# Synthesis and Sorption Behaviour of Some Radioactive Nuclides on Sodium Titanate as Cation Exchanger

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**Abstract.** Crystalline ($Na_4TiO_4 \cdot 0.32H_2O$) and amorphous ($Na_2TiO_3 \cdot 1.45H_2O$) forms of sodium titanate were prepared by fusion reaction of $TiO_2$ and $Na_2CO_3$ at $1100°C$ in molar ratios of 2:1 and 1:2, respectively. The prepared products were characterized using IR, DTA-TG, X-ray and elemental analyses. Kinetic studies of the order of reaction ($n$) and activation energy ($E_a$) for crystallization transformation step (for crystalline sodium titanate only) have been determined from DTA thermogram and their values were found to be 0.87 (univalent order) and 3.97 kJ mol$^{-1}$, respectively. Ion exchange capacities and some distribution studies were carried out at different conditions in the presence of some complexing agents (EDTA, boric and citric acids) and the results showed that the capacities of the crystalline form are always less than the amorphous one.

**Keywords:** sodium titanate, cation exchanger, sorption, radioactive nuclides

## Introduction

There are many accounts in the literature describing the chemistry and formation of sodium titanates prepared by precipitation or fusion reaction (Izaw et al., 1983; Abe, 1974; Manku, 1984; Parakash et al., 1971). The physicochemical properties of the products depend on the reactants and the method of preparation (Izaw et al., 1983; Abe, 1974). Alkali metal titanates have been synthesized which confirm to either of the following two series [$M_nTi_nO_{2n+1}$] and $Na_4Ti_nO_{2n+2}$ (Bouziz and Mayer, 1971; Wefors, 1967; Andersson and Wadsley, 1961; Dion et al., 1978; Beloyev et al., 1968; Andersson and Wadsley, 1962; Watanabe et al., 1979; Marchand et al., 1980). In the former series; members with $n = 1$–9 have been prepared, while in the later series; compounds with $n =$ odd ($n = 1, 3, 5$). $K_2Ti_2O_5$, $Na_2Ti_3O_7$, $Na_2Ti_4O_9$ and $Na_4Ti_5O_{12}$ have been synthesized and gave a layered structure (Watanabe et al., 1979; Marchand et al., 1980; Olazcuage et al., 1975; Werthmann and Hoppe, 1984; Izawa et al., 1982). Whereas, thermally synthesized sodium titanates by fusion reaction led to more chemically and thermally stable than

that obtained by precipitation and is more convenient to use in nuclear technology purposes. New sodium titanates were prepared by reaction of $TiO_2$ with NaOH, this compound has a layered structure and it has the formula of $Na_4Ti_9O_{20} \cdot nH_2O$ (Clearfiled and Lehto, 1988). Analysis of literature data provided that, few published paper discussed the applications of titanates as ion exchanger in the separation technology purposes.

The overall objective of this study was directed to prepare thermally stable sodium titanate as cation exchanger in both crystalline and amorphous forms by the fusion reaction of $Na_2CO_3$ and $TiO_2$ at different molar ratios. Investigation of the possible use of thermally synthesized sodium titanate in the treatment of radioactive liquid waste is assessed.

## Materials and Methods

Titanium dioxide was used of 99.9% purity. All other reagents were of analytical grade. In all experiments bidistilled water was used for analytical purposes and for final washing of the exchangers.

Two samples of sodium titanate were prepared as reported earlier (Manku, 1984; Parakash et al., 1971) by heating a finally divided mixtures of $TiO_2$ and $Na_2CO_3$ in 2:1 and 1:2 molar ratios, up to fusion and continuous heating to 1100°C for 6 hours. The products were immediately separated as micro rocks from the platinum crucible and uniformly dispersed into bidistilled water. The prepared samples were washed with bidistilled water to remove fine adherent particles and soluble matters, then dried at 50°C. The solids were broken to smaller particle sizes, sieved (0.01–0.1 mm) and stored at room temperature.

Sodium titanate in $H^+$-form (titania) were obtained using glass column (2.5 cm i.d.) packed with 15 g of the solids in $Na^+$ form and treated with 0.5 M HCl until the filtrate becomes free from $Na^+$ ions. Then the solid was washed with water to remove excessive acid until the pH of the effluent was reached to ∼6. The resulting products were dried at 50°C and stored over a saturated NaCl solution to a constant weight.

The elemental analysis of the synthesized sodium titanate was carried out by dissolving the solid in HF and the resulting solutions were analyzed for $Na^+$ and $Ti^{4+}$ by using flame photometry and total reflection X-ray fluorescence (TXRF), respectively. The water content of the samples were determined from TG-Thermograms up to 850°C, and by calcination of 1 g of the samples at the same temperature.

The water content in the crystalline sodium titanate $[Na_4TiO_4 \cdot nH_2O]$ and its protonated phase $[H_4TiO_4 \cdot nH_2O]$, was found to be in the range $0.36 > n > 0.3$. Also, the water content in the amorphous sodium titanate $[Na_2TiO_3 \cdot nH_2O]$ and its protonated phase $[H_2TiO_3 \cdot nH_2O]$ was found to be in the range $1.45 > n > 1.42$.

Capacities of the products were determined as reported earlier (El-Naggar et al., 1999; Aly and El-Naggar, 1995) by equilibration of 0.1 g of the solid with 10 ml of the desired solution in a shaking thermostated water bath adjusted at $25 \pm 1°C$. The capacity was calculated by the following equation;

$$Capacity = \%Uptake \cdot C_o \cdot V/m \cdot Z \text{ meq/g}$$

where $C_o$: the initial concentration of the solution (M), $V$: volume of the solution (ml), $m$: weight of the exchanger (g) and $Z$: valence of cation.

