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Hydrothermal Synthesis and Characterization of a Novel Zirconium Oxide and Its Application as an Ion Exchanger

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Abstract

A novel hydrothermal zirconium oxide (ZrO_2) ion exchange material was successfully synthesized by hydrothermal technique. The material has been characterized using different tools such as thermal analysis (DTA-TGA), FT-IR and X-ray diffraction studies. The results show that the prepared ZrO_2 is pure and with a unique shape and it belongs to the hexagonal system. Chemical resistively of the material for various media such as, water, acids and bases have been assessed. The capacity of ZrO_2 ion exchanger for Na^+, Cu^{2+}, Ni^{2+} and Zn^{2+} ions at natural pH has been determined. The effect of heating treatment for ZrO_2 on ion exchange capacity was studied. The sorption/ion exchange behaviour of Cu^{2+}, Ni^{2+} and Zn^{2+} ions towards ZrO_2 in different pH media has been investigated. The distribution coefficients and separation factors were determined. Finally, Freundlich isotherms for Cu^{2+}, Zn^{2+} and Ni^{2+} ions on hydrothermal ZrO_2 ion exchanger were investigated and the Freundlich isotherm constants were conduced.

1. Introduction

The methods for the synthesis of metal oxide ion exchange material mainly include chemical deposition, sol-gel process, chemical vapor decomposition, gas-phase reaction and hydrothermal synthesis. Among these methods, hydrothermal method is a promising method for synthesizing ideal CdO material with special morphology via a simple, fast, low cost, low temperature, high yield and scalable process [1]. Additional, high-crystallized powders with narrow grain size-distribution and high purity without heat treatment at high temperature are the advantages of hydrothermal technique [2-5]. Literature show many publications [6-9] on metal oxide ion exchangers such as ZnO and TiO_2 that have been used extensively as photocatalyst due to their high photocatalytic activity, non-toxic nature, inexpensive, excellent chemical and mechanical stability. ZnO can be also a suitable alternative to TiO_2 because it is lower cost and has the similar band gap energy around 3.2 eV. In addition, ZnO shows better performance compared to TiO_2 in the degradation of several organic contaminants in both acidic and basic medium, which has stimulated many researchers to further explore the properties of

ZnO in many photocatalytic reactions [6-8]. As we know, the shape, crystalline structure, and size of semiconductors are important elements in determining their physical and chemical properties [9]. On the other hand, recent literature indicates few works carried out on ZrO_2 as ion exchange materials. Additional, inorganic ion exchange materials have found extensive applications in analytical and industrial chemistry and played a vital role in the treatment of environmental pollutants. Ion exchange materials with higher selectivities are continuously being investigated [10,11].

Hopefully, the results of this work might provide a promising data for the synthesis and characterization of ZrO_2 as inorganic ion exchange material and its applications for the removal of some toxic elements from hazardous wastewater.

2. Experimental

2.1. Hydrothermal Preparation of ZrO_2 Ion Exchanger

Zirconium oxide (ZrO_2) inorganic ion exchange material was synthesized hydrothermally by the reaction of

equi-concentrations (5%) solutions of zirconium oxy-chloride ($ZrOCl_2$) and NH_4OH with volumetric ration 2:1 under magnetic stirring. After mixing, the reaction mixture was further stirred for 60 min under constant stirring rate at room temperature to ensure all of the reagents react completely. Subsequently, the mixture was transferred to a Teflon-lined stainless steel autoclave which were sealed and maintained at 130 ± 1°C for 24 h, and then it was natural cooled at room temperature. After hydrothermal reaction, the resulting solid products were filtered and washed with deionized water for several times in order to remove Cl^- ions. Finally, the solid ZrO_2 ion exchanger was dried in drying oven at 70 ± 1°C for overnight, and then ground, sieved and stored at room temperature.

2.2. Characterization of Prepared ZrO_2 Ion Exchanger

FTIR spectrum of ZrO_2 ion exchange material was carried out using FTIR Spectrometer; BOMEN, MB-series and the measurements were carried out using KBr disc method technique. X-ray diffraction pattern of ZrO_2 ion exchange material was carried out using SHIMADZO X-ray diffractometer, XD-D1, with a nickel filter and a Cu-Kα radiation. Differential thermal and Thermogravimetric analyses for ZrO_2 was carried out using a SHIMADZU (DTA-TG) thermal analyzer obtained from Shimadzu Kyoto "Japan". The sample was measured for ambient temperature up to 850°C with heating rate of 5 deg./min. The surface area values of ZrO_2 were measured using BET-technique as an adsorption phenomenon of nitrogen gas on the powder surface at 77 K.

