

**REMOVAL OF BARIUM IONS FROM AQUEOUS SOLUTIONS BY
BARIUM TITANATE USING RADIOTRACER TECHNIQUE:****¹ S.P.MISHRA AND ^{2*} N.SRINIVASU**

¹ Nuclear and radiation chemistry laboratory, Department of Chemistry,
Banaras Hindu University, Varanasi – 221005, India

² Department of Science & Humanities, Vignan University, Vadlamudi, A.P., India

ABSTRACT

The adsorption of barium ions on barium titanate in an aqueous solution was studied by means of batch technique as a function of Ba(II) concentration, temperature and solution pH using Ba-140 as radiotracer. The results show that adsorption is essentially complete in ca 180min and the steady state values of adsorption at various concentrations agree well with the classical Freundlich isotherm and follow first order kinetics. The pH and temperature of the solution markedly affect the extent of adsorption. Exposure of the activated barium titanate adsorbent to neutrons and γ irradiation from a (Ra-Be) neutrons source having an integral flux of 3.85×10^6 neutrons/cm² / sec and associated with a nominal γ dose of Ca 172 rads/h, affects its adsorption capacity markedly.

KEYWORDS: barium ions radiotracer barium titanate

**N.SRINIVASU**

Department of Science & Humanities, Vignan University, Vadlamudi, A.P., India

INTRODUCTION

Barium and strontium ions from the by product of nuclear fission reaction and the leakage of the nuclear reactor, can cause long term issues that seriously threaten the health of a large population¹⁻⁴. Treatment of the radioactive wastes is needed to produce a waste product suitable for long term storage and disposal. Advanced materials for this purpose are of great interest as more nuclear power stations are in operation or construction and quantity of nuclear waste is increasing⁵. Natural inorganic cation exchangers, such as clay and zeolites have been extensively used for the removal of the radioactive ions from water by ion exchange process and subsequent safe disposal^{6,7}, because of their stability against radiation, chemicals and thermal changes. Synthetic exchangers are far superior to the natural materials for selective removal of the radioactive cations from water⁸. The titanates have good stability against high temperature and radiation⁹. Adsorption studies of Ba (II) on titanium (IV) oxide (Mishra et al 1992) powder using a radiotracer technique have been

reported¹⁰. The present work deals with the adsorption of Ba^{2+} ions on barium titanate powder as a function of concentration, temperature of the adsorptive solution. The effect of neutron and γ -irradiation of the titanate adsorbent for different exposure periods on the extent of adsorption was also studied.

MATERIALS AND METHODS

Experimental

Commercially available barium titanate (Alpha product) was activated at 1173K for about 10hours and cooled slowly to room temperature. The powder was ground in porcelain mortar and sieved to get a particle size 120-170 mesh (B.S.Sieve) and was characterized through powder XRD analysis (cf Fig1). The material was found to be crystalline and gave identical XRD data as standard ASTM charts. The crystal structure was found to be tetragonal with lattice parameters $a = 3.99 \text{ \AA}$ and $C = 4.038 \text{ \AA}$.