Batch technique was followed to determine the distribution coefficient ($k_d$) values of $Cs^+$ and $Sr^{2+}$ ions on sodium titanates in the presence of complexing agents,

according to the following formula:

$$K_d = \frac{A_o - A_f}{A_f} \times \frac{V}{m} \text{ ml/g}$$

where $A_o$ and $A_f$, are the initial and final counting rate of the considered element in solution, respectively; $V$ and $m$, are the volume of the solution (ml) and the weight of exchanger (g), respectively.

## Results and Discussion

### Synthesis of Sodium Titanate

Two forms of sodium titanate were prepared by fusion reactions of $TiO_2$ and $Na_2CO_3$ at 1100°C in two molar ratios of 2:1 and 1:2. Details of additive and preparations are summarized in Table 1. The reaction of powdered of $TiO_2$ with $Na_2CO_3$ as solid-solid interaction was studied by thermal analysis techniques (DTA-TG) and the results are presented in Fig. 1. Figure 1(a)–(d)
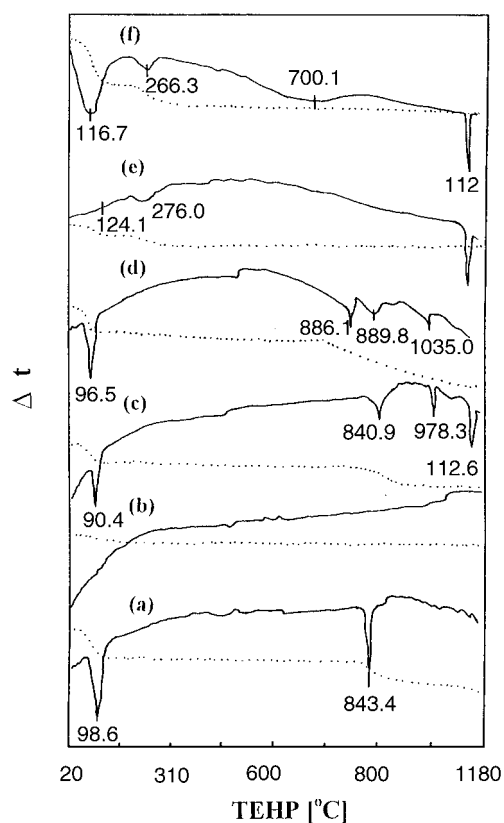


*Figure 1.* DAT-TG curves of $Na_2CO_3$ (a), $TiO_2$ (b), mixture of $TiO_2$ and $Na_2CO_3$ (2:1) (c), mixture of $TiO_2$ and $Na_2CO_3$ (1:2) (d), crystalline sodium titanate (e) and amorphous sodium titanate (f).

*Table 1.* Details of preparation conditions and some characteristics of sodium titanate forms.

| Sample | | Molar ratio of rectants in mixed powder $TiO_2$:$Na_2CO_3$ | Elemental analysis | | | | | Expected molecular formula (M. wt) | M.P. (°C) | Colour | XRD analysis | Capacity (Meq./g) | |
| | | | Na% | | Ti% | | | | | | | | |
| | | | Exp.[a] | Cal. | Exp.[a] | Cal. | $H_2O$[c] | | | | | $Na^+$ | $Cs^+$ |
| Prod. I | Na-form | | 45.1 | 43.9 | 23.8 | 22.8 | 2.7 | $Na_4TiO_4 \cdot 0.32H_2O$ | 1126 | White | Crystalline | 2.1 | 1.42 |
| | H-form | 2:1 | 30.5 | 34.1 | 27.6 | 26.3 | 3.8 | M. wt = 209.28 | | | | | |
| | | | | | | | | $Na_2H_{1.3}TiO_4 \cdot 0.36H_2O$ | 1126 | White | Crystalline | 0.23 | 0.17 |
| | | | | | | | | M. wt = 181.76 | | | | | |
| Prod. II | Na-form | | 27.0 | 27.3 | 28.1 | 28.5 | 15.5 | $Na_2TiO_3 \cdot 1.45H_2O$ | 1120 | Orange | Amorphous | 3.78 | 2.45 |
| | H-form | 1:2 | 28.0 | 1.35 | 38.6 | 40.1 | 19.7 | M. wt = 167.98 | | | | | |
| | | | | | | | | $NaO_{.07}H_{1.93} \cdot TiO_4H_2O$ | 1120 | Orange | Amorphous | 0.38 | 0.2 |
| | | | | | | | | M. wt = 119.2 | | | | | |

Prod. I: Crystalline sodium titanate, Prod. II: Amorphous titanate, XRD: X-ray diffraction, M.P.: Melting point, Cal.: Theoretical.
[a]Measured by flame spectrophotometer.
[b]Measured by total X-ray florescence.
[c]Measured by TG analysis.

shows the DTA and TG curves of both reactants during the formation of product I and product II, while Fig. 1(e) and (f) represents DTA-TG curves of the finally obtained products. The thermal decomposition of $Na_2CO_3$, Fig. 1(a), shows the first endothermic peak at ~98.6°C with mass loss ~5.1%. This stage may be due to the evaporation of surface adsorbed water. The second endothermic peak at ≈843.4°C may be attributed to the melting of $Na_2CO_3$ which accompanied with a continuous mass loss relative to the partial decomposition of $Na_2CO_3$ (Anonymous, 1972; Nobuyuki et al., 1998). The thermal decomposition of $TiO_2$ (Fig. 1(b)) shows thermal stability through heating program (m.p. ≈1870°C) due to loss of unaccompanied surface water at the start of heating (Anonymous, 1972).

