

## Recent Advances in Radioanalytical Separation by Nanomaterials: A Review

R. Chakraborty, Sadhan Pramanik and P. Chattopadhyay\*

Department of Chemistry,  
The University Burdwan, Golapbag, Burdwan-713104, INDIA.

(Received on: December 22, 2017)

### ABSTRACT

The rapidly expanding field of nano science and technology is generating many exciting new materials with novel properties. Apart from the all other applications, nano materials are expected to act as a new class solid phase sorbent for radioanalytical separation in due to their unique surface and morphological features. The present review provides a summary of the novel nano-sorbent for radioanalytical separation as reported till now. The sorbent materials include the magnetic Fe<sub>3</sub>O<sub>4</sub> nano-particles, hybrid nano materials and the oxide and phosphate based nano materials of group 4/5. Magnetic nanoparticles are reportedly employed for the sorption of isotopes as <sup>109</sup>Cd, <sup>60</sup>Co, <sup>152</sup>Eu, <sup>226</sup>Ra, <sup>140</sup>Nd, <sup>238</sup>U, <sup>239</sup>Pu etc. Other nano sorbents are employed for the development of some generator systems like <sup>99</sup>Mo/<sup>99m</sup>Tc, <sup>188</sup>W/<sup>188</sup>Re, <sup>68</sup>Ge/<sup>68</sup>Ga and also for some parent-daughter separations like <sup>137</sup>Cs-<sup>137m</sup>Ba and <sup>90</sup>Sr-<sup>90</sup>Y. The synthesis, structural features and exchange behavior of these materials are also discussed in brief.

**Keywords:** Radioanalytical separation, Nano-sorbent. Magnetic nano-particle, Generator Systems, Parent-daughter separation.

### 1. INTRODUCTION

Necessity is the mother of invention. In the course of the evolution of human civilization, many innovative ideas of science and technologies have come and gone. The development of today's nano-science is also a part of the continuous evolution process of mankind. The practice on nano-science began long ago. In the Indian scriptures related to Ayurveda, gold was used in several preparations. All these preparations use finely ground gold. Over 5,000 years ago the metal was also used for medical purposes in ancient Egypt. In Alexandria, alchemists developed a powerful colloidal elixir known as liquid gold, which used to be incorporated in glasses and vases to give them colour. Faraday may be considered as

pioneer of synthesis of colloidal gold in 1856 and called it divided metals. In his diary dated 2 April 1856, Faraday called the particles he made the 'divided state of gold'. The solutions he prepared are preserved in the Royal Institution. Metallic gold, when divided into fine particles ranging from sizes of 10–500 nm particles, can be suspended in water.

In 1959, noble laureate Richard Feynman presented a visionary lecture at a meeting of the American Physical Society, entitled "There is plenty of room at the bottom", where he focused on the possibility and potential of nanosized materials<sup>1-2</sup>. But, the emergence of appropriate methods of fabrication of nanostructures that a notable increase in research activity occurred, 1990s and a number of significant developments resulted. This period was also marked by the phenomenal success in developing important tools for viewing, characterizing and for atomic manipulation of the nanostructures. So many sophisticated instruments for characterization and manipulation such as scanning electron microscopy, transmission electron microscopy and scanning probe microscopy became available for researchers to explore the nanoworld.

Owing to their unique properties, nanomaterials are now used in various diverse fields like nanophotonics, lasers, nanoelectronics, solar cells, resonators, high sensitivity sensors, catalysis, functional coatings, energy storage, drug delivery and biomedicines<sup>3</sup>. Today, nanomaterials are revolutionizing social and economic development by offering innovative and viable solutions to some of the most pressing problems of the world community. However, these are only a limited part of the fast developing applications of nanomaterials and numerous other applications of these materials are yet to be explored. One of such novel application of nano materials is the use of these materials in radio chemical separation studies. So far literature is concern this particular application of nano material is not so wide-spread.

## 2. RADIO ANALYTICAL SEPARATION

Analytical chemistry is concerned with the theory and practice of methods used to determine the composition of matter. Analytical chemistry is an ancient branch of science, yet may be regarded as one of the youngest science with the growing global awareness in health hazards and environmental pollution. The practice of analytical chemistry which focuses on the both qualitative and quantitative analysis of sample for their radionuclide content, gives to rise to the field of radioanalytical chemistry. The field of radioanalytical chemistry was originally developed by Marie Curie with contributions by Ernest Rutherford and Frederick Soddy. They developed chemical separation and radiation measurement techniques on terrestrial radioactive substances. During the twenty years that followed 1897 the concepts of radionuclides was born. Since Curie's time, applications of radioanalytical chemistry have proliferated. Modern advances in nuclear and radiochemistry research have allowed practitioners to apply chemistry and nuclear procedures to elucidate nuclear properties and reactions, used radioactive substances as tracers, and measure radionuclides in many different types of samples.

The importance of radioanalytical chemistry spans many fields including chemistry, physics, medicine, pharmacology, biology, ecology, hydrology, geology, forensics,

atmospheric sciences, health protection, archeology, and engineering. Applications include: forming and characterizing new elements, determining the age of materials, and creating radioactive reagents for specific tracer use in tissues and organs. The ongoing goal of radioanalytical researchers is to develop more radionuclides and lower concentrations in people and the environment.

### 3. SYNTHESIS OF NANOMATERIALS

The synthesis of nanoparticles is to be considered with great attention in the discussion of nanoscience. This is because proper control over size, shape and crystalline nature, is to be determined in order to make their proper utilization for the desired applications. Several methods of synthesis of nanoparticles have been reported in the literature, which include high energy milling, sputtering, laser ablation, utilization of plasma generated by radiofrequency heating coils, thermolysis, combustion, chemical-vapor deposition, electrodeposition, sol-gel and solvothermal methods<sup>4-5</sup>. Of these, the last two methods are the hard-core chemical route for the synthesis of nanomaterial and at the same time these are probably the most useful method of synthesis of based sorbents for radionuclide generators. This is primarily due to the suitability of this method to be scaled up for the routine synthesis of large quantities of nanomaterials using inexpensive and less complicated apparatus. Moreover, chemical methods have proved to be much more effective than other methods, as they provide better size-control, homogeneity and enable different shapes and functionalization. In this thesis, therefore sol-gel and solvothermal methods have been used for the syntheses of various nanomaterials based sorbents for use in radionuclide generators.

### 4. CHARACTERIZATION OF NANOMATERIALS FOR RADIOCHEMICAL EXTRACTION

Several techniques are available in each of these areas and a systematic application of several tools leads to a complete understanding of structural features of the materials in the nanoscale. The observation may be done including electrons, photons, scanning probes, ions, atoms, etc. Some of the very common and useful techniques are described below.