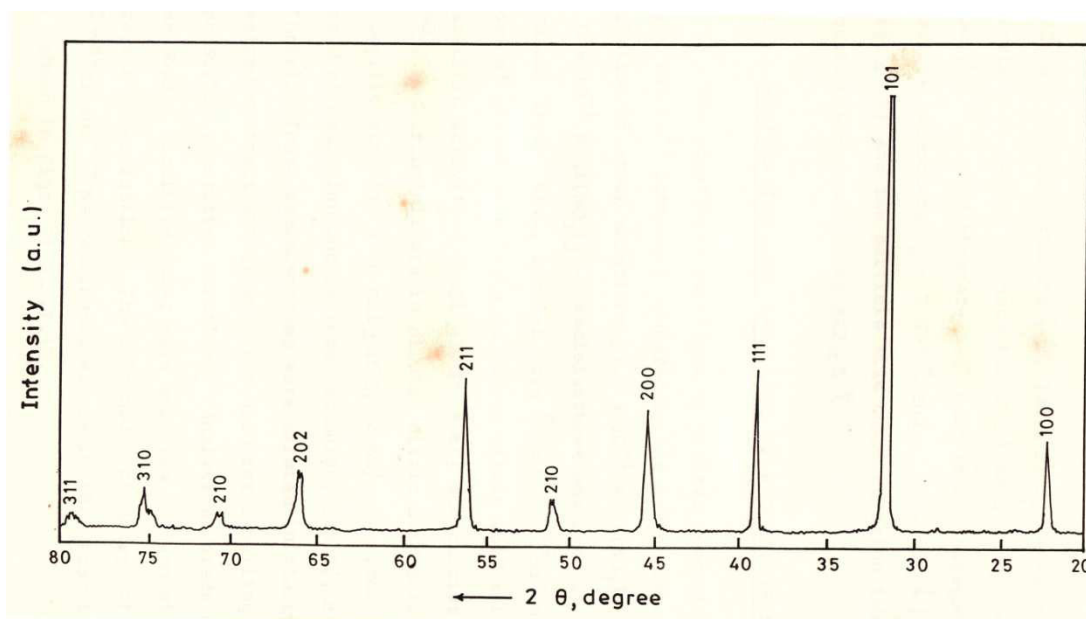


Figure 1
X-ray diffraction pattern of barium titanate annealed at 1173 K

Carrier free barium – 140, as barium nitrate in dilute HNO_3 solution (Specific activity about 3.98

m Ci \pm 10%; 2ml) obtained from the Board of Radiation and Isotope Technology, Bombay,

India, was used for labeling the adsorptive solutions. The sorption was measured by equilibrating 0.1g of barium titanate with 10.0mL of barium nitrate solution of desired concentration (10^{-3} to 10^{-7} M) containing known quantity of radiotracer; the solution was centrifuged for phase separation and then the supernatant solution was analyzed by its β -activity measurement. The desired pH of the solution was measured with the help of digital pH meter. The experimental procedure for measurement of adsorption and estimation of amounts adsorbed are described in detail elsewhere¹¹.

RESULTS AND DISCUSSION

Effect of Concentration

The concentration dependence study (10^{-3} – 10^{-7} M) on the adsorption of barium (II) on barium titanate as a function of contact time (See Fig 2) reveals a rapid initial rise on adsorption and thereafter gradual slowing down and finally reaching to an apparent equilibrium. The time taken for reaching equilibrium was found to be ca 180 minutes at all concentrations of the adsorptive solution. The result show that the amount adsorbed at equilibrium increased from 0.408×10^{-8} to 0.252×10^{-4} mol g^{-1} with the increase in adsorptive concentration from 10^{-7} to 10^{-3} M. This would mean that the relative change in the uptake, i.e percent adsorption, increases from 25.2 to 40.8% with the dilution increasing from 10^{-3} M to 10^{-7} M at pH 10.7. This increase in the uptake is due to relatively smaller number of adsorptive species available for an equal number of surface sites of barium titanate.