Figure 1(c) and (d) show the DTA-TG thermograms of 2:1 and 1:2 molar ratios of $TiO_2$ with $Na_2CO_3$, leading to the formation of crystalline and amorphous forms of sodium titanate, respectively. Figure 1(c) shows the melting of $Na_2CO_3$ at $T_{max}$ 841°C which is considered the starting point of the reaction with $TiO_2$ through its decomposition up to ~950°C, and followed by irreversible endothermic peak at $T_{max}$ 977°C without mass change which may be due to crystallization of the product I (crystalline form). It follows by the last reversible endothermic peak at $T_{max} \approx 1126$°C which may be attributed to the melting point of the product I. Also, the TG curve, Fig. 1(c) shows a mass loss in the range 800–950°C is ~12% which may be due to

loss of $CO_2$ gas. The above results led to assume the reaction may be follows the equation;

$$4TiO_2 + 2Na_2CO_3 = Na_4TiO_4 + 3TiO_2 + 2CO_2\uparrow$$
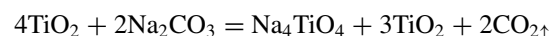
On the other hand, Fig. 1(d) shows different behavior for the fusion reaction of $TiO_2$ with $Na_2CO_3$ (1:2 molar ratio). The melting of $Na_2CO_3$ starts the thermal reaction at $T_{max}$ 823°C followed by a series of endothermic peaks at $T_{max}$ ~895 and ~1033°C. These accompanied by continuous mass loss in the range 800–1000°C, with mass change ~28% which may be mainly relative to $CO_2$ gas and trace of some evolved sodium as side products (Nobuyuki et al., 1998). These changes may be corresponding to the formation reaction followed by different rearrangements of the yellow intermediate product to the final orange yellow product II (amorphous form). The results led to assume the reaction to be proceeds as follows;

$$TiO_2 + 2 Na_2CO_3 = Na_2TiO_3 + Na_2O + 2CO_2\uparrow$$
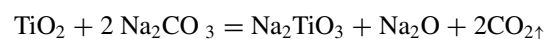
It was found that, after cooling the last equation products the excess of $Na_2CO_3$ or $Na_2O$ decomposed as side products and can be hydrated by air moisture giving NaOH, which is determined by $FeCl_3$ (Andersson and Wadsley, 1962). Therefore, the isolation of the product from the air is necessary and the continuous washing by distilled water was carried out to separate and remove all adherent particles. The side products must be

considered and finally pure orange color material was obtained (Andersson and Wadsley, 1962).

Figure 1(e) and (f) shows the thermal analysis of the finally obtained crystalline and amorphous structure of sodium titanate, respectively. It was found that, very broad endothermic peak at $T_{max}124°C$ and sharp endothermic peak at $116.7°C$ were obtained and resulting from the loss 1.52% and $\approx 10.53%$ of free water, respectively. Two broad endothermic peaks at 250–300°C and $T_{max} \approx 265°C$ were obtained and resulting from loss of amount of coordinated water with mass change = 1.35% and 4.38%, respectively. Finally the reversible endothermic peaks at $T_{max} \approx 1128$ and 1121°C corresponding to the melting of crystalline and amorphous sodium titanate products, respectively. These melting points of titanate products were supported by the melting point of sodium trititanate ($Na_2TiO_3$) in literature data that was found at 1128°C (Anonymous, 1972). From the above analysis, it's clear that the amorphous sodium titanate contains $\sim 15.5%$ water from its original weight, but the crystalline sodium titanate contains small quantity of water ($\sim 2.8%$) which may be considered as a great influence on its properties as ion exchanger. Similar behavior was reported by El-Naggar et al. for other ion exchangers such as, tin, iron and cerium (IV) antimonate (Aly et al., 1999; El-Naggar et al., 1993, 1997).

*IR-Spectra*

The IR spectra of the reactant materials ($Na_2CO_3$ and $TiO_2$) and the final products of sodium titanates (dried at 50, 200, 400, 600 and 850°C) are presented in Figs. 2–4. It was found that, the two spectra of product I and II, Fig. 2(c) and (d), are completely different from that of $Na_2CO_3$ (Fig. 2(b)) but the same two spectra are nearly similar to the spectrum of $TiO_2$ (Fig. 2(a)). Furthermore, the vibration diagnostic bands for both H-form and Na/H-form for the synthesized products are similar. Continuously, the two spectrum of product I and product II (Fig. 2(c) and (d)) revealed a broad absorption peak in the range 3600–3050 $cm^{-1}$ that could be assigned to the stretching vibrational mode of water. While the absorption band at 1635–1645 $cm^{-1}$ may be due to the bending modes of water molecules absorbed on the surface of titanate samples (Mishra and Srinivasu, 1992).

The absorption bands at 910 $cm^{-1}$ indicates the presence of Ti—O in the synthesized compounds (Nakamoto, 1978). This bending peak in the case of
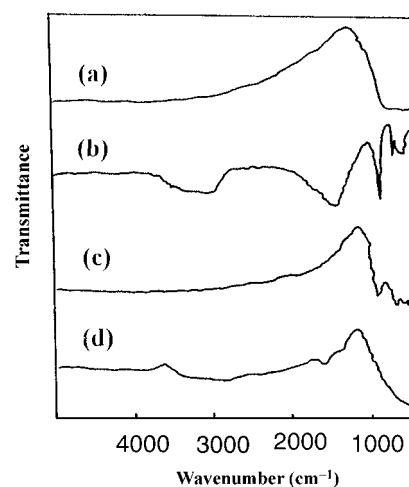