- ❖ **Powder X-ray diffraction:** This is important technique which indicates the crystalline nature of the nano materials.
- ❖ **Dynamic Light scattering method (DLS):** This method is used to determine the average size distribution profile of the nanoparticles in suspension.
- ❖ **Scanning Electron Microscopy (SEM):** This is the most useful technique to observe the surface morphology of the nanoscale materials.
- ❖ **Energy Dispersive Spectroscopy (EDS):** SEM followed by EDS correctly predicts the key elements present in the material.
- ❖ **Transmission Electron Microscopy (TEM):** TEM is very useful tool to which provides information about the size, shape and structure of the nano scale particles in details. It also tells about the polycrystalline nature of the material through selected area diffraction pattern (SAED).

❖ **Scanning Transmission Electron Microscopy (STEM):** STEM is a hybrid instrument with the features of both SEM and TEM.

❖ **Atomic Force Microscopy (AFM):** In this technique, the interactions between a sharp probe and a sample are used for imaging. A resolution of 1 nm can be observed by AFM.

All these above-mentioned tools are widely used in characterization of nano-materials. Apart from those some other techniques X-ray Photoelectron spectroscopy (XPS), secondary ion mass spectrometry (SIMS), scanning tunneling microscopy (STM) etc are also important techniques in the characterization of nano-materials.

## 5. RADIONUCLIDE GENERATOR

In a radionuclide generator, a 'parent' radionuclide (A) decays to a daughter radionuclide (B) which further decays to stable/nearly stable grand-daughter nuclide (C) as shown in **Fig.1**. When a radionuclide decays (the parent, denoted by subscript 1) to form another radionuclide (the daughter, denoted by subscript 2), the behavior of the parent follows the decay law  $N_1^t = N_1^0 e^{-\lambda_1 t}$  the number of atoms  $N_2^t$  of daughter at time 't' can be shown to be 
$$N_2^t = \left[ \frac{\lambda_1}{\lambda_2 - \lambda_1} \right] N_1^0 [e^{-\lambda_1 t} - e^{-\lambda_2 t}] + N_2^0 e^{-\lambda_2 t} \quad (i)$$

Where  $N_1^0$  and  $N_2^0$  are the number of atoms of parent and daughter respectively at  $t = 0$ ,  $\lambda_1$  and  $\lambda_2$  are the decay constants ( $0.693 / T_{1/2}$ ) of parent and daughter with a half-life  $T_{1/2}^1$  and  $T_{1/2}^2$  respectively. In the case of  $T_{1/2}^1 \text{ parent} \gg T_{1/2}^2 \text{ daughter}$ , the maximum activity of the daughter occurs at the time, t, which is calculated from the expression (i) is

$$t = \left[ \frac{1}{\lambda_2 - \lambda_1} \right] \ln \lambda_2 / \lambda_1 \quad (ii)$$

Once transient equilibrium is reached, the number of daughter atoms at 't' is given by

$$N_2^t = \left[ \frac{\lambda_1}{\lambda_2 - \lambda_1} \right] N_1^0 e^{-\lambda_1 t} \quad (iii)$$

Equation (ii) helps to find the frequency at which the daughter can be theoretically separated at its maximum yield. For many of the medical radionuclide generators, the half life of the daughter is usually very short in comparison to the parent, i.e.  $T_2 \gg T_1$ . Therefore, after eluting the daughter from the generator, 50 % of the maximum daughter activity is retained on the generator after one daughter half-life and 75 % after two daughter half-lives. Equation (iii) can be used to determine the quantity of daughter radionuclide that can be separated at any given time, by recalling that  $dN/dt = -\lambda N$ .

## 6. NANOMATERIALS AS SORBENT FOR RADIONUCLIDE GENERATOR SYSTEM

Nanomaterials are expected to provide unprecedented opportunities in developing a new class of sorbents for chromatographic applications due to their uniqueness in surface and morphological features. While the structural features of those materials are in between of those of atoms and the bulk materials, the properties of materials with nanometer dimensions are significantly different from those of atoms and bulks materials.

Due to their small dimensions, nanomaterials have extremely large surface area to volume ratio, which makes a large fraction of atoms of the materials to be the surface. These surface atoms are unsaturated, exhibit intrinsic surface reactivity and have a tendency to

chemisorb charged species in aqueous solution in order to achieve surface stabilization. Moreover, the small size of nanomaterials either renders them free of internal structural imperfections or impurities present cannot multiply sufficiently in them to cause mechanical failure<sup>6</sup>. The imperfections within the nano dimension are highly energetic and will migrate to the surface to relax themselves under annealing, thereby leaving pure and perfect material structures inside the nanomaterials. This phenomenon of increased materials perfection affects the properties of nanomaterials. For example, the chemical stability for certain nanomaterials may be enhanced and the mechanical properties of nanomaterials will be better than the corresponding bulk materials<sup>7</sup>.

Further, it is reported that nanocrystalline materials are more radiation resistant than their bulk counterparts with larger grain sizes. There are few reports available in the literature on the exploitation of nanomaterial based sorbents in the chromatographic separation of metal ions<sup>8</sup>. Owing to their high surface area and intrinsic surface reactivity, nanomaterial based sorbents has much higher sorption capacity and selectivity compared to the conventional sorbents. Consequently, parent radioisotopes obtained from medium flux reactors with low specific activity can also be used for the preparation of radionuclide generators and the daughter activity can be availed with appreciably high radioactive concentration and purity. The enhanced mechanical and chemical stability of such sorbents ensure that the column matrix does not dissolve even after multiple elutions and use of the generator for a prolonged time, thereby preventing the addition of chemical impurities in the eluate. Further, owing to the high radiation stability, nanomaterials demonstrate consistently good performance over a prolonged period of time.

## 7. RADIOCHEMICAL SEPARATION BY MAGNETIC NANOMATERIALS

Magnetic field-based separation, using magnetic nanoparticles as sorbent in solid phase extraction, has been used for radiocesium and radiostrontium removal from soil suspension<sup>9</sup>. Enhanced sorption by external magnetic field shows promising prospects for rendering improvements. Iron oxides nanoparticles, in various forms, have been used as sorbent for radioactive and heavy metals scavenger on water and waste water solutions<sup>10-11</sup>. Its large surface area, high capacity, stability and high reactivity, significantly improve their performance compared to processes with microparticles. Magnetic nanoparticles ( $\text{Fe}_3\text{O}_4$ ) are widely studied functional materials employed for radio analytical sorption and extraction of a several number of radio elements. Synthetic approach and some of the very interesting separations by magnetic nanoparticles obtained in literature are given as follows:

**7.1 Synthesis of magnetic nanoparticles:**  $\text{Fe}_3\text{O}_4$  nano-particles have been synthesized by different methods such as co-precipitation<sup>12</sup>, sol gel<sup>13</sup> and sonochemistry<sup>14</sup>. Solid state mechano chemical method is the most reported method for synthesis of  $\text{Fe}_2\text{O}_3$  nano-particles with the mixture of  $\text{FeCl}_2 \cdot 4 \text{H}_2\text{O}$  and  $\text{FeCl}_3$  and as precursor material. The following method of synthesis is the most popular synthetic route for the synthesis of magnetic nanomaterial.