2.3. Chemical Resistively of ZrO_2 Ion Exchanger

The chemical resistively of the ZrO_2 in various media H_2O, HNO_3, HCl, NaOH and KOH was studied by taking 0.5 mg of sample in 50 ml of the particular medium and allowing it to stand for 24 h. The percent of solubility was calculated and summarized in **Table 1**.

2.4. Sorption Studies:
Capacity of ZrO_2 for Na^+, Cu^{2+}, Ni^{2+} and Zn^{2+} Ions:

The capacity of ZrO_2 ion exchanger for Na^+, Cu^{2+}, Ni^{2+} and Zn^{2+} ions (in nitrate from) was carried out by equilibrium batch technique. 0.1 g of ion exchanger was equilibrated with 10 ml of 50 ppm of Na^+, Cu^{2+}, Ni^{2+} and Zn^{2+} ion solutions (natural pH) in a shaker thermostat at 25 ± 1°C. The capacity value was calculated by the following formula;

$$Capacity = \frac{\%Uptake}{100} \cdot C_o \cdot V/m. \quad mmol/g \qquad (1)$$

where % uptake is the percent uptake of metal ions equal $\{(C_o - C_f)/C_o\} \times 100$, and C_o, C_f is the initial and final concentration of the ions in solution, V is the solution volume and m is the sorbent mass.

The effect of heating temperature treatment of ion exchanger on ion exchange capacity of ZrO_2 ion exchanger for Na^+, Cu^{2+}, Ni^{2+} and Zn^{2+} ions was studied by pretreatment of 1 g portion of the material at different heating temperature for 4 h at temperatures between 50°C and 600°C in a muffle furnace. Then the capacity was carried out as described previously.

2.5. Effect of pH Medium on Sorption Behaviour of ZrO_2 Ion Exchanger:

Effect of pH medium on the sorption behaviour of various metal ions Cu^{2+}, Ni^{2+} and Zn^{2+} (in nitrate from) on ZrO_2 ion exchanger was investigated. A series of metal solutions was prepared with concentrations equal 50 ppm at different pH adjusted using nitric acid from pH (1) to (5). The experiment was carried out by equilibration of 0.1 g of ion exchanger with 10 ml of metal ion solution. The mixture shaken for 3 h in shaker thermostat at 25 ± 1°C. Then the solutions were separated and the metal ion concentrations were determined using the supernatant liquid by atomic absorption spectrometer. The sorption percent, distribution coefficients and separation factors were determined using the following expressions;

$$Sorption\ Percent = \frac{C_o - C_e}{C_o} \cdot 100 \qquad (2)$$

$$Distribution\ coefficient\ (K_d) = \frac{C_o - C_e}{C_e} \cdot V/m \quad ml/g \quad (3)$$

$$Separation\ factor\ (a)_B^A = \frac{K_d(B)}{K_d(A)} \qquad (4)$$

Where;
 $K_d(A)$ is the distribution coefficient of (A) ion,
 $K_d(B)$ is the distribution coefficient of (B) ion,
 C_o is the initial concentration of metal ion,
 C_e is the final concentration of metal ion,
 V is the solution volume,
 m is the mass of ion exchanger.

2.6. Sorption Isotherm

For adsorption isotherms for Cu^{2+}, Ni^{2+} and Zn^{2+} ions on ZrO_2 ion exchanger were investigated, 10 ml metal ion solution of different metal ion concentrations varied from 2×10^{-2} M to 5×10^{-4} M were equilibrated for a specific

period of time (3 h) with 0.1 g of exchanger. After 3 h (time sufficient to attain equilibrium) the supernatant liquid was removed immediately and the metal ion concentration evaluated by atomic absorption spectrometer. The experiments were carried out in shaker thermostat at $25 \pm 1°C$. The equilibrium concentration ($C_{eq.}$) and amount uptake (W) were calculated in mmol/g as follows;

$$W = Uptake \cdot C_o \cdot V/m \quad mmol/g \quad (5)$$

$$C_{eq} = (1 - Uptake) \cdot C_o \quad (6)$$

Plot of C against C/W and/or log $C_{eq.}$ against log W/m were performed to obtain the required isotherm.