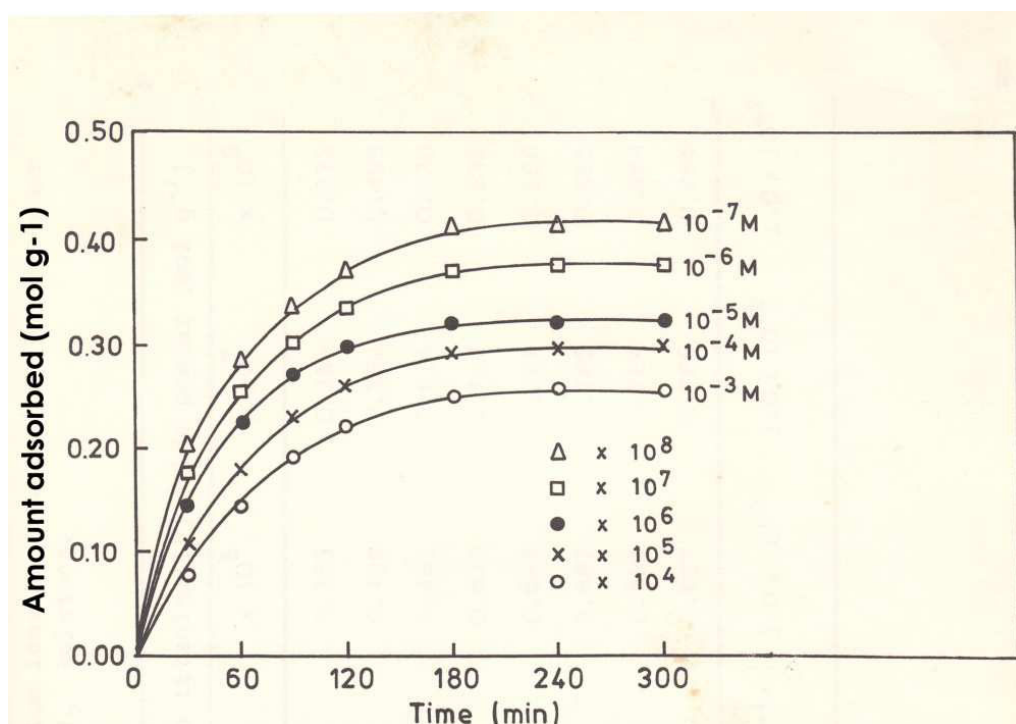


Figure 2
Time variation of adsorption of barium ions on barium titanate powder at various concentrations (Temperature : 303K; Initial pH: 10.7)

Adsorption data were further analyzed using the Freundlich adsorption isotherm (Fig.3) in its logarithmic form.