## **7.2 Separations of different radio isotopes by magnetic nanoparticles (MNPs) and functionalized MNPs**

Magnetic nanoparticles are reportedly employed for the sorption of isotopes as  $^{109}\text{Cd}$ ,  $^{60}\text{Co}$ ,  $^{152}\text{Eu}$ ,  $^{226}\text{Ra}$ ,  $^{140}\text{Nd}$ ,  $^{238}\text{U}$ ,  $^{239}\text{Pu}$  etc. Some notable radiochemical separations, as reported in the literature are described below:

### **7.2.1 Magnetic nano-particles and its application as radionuclidic sorbant to purify $^{109}\text{Cd}$ radionuclide:**

This report<sup>15</sup> shows  $^{109}\text{Cd}$  radiochemical separation starts with Ag activities precipitated with HCl 0.0015 M followed by, on a second step,  $^{109}\text{Cd}$  separation from Cu carrier and  $^{65}\text{Zn}$  (243.8 days) using  $\text{Ca}(\text{NO}_3)_2$  0.01 M. Experimental parameters such, pH and sorbent concentration, on  $^{109}\text{Cd}$  extraction efficiency were investigated<sup>16-17</sup>.

### **7.2.2 Sorption study of radiocobalt ( $^{60}\text{Co}$ ) by magnetic hydroxyapatite nanoparticles**

Novel  $\text{Fe}_3\text{O}_4$ - hydroxyapatite (HAP, apatite mineral) composite was prepared from biowaste chicken eggshell and was used as a magnetic adsorbent<sup>18-21</sup>. The experimental results confirm that this adsorbent has the potential application for the removal of  $\text{Co}^{2+}$  from aqueous solutions. The  $\text{Fe}_3\text{O}_4/\text{HAP}$  can be utilized as environment friendly adsorbent for the removal of  $\text{Co}^{2+}$  ions from aqueous solutions due to the efficient and fast sorption process, as well as simple and convenient magnetic separation.

### **7.2.3 Synthesis and characterization of magnetic nano-material for removal of Eu(III) ions from aqueous solutions**

In this study<sup>22</sup>, a magnetic nano-adsorbent composed from iron ferrite core and hydroxyapatite shell<sup>23-25</sup> was successfully synthesized. The prepared nano-material had a high thermal stability and possessed a crystalline structure. The sorption of  $\text{Eu}^{3+}$  was highly attained from acid solution and slightly affected by the value of ionic strength. The results highlight the promising application of this material in separation and recovery of lanthanide elements from their aqueous solutions.

### **7.2.4 Preparation and sorption performance of magnetic 18-crown-6/ $\text{Fe}_3\text{O}_4$ nanocomposite for uranium(VI) in solution**

Based on the combination Magnetic nanoparticles and 18-crown-6, a new magnetic nanocomposite material (MCFN) was synthesized via coprecipitation approach<sup>26-29</sup>. The U(VI) adsorption mechanism and performance of MCFN were further investigated via orthogonal experiment and variance analysis based on four impact factors (the adsorption temperature, crown ether amount, pH and contact time). The result suggested that MCFN exhibited high affinity, selectivity and fast kinetic process for the adsorption of U(VI) ions.

### **7.2.5 Application of magnetic nanoparticles for the extraction of radium-226 from water samples**

In this study<sup>30</sup>, crown ether functionalised MNPs<sup>31-33</sup> were employed for extraction of <sup>226</sup>Ra from aqueous samples exploiting the unique physical and chemical properties of MNPs along with the selective nature of 18-crown-6 for <sup>226</sup>Ra. An extraction efficiency of  $94 \pm 1\%$  was obtained using 0.01 M picric acid at pH 4 with 25 mg of CE-modified MNPs. A recovery of  $95 \pm 1\%$  was obtained from the stripping of <sup>226</sup>Ra from CE-modified MNPs. Further method development is underway to apply the CE-modified MNPs for determination of <sup>226</sup>Ra from drinking water and urine samples.

### **7.2.6 Adsorption of uranium ions from aqueous solution by amine group functionalized magnetic Fe<sub>3</sub>O<sub>4</sub> nanoparticle**

In the present work<sup>34</sup>, the magnetic nanoparticle was amine-functionalized using APTMS<sup>35-37</sup> for the adsorptive removal of uranium ions from aqueous solution. The Fe<sub>3</sub>O<sub>4</sub>-NH<sub>2</sub> showed a better adsorption capacity onto uranium ions as the monolayer adsorption capacity was as high as 268.49 mg/g, which was larger than the Fe<sub>3</sub>O<sub>4</sub> nanoparticle (85.35 mg/g) at 298.15 K. The results indicate that the Fe<sub>3</sub>O<sub>4</sub>-NH<sub>2</sub> is a potentially useful adsorbent for removal uranium ions from aqueous solution with higher efficiency.

### **7.2.7 Neodymium (III) removal by functionalized magnetic nanoparticles**

In this study<sup>38</sup>, the sorption capacities of Nd<sup>3+</sup> on magnetic nanoparticles grafted by poly(aminoethylene Nmethyl 1-formic acid, 1-phosphonic acid) were studied by batch tests<sup>39-41</sup>. Liquid–solid extraction of neodymium<sup>3+</sup> is made by magnetic particles with two different sizes. The results obtained in this study by large and fine magnetic particles are very close and there is moderate difference but this study makes this magnetic particle a promising material for sorption, immobilization and preconcentration.

## **8. Other nanoparticles for successful radio analytical separation**

### **8.1 Fe(III)<sub>x</sub>Sn(II)<sub>y</sub>Sn(IV)<sub>12x2y</sub>Hn[P(Mo<sub>3</sub>O<sub>10</sub>)<sub>4</sub>] xH<sub>2</sub>O new nano hybrid, for effective removal of Sr(II) and Th(IV)**

This work<sup>42</sup> shows that Fe(III)<sub>x</sub>Sn(II)<sub>y</sub>Sn(IV)<sub>12x2y</sub>Hn[P(Mo<sub>3</sub>O<sub>10</sub>)<sub>4</sub>] xH<sub>2</sub>O nano particle has been successfully prepared via a simple chemical precipitation method<sup>43</sup>. This cost effective and environment friendly adsorbent was proved to be a very good adsorbent for the removal of Sr(II) and Th(IV) ions from aqueous solutions.