3. Results and Discussions

Chemical resistively of ZrO_2 ion exchange material was checked in different media such as H_2O, HNO_3, HCl, NaOH and KOH. The data represented in **Table 1** indicated that ZrO_2 is very stable in water and stable in acid medium, maximum tolerable limits being 2 N HNO_3 and 2 N HCl, and it is not stable in base medium, maximum tolerable limits being 1 N NaOH and 0.5 N KOH. This means that ZnO_2 ion exchange material is chemically stable in acid medium and hence can be used for analytically important separations.

The FTIR adsorption analysis of the synthesized ZrO_2 ion exchanger is represented in **Figure 1**. **Figure 1** shows a broad transmittance peak in the range of 3600-2500 and ~1640 cm^{-1}, which could be assigned to the stretching and the bending modes of water molecules adsorbed on ZrO_2 sample [12,13]. The transmittance peak in the range of 500-450 cm^{-1} may be related to Zr-O bond [12,13].

X-ray diffraction pattern of ZrO_2 ion exchanger is represented in **Figure 2**. This figure manifested that the synthesized ZrO_2 had a crystalline structure and the ma-
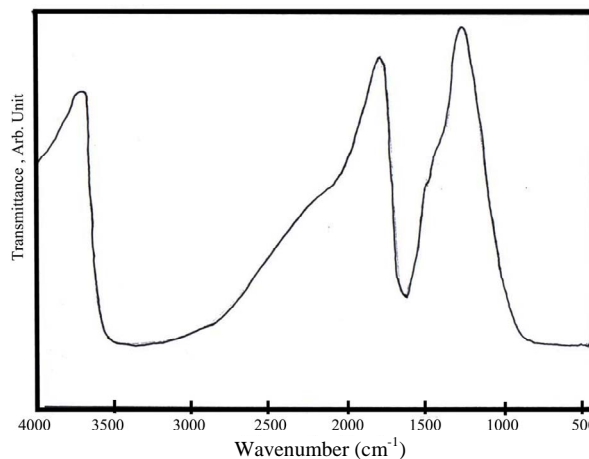

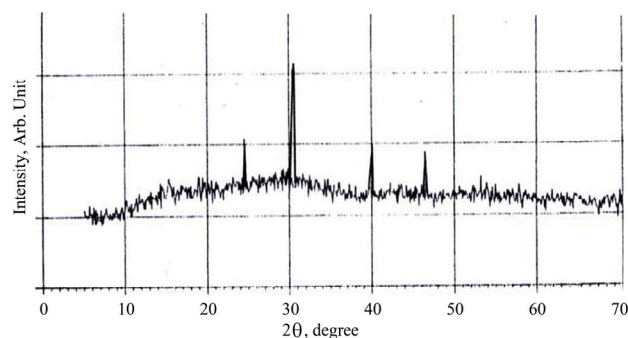Figure 1. Infrared spectrum of ZrO_2 ion exchanger at $25 \pm 1°C$.

Figure 2. X-ray diffraction pattern of ZrO_2 ion exchanger at $25 \pm 1°C$.

terial is present in one phase **Figure 2**. According to Joint Committee for Powder Standard Diffraction (JCPSD) the peaks well matched with these peaks of the hexagonal cards that means ZrO_2 was belong to hexagonal system.

Differential thermal and Thermogravimetric analyses for ZrO_2 is represented in **Figure 3**. **Figure 3** indicated two endothermic peaks at 92 and 380°C that may be related to dehydration of free water and interstitial water, respectively. From TG curve we found that the weight firstly is high related to loss of water, then there are gradually stable in the curve during the heating process. These data confirm the thermal stability of ZrO_2 compared to other organic and inorganic ion exchanger. Also, these data indicates the suitability of application of ZrO_2 at higher temperatures.

The surface area value of ZrO_2 was found to be 33.44 m^2/g as determined by the BET adsorption of nitrogen gas.

Preliminary studies for the time required for equilibrium of the studied cations on ZrO_2 ion exchange material was carried out and the results indicated the equilibrium was attained within 3 h.

