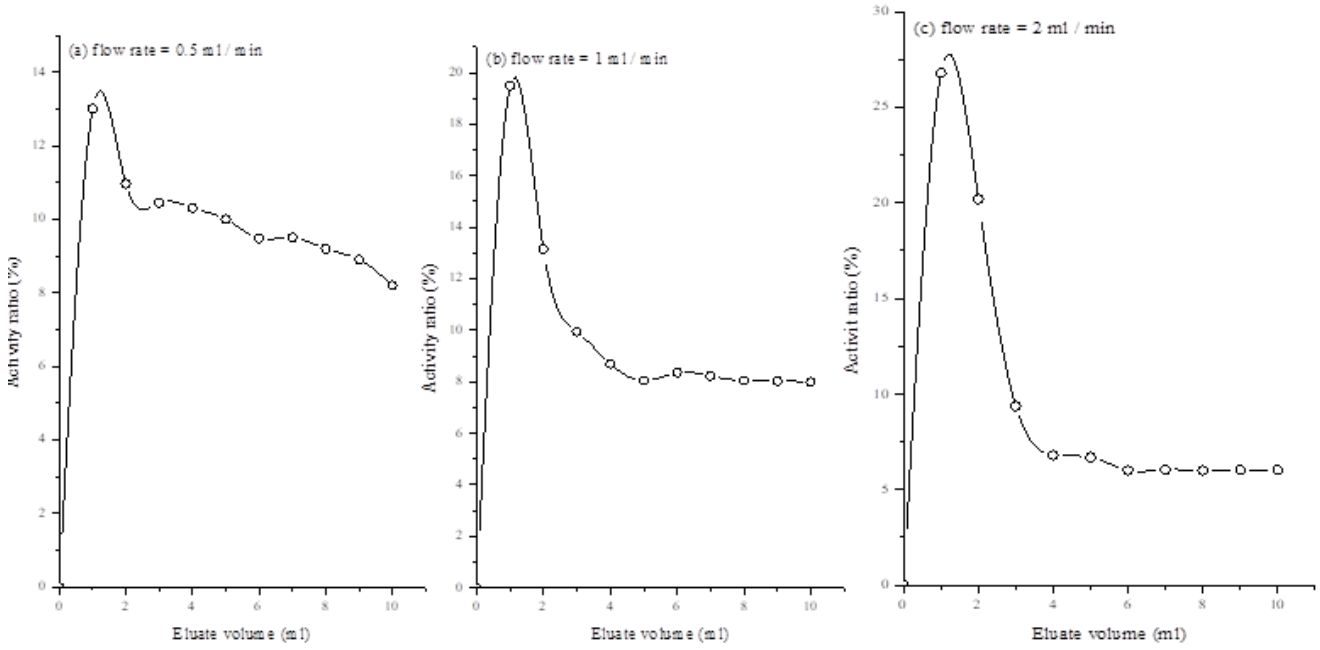
It was found that, elution yield decreased with increasing elution flow rate from 0.5 ml/min to 1ml/min ,then increased again with increasing flow rate to 2 ml/min where the elution yield values were found to be 58 ± 9, 30 ± 7 and 72 ± 3 % at elution flow rates of 0.5, 1 and 2 ml/min. The best elution yield was found at 2 ml/min flow rate.

Conclusion

Nano zirconia gel was synthesized by hydrothermal route.

The effect of different parameters (i. pH, ii. urea: zirconium molar ratio, iii. equilibration media, Cl^- and NO_3^- media, iv. drying temperature and v. hydrothermal temperature) on the distribution coefficient (k_d) of tungstate (VI)-^{188}W was studied. It was found that the optimum conditions were urea : zirconia molar ratio of (1.25), pH 1.5, Cl^- medium, hydrothermal reaction of 150 °C and drying temperature of 350 °C.

The gel was characterized by IR spectroscopy, XRD, SEM, HRTEM. It was found that sorption of tungstate(VI)-^{188}W gel obeyed the pseudo second-order kinetic rate at different temperatures [25, 40 and 60] °C. The sorption was found to be endothermic. The performance of $^{188}W/^{188}Re$ chromatographic column generators, based on gel was studied. Specifications of ^{188}Re eluates from generator was found to meet the requirements of nuclear medicine applications.



(a) **(b)** **(c)**

Fig. 11: ^{188}Re elution profiles obtained from$^{188}W/^{188}Re$ at flow rates of (a) 0.5 ml / min, (b) 1 ml / min and (c) 2 ml / min at 25 °C.

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