### **8.2 Sorption of plutonium from low level liquid waste using nano MnO<sub>2</sub>**

This article<sup>45</sup> describes that Pu<sup>4+</sup> is sorbed by nano MnO<sub>2</sub><sup>46-48</sup> at pH in the pH range of 3–5 almost quantitatively. The kinetics of the sorption process is quite fast with the nearly 100% sorption attained in 15 h. A small but finite effect of ionic strength was observed on the

sorption of  $\text{Pu}^{4+}$  by  $\text{MnO}_2$  suggesting the mechanism of sorption via outer sphere complexation at lower pH values. Thus the present study has shown that nano- $\text{MnO}_2$  can be effectively used for removing Pu from low level waste solutions before their further treatment.

### 8.3 Magnesium oxide nanoparticles: Preparation, characterization, and uranium sorption properties

This study<sup>49</sup> is focused on the investigation of sorption characteristics of  $\text{U}^{6+}$  onto MgO from aqueous solution. The operating parameters, pH of solution, uranium concentration, contact time, and temperature, were effective on the removal efficiency of  $\text{U}^{6+}$ . For the solution with  $40 \mu\text{g mL}^{-1}$  metal ion, the maximum removal efficiency was found as  $87.61 \pm 3.10\%$  for  $\text{U}^{6+}$  ion without pH control with a shaking time of 120 min at temperature  $25^\circ\text{C}$ .

### 9. Some high capacity nanosorbents such for development of some generator system

R Chakravarty *et al.*<sup>50-56</sup> has reported several numbe of high capacity nano based sorbents such as polymer embedded nanocrystalline titania (TiP), mixed phase nano-zirconia (nano- $\text{ZrO}_2$ ) tetragonal nano-zirconia (t- $\text{ZrO}$ ) nanocrystalline alumina ( $\gamma\text{-Al}_2\text{O}_3$ ) and nano-ceria-polyacrylonitrile composite ( $\text{CeO}_2\text{-PAN}$ )vfor the development of some generator systems like  $^{99}\text{Mo}/^{99\text{m}}\text{Tc}$ ,  $^{188}\text{W}/^{188}\text{Re}$ ,  $^{68}\text{Ge}/^{68}\text{Ga}$ . A comparative study on the Structural characteristics of the nanosorbents is given in the **table 1**. The separation processes could be demonstrated by developing generators using these nanosorbents. The sorption capacities of these sorbents are shown below in tabular from (**table 2**) as obtained from the literature.

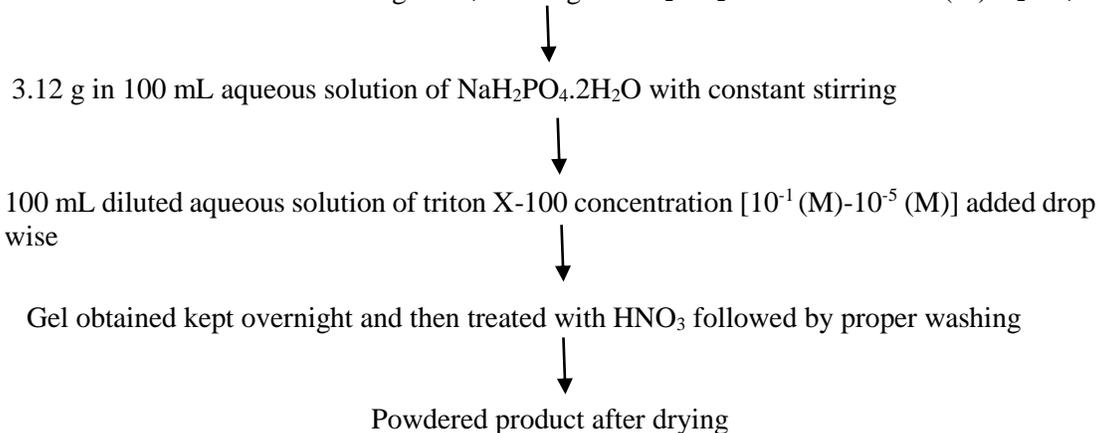
### 10. Some newly designed nanocomposites for radioanalytical separation with modified Route of synthesis and size-dependent properties

It is expected that the exchanger material will definitely exhibit superior exchange capacity due to their smaller size and large surface to volume ratio compared to that of macro state. Macro state sorbent base on group 4/5 metals oxides and phosphates are established ion exchange type material. It is reported that surfactant controlled synthesis of these nanocomposite not only shows enhanced exchange capacities but also provides interesting studies on size-dependent properties. A brief account of some of this novel class of nanocomposites is described herein like titanium phosphate (TiP), Zirconium phosphate, Zirconium titanium phosphate (ZTP) is an belonging to the class of polyoxometalates. It is reported that surfactant Controlled synthesis of nanocomposite ZTP exhibit superior exchange capacity.

**10.1 Hydrogen titanate nanotubes ( $\text{H}_2\text{Ti}_3\text{O}_7$ ):**  $\text{H}_2\text{Ti}_3\text{O}_7$  were synthesized by hydrothermal process using 10 M NaOH and  $\text{TiO}_2$  anatase powder followed by acidification using 1 M HCl. The scanning electron micrograph (**Fig.2A**) shows the formation of one dimensional (1-D) nanostructures. Further TEM study (**Fig.2B**) clearly shows that all the 1-D units are actually hollow, multiwall nanotubes<sup>57</sup>. This nanosized material behaved as a cation exchanger and it was employed to separate carrier-free  $^{137\text{m}}\text{Ba}$  from  $^{137}\text{Cs}$  in column chromatographic technique using 1.0 M  $\text{HNO}_3$  as eluting agent. Ion exchange capacities  $\text{H}_2\text{Ti}_3\text{O}_7$  towards different metal ions are given in the **table 3**.

**10.2 Zirconium titanium phosphate nanocomposite (ZTP):** ZTP<sup>58</sup> of different sizes were employed to separate carrier-free <sup>137m</sup>Ba from <sup>137</sup>Cs in column chromatographic technique using 1.0 M HNO<sub>3</sub> as eluting agent at pH = 5. The structural and morphological details of the material were obtained by SEM (**Fig.3A**) and TEM (**Fig.3B**). The size dependent ion exchange property is shown in the **table 4**.