*Figure 2.*    Infrared spectra of $TiO_2$ (a), $Na_2CO_3$ (b), crystalline (c) and amorphous (d) sodium titanates.
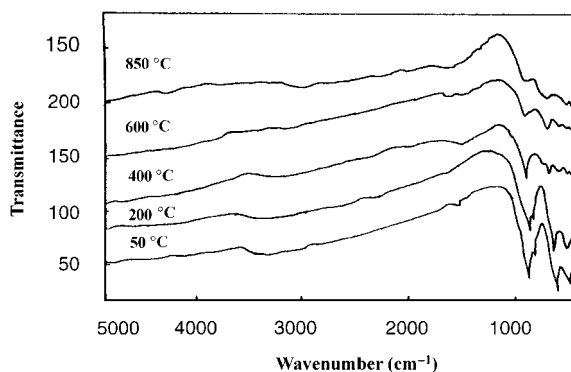


*Figure 3.*    Infrared spectra of crystalline sodium titanate at different drying temperatures.
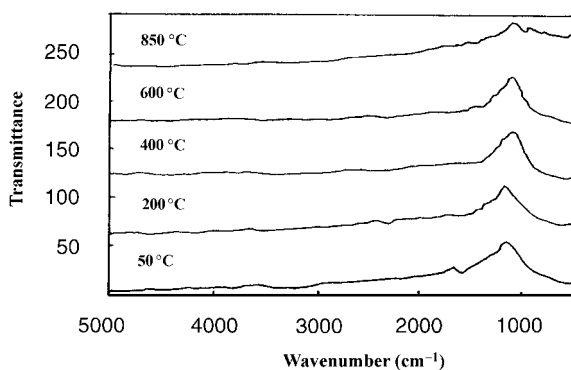


*Figure 4.*    Infrared spectra of amorphous sodium titanate at different drying temperatures.

product II (Fig. 2(d)) is neglected relative to product I (Fig. 2(c)), which may be due to some differences in the structure, feature in the case of product I (crystalline form). The absorption peaks in the range (920–450 $cm^{-1}$) may be due to the vibration of M—O bond of the crystalline form (Nakamoto, 1978). From all the above results, the comparison between the spectrum of $TiO_2$ (Fig. 2(a)) and the spectrum of the synthesized products, Fig. 2(c) and (d), led to assume that, the obtained sodium titanates in different forms have the structure of $Na_2O \cdot nTiO_2 \cdot nH_2O$ which indicated that the hydrous $TiO_2$ is the basic matrices of the structure and the sodium ions distributed between its layer in the case of crystalline form and randomly in the case of amorphous form (Clearfiled and Lehto, 1988; Sasaki et al., 1985a).

Moreover, the protonated samples of crystalline sodium titanate (Fig. 3) and amorphous sodium titanate (Fig. 4) heated at higher temperatures showed essentially the same absorption band for the samples dried at 50°C but clearly steadily decrease in the band characteristic at 3300 and 1650 $cm^{-1}$ of molecular water. This goes parallel to increase in drying temperatures from 50°C to 850°C, where the characteristics two bands of water disappeared at 850°C. Similar results were obtained by Clearfield et al. (1997) through treating sodium titanium silicate to higher temperatures.

*XRD Analysis*

The X-ray diffraction patterns of thermal synthesized sodium titanates showed that the product I of 2:1 molar ratio (Ti/Na) has crystalline structure but the product II of 1:2 molar ratio has completely amorphous structure as shown in Figs. 5(a) and 6(a), respectively. The results of X-ray diffraction for reactants ($TiO_2$ and $Na_2CO_3$) and final products are inagreement with the IR-spectra and DTA-TG analysis. As shown in Figs. 5(a) and 6(a), all the diffraction lines of the reactants disappeared from the pattern of the product due to the chemical reaction. Consequently, the product of the reaction of $TiO_2$ with $Na_2CO_3$ of 2:1 ratio shows clearly new lines characteristic for the new sodium titanate with crystalline structure with sharp peak at 10.7° $2\theta$ (Fig. 5(a)). But for 1:2 molar ratio of the same reactants (Fig. 6(a)) completely amorphous sodium titanate is obtained.

Additional informations concerning the thermal decomposition of sodium titanate were obtained by using X-ray diffraction patterns. The XRD patterns of the product I (crystalline form) and product II (amorphous
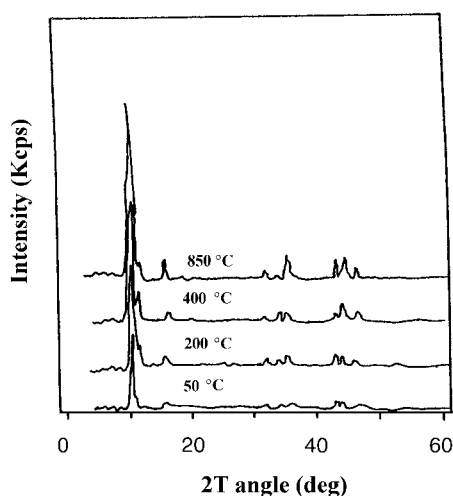


*Figure 5.* X-ray diffraction patterns of crystalline sodium titanate at different drying temperatures.
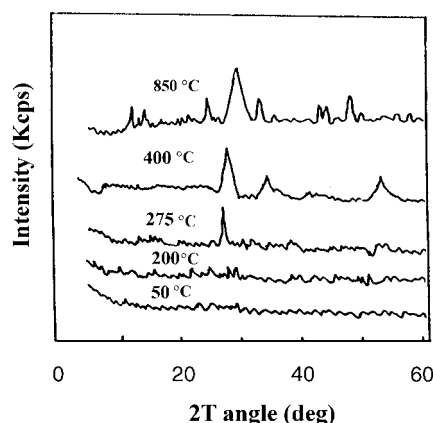


*Figure 6.* X-ray diffraction patterns of amorphous sodium titanate at different drying temperatures.