Table 1. Chemical resistively of ZrO_2 ion exchange material for H_2O, acid and base media at $25 \pm 1°C$ (standard error 0.01 %).

Medium	Concentration, M	% Solubility	Medium	Concentration, M	% Solubility
H_2O	--	--		0.1	--
	0.1	0.12		0.5	0.25
	0.5	0.19	NaOH	1.0	1.52
	1.0	0.25		2.0	3.50
HNO_3	2.0	1.70		4.0	5.40
	4.0	2.50		6.0	25.25
	6.0	13.0		0.1	0.15
	0.1	--		0.5	2.5
	0.5	0.12	KOH	1.0	15.52
	1.0	0.22		2.0	18.50
HCl	2.0	1.20		4.0	20.23
	4.0	2.80		6.0	26.22
	6.0	4.90			
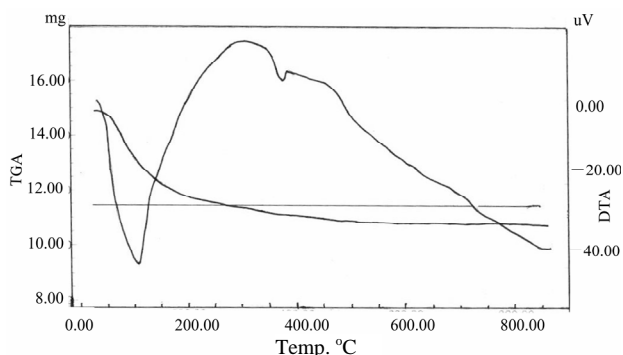
Figure 3. DTA and TG curves for ZrO₂ ion exchanger.

Table 2. Capacity of ZrO₂ for Na⁺, Cu²⁺, Ni²⁺ and Zn²⁺ ions at Natural pH , V/m = 100 ml/g and t = 25 ± 1˙C.

Cation	Capacity, mmol/g			
	At 50˙C	At 200˙C	At 400˙C	At 600˙C
Na⁺	1.49	1.22	1.1	0.95
Cu²⁺	1.33	1.30	1.15	1.03
Ni²⁺	0.80	0.74	0.69	0.55
Zn²⁺	0.95	0.88	0.80	0.65

Figure 4. Effect of pH of the medium on the sorption percent of Cu²⁺, Zn²⁺ and Ni²⁺ ions on ZrO₂ ion exchanger at 25 ± 1˙C.

The capacity of ZrO₂ ion exchanger for Na⁺, Cu²⁺, Ni²⁺ and Zn²⁺ ions was carried out by equilibrium batch technique and the data was represented in **Table 2**. The data in **Table 2** shows that the selectivity sequence of ZrO₂ for the studied cations was fond to Na⁺ > Cu²⁺ > Zn²⁺ > Ni²⁺. This sequence may be due to the generally stronger electrostatic interactions of divalent cations compared to mono valent ones. Also, this sequence is parallel to the order of ionic radii and stated that the studied cations are absorbed in hydrated state [14].

The effect of heating temperature of ion exchanger on ion exchange capacity was studied and the data represented in **Table 2**. The data indicated that as the heating temperature of ZrO₂ increased the capacity for Na⁺, Cu²⁺, Ni²⁺ and Zn²⁺ ions decreased. This may be due to as the heating temperature increased the loss of water content of ZrO₂ are increased as shown in DTA-TG curves (**Figure 3**). This behaviour can be interpreted by the heating effect. Since, in the early stage of the heating only water molecules present in the cavity of the exchanger will be lost (cavity water), and by increasing the heating temperature the water molecules present in the structure will be lost during condensation (condensation water) leading to shrinkage in the cavity and channels of the exchanger at higher temperatures [14]. This shrinkage in the structure leads to some strike difficulties and decrease in the number of exchangeable active sites of the exchanger.

Effect of pH on the sorption behaviour of various metal ions Cu²⁺, Ni²⁺ and Zn²⁺ (in nitrate form) on ZrO₂ ion exchanger was carried out at different pH and the data are represented in **Figure 4**. The data indicated that the sorption percent of Cu²⁺, Ni²⁺ and Zn²⁺ ions on ZrO₂ are increased with increasing the pH of the medium.