**Scheme:** Mixed solution of 1.00 g TiCl<sub>4</sub> + 1.53 g ZrOCl<sub>2</sub>.8H<sub>2</sub>O in 50 mL in 1.0 (M) H<sub>2</sub>SO<sub>4</sub>



### 10.3 TiP nanocomposite:

Synthesis Nanocomposite titanium-phosphate (TiP) of different sizes was synthesized using triton X-100. The nanomaterial of the smallest size of around 43 nm was employed to separate carrier-free <sup>137m</sup>Ba from <sup>137</sup>Cs in column chromatographic technique using 1.0 M HNO<sub>3</sub> as eluting agent at pH = 5. The size dependent ion exchange property is shown in the **table 5**.

**Figure 4A and 5A** shows the SEM and TEM images followed by SAED pattern (**Fig. 5B**) of the nanostructured material. Sample does not have unique morphology. EDS analysis (**Fig. 4A**) ensures that the dominant chemical elements present in the samples are P, Ti and O.

### 10.4 ZP nanocomposite:

Zirconium phosphate nanoparticles (ZPs) of different sizes were synthesized using triton X-100 as earlier. Ion exchange capacity was measured for different metal ions with sizes of the ZP nanoparticles and size-dependent ion exchange property (**table 6**) of the material was investigated thoroughly. The nanomaterial was employed to separate carrier-free <sup>137m</sup>Ba from <sup>137</sup>Cs in column chromatographic technique using 1.0 M HNO<sub>3</sub> as eluting agent at pH = 4. **Figure 6A and 7A** shows the SEM and TEM images followed by SAED pattern (**Fig. 6B**) of the nanostructured material with different magnification. Sample does not have

specific morphology but particles (blocks) consist of small grains with the size range of nanometers. EDS analysis (corresponding to (Fig. 6B) shows that the dominant chemical elements present in these samples are P, Zr and O. The size dependent ion exchange property is shown in the table.

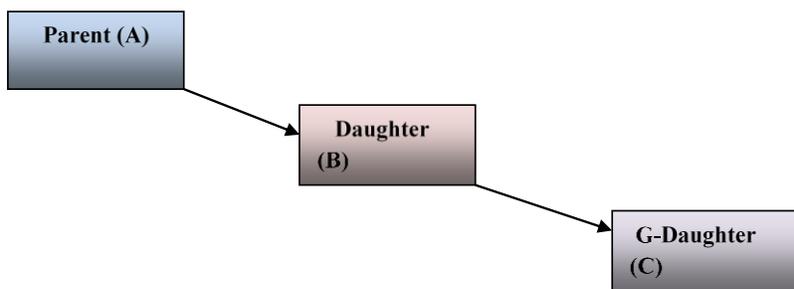


Fig. 1. Decay scheme of parent-daughter radionuclide pair

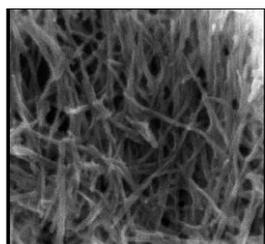


Fig.2A. SEM image of  $H_2Ti_3O_7$

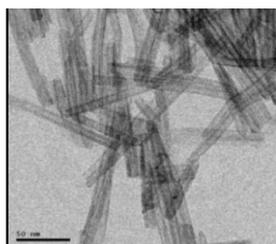


Fig.2B. TEM image of  $H_2Ti_3O_7$

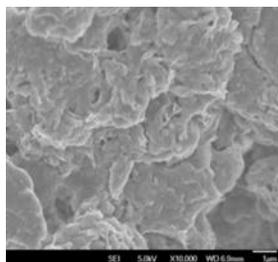


Fig. 3A. SEM image of ZTP

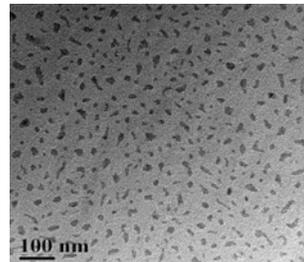


Fig. 3B. TEM image of ZTP

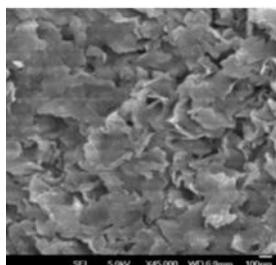


Fig.4A. SEM image of TIP

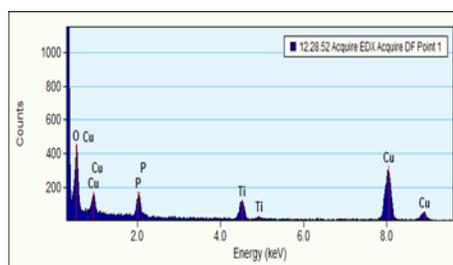
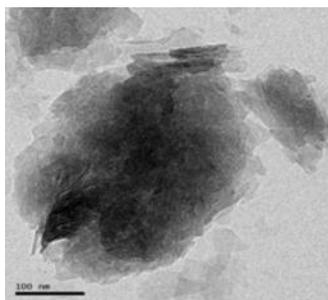
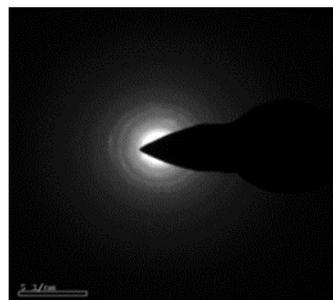


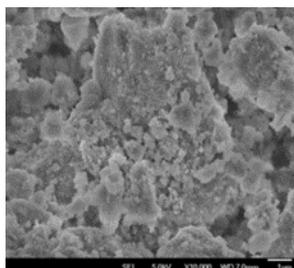
Fig.4B. EDS spectrum of TiP



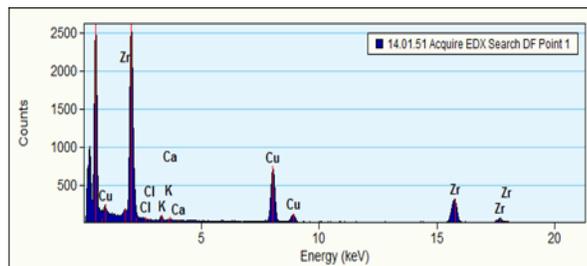
**Fig.5A. TEM image of TiP**



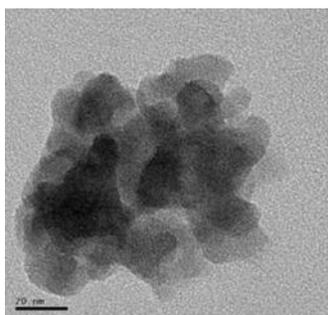
**Fig.5B. SAED pattern**



**Fig.6A. SEM image of ZP**



**Fig.6B. EDS spectra of ZP**



**Fig.7A. TEM image of ZP**



**Fig.7B. SAED Pattern**

**Table 1 structural characteristic of the nanosorbents**

Nanosorbent	Crystallinity and phase as evidenced from XRD pattern	Size of the particles from XRD in nm	Agglomeration from TEM
TiP	Nanocrystalline rutile	5	Dispersed titania in the network polymer
nano-ZrO <sub>2</sub>	Nanocrystalline mixed phase	15	Agglomerated
t-ZrO <sub>2</sub>	Nanocrystalline tetragonal	7	Agglomerated
γ-Al <sub>2</sub> O <sub>3</sub>	Nanocrystalline gamma	5-6	Agglomerated
CeO <sub>2</sub> -PAN	Nanocrystalline cubic	8-10	Agglomerated

