Assessment removal of tritium radionuclide from liquid waste using sequential ion exchange resin

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ABSTRACT

Tritium (³H) readily combines with oxygen to form water, so its behavior in aqueous systems is controlled by hydrologic processes and it migrates at essentially the same velocity as surface and ground water. In this study removal of tritium from radioactive aqueous solution by using a strongly acidic resin (KU-2) and weakly basic resin (AN-31) by batch and column technique was investigated. Batch studies were performed to estimate the effect of pH, contact time and resin weight in the removal process as well as desorption process. The optimum pH was found to be 7.8. The maximum uptake was reached within one hour and the equilibrium was reached within 1.5 h. Desorption of radioactive tritium was achieved using 3 M HNO₃ and 2 M NaOH. The removal of tritium from liquid radioactive waste using the sequential cationic and anionic columns exchangers that are being used in Egyptian liquid radioactive waste treatment plant was applied. The obtained purified water reaches the permissible level to save our environment. Finally, results indicate that KU-2 resin is an efficient ion exchanger for the removal of ³H from aqueous solution.

Keywords: Removal; Tritium; Tritiated water; Ion exchange; XRD; SEM; Raman spectroscopy

1. Introduction

Among different isotopes of hydrogen is tritium (³H) that emits beta particles at the energy of 5–18.6 KeV. It is considered hazardous to the environment due to its long half-life of 12.3 years [1]. Tritium occurs naturally in both liquid and vaporized water [2]. Naturally, tritium which is generated by the interaction of cosmic radiation with the gases present in the upper atmospheric layers and is estimated to contribute the annual effective dose equivalent about 0.01 μSv [3]. There are different sources of tritium due to human activities that include atmospheric nuclear testing [4], tritium from a nuclear reactor under normal operations [5]. Nuclear power plants also produce tritium by fission and neutron activation [6]. The production rates from power reactors vary due to differences in plant designs: heavy water reactors, which use deuterium as a coolant and moderator, produce hundreds to thousands of times greater quantity of tritium than boiling water or pressurized water reactors [7,8].

Tritium readily forms a chemical bond with oxygen (O) and another H atom to form tritiated water (HTO, as opposed to stable H₂O) [9,10]. Tritium behaves nearly identically to its stable isotope, and thus takes a similar path through biological and chemical systems in the environment. The physico-chemical similarity of HTO to water is because the supplemental H and O atoms in HTO effectively reduce the relative significance of the mass of the two extra neutrons on the radioactive isotope [11].

Tritium, which is deposited into the soil as HTO can be incorporated into plants, animal tissues, and human body causes internal radiation doses [12]. Tritium atoms reversibly
replaced H in OH, NH and SH bonds of organic molecules in the body, while about 1% of the activity is incorporated into stable CH bonds [13,14]. These forms are called organically bound tritium (OBT). A major part of OB T (>90%) is oxidized and excreted as HTO, this tritium is called the exchangeable tritium fraction. The non-exchangeable tritium fraction is normally released only as a result of an enzymatic breakdown of the molecules containing tritium bound to carbon. The major of HTO is excreted in urine.

Traditional methods of tritium separation and removal such as water distillation, electrolysis, and catalytic exchange process are costly [15]. Ion exchange resins have been used in water softening, removal of toxic metals from water in the environment and radioactive liquid waste treatment [16,17]. They are environmentally compatible since the cycle of loading/regeneration/reloading allows them to be used for many years. Kobayashi et al. [18] studied the sorption and desorption of tritiated water vapor on four kinds of materials (epoxy paint, butyl rubber, stainless steel 304 and acrylic resin) and it was found that the amount of tritium sorbed take the order of epoxy paint > acrylic resin = butyl rubber > stainless steel 304. Ono et al. [19] studied the sorption of tritiated water on organic materials such as organic rubber, linoleum, and acrylic resin. It was found that the sorption amount increases slightly with contact time. In another study [20], Teng et al. investigated the sorption of tritium on four soil samples, and the results showed that the distribution coefficient is small but noticeable. It is worthy to consider that migration of $^3$H can be distinctly slower, from its sorption onto geological media, than the flow rate of the ground water. The purpose of this study is to investigate the affinity of tritium removal using both cation (KU-2) and anion exchange resins (AN-31) that the Egyptian Atomic Energy Authority (EAEA) has already used; purified water will reach the level allowed for safe release into our environment.