form) that dried at 50, 200, 400 and 850°C, are given in Fig. 5(a)–(d) and Fig. 6(a)–(d), respectively. Analysis of the data obtained shows that practically no changes are observed in XRD patterns for product I (crystalline sodium titanate) after thermal treatment at elevated temperatures, even at 850°C. There is only little increase in the diffraction lines characteristic of the crystalline form of sodium titanate as a result of water dehydration. This suggests that the basic structure of this compound remains unchanged and shows high thermal stability. The XRD patterns of product II (amorphous sodium titanate) show some degree of crystallinity by increasing temperatures from 50°C to 850°C, Fig. 6(a)–(d). The first diffraction line at 25° $2\theta$ appears only after drying up to 275°C, Fig. 6(c). This

change is corresponding to the second irreversible dehydration endothermic peak at $T_{max}$ 275°C as shown in DTA-thermogram Fig. 1(d). This inflection to poor crystalline form may be also due to the dehydration process parallel to the $TiO_2$ formation (Mishra and Srinivasu, 1992; Sasaki et al., 1985b). These observations were also reported by different authors (Mishra and Srinivasu, 1992; Dubrovin and Malimonova, 1985; Yamazaki et al., 1990).

**Reaction Order and Activation Energy**

Differential thermal analysis has long been used to investigate and identify many endothermic and/or exothermic reactions that occur when a material is heated or cooled using a carefully standardized procedure. DTA apparatus may be calibrated and used as a semi-quantitative calorimeter for estimating both chemical and physical heat changes (Ingahan and Manes, 1965). So, from Fig. 1(c), the DTA thermogram of the mixture of $TiO_2$ with $Na_2CO_3$ (2:1 molar ratio) leading to the formation of purely crystalline sodium titanate, the peak responsible for the crystallization process in this thermal reaction can be determined (Ingahan and Manes, 1965). Thus, X-ray diffraction patterns for samples heated at different $T_{max}$ after starting the fusion reaction were measured as shown in Fig. 7(a) and (b). Consequently, Fig. 7(a) shows no diffraction lines for the mixture samples heated up to 950°C for 6 h while, Fig. 7(b) shows clearly diffraction lines for the sample heated up to 1000°C for 6 h, diagnostic of crystalline sodium titanate. Thus, we can assume that the irreversible endothermic peak in the

Fig. 1(c) at $T_{max}$ 978°C must be corresponding to rearrangement from amorphous to crystalline structure of the product I. This is clear from Fig. 7 by zooming the crystallization peak at 978°C as given in Fig. 7(c). The order of reaction ($n$) of this transformation state from amorphous to crystalline form may be calculated using Kissinger empirical relation (Kissinger, 1957) as follows:

$$n = 1.26 \, S^{1/2} \quad \text{and} \quad S = a/b$$

where, $n$ is the order of reaction, $S$ is the peak shape factor (the reaction DTA peak symmetry), $a$ and $b$ are the length in cm on base line as shown in Fig. 7(c). The values of these parameter were calculated from the peak at $T_m = 978$°C of the crystallization reaction (which may be considered as solid-state reaction of single reactant). These types of reactions are assumed to be controlled by nucleation, diffusion phase, and boundary advancement or by partial liquefaction (Reich, 1966). So, the order of rearrangement to crystalline form of sodium titanate is calculated and found to be close to unity (0.87). Therefore, from the above results we can conclude that solid-state reaction follows first order reaction and the rate determining step is mainly nucleation process and there is equal probability of the nucleation step occurring instantaneously (Byrn, 1982). Thus, the surface of each particle is covered with a layer of product (Byrn, 1982); nucleation of the reactant however may be a random process not followed by rapid surface growth (Byrn, 1982). This process has been recorded by Avrami and Erofeav (Byrn, 1982).
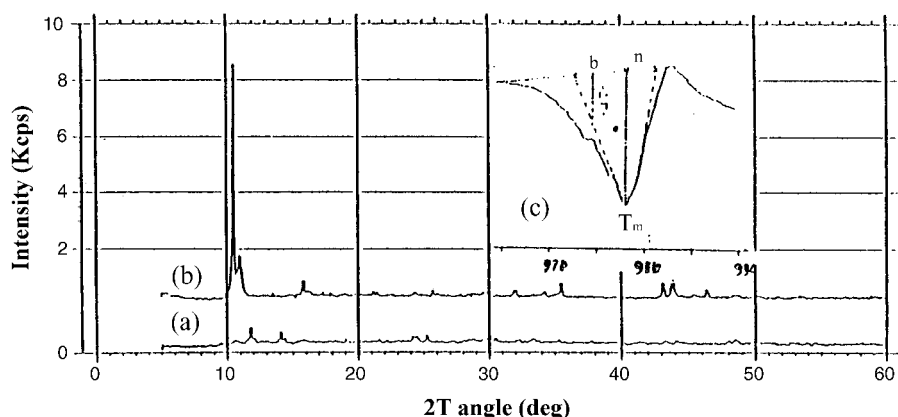


*Figure 7.* X-ray diffraction patterns of mixture of $TiO_2$ and $Na_2CO_3$ in 2:1 molar ratio heated to 900°C (b) and zooming of thermopeak of the crystallization of crystalline sodium titanate (c).
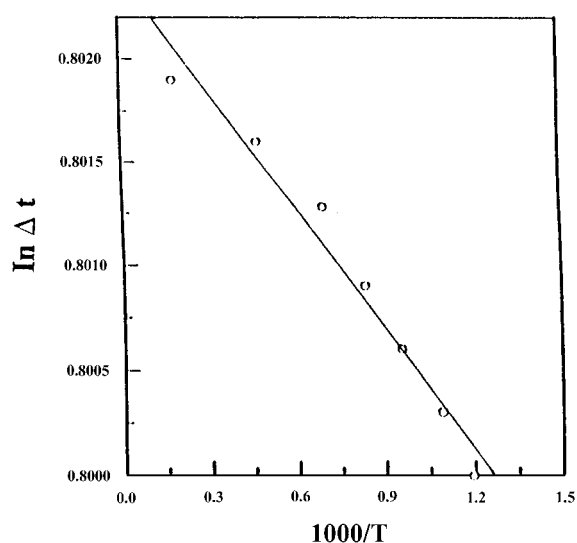
*Figure 8.* Plot of ln $\Delta t$ vs. 1000/T K$^{-1}$ for crystalline sodium titanate.