**Table 2. A comparative study on sorption capacities of these nano sorbents**

Generator system	Sorption Capacities in mg/g of sorbent	
<sup>99</sup> Mo/ <sup>99m</sup> Tc	Static	dynamic
	TiP	88±4
	t-ZrO <sub>2</sub>	155±12
	γ-Al <sub>2</sub> O <sub>3</sub>	148±3
<sup>188</sup> W/ <sup>188</sup> Re	TiP	98 ± 2
	t-ZrO <sub>2</sub>	110 ± 5
	γ-Al <sub>2</sub> O <sub>3</sub>	298±6
	CeO <sub>2</sub> -PAN	76±3
<sup>68</sup> Ge/ <sup>68</sup> Ga	t-ZrO <sub>2</sub>	20±2
	CeO <sub>2</sub> -PAN	135±10

Note: '±' indicates standard deviation (n = 3)

**Table 3: Ion exchange capacity of different cations**

Ions	Exchange capacity (meq/g)
Na <sup>+</sup>	2.625
K <sup>+</sup>	2.409
Cs <sup>+</sup>	2.021
NH <sub>4</sub> <sup>+</sup>	1.637
Mg <sup>2+</sup>	1.732
Ca <sup>2+</sup>	1.735
Ba <sup>2+</sup>	1.965

**Table 4: Exchange capacities of ZTPs of different particle sizes towards metal ions**

Ion	IEC in meq/g onto ZTPs of different particle sizes <sup>a</sup>				
	ZTP-1	ZTP-2	ZTP-3	ZTP-4	ZTP-5
Na <sup>+</sup>	1.468	1.488	1.504	1.522	1.682
K <sup>+</sup>	1.558	1.583	1.598	1.613	1.825
Cs <sup>+</sup>	1.684	1.735	1.751	1.768	1.887
Ca <sup>2+</sup>	2.631	2.649	2.670	2.687	2.801
Ba <sup>2+</sup>	2.839	2.886	2.906	2.924	3.185

<sup>a</sup>average size of ZTPs (in nm): ZTP-1, 101.1; ZTP-2, 78.82; ZTP-3, 58.77; ZTP-4, 30.22; ZTP-5, 4.849

**Table 5: Exchange capacities of TiPs of different particle sizes towards metal ions**

IEC in meq/g onto TiPs of different particle sizes <sup>b</sup>					
Ions	TiP 1	Tip 2	TiP 3	TiP 4	TiP 5
Na <sup>+</sup>	1.906	1.880	1.857	1.832	1.811
K <sup>+</sup>	2.116	2.09	2.067	2.046	2.021
Cs <sup>+</sup>	2.285	2.264	2.240	2.196	2.171
Ca <sup>+</sup>	3.072	3.048	3.025	3.001	2.976
Ba <sup>+</sup>	3.326	3.305	3.284	3.259	3.234

<sup>b</sup>average size of TiPs (in nm):TiP-1, 43.82; TiP-2, 68.06; TiP-3, 91.28; TiP-4, 122.4; TiP-5, 141.8

**Table 6 Exchange capacities of ZPs of different particle sizes towards metal ions**

IEC in Meq/g onto ZP of different particle size <sup>c</sup> (nm)					
Ions	ZP 1	ZP 2	ZP 3	ZP 4	ZP 5
Na <sup>+</sup>	1.375	1.340	1.308	1.277	1.237
K <sup>+</sup>	1.875	1.836	1.801	1.768	1.737
Cs <sup>+</sup>	2.593	2.491	2.445	2.399	2.358
Ca <sup>2+</sup>	3.299	3.157	3.102	3.046	2.995
Ba <sup>2+</sup>	4.129	3.932	3.856	3.763	3.710

<sup>c</sup>average size of ZPs (in nm): ZP-1, 21.04; ZP-2, 41.6; ZP-3, 65.06; ZP-4, 78.82; ZP-5, 91.28

## 11. CONCLUSION

Synthesis of nanoparticles along with different size distribution has emerged as an important field of investigation in materials chemistry because of their several non conventional physical properties like catalytic, optic, electric and magnetic and so on. But with such great promises, the affectivities of using nano material in radioanalytical separation process are a small area of research till date. Perspectives of this review are to focus on the great affectivities of the nano materials as sorbent in trace level radioanalytical separations.

The design of the conventional exchanger in nanoscale range and its characterization has demonstrated its applicability towards attaining a novel separation in trace level analysis with enhanced efficiency. Use of nanoscopic material as sorbent in radio-analytical separation will reduce the cost and will lead to portability of the exchanger devices. Moreover it will fulfill the increasing demand for chemical surveillance in environmental protection, medicine, and many other industrial processes. Moreover it is also noteworthy that eco-friendly synthetic route is followed for the preparation of the most of the nano material based sorbent which is in very much favor of today's worldwide campaign of green chemistry.

## REFERENCES

1. Bhattacharyya D. K., Basu S., Use of Alumina as an Ion Exchanger In the Separation of Carrier-Free <sup>144</sup>Pr from <sup>144</sup>Ce, *Sepa. Sci*,11, 503-508 (1976).
2. Bhattacharyya D. K., De. A., Separation of Carrier-free <sup>99m</sup>Tc from Mo and <sup>144</sup>pr from <sup>144</sup>Ce Over a Column of Zirconium Arsenate, *Sepa. Sci*, 17, 925-933 (1982).