$$\log a_e = \log K + \frac{1}{n} \log C_e \quad \text{--- (1)}$$

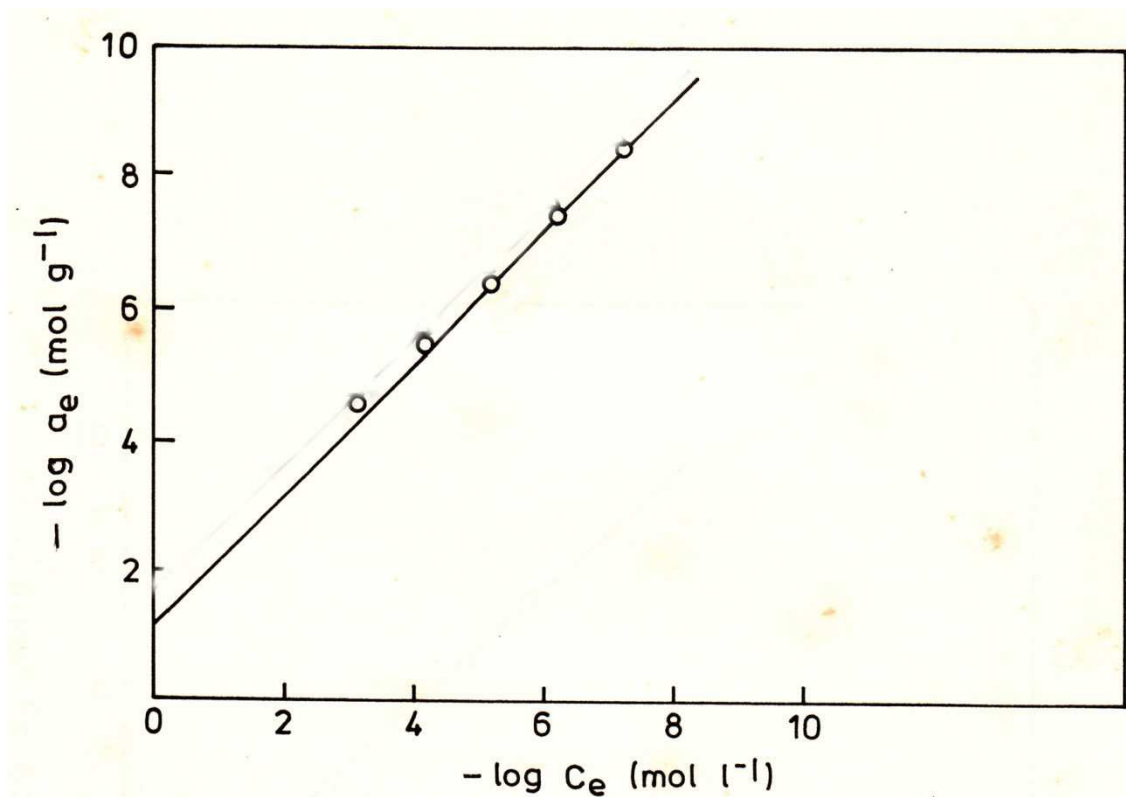


Figure 3

Freundlich adsorption isotherm for Ba (II) ions on barium titanate at 303 K.

Where 'a_e' is the amount adsorbed at equilibrium, C_e is the equilibrium bulk concentration, K and 1/n is Freundlich constants. These constants were estimated for the intercept and slope of the straight line. In the present case, the isotherm with 1/n equal to 0.91 (0 < (1/n) < 1) is necessarily due to the heterogeneous nature of the surface structure with exponential distribution of surface sites¹². The observed Freundlich constant K of 0.63 (or) 6.3 × 10⁻² mol g⁻¹ further confirms a significant affinity to the barium titanate towards barium (II) ions. The applicability of Freundlich isotherm has also been reported previously for adsorption of

barium ions on sodium titanate and potassium titanate¹³⁻¹⁴.

Effect of temperature

The uptake of barium ions on barium titanate has been studied as a function of temperature (303 – 333K) with 1.0 × 10⁻⁵ M Ba(NO₃)₂ solutions at pH. It is interesting to note that while the extent of adsorption changed with temperature, the time required to attain saturation was not affected. The results in Table 1 reveal that the amount of barium ions adsorbed on barium titanate increased from 0.328 × 10⁻⁶ mol g⁻¹ to 0.392 × 10⁻⁶ mol g⁻¹ with a rise in temperature from 303 to 333K.

Table 1

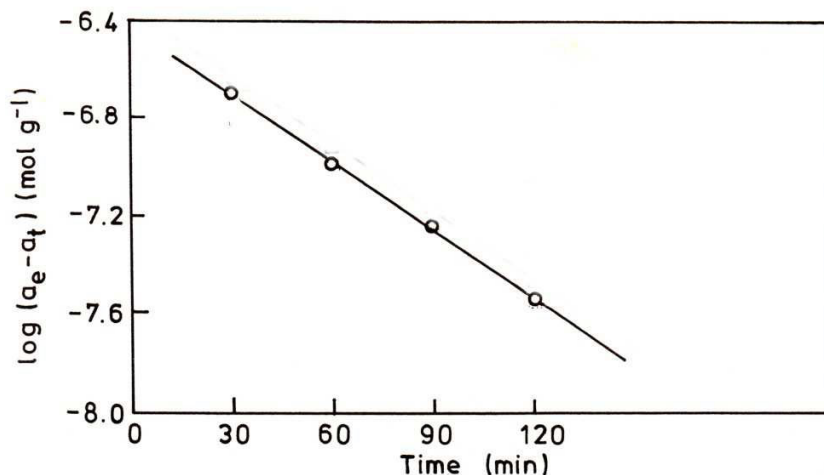
Effect of temperature on the adsorption of barium ions on barium titanate powder at different time intervals. Initial concentration of adsorptive solution = 1.0×10^{-5} M; pH = 10.7.