Also, the activation energy ($E_a$) for this transformation reaction from amorphous to crystalline form (product I), can be calculated using the formula of Piloyan et al. (1966) as following;

$$\ln \Delta t = C - E_a / RT$$

Where, $\Delta t$ is the deviation from base line (its values was taken directly from the DTA curve in unit of length cm or mm), as shown in Fig. 7(c), $E_a$ is the energy of activation, $R$ is the universal gas constant and $T$ is the absolute temperature.

By plotting ln $\Delta t$ vs. 1000/$T$, straight line with slope equal to $-E_a/R$ was obtained as shown in Fig. 8, $E_a$ was found to be 3.97 kJ mol$^{-1}$.

### Sorption Behavior of Na and Cs

Table 1 shows that the Na$^+$ capacities (2.1 and 3.78 meq/g) are higher than Cs$^+$ capacities (1.42 and
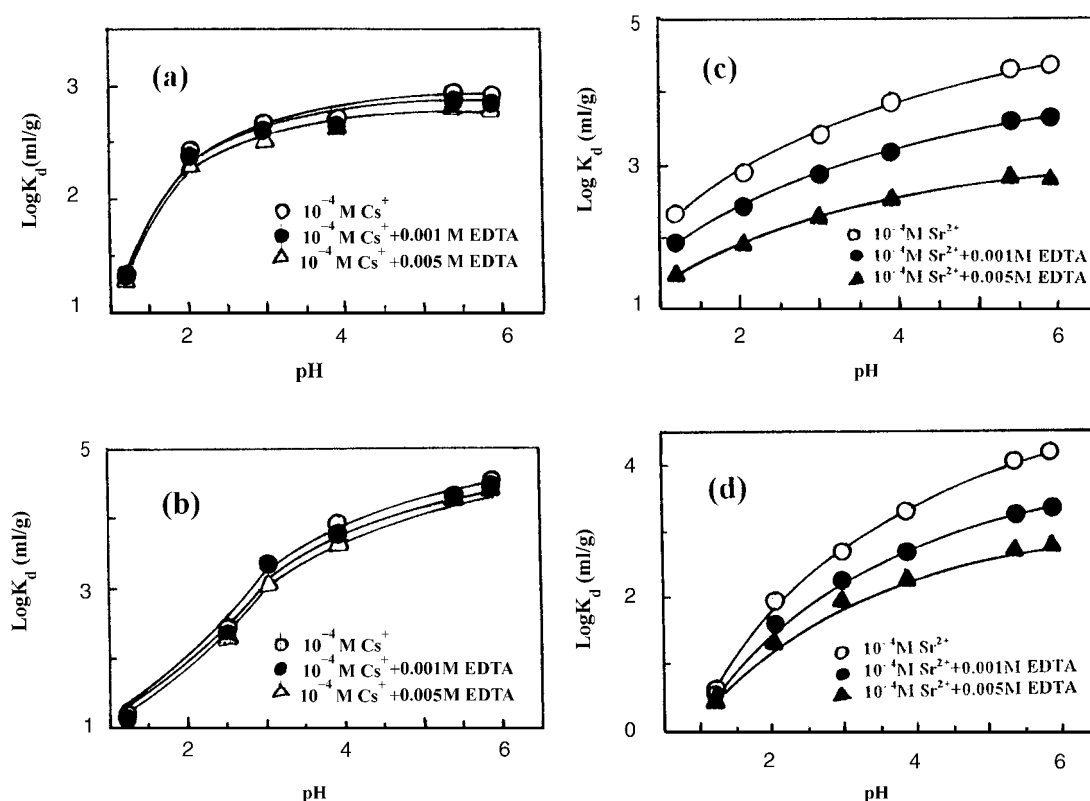


*Figure 9.* (a) Distribution coefficient values of Cs$^+$ ($10^{-4}$) as a function of PH on crystalline sodium titanate at different EDTA concentrations at $25 \pm 1°$C. (b) Distribution coefficient values of Cs$^+$ ($10^{-4}$) as a function of PH on amorphous sodium titanate at different EDTA concentrations at $25 \pm 1°$C. (c) Distribution coefficient values of Sr$^{+2}$ ($10^{-4}$) as a function of PH on crystalline sodium titanate at different EDTA concentrations at $25 \pm 1°$C. (d) Distribution coefficient values of Sr$^{+2}$ ($10^{-4}$) as a function of PH on amorphous sodium titanate at different EDTA concentrations at $25 \pm 1°$C.

2.45 meq/g) for both crystalline and amorphous sodium titanate, under the same conditions. This may be attributed to two reasons; the first is the higher complexing ability of $Na^+$ with the surface sites and the second is that, both of the cations are exchanged in dehydrated state whereas the ionic radii of $Na^+$ ion is smaller than that of $Cs^+$ ion. This may lead to increase the electrostatic interaction of $Na^+$ ion with the exchange sites as a result of the higher mobility of $Na^+$ compared with $Cs^+$. The capacities of amorphous form are higher than that of crystalline one; for both cations this may be attributed to the water content of both materials, which act as active sites, Table 1.