3. Herring C., Galt J.K. Elastic and plastic Properties of Very Small Metal Specimens. *Phys. Rev.*, 85, 1060 (1952).
4. Bai X.M., Voter A.F, Hoagland R.G., Uberuaga, M, Efficient annealing of radiation damage near grain boundaries via interstitial emission. B.P, *Science*, 327,1631-1634 (2010).
5. Okuyama K. I., Lenggono W., Preparation of nanoparticles via spray route. *Chem. Eng. Sci.*, 38, 537-547 (2000).
6. Szostak R., Szostak R., Molecular Sieves, Van Nostrand Reinhold, York (1989).
7. Rao C.N.R., Vivekchand S.R K., Govindaraj, A., Synthesis of inorganic Nanomaterials, *Dalton Trans.* 37, 3728-3749 (2007).
8. Rao C.N.R., Thomas P.J., Kulkarni G.U., Nanocrystals: synthesis, properties and applications 95, Hong Kong (2007).
9. Rao C.N.R., Muller A., Cheetham A.K., The Chemistry of Nanomaterials: Synthesis, Properties and Applications, 1st ed, Wiley-VCH, Verlag, Germany (2004).
10. Macasek F., Bartos P., A magnetic sorbent for radiocesium and radiostrontium Removal from clay and soil suspensions, *J. Radioanal. Nucl. Chem.* 246, 565-569 (2000).
11. Misa N.Z., Ghoniemy H.F., Morcos T.N., Adsorption of  $\text{Co}^{2+}$  and  $\text{Zn}^{2+}$  ions on hydrous Fe (III), Sn (IV), and Fe (III)/Sn (IV) oxides: II. Thermal behavior of loaded oxides, isotopic exchange equilibria, and percentage adsorption–pH curves. *J. Colloid. Interface. Sci.* 184, 31-43 (1996).
12. Ghoniemy H.F., Morcos T.N., Misak, N.Z., Characteristics of the hydrous oxides, apparent capacity and some equilibria measurements, *Physicochem. Eng. Aspects.* 122,13-26 (1997).
13. Lee S.J., Jeong J.R., Shin S.C., Kim J.C., Kim J.D., Synthesis and characterization of superparamagnetic maghemite nanoparticles prepared by coprecipitation technique, *J. Magn. Mater.*, 282,147-150 (2004).
14. Battisha I.K., Afify H.H., Ibrahim M. J., Surfactant-free synthesis of magnetic polypropylene nanocomposites *J. Magn. Mater.*, 306, 211-217 (2006).
15. Vijayakumar R., Koltypin Y., Felner I., Gedanken A., Sonochemical synthesis and characterization of pure nanometer-sized  $\text{Fe}_3\text{O}_4$  particles, *Mater. Sci. Eng. A*, 286,101- 105 (2000).
16. Geotz L.E., Sabbioni E., Marafante C., Bondari, M., Cyclotron production of  $^{107,109}\text{Cd}$  for use in metallobiochemistry of heavy metal pollution. *Radiochem. Radioanal. Lett.*, 45, 51-59 (1980).
17. Long X., Peng X., Fuqing H., Mantian L., Production of cadmium-107 and cadmium-109 by deuteron bombardment of silver. *Appl. Radiat Isot.*, 42, 1234-1336 (1991).
18. Hongqin X., Duilin W., Zhe J., Xiaowei Li., Cheng J., Kinetic and thermodynamic sorption study of radiocobalt by magnetic hydroxyapatite nanoparticles. *Radioanal. Nucl. Chem.*, 292, 637-647 (2012).
19. Zhang S.W., Guo Z.Q., Xu J.Z., Niu H.H., Z.S. Chen, Xu J.Z., Effect of environmental conditions on the sorption of radiocobalt from aqueous solution to treated eggshell as biosorbent, *J. Radioanal. Nucl. Chem.* 288, 121-130 (2011).
20. Wang X.K., Chen C.L., Hu W.P., Ding A.P., Xu D., Zhou X., Sorption of  $^{243}\text{Am(III)}$  to multiwall carbon nanotubes. *Environmental Science & Technology Environ. Sci. Technol.*, 39, 2856 (2005).

21. Tan X.L., Wang X.K., Geckeis H., Rabung T., Sorption of Eu(III) on Humic acid or fulvic acid bound to hydrous alumina studied by SEM-EDS, XPS, TRLFS, and batch techniques, *Environ. Sci. Technol.* 42, 6532-6537 (2008).
22. Moussa S. I., Sheha. R. R., Saad, E. A., Tadros, N. A., Synthesis and characterization of magnetic nano-material for removal of Eu<sup>3+</sup> ions from aqueous solutions. *J. Radioanal. Nucl. Chem.* 295, 929-935 (2013).
23. Fan Q.H., Zhang Y., Ding K.F., Yang Z.Q., Wu W.S., Sorption of Eu(III) and Am(III) on attapulgite: effect of pH, ionic strength and fulvic acid, *Radiochim. Acta.*, 98, 19-25 (2010).
24. Shao D.D., Fan Q.H., Chen Y.X., Wang X.K., Removal of Eu(III) from aqueous solution using ZSM-5 zeolite, *Micro Meso Mater.*, 123, 1-9 (2009).
25. Tan X., Fang M., Li J., Lu Y., Wang X., Adsorption of Eu(III) onto TiO<sub>2</sub>: effect of pH, concentration, ionic strength and soil fulvic acid. *J. Hazard. Mater.*, 168, 458-465 (2009).
26. Bhattacharyya D. K., De A., Ceric tungstate as sorbent for polyvalent tracer cations and as an ion exchanger for separation of carrier-free <sup>95</sup>Nb from <sup>95</sup>Zr and <sup>113m</sup>In from <sup>113</sup>Sn, *J. Radioanal. Chem.*, 108, 109-124 (1986).
27. Dam H.H., Reinhoudt D.N., Verboom W., Multicoordinate ligands for actinide/lanthanide separations. *Chem. Soc. Rev.* 36, 367-377 (2007).
28. Jain V. K., Pandya R.A., Pillai S.G., Shrivastav P.S. Simultaneous preconcentration of uranium(VI) and thorium(IV) from aqueous solutions using a chelating calixarene anchored chloromethylated polystyrene solid phase, *Talanta.* 70, 257 (2006).
29. Sheng G.D., Hu J., Wang X.K., Development and application of an on-line sequential injection system for the separation of Pu, <sup>210</sup>Po and <sup>210</sup>Pb from environmental samples, *Appl. Radiat. Isot.* 66, 223-230 (2008).
30. Natalie M., Baki S., Chunsheng Li., Edward L., Application of magnetic nanoparticles for the extraction of radium-226 from water samples. *J. Radioanal. Nucl. Chem.* 298, 1501-1509 (2013).
31. Faraji M., Yamini Y., Rezaee M., Magnetic nanoparticles: Synthesis, stabilization, functionalization, characterization, and applications, *J. Iran. Chem. Soc.* 7, 1-37 (2010).
32. Gao J., Gu H., Xu B., Multifunctional magnetic nanoparticles: design, synthesis, and biomedical applications, *Acc. Chem. Res.* 42, 1097-1107 (2009).
33. Vatta L.L., Sanderson R.D., Koch K.R., Magnetic nanoparticles: Properties and potential applications, *Pure Appl. Chem.* 78, 1793-1801 (2006).
34. Peng G. W., Ding D. X., Xiao F. Z., Wang X. L., Hun N., Wang Y. D., Dai Y., Cao M. Z., Adsorption of uranium ions from aqueous solution by amine-group functionalized magnetic Fe<sub>3</sub>O<sub>4</sub> nanoparticle. *J. Radioanal Nucl Chem.* 301, 781 (2014).
35. Mezaguer, M., Kamel, N., Lounici, H., Kamel, Z., Characterization and properties of *Pleurotus mutilus* fungal biomass as adsorbent of the removal of uranium(VI) from uranium leachate, *J. Radioanal. Nucl. Chem.* 295, 393-403 (2013).
36. Wang, X.L., Peng, G.W., Yang, Y., Wang, Y.F., He, T.T., Uranium adsorption by dry and wet immobilized *Saccharomyces cerevisiae*, *J. Radioanal. Nucl. Chem.* 291, 826-830 (2012).