2. Experimental

2.1. Chemicals and reagents

All chemicals and reagents used in this work were of analytical grade purity and used without further purification. Radioactive liquid waste with beta emitters was collected from the storage tank in the LRWTF at the hot laboratories center, located at Abu Zaabal, Cairo, Egypt. The cation exchanger (KU-2) used as a strongly acidic resin functionalized with a polystyrene sulfonic group, with a particle size 0.3–1.2 mm, while the anion exchange (AN-31) is a weakly basic resin with a particle size 0.4–2 mm. The specific volume in (H$^+$)-form and (OH$^-$)-form is 2.7 and 3.3 cm$^3$/g for KU-2 and AN-31, respectively. The dynamic exchange capacities were 1600 and 1280 mol/cm$^3$ for KU-2 and AN-31, respectively.

2.2. Batch experiments

Batch experiments were carried out as follow: a certain weight of resin (KU-2 or AN-31) was placed into a polypropylene tube and 10 mL of radioactive liquid waste was transferred to the tube. The tubes were shaken for the required time at 250 rpm at ambient temperature (25 ± 1°C). In order to study the optimum conditions for the batch adsorption, various experimental parameters were studied including the effects of pH (2–10), contact time (5–180 min) and resin weight (0.5–1 g). After the required shaking time, the mixture was centrifuged and the clear supernatant phase was filtered through a 0.1 mm ion chromatograph filter. The radioactivity of the liquid waste was determined before and after the treatment process using liquid scintillation counter TRI-CARB model (2700TR series). The load resins (0.1 g resin after the treatment process by batch mode) have been used for desorption (regeneration) studies. Aliquots (10 ml) of different concentration (0.1–3 M) of HNO$_3$ and (0.1–2 M) of NaOH solutions were used for desorption of the sorbed tritium onto KU-2 resin. The removal percent (R %) and desorption percent (D %) were calculated from the following equations:

$$R(\%) = \frac{C_i - C_f}{C_i} \times 100$$

$$D(\%) = \left(\frac{C_f}{C_i - C_f}\right) \times 100$$

where $C_i$, $C_f$, and $C_d$ are the initial, final and desorbed tritium counts, respectively, per unit time per unit volume. The TDS, conductivity and pH values of liquid waste were measured using Consort C 932 model 86561 made in Belgium.

2.3. Application using ion exchanger column

The Egyptian Atomic Energy Authority (EAEA) has a liquid radioactive waste treatment facility (LRWTF). It is running based on the combined process including the precipitation and ion exchange processes as shown in Fig. 1. LRWTF has two kinds of columns employed for ion exchange processes including the cationic and anionic columns. The capability of both columns (KU-2 and AN-31) for the removal of tritium from real collected low level liquid radioactive waste (LLLRW) was evaluated. The cationic (KU-2) and anionic (AN-31) columns were preconditioned using 1.5 M HNO$_3$ and 0.75 M NaOH, respectively. Then, the dynamic experiments were carried out by pumping tritium solution in an up-flow mode through the columns at room temperature (25 ± 1°C). About 10 m$^3$ of LLLLW (of pH 7.8) containing tritium from the storage tanks in the LRWTF was treated using an ion exchange columns. Sequential cationic (KU-2) and anionic (AN-31) columns at a flow rate of 1.5 m$^3$/h were applied for the treatment of liquid radioactive waste. Two circulation passes of each of KU-2 and AN-31 were employed in order to get purified water that can be safely released to the environment as shown in Fig. 1.

3. Results and discussion

3.1. Characterization

3.1.1. Characterization of liquid radioactive waste

Liquid scintillation analyzer was used to characterize the LLLRW sample and compare the spectrum obtained
from the radioactive tritium standard, as shown in Fig. 2. Tritium decays by the emission of a low-energy (18.6 KeV) beta particle [21]. The spectrum of waste was close to that of the spectrum of the tritium standard, which confirms the contamination of an aqueous solution with radioactive tritium ($^3$H). Some of the physico-chemical properties of this radioactive waste are listed in Table 1. The total dissolved salts (TDS) and the conductivity of the radioactive waste are 427 mg/L and 804 μS/cm, respectively, as reported in Table 1. The density and boiling point of liquid waste is 1.20 g/cm$^3$ and 101.2°C, respectively. These results indicated that the density and boiling point values of liquid waste are higher than the values of H$_2$O. Tritium is extremely mobile in the environment. The tritium is released mainly in two forms – tritium gas (HT) and tritiated water (HTO). However, in the environment, tritium atoms in HT are relatively quickly exchanged with stable H atoms in water through the phenomenon of molecular exchange. That means HT is transferred to HTO. According to the above-mentioned characterization and discussion, in this study, all tritium (HT and HTO) releases are treated as HTO [22].