Time (min)	Amount of barium ions adsorbed on barium titanate powder (mol g ⁻¹) x 10 ⁻⁵ at temperatures of			
	303K	313K	323K	333K
30	0.145	0.176	0.214	0.264
60	0.225	0.245	0.281	0.315
90	0.271	0.295	0.325	0.356
120	0.300	0.322	0.352	0.378
180	0.328	0.348	0.374	0.392
240	0.325	0.350	0.373	0.398
300	0.326	0.346	0.372	0.401

The order of reaction for adsorption of barium ions on barium titanate has been investigated using Lagergren's equation in the form

$$\log(a_e - a_t) = \log a_e - \frac{k_1}{2.303} t \quad \text{--- (2)}$$

Where a_e is the amount adsorbed at equilibrium, a_t is the amount adsorbed at time t and k_1 denotes the rate constant of adsorption. The plot of $\log(a_e - a_t)$ vs. time gives as straight line (cf. Fig 4) indicating that the process is of first order with respect to adsorptive concentration.

**Figure 4**

Adsorption kinetics of barium ions on barium titanate at 303 K (Initial concentration of adsorptive solution: 1.0×10^{-5} M. Initial pH: 10.7)

The temperature dependent data on the adsorption kinetics has been further utilized for calculating the energy of activation of adsorption through slope of Arrhenius plot ($\log k_1$ vs. $1/T$) as show in Fig. 5 and the value are reported in table. 2 along with rate constants of

system studied. The low value of energy of activation 3.2KJ/mol indicates that the forces of attraction between the adsorbent (barium titanate) and adsorptive species (Ba^{2+} ions) are relatively stronger and the uptake process can occur ordinary conditions.

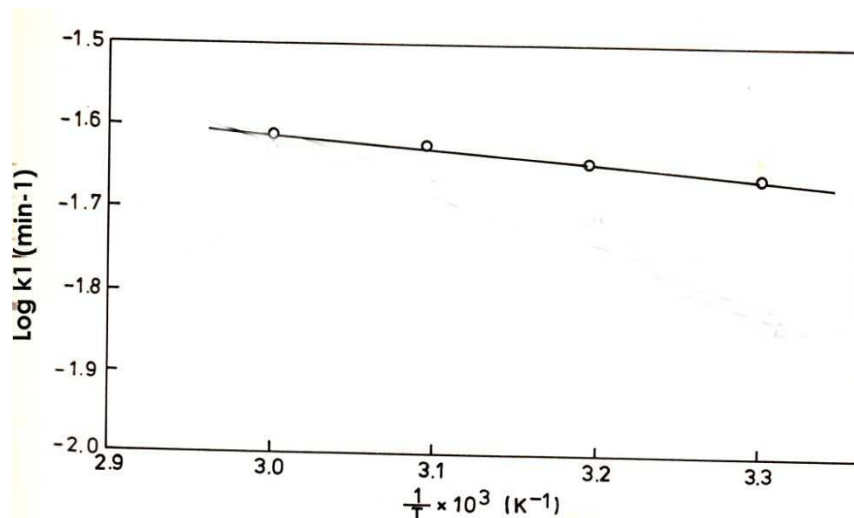


Figure 5
Arrhenius plot for the adsorption of Ba²⁺ on barium titanate (Initial concentration of adsorptive : (1.0 x 10⁻⁵ M. Initial pH: 10.7)

Table 2
Rate constants and energy of activation for the adsorption of barium ions on barium titanate surfaces at different temperatures. Initial adsorptive concentration: 1.0 x 10⁻⁵ M.

Adsorptive	Adsorbent	Temperature (k)	Rate Constant k ₁ (min ⁻¹)	Energy of activation (KJ mol ⁻¹)
Ba ²⁺	Barium Titanate	303	21.8 x 10 ⁻³	3.2
		313	22.9 x 10 ⁻³	
		323	24.0 x 10 ⁻³	
		333	24.4 x 10 ⁻³	

Effect of pH

The influence of pH (4.2 to 11.4) on the adsorption to barium ions on barium titanate surface was studied in a 1.0 x 10⁻⁵ M Ba (NO₃)₂ solutions (cf Fig.6). An inspection of this curve reveals it to be essentially similar to that of Fig. 2; and the time necessary to reach equilibrium also remains almost unaffected. However, the rate and the amount adsorbed at equilibrium are

affected markedly by a change in the pH the adsorptive solution. The amount adsorbed at equilibrium increases from 0.102x10⁻⁶ to 0.375x10⁻⁶ mol g⁻¹ with an increase in pH from 4.2 to 11.4. A similar increase in amount adsorbed with an increase in the pH of solution for adsorption of Sr (II) on sodium titanate has been reported by Heinonen etal¹⁵.