37. Kazy, S.K., Souza, S.F., Sar, P., Uranium and thorium sequestration by a Pseudomonas sp: Mechanism and chemical characterization, *J. Hazard. Mater.* 163, 65-72 (2009).
42. Yousefi, T., Yavarpour, S., Hamed, S., Meisam, M., Davarkhah, R., Hossei G., FeIII<sub>x</sub>SnII<sub>y</sub>SnIV<sub>1-x-y</sub>H<sub>n</sub>[P(Mo<sub>3</sub>O<sub>10</sub>)<sub>4</sub>].xH<sub>2</sub>O new nano hybrid, for effective removal of Sr(II) and Th(IV), *J. Radioanal. Nucl. Chem.* 307, 941-953 (2016).
43. Pathania, D., Sharma, G., Thakur, R., Fabrication of nanocomposite polyaniline zirconium (IV) silicophosphate for photocatalytic and antimicrobial activity, *Chem. Eng. J.* 267, 235-244 (2015).
44. Bhagyashree K., Mishra R. K., Shukla R., Sharayu K., Kar A., Kumar S., Kaushik C. P., Tyagi A. K., Tomar, B. S., Sorption of plutonium from low level liquid aste using nano MnO<sub>2</sub>. *J. Radioanal. Nucl. Chem.* 295, 1561-1566 (2013).
45. Raj K., Prasad K.K., Bansal N.K., Radioactive waste management practices in India, *Nucl. Eng. Design.* 236, 914-930 (2006).
46. Hua M., Zhang S., Pan, B., Zhang W., Lv L., Zhang, Q., Heavy metal removal From water/ wastewater by nanosized metal oxides: a review. *J. Hazardous Mater.* 211, 317-331 (2012).
47. Manceau A., Charlet L., Boisset M.C., Spadini B. L., Sorption and speciation of heavy metals on Fe and Mn hydrous oxides. From microscopic to macroscopic, *Appl. Clay. Sci.* 7, 201-223 (1992).
48. Luo X. C., Wang S., Luo R., Dong T.U., Zeng G., Adsorption of As (III) and as (V) from water using magnetite Fe<sub>3</sub>O<sub>4</sub>-reduced graphite oxide–MnO<sub>2</sub> nanocomposites, *Chem. Eng. J.* 187, 45-52 (2012).
49. Camtakan Z., Sema E., Yusan S., *Environ. Progress Sustainable Energy.* 31, 536 (2012).
50. Chakravarty R., Shukla, R., Gandhi, S., Ram, R., Dash, A., Exploitation of nano alumina for the chromatographic separation of clinical grade 188Re from 188W: a renaissance of the 188W/188Re generator technology. *Anal. Chem.* 83, 6342-6348 (2011).
51. Chakravarty R., Ram R., Dash A., Pillai M. R. A., Preparation of clinical-scale <sup>99</sup>Mo/<sup>99m</sup>Tc column generator using neutron activated low specific activity <sup>99</sup>Mo and nanocrystalline γ-Al<sub>2</sub>O<sub>3</sub> as column matrix, *Nucl. Med. Biol.* 39. 916-922 (2012).
52. Chakravarty R., Shukla R., Gandhi S., Ram R., Dash A., Venkatesh M., Tyagi K., Polymer embedded nanocrystalline titania sorbent for <sup>99</sup>Mo-<sup>99m</sup>Tc generator, *J. Nanosci. Nanotechnol.* 8, 4447-4452 (2008).
53. Chakravarty R., Shukla R., Gandhi S., Ram R., Dash A., Nanocrystalline zirconia: A novel sorbent for the preparation of 188 W/188 Re generator, *Appl. Radiat. Isot.* 68, 229 (2010).
54. Chakravarty R., Shukla R., Gandhi S., Ram R., Dash A., Practicality of tetragonal nano-zirconia as a prospective sorbent in the preparation of <sup>99</sup>Mo/<sup>99m</sup>Tc generator for biomedical applications, *Chromatographia.* 72, 875-884 (2010).
55. Chakravarty R., Shukla R., Gandhi S., Ram R., Dash A., Nanoceria-PAN composite-based advanced sorbent material: A major step forward in the field of clinical-grade <sup>68</sup>Ge/<sup>68</sup>Ga generator, *ACS Appl. Mater.* 2, 2069-2075 (2010).
56. Chakravarty R., Dash A., Role of Nanoporous Materials in Radiochemical Separations for Biomedical Applications, *J. Nanosci. Nanotechnol.* 13, 2431 (2013).

57. Chakraborty R., Chatterjee S., Chattopadhyay P., One-dimensional Ti-O based nanotubes as ion exchanger: synthesis, characterization and application in radiochemical separation of carrier-free  $^{137\text{m}}\text{Ba}$  from  $^{137}\text{Cs}$ . *Radiochim. Acta.* 101, 33-36 (2013).
58. Chakraborty R., Bhattcharaya K., Chattopadhyay P., Nanostructured zirconium phosphate as ion exchanger: Synthesis, size dependent property and analytical application in radiochemical separation. *Appl. Radiat. Ist.* 85, 34-38 (2014).
59. Chakraborty R., Chatterjee S., Chattopadhyay P., Radioanalytical separation and size-dependent ion exchange property of micelle-directed titanium phosphate nanocomposites. *J. Radioanal. Nucl. Chem.* 299,1565-1570 (2014).
60. Chakraborty R., Sen B., Chattopadhyay P., Zirconium-titanium-phosphate nanoparticles: Triton X-100 based size modification, characterization and application in radiochemical separation. *Radiochim. Acta.* 102, 363 (2014).