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 (ZrO₂) 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 ZrO₂ 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 ZrO₂ ion exchanger for Na⁺, Cu²⁺, Ni²⁺ and Zn²⁺ ions at natural pH has been determined. The effect of heating treatment for ZrO₂ on ion exchange capacity was studied. The sorption/ion exchange behaviour of Cu²⁺, Ni²⁺ and Zn²⁺ ions towards ZrO₂ in different pH media has been investigated. The distribution coefficients and separation factors were determined. Finally, Freundlich isotherms for Cu²⁺, Zn²⁺ and Ni²⁺ ions on hydrothermal ZrO₂ ion exchanger were investigated and the Freundlich isotherm constants were conduced.

Keywords: Hydrothermal Synthesis, Zirconium Oxide, Ion Exchanger

1. Introduction

Hydrothermal Synthesis, Zirconium Oxide, Ion Exchanger

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]. Additionally, 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 TiO₂ 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 TiO₂ because it is lower cost and has the similar band gap energy around 3.2 eV. In addition, ZnO shows better performance compared to TiO₂ 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 ZrO₂ 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 ZrO₂ 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 ZrO₂ Ion Exchanger

Zirconium oxide (ZrO₂) inorganic ion exchange material was synthesized hydrothermally by the reaction of...
equi-concentrations (5%) solutions of zirconium oxychloride (ZrOCl₂) and NH₄OH 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 \( \pm \) 1 \( ^\circ \)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 \( \pm \) 1 \( ^\circ \)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-K\(\alpha\) 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 \( ^\circ \)C with heating rate of 5 \( ^\circ \)/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\(_2\)O, 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 \( \pm \) 1 \( ^\circ \)C. The capacity value was calculated by the following formula:

\[
\text{Capacity} = \frac{\% \text{Uptake} \times V}{m \cdot \text{mmol/g}}
\]

where \( \% \text{ uptake} \) is the percent uptake of metal ions equal \( \left\{ \left( C_o - C_f \right) / C_o \right\} \times 100 \), 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\( ^\circ \)C and 600\( ^\circ \)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 \( \pm \) 1 \( ^\circ \)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:

\[
\text{Sorption Percent} = \frac{C_o - C_f}{C_o} \times 100
\]

\[
\text{Distribution coefficient} \ (K_d) = \frac{C_o - C_f}{C_o} \cdot V/m \ \text{ml/g}
\]

\[
\text{Separation factor} \ (a) = \frac{K_d(A)}{K_d(B)}
\]

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,
- \( C_f \) 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 \( 2 \times 10^{-2} \) M to \( 5 \times 10^{-4} \) 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 ± 1˚C. The equilibrium concentration \( C_{eq} \) and amount uptake \( W \) were calculated in mmol/g as follows:

\[
W = \text{Uptake} \cdot C_{eq} \cdot V / m \text{ mmol/g} \tag{5}
\]

\[
C_{eq} = (1 - \text{Uptake}) \cdot C_{o} \tag{6}
\]

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\(_2\)O, 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 material is present in one phase Figure 2. According to Joint Committee for Powder Standard Diffraction (JCPDS) 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\(_2\)O, acid and base media at 25 ± 1˚C (standard error 0.01 %).

<table>
<thead>
<tr>
<th>Medium</th>
<th>Concentration, M</th>
<th>% Solubility</th>
<th>Medium</th>
<th>Concentration, M</th>
<th>% Solubility</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(_2)O</td>
<td>--</td>
<td>--</td>
<td>NaOH</td>
<td>0.5</td>
<td>0.25</td>
</tr>
<tr>
<td>HNO(_3)</td>
<td>0.1</td>
<td>0.12</td>
<td>0.5</td>
<td>0.25</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>0.19</td>
<td>1.0</td>
<td>1.52</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>0.25</td>
<td>2.0</td>
<td>3.50</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>1.70</td>
<td>4.0</td>
<td>5.40</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4.0</td>
<td>2.50</td>
<td>6.0</td>
<td>25.25</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6.0</td>
<td>13.0</td>
<td>0.1</td>
<td>0.15</td>
<td></td>
</tr>
<tr>
<td>HCl</td>
<td>--</td>
<td>--</td>
<td>KOH</td>
<td>0.1</td>
<td>2.5</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>0.12</td>
<td>1.0</td>
<td>15.52</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>0.22</td>
<td>2.0</td>
<td>18.50</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>1.20</td>
<td>4.0</td>
<td>20.23</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4.0</td>
<td>2.80</td>
<td>6.0</td>
<td>26.22</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6.0</td>
<td>4.90</td>
<td>--</td>
<td>--</td>
<td></td>
</tr>
</tbody>
</table>
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 found 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⁺, Zn²⁺ and Ni²⁺ ions on ZrO₂ ion exchanger at 25 ± 1°C.

\[ nH^+ + M^{n+} \leftrightarrow M^{n+} + nH^+ \]  

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

\[ K_{HM}^M = \frac{[M^{n+}][H^+]}{[M^{n+}]} \]  

(8)

where \([M^{n+}]\) and \([H^+]\) denote to the concentrations of \(M^{n+}\) and \(H^+\) ions in the exchanger, respectively, and \([M^{n+}]\) and \([H^+]\) 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

\[ K_{d_H}^M = K_d \frac{[H^+][M^{n+}]}{[H^+]^n} \]  

\[ K_{d_H}^M = K_d \frac{[H^+]^n}{[H^+]^n} \]  

by taking the logarithm of the two sides

\[ \log K_d = \log K_{d_H}^M \frac{[H^+]}{[H^+]^n} = \log [H^+] \]  

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

<table>
<thead>
<tr>
<th>Cation</th>
<th>Capacity, mmol/g</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>At 50°C</td>
</tr>
<tr>
<td>Na⁺</td>
<td>1.49</td>
</tr>
<tr>
<td>Cu²⁺</td>
<td>1.33</td>
</tr>
<tr>
<td>Ni²⁺</td>
<td>0.80</td>
</tr>
<tr>
<td>Zn²⁺</td>
<td>0.95</td>
</tr>
</tbody>
</table>

Figure 3. DTA and TG curves for ZrO₂ ion exchanger.