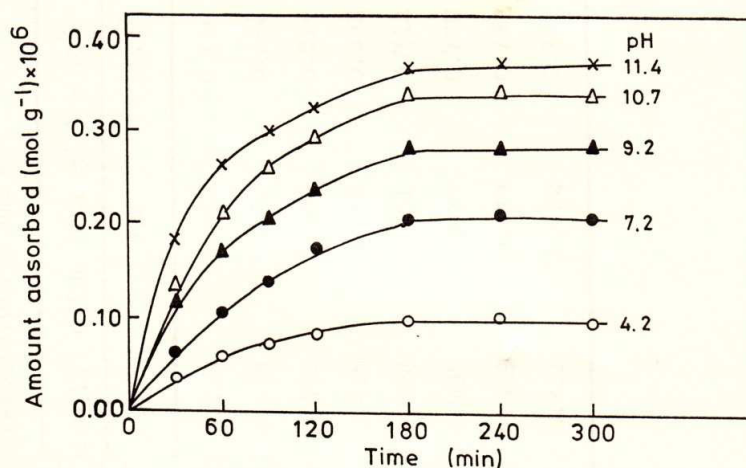


Figure 6

Adsorption of barium ions on barium titanate as a function of time at various pH.
(Initial concentration of Ba (II) : $1.0 \times 10^{-5} M$; Temperature : 303K)

Effect of irradiation

Results of adsorption of Ba^{2+} ions on irradiated as well as un irradiated barium titanate are represented in Fig. 7

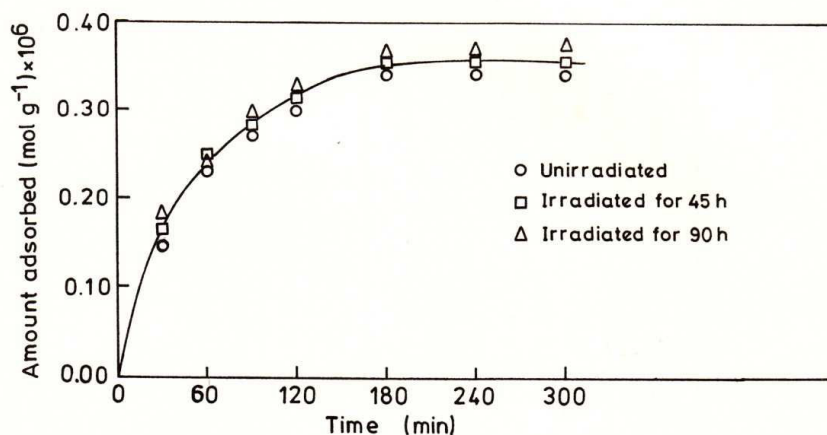


Figure 7

Comparative adsorption of barium ions by irradiated and unirradiated barium titanate.
Initial concentration of Ba (II) : $1.0 \times 10^{-5} M$; Temperature : 303K.

The general nature of these time rate curves is similar to that of an irradiated adsorbent and the time required to attain the equilibrium state is not affected by irradiation to an appreciable extent. It is evident that the amounts adsorbed at equilibrium were not significantly affected due to irradiation of barium titanate thus indicating that barium titanate has good radiation stability.

CONCLUSION

The barium (II) adsorption data indicate that the uptake of barium ions on barium titanate is favored at higher concentration, temperature and pH of the adsorptive solutions. The kinetics of the decontamination process follows first order rate law and obeys the Freundlich

isotherm, and the process involved appears to be chemical (ion exchanges type) in nature. The barium titanate has a stabilizing effect on radiation damage, and hence it can be said that barium titanate may be used effectively for the online treatment of radioactive wastes and can be used for long term storage in reduced solid form.