3.1.2. Resin characterization

SEM, Raman, and XRD were used for characterization of KU-2 and AN-31 before and after activation as shown in Figs. 3–6. From these figures, it shows that in the micrographs apparently original porous resin possesses many vacant pores (Fig. 3A). A small amount of tritium hardly changes the appearance of the surface of the anionic (AN-31) resin, (Fig. 3B). However, after the sorption of tritium cation, the surface changes by the formation of complexes. Raman and XRD spectrum confirmed the sorption of tritium ion onto the surface of AN-31 and KU-2 activity impregnated resins is amorphous and the noise signal spectra for these samples are similar (Figs. 4 and 5).

3.2. Batch technique

3.2.1. Effect of pH

The removal of tritium was examined in a pH range of 2–10 at room temperature as demonstrated in Fig. 6. The maximum removal percent of $^3$H was 83% and it is clear that there was no influence of pH on the removal of tritium by KU-2. This may be due to using the hydrogen form of this strong acid resin, so it was highly dissociated and the exchangeable hydrogen ion was readily available for exchange with $^3$H over the entire pH range. Consequently, the exchange removal of the strong acid resin was independent of the solution pH. Teng et al. [20] also showed that there is no clear influence of pH on the sorption of tritium as tritiated water at four different kinds of soil materials. In the case of the AN-31 resin, the removal percent of tritium was 7% at pH = 2 and this increased gradually up to 15% at pH = 5. This is because the degree of ionization of the weak base resin was strongly influenced by pH. Also, increasing uptake of $^3$H on a weak base resin (R-NH$_3$OH) with increasing pH may be explained by a mechanism involving the hydrolysis of the tritium ion (H$^+$) in a solu-

<table>
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<th>Properties</th>
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<tr>
<td>TDS</td>
<td>427 ± 4.9 mg/L</td>
</tr>
<tr>
<td>Conductivity</td>
<td>804 ± 7 μS/cm</td>
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<tr>
<td>Boiling point</td>
<td>101.2°C</td>
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<tr>
<td>Density</td>
<td>1.20 g/cm$^3$</td>
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Fig. 1. Column technique used in the purification of radioactive waste in LRWTF.

Fig. 2. Beta-spectrum of (a) the radioactive tritium standard and (b) the real waste containing radioactive tritium.
tion to give a hydrolysis product, which is more strongly adsorbed or by a mechanism involving the direct exchange of un-hydrolyzed ions with a specific group on the adsorbing surface in a relatively low pH value. It was clear that the cation exchange resin (KU-2) was more efficient than anion exchange resin (AN-31) in the removal of tritium.

3.2.2. Effect of contact time

The effect of contact time on the removal of tritium using KU-2 and AN-31 resin at 25°C and pH 7.8 is given in Fig. 7. The removal percent was 80% and 20% in the first one hour for both KU-2 and AN-31, respectively. The equi-

Fig. 3A. SEM for KU-2 before (a) and after activation (b).

Fig. 3B. SEM for AN31 before (a) and after activation (b).
Equilibrium was attained within 1.5 h. It is deduced that the cationic exchange (KU-2) has fast kinetic.

H is the constituent of water; it can penetrate into the porous of resin as well as exchanges in functional surface onto KU-2 and AN-3 with the different forms of water. Thus, different isotope exchange reactions may take place onto KU-2 and AN-3: molecular HTO-H2O exchange reaction, ionic T+ and OT¯ isotope exchange reactions, and both molecular and ionic reactions. In this case, it might be the retained 3H onto KU-2 and AN-3 is bound to organic molecules via reversibly replaced H in OH, SH, and CH to form organically bound tritium (OBT) [13,14].

3.2.3. Effect of resin weight

The resin amount is also an important parameter influencing the quantitative removal of radioactive waste. The retention of the tritium isotope was examined in relation to the amount of resin used (KU-2 and AN-3), in the range of 0.05–1 g and equilibrated for two hours, as shown in Fig. 8. It was observed that the amount of tritium removed per unit mass increased with increases of the resin amounts. The maximum uptake by KU-2 and AN-3 resins was achieved with an adsorbent mass of 0.2 g, and finally, the removal percentage remained constant up to 1 g of resin. The increase in removal percentage was due to the greater surface area and an increased number of exchanging sites [23]. By increasing the resin mass, the binding of 3H remained constant. This effect might be attributed to the clumping of the resin, resulting in a decrease in the total surface area of the adsorbent [24].

3.3. Desorption of tritium

After use, the resin was converted back to the hydrogen form (regenerated). Most ion exchange media can be regenerated by using an appropriate strong acid (such as HNO3) for cation resins or alkali (such as NaOH) for anion resins to replace the bound contaminant ions on the medium and return the resin to its original chemical form. Resin life can be extended by regeneration, which saves cost and disposal concerns. Sodium hydroxide and nitric acid were used in a
different concentration range for the regeneration resin KU-2, as shown in Fig. 9. The most important factor in cation resin regeneration efficiency is the acid concentration. Since the resin active sites have a greater affinity for ions they have picked up than for hydrogen ions, a sufficient acid concentration is required to overcome and drive the ions from these sites.