The K_d values of Cu²⁺, Ni²⁺ and Zn²⁺ on ZrO₂ ion exchanger as a f **Figure 5**. Non-linear relations between log K_d and pH was observed.

When the simple ion exchange proceeds by the following reaction unction of pH of solution are represented in

$$n\overline{H^+} + M^{n+} \leftrightarrow \overline{M^{n+}} + nH^+ \qquad (7)$$

in sufficiently diluted solution, where activity coefficient may be neglected, the selectivity coefficient can be defined by the following equation [15];

$$K^M_H = \frac{\left[\overline{M^{n+}}\right]\left[H^+\right]^n}{\left[\overline{H^+}\right]^n\left[M^{n+}\right]} \qquad (8)$$

where $\left[\overline{M^{n+}}\right]$ and $\left[\overline{H^+}\right]$ denote to the concentrations of M^{n+} and H^+ ions in the exchanger, respectively, and $\left[M^{n+}\right]$ and $\left[H^+\right]$ are their concentrations in solution. Since the K_d value is the ratio between the metal ion concentration in the exchanger and in the solution, then

$$K^M_H = K_d \frac{\left[H^+\right]^n}{\left[\overline{H^+}\right]^n} \qquad (9)$$

Or

$$K^M_H = K_d \frac{\left[\overline{H^+}\right]^n}{\left[H^+\right]^n} \qquad (10)$$

by taking the logarithm of the two sides

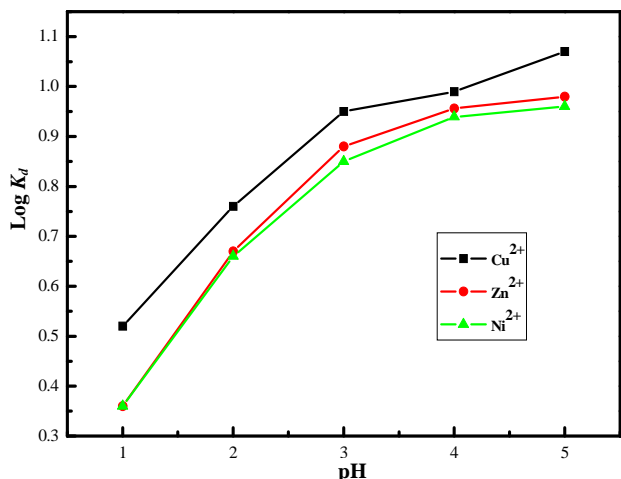$$logK_d = logK^M_H\left[\overline{H^+}\right]^n - nlog\left[H^+\right] \qquad (11)$$

Figure 5. Log K_d of Cu^{2+}, Zn^{2+} and Ni^{2+} ions versus pH of medium on ZrO_2 ion exchanger at $25 \pm 1°C$.

When $\left[\dfrac{\overline{M^{n+}}}{K_H^M}\right] \le \left[\dfrac{\overline{H^+}}{H^+}\right]_n$ and $\left[M^{n+}\right] < \left[H^+\right]$, the magnitude is considered constant, thus Equation (11) can be reduced to

$$logK_d = C + npH \qquad (12)$$

Which implies that a plot of log K_d versus pH should be linear with a slope (*n*). **Figure 5** shows the dependency of log K_d values of Cu^{2+}, Zn^{2+} and Ni^{2+} ions on pH of the solution with non-ideality of the exchange reaction for Cu^{2+}, Zn^{2+} and Ni^{2+} ions on ZrO_2 ion exchanger. The non-ideality results may be due to the presence of other mechanism beside the ion exchange mechanism such as the physical adsorption between the metal ions and the exchanger that could be related to the ionic potential of the cations [15].

The distribution coefficients (K_d) and separation factors (α) for the mentioned cations in different pH medium were calculated and tabulated in **Table 3**. The data in **Table 3** indicated that the distribution coefficients have the affinity sequence $Cu^{2+} > Zn^{2+} > Ni^{2+}$ for ZrO_2. This sequence supports the sorption of metal ions in hydrated state. The separation factors for the studied cations were calculated and indicated that Cu^{2+} ion can easily separated from Zn^{2+} and Ni^{2+} ions in waste water solutions.