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REFERENCES

1. Komaraneni.S; Roy.R, 'Use of γ -Zirconium phosphate for CS removal from, radioactive waste', *Nature* 299, 707, 1982.
2. Paulus W.J, Komarneni, S. Roy.S, 'Bulk synthesis and selective exchange of strontium ions in $\text{Na}_4 \text{Mg}_6 \text{Al}_4 \text{Si}_4 \text{O}_{20} \text{F}_4$ mica, *Nature*. 357, 571, 1992,
3. Komarameni.S, Koza.N, Paulus W.J. 'Environment super selective clay for radium uptake', *Nature* 410, 771, 2001.
4. Nyman. M, Tripathi.A, parise J.b, Maxwell R.S; Nenoff T.M. J.Am.Chem. Soc, 'Sandia octahedral molecular sieves (SOMS) structural and property effects of charge balancing the M-IV substituted (M=Ti, Zr) Niobate frame work', 124, 1704, 2002.
5. Zhu.H.Y; Zheng.Z, Gao.X, Huang.Y., Yanz, Zo.J, Yin,H, Zoua, Kable S.H, Zhao.J, Xi, y Martens, W.N. Frost, 'Structural Evolution in a Hydrothermal reaction between $\text{Nb}_2 \text{O}_5$ and NaOH solutions. From $\text{Nb}_2 \text{O}_5$ grains to micro porous $\text{Na}_2 \text{Nb}_2 \text{O}_6 \cdot 2/3 \text{H}_2 \text{O}$. Fibers and NaNbO_3 cubes', *J.Am.Chem.Soc.* 128, (7) 2373, 2006.
6. Amphlett.C.B, MC Donald I.A, Redman, M.J., 'Synthetic inorg.ionex change materials, Zirconium phosphate;', 'Radiation stability of synthetic organic ion-exchange resin', *J.Inorg. Nucl. Chem*, Vol. 6(3), 220, 1958.
7. Mercer.W. Ames L.L, Smith P.W. Radionuclide Present in the radio contaminants of nuclear wastes' *Nucl. Appl. Technol*, 8, 62, 1970.
8. Clearfield and Lehto ' Preparation, structure and ion exchange properties of $\text{Na}_4 \text{Ti}_9 \text{O}_{20} \times \text{H}_2 \text{O}$; *J. Solid state chem.* 73, 98, 1988.
9. Lehto.J, Szirtes.L 'Effects of gamma radiation on sodium titanate and on α -zirconium phosphate in monosodium form *J.Radiochem. radional.Lett*, 50, 375, 1982.
10. Mishra S.P. Srinivasu.N, Tiwary.D, 'Ion exchangers in radioactive waste management –V and case of efficient removal of Ba (II) from aqueous solutions by Tio_2 powder – radiotracer study', *Appl. Radiat.Isot*, 43, 1253, 1992.
11. Mishra S.P and Singh.S.N 'Radiotracer technique in adsorption study part VI adsorption of chromate ions on chromium (IV) oxide powder. *Appl. Radiat. Isot.* 38, 541, 1987.
12. Benes., Majer.V, Trace Chemistry of Aqueous solution, *Elsevier*, Amsterdam, 1980
13. Shuddhodan P.Mishra, Srinivasu.N, 'Ion exchangers in radioactive waste management part VI : Radiotracer studies on adsorption of barium ions on potassium titanate', *Radiochimica Acta*,61, 47, 1993.
14. Mishra.S.P, Srinivasu.N, 'Ion exchangers in radioactive waste management part IV. Radiotracer studies on adsorption of strontium ions over sodium titanate', *J.Radioanal and Nucl. Chem Art.*, 162(2), 299, 1992.
15. Heinonen O.J, Lehto.J, Miettinen J.K. 'Sorption of strontium (II) and Radio strontium ions on sodium titanate', *Radio Chim.Acta* 28, 93, 1981.