*Effect of Complexing Agents*

The effect of EDTA concentrations on the sorption behaviour of $Cs^+$ and $Sr^{2+}$ for both crystalline and amorphous sodium titanate, were studied as shown in Fig. 9(a)–(d). Figure 9(a) and (b) shows that the sorption of $Cs^+$ on crystalline and amorphous sodium

titanate was slightly decreased as the concentration of EDTA increased. The $k_d$ values are not affected for the two forms of titanate in the presence of $10^{-3}$ M EDTA as interfering ions in the feed solution at different range of pH values. This effect was increased to be 4.35 and 2.50% for crystalline and amorphous sodium titanate, respectively, at $5 \times 10^{-3}$ M EDTA.

Figure 9(c) and (d) shows that the sorption of $Sr^{2+}$ on crystalline and amorphous sodium titanate was decreased as the concentration of EDTA increased, where the $k_d$ values decreased by 18.24% and 20.43% for crystalline and amorphous titanate in the presence of $10^{-3}$ M EDTA as interferring ions in the feed solution, respectively. This effect was increased to be 34.36% and 35.10% for crystalline and amorphous sodium titanate at $5 \times 10^{-3}$ M EDTA, respectively.

Citric acid in the feed solution as interfering ion has a bad effect on the sorption behavior of both $Cs^+$ and $Sr^{2+}$ ions on crystalline and amorphous titanate, Fig. 10(a)–(d). Figure 10(a) and (b), indicated that $5 \times 10^{-2}$ M citric acid reduced the $k_d$ values of
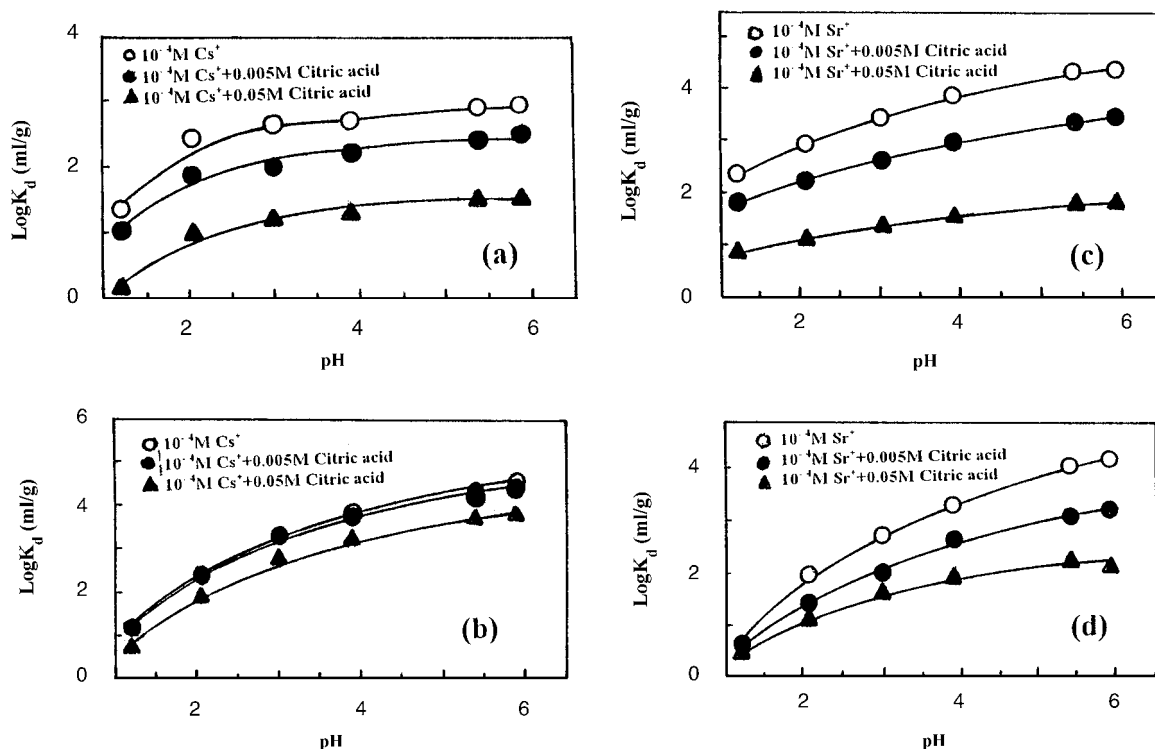