It was found that the high acid concentration regenerated the resin more completely. According to Fig. 9 the recommended concentration for regeneration of KU-2 resin and 100% removal of tritium was 3 M of HNO₃ and 2 M of NaOH. Sodium hydroxide is more efficient than nitric acid at the same concentration and this may be due to sodium ions have a higher affinity for the resin active sites than the hydrogen ions and tritium was desorbed mainly in the form of tritiated water. In comparison with other studies, desorption of tritium from the surface of epoxy paint and acrylic resin reached about 20–50% using nitrogen purging and water vapor technique [18].

Several regeneration cycles were carried out on the loaded KU-2 resin using nitric acid, as shown in Table 2, it was found that the four cycles for each concentration range allowed fewer regenerations but with a significantly reducing regeneration cost and increasing resin lifetime.

### 4. Applicability of columns at Egyptian LRWTF

Egyptian radioactive waste management program constructed the LRWTF to treat low and intermediate level radioactive liquid wastes. It is mainly based on the combined process, including precipitation and coagulation as well as the cationic and anionic ion exchange processes [25]. Treatment of tritium using sequential cationic (KU-2) and anionic (AN-31) in LRWTF was a highly efficient treatment (Table 3). About 98% of tritium was retained onto KU-2 and AN-31. In comparison with other investigations, Jeppson (2000) studied the uptake of tritium using a commercial sulfonated polystyrene/divinylbenzene resin. After resin pre-treatment, column technique was applied and the removal percent reach to about 83% [15].

In most countries, the guidelines for radio nuclides in drinking water are based on international radiation protection methodologies, including recommendations of the International Commission on Radiological Protection (ICRP) and the World Health Organization (WHO) [26,27]. Most EU member states have transposed the 1998 EU directive into national law, regulation or standard, and most have followed the logic of using the 100 Bq/L value for tritium only as a screening value. United States Environmental Protection Agency (USEPA) was referred to a Maximum Contaminant Level (MCL) at 20,000 pCi/L (740 Bq/L) based on a 4 mrem (0.04 mSv) per year dose limit [28,29]. In Canada, the guideline reference level (GL), or maximum acceptable concentration (MAC), for tritium in drinking water is 30,000 Bq/L. Finland’s standard for tritium in drinking water was 30,000 Bq/L. The Tritium limit in drinking water was 10,000 Bq/L as reported

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**Table 2**

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<tr>
<th>Conc. HNO₃</th>
<th>Regeneration , %</th>
<th>1 Cycle</th>
<th>2 Cycle</th>
<th>3 Cycle</th>
<th>4 Cycle</th>
<th>Total</th>
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<td>0.1 M</td>
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<td>13.5</td>
<td>3.5</td>
<td>7.8</td>
<td>24.9</td>
<td></td>
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<tr>
<td>0.5 M</td>
<td>28.1</td>
<td>23.1</td>
<td>14.2</td>
<td>12.6</td>
<td>44.2</td>
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<tr>
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<td>30.3</td>
<td>25.3</td>
<td>15.2</td>
<td>11.9</td>
<td>52.4</td>
<td></td>
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<tr>
<td>2.0 M</td>
<td>49.5</td>
<td>34.5</td>
<td>19.2</td>
<td>9.4</td>
<td>63.2</td>
<td></td>
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<tr>
<td>3.0 M</td>
<td>100</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>100</td>
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**Table 3**

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<th>Properties</th>
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<th>After treatment</th>
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<tr>
<td>Activity (Bq/L)</td>
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<tr>
<td>pH</td>
<td>7.8</td>
<td>7.36</td>
</tr>
<tr>
<td>TDS (mg/L)</td>
<td>427</td>
<td>111</td>
</tr>
<tr>
<td>Conductivity (μS/cm)</td>
<td>804</td>
<td>205</td>
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</tbody>
</table>
by WHO and Switzerland [28]. It can be concluded that the purified water that has been obtained after the treatment process can be safely released into the environment.

5. Conclusion

Removal of tritium from aqueous solution using strongly acidic resin (KU-2) and weakly basic resin (AN-31) was investigated. The experimental results indicated that these resins can be successfully used for the removal of tritium, but cation exchange resin was more efficient than anion exchange resin. Removal of tritium by KU-2 is a pH-independent. Removal by AN-31 was pH dependent and the optimum pH was 7.8. Batch kinetic study shows that a rapid uptake occurred within the first one hour and the equilibrium was attained within 1.5 h. Tritium was desorbed from the resin by using different concentrations of both sodium hydroxide and nitric acid. The purified water that obtained after an efficient treatment process is safe for release into the environment.

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References