The nature of adsorption processes for Cu^{2+}, Zn^{2+} and Ni^{2+} ions on ZrO_2 were investigated by gradual increase of the sorbate concentration and measuring the amount sorbed at each equilibrium concentration. The freundlich isotherm most widely used mathematical model, given an empirical expression encompassing the surface heterogeneity and exponential distribution of active sites and their energies was tested in the following form;

Table 3. Distribution coefficients and separation factors for Cu^{2+}, Zn^{2+} and Ni^{2+} ions on ZrO_2 in different pH media at $25 \pm 1°C$.

pH of medium	Parameter	Cu^{2+}	Zn^{2+}	Ni^{2+}
1	K_d, ml/g	3.31	2.28	2.3
	Separation factor, α		0.69	0.69
				1.01
2	K_d, ml/g	5.82	4.66	4.60
	Separation factor, α		0.80	0.79
				1.00
3	K_d, ml/g	8.93	7.53	7.18
	Separation factor, α		0.84	0.81
				0.95
4	K_d, ml/g	9.89	9.05	8.69
	Separation factor, α		0.92	0.88
				0.96
5	K_d, ml/g	11.73	9.59	9.19
	Separation factor, α		0.82	0.78
				0.96

$$log\,W/m = LogK + 1/n\,log\,C_{eq} \qquad (13)$$

where *W*: is the amount uptake, $C_{eq.}$: the equilibrium concentration, *m*: mass of the ion exchanger, and, *n* and *K* are the freundlich constants measure the adsorption intensity and adsorption capacity of the sorbent, respectively, and computed from the slope and intercept of the linear relationship.

Plots of log W/m against log $C_{eq.}$ linear relationships were obtained for Cu^{2+}, Zn^{2+} and Ni^{2+} ions on ZrO_2 as shown in **Figure 6**. The data in **Figure 6** show the applicability of freundlich isotherm for Cu^{2+}, Zn^{2+} and Ni^{2+} ions on ZrO_2 ions and all of these cations are physically sorbed on ZrO_2. The values of adsorption capacity (*K*) and adsorption intensity (*n*) for Cu^{2+}, Zn^{2+} and Ni^{2+} ions on ZrO_2 were computed from the linear relationships in **Figure 6** and tabulated in **Table 4**. As seen from **Table 4** the numerical values of ($0 < n < 1$) suggest the surface of the sorbent of heterogeneous type [16]. Also the numerical value of (*n*) is only reduced at lower equilibrium concentrations. Freundlich sorption isotherm does not predict any saturation of the solid surface thus envisages infinite surface coverage mathematically.

Similar results were also reported for the adsorption of

Table 4. Freundlich constants (*n* and *K*) for sorption of Cu^{2+}, Zn^{2+} and Ni^{2+} ions on ZrO_2 at t = $25 \pm 1°C$.

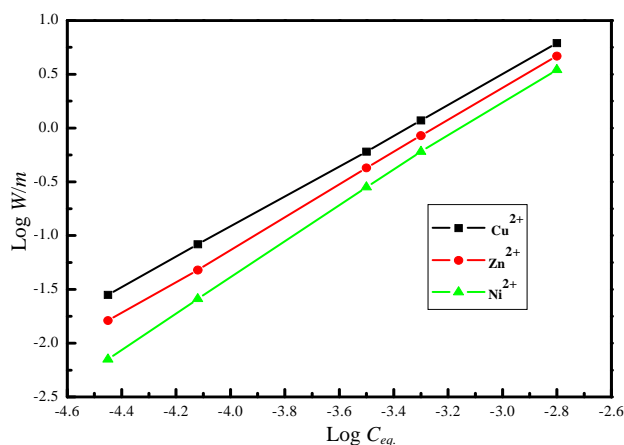| Cations	Freundlich constants	
	n	*K*
Cu^{2+}	0.71	1.80×10^{-2}
Zn^{2+}	0.67	7.76×10^{-3}
Ni^{2+}	0.63	4.17×10^{-3}

Figure 6. Freundlich adsorption isotherms for Cu^{2+}, Zn^{2+} and Ni^{2+} ions on ZrO$_2$ ion exchanger at 25 ± 1°C.

Zn^{2+}, Cu^{2+}, Cd^{2+} and Ni^{2+} ions on poly acrylamide acrylic acid impregnated with silico-titanate ion exchanger [17] and UO$_2$$^{2+}$ and Th^{4+} ions on titanium antimonate [18].

4. References

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