*Figure 10.* (a) Distribution coefficient values of $Cs^+$ ($10^{-4}$) as a function of PH on crystalline sodium titanate at different citric acid concentrations at $25 \pm 1°C$. (b) Distribution coefficient values of $Cs^+$ ($10^{-4}$) as a function of PH on amorphous sodium titanate at different citric acid concentrations at $25 \pm 1°C$. (c) Distribution coefficient values of $Sr^{+2}$ ($10^{-4}$) as a function of PH on crystalline sodium titanate at different citric acid concentrations at $25 \pm 1°C$. (d) Distribution coefficient values of $Sr^{+2}$ ($10^{-4}$) as a function of PH on amorphous sodium titanate at different citric acid concentrations at $25 \pm 1°C$.
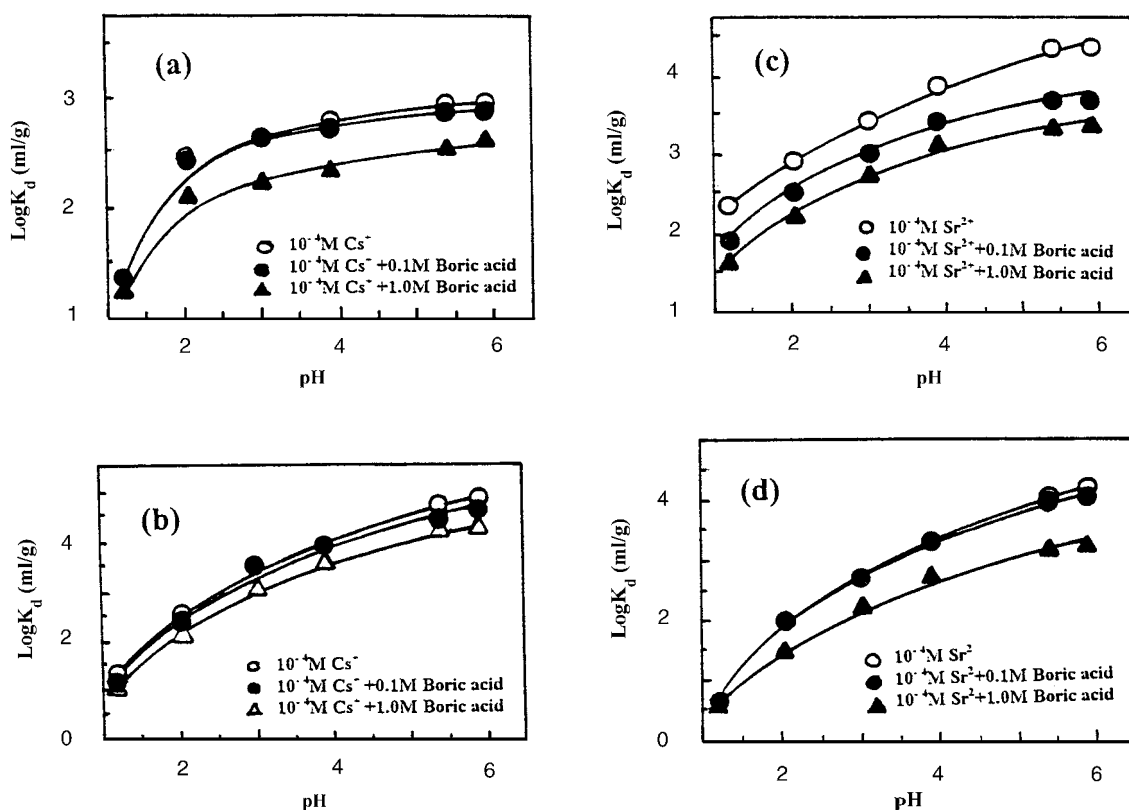
*Figure 11.* (a) Distribution coefficient values of $Cs^+$ ($10^{-4}$) as a function of PH on crystalline sodium titanate at different boric acid concentrations at $25 \pm 1°C$. (b) Distribution coefficient values of $Cs^+$ ($10^{-4}$) as a function of PH on amorphous sodium titanate at different boric acid concentrations at $25 \pm 1°C$. (c) Distribution coefficient values of $Sr^{+2}$ ($10^{-4}$) as a function of PH on crystalline sodium titanate at different boric acid concentrations at $25 \pm 1°C$. (d) Distribution coefficient values of $Sr^{+2}$ ($10^{-4}$) as a function of PH on amorphous sodium titanate at different boric acid concentrations at $25 \pm 1°C$.

$Cs^+$ by 50 and 17.4% for crystalline and amorphous sodium titanate at ~5.9 pH, respectively. But the data in Fig. 10(c) and (d) shows the effect of the same concentration of citric acid reduced $k_d$ values of $Sr^{2+}$ by 59.1% and 47.62% for crystalline and amorphous sodium titanate, respectively.

The effect of boric acid on the sorption of $Cs^+$ and $Sr^{2+}$ ions in both crystalline and amorphous titanate, was also studied and the results are given by Fig. 11(a)–(d), respectively. Figure 11(a) and (b) shows that the sorption of $10^{-4}$ M $Cs^+$ on crystalline and amorphous sodium titanate is not affected up to 0.5 M $H_3BO_3$ as interfering ions in the feed solution at pH $\approx 5.9$. Some decrease in the $k_d$ values of $Cs^+$ by 10.34% and 4.44% on both crystalline and amorphous titanate, respectively was obtained by increasing the $H_3BO_3$ up to 1 M. Figure 11(c) and (d) shows the sorption of $Sr^{2+}$ on crystalline and amorphous sodium titanate in the presence of 0.5 M boric acid was decreased by 15.9% and 1%,

respectively; this bad effect was increased to be 25% and 23.81% for crystalline and amorphous titanate, in 1 M $H_3BO_3$, respectively.

From the above results, we can concluded that the presence of EDTA, citric acid or boric acid as interfering ions in the feed solutions had slight effect on the sorption behavior for $Cs^+$ and $Sr^{2+}$ on the two forms of sodium titanate. But this bad effect is large for crystalline form than that for amorphous form, this may be due to the weaker cationic exchange of crystalline form than amorphous one (Defilippi et al., 1997). Also, the above results assume the chelation of metal ions with the chelating agents to form metal chelates, leads to decrease in the metal ion concentration in the solution and decrease the $k_d$ values of metal ions on the sorbents. It was found that, by increasing the concentration of complexing agents the above observation increase (Defilippi et al., 1997). The presence of EDTA, citric acid and boric acid has a bad effect on the $k_d$

values of $Sr^{2+}$ larger than that with $Cs^+$ (Defilippi et al., 1997).

## Conclusion

– High thermally stable sodium titante obtained in two different structures (crystalline and amorphous forms) and used as new cation exchanger.

– These thermoproduct materials can be used in their initial forms ($Na^+$-form) for treatment of radioactive liquid wastes with high efficiency through broad spectrum of pH (from 1 to 6), even in the presence of some salts or complexing agents.

– Due to the high thermal, chemical and radiation stabilities of these materials, they can be used for separation and removal of the investigated radionuclides from liquid waste solutions.

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