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.
When \( \left[ \frac{M^{n+}}{K^M_n} \right] < \left[ \frac{H^+}{H^+} \right] \) and \( \left[ \frac{M^{n+}}{K^M_n} \right] < \left[ \frac{H^+}{H^+} \right] \), the magnitude of the equilibrium constant is considered constant, thus Equation (11) can be reduced to

\[
\log K_d = C + npH
\]  

(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 \( \log K_d \) versus pH of the solution with non-ideality of the exchange reaction for Cu\( ^{2+} \), Zn\( ^{2+} \) and Ni\( ^{2+} \) ions on \( \text{ZrO}_2 \) 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 \( (\alpha) \) 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 \( \text{ZrO}_2 \). 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 \( \text{ZrO}_2 \) 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;

\[
\log W/m = \log K + 1/n \log C_{eq}
\]  

(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 \( \text{ZrO}_2 \) 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 \( \text{ZrO}_2 \) ions and all of these cations are physically sorbed on \( \text{ZrO}_2 \). The values of adsorption capacity \( (K) \) and adsorption intensity \( (n) \) for Cu\( ^{2+} \), Zn\( ^{2+} \) and Ni\( ^{2+} \) ions on \( \text{ZrO}_2 \) 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 Cu\( ^{2+} \), Zn\( ^{2+} \) and Ni\( ^{2+} \) ions on \( \text{ZrO}_2 \) at \( t = 25 \pm 1^\circ C \).

**Table 3. Distribution coefficients and separation factors for Cu\( ^{2+} \), Zn\( ^{2+} \) and Ni\( ^{2+} \) ions on \( \text{ZrO}_2 \) in different pH media at 25 \( \pm 1^\circ C \).**

<table>
<thead>
<tr>
<th>pH of medium Parameter</th>
<th>Cu( ^{2+} )</th>
<th>Zn( ^{2+} )</th>
<th>Ni( ^{2+} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( K_d, \text{ml/g} )</td>
<td>3.31</td>
<td>2.28</td>
<td>2.3</td>
</tr>
<tr>
<td>Separation factor, ( \alpha )</td>
<td>0.69</td>
<td>0.69</td>
<td>0.69</td>
</tr>
<tr>
<td>( K_d, \text{ml/g} )</td>
<td>5.82</td>
<td>4.66</td>
<td>4.60</td>
</tr>
<tr>
<td>Separation factor, ( \alpha )</td>
<td>0.80</td>
<td>0.79</td>
<td>0.79</td>
</tr>
<tr>
<td>( K_d, \text{ml/g} )</td>
<td>8.93</td>
<td>7.53</td>
<td>7.18</td>
</tr>
<tr>
<td>Separation factor, ( \alpha )</td>
<td>0.84</td>
<td>0.81</td>
<td>0.81</td>
</tr>
<tr>
<td>( K_d, \text{ml/g} )</td>
<td>9.89</td>
<td>9.05</td>
<td>8.69</td>
</tr>
<tr>
<td>Separation factor, ( \alpha )</td>
<td>0.95</td>
<td>0.95</td>
<td>0.95</td>
</tr>
<tr>
<td>( K_d, \text{ml/g} )</td>
<td>11.73</td>
<td>9.59</td>
<td>9.19</td>
</tr>
<tr>
<td>Separation factor, ( \alpha )</td>
<td>0.96</td>
<td>0.96</td>
<td>0.96</td>
</tr>
</tbody>
</table>

**Table 4. Freundlich constants \( (n \) and \( K) \) for sorption of Cu\( ^{2+} \), Zn\( ^{2+} \) and Ni\( ^{2+} \) ions on \( \text{ZrO}_2 \) at \( t = 25 \pm 1^\circ C \).**

<table>
<thead>
<tr>
<th>Cations</th>
<th>( n )</th>
<th>( K )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu( ^{2+} )</td>
<td>0.71</td>
<td>( 1.80 \times 10^2 )</td>
</tr>
<tr>
<td>Zn( ^{2+} )</td>
<td>0.67</td>
<td>( 7.76 \times 10^4 )</td>
</tr>
<tr>
<td>Ni( ^{2+} )</td>
<td>0.63</td>
<td>( 4.17 \times 10^5 )</td>
</tr>
</tbody>
</table>
$\text{Zn}^{2+}$, $\text{Cu}^{2+}$, $\text{Cd}^{2+}$ and $\text{Ni}^{2+}$ ions on poly acrylamide acrylic acid impregnated with silico-titanate ion exchanger [17] and $\text{UO}_2^{2+}$ and $\text{Th}^{4+}$ ions on titanium antimonate [18].